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A review of highly reliable flexible encapsulation technologies towards rollable and foldable OLEDs

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ABSTRACT
As the demand for flexible, rollable, and foldable displays grows, various state-of-the-art component technologies, including thin-film transistors (TFTs), electrodes, thin-film encapsulations (TFEs), and touch screen panels, have been developed based on organic light-emitting diodes (OLEDs) with flexible organic layers. Developing highly reliable flexible OLEDs is essential to realize flexible displays, but the flexible encapsulation technology still has technical difficulties and issues to be addressed. This review covers the recent developments in encapsulation technologies, particularly their material and structural designs, for highly reliable, flexible OLEDs. The solution concepts for the existing technical hurdles in flexible encapsulations are addressed. Among the various advanced flexible encapsulation technologies developed so far, neutral-axis engineering with a thin metal layer and a crack arrester is introduced.

1. Introduction
In the emerging Fourth Industrial Revolution, Internet of things (IoT) will be widely used by people in their daily lives as smart devices provide added convenience. The display technologies for these smart devices have become increasingly important to the market and consumers [1–3]. They act as a communication tool between the devices and humans to help directly express the purpose and operation of the device. One of the easiest and most powerful forms of this communication is to use displays to show the present status of the device.

The displays that have been widely used in many products have flat and fixed shapes, but there is a growing interest in the use of flexible displays for various applications. When rollable and foldable displays become available, devices can have bigger screens and greater portability. The efforts to develop rollable and foldable flexible displays continue. Various approaches have been investigated, and prototypes have been launched [4–7].

Since the first report on organic light-emitting diodes (OLEDs), they have been the subject of intensive development and study [8–17]. The OLED technology has its origins in observations of electroluminescence [18–21]. The basic structure of OLEDs was proposed by Tang and VanSlyke in 1987 [22]. In 1988, three-layered OLEDs [23] were introduced, and the layered structure has since been extended up to five layers [24]. The fundamental OLED device structure includes a substrate, an anode through which holes are injected, a cathode through which electrons are injected, and an organic layer where the injected holes and electrons move to form excitons, emitting light. Among their advantages, OLEDs are slim, flexible, and provide an esthetically pleasing image due to their high contrast ratio and good response time, but for the commercialization of flexible displays, their flexibility is their most attractive feature.

Organic materials are much more vulnerable to water vapor and oxygen compared to inorganic materials. The mechanism of degradation is quite complicated and not yet fully understood, but progress has been reported in this regard [25–30]. Unfortunately, when OLEDs are exposed to water vapor and oxygen, the organic layers can be easily oxidized and crystalized, which leads to the formation of dark spots [31–35]. To address this issue, packaging technologies that can seal out water vapor and oxygen, called ‘encapsulation’ or ‘passivation,’ have been investigated. The fundamental principles of the permeation barrier technology have their origins in food and medical packaging [36–38]. Such methods have long been applied to protect foods and electronic devices.
against environmental degradation, and to ensure the reliability of products over time.

To meet the requirements of organic electronic devices (OEDs), the encapsulation technology needs a gas barrier coating with a much higher performance. Specifically, the water vapor transmission rate (WVTR) for an OLED should be less than $10^{-6}$ g/m²/day [38,39]. The recent breakthroughs in the deposition technology, such as thermal evaporation, chemical vapor deposition (CVD), and atomic layer deposition (ALD), have led to dramatic improvements in the gas barrier technology. Accordingly, such encapsulation technologies have been actively studied to guarantee the long-term reliability of OLEDs.

In the past, rigid OLEDs were given glass lid encapsulation with a desiccant of barium oxide (BaO) or calcium oxide (CaO), which provides an acceptable level of WVTR. The brittle nature of glass, however, limits its application to flexible OLEDs, which require flexible encapsulation. Many types of encapsulation technologies have been studied and proposed as alternatives to solve this problem. Among them, thin-film encapsulation (TFE) is considered highly promising because it can eliminate edge permeation and has some flexibility due to its thickness. Many types of TFE have been developed for flexible OLEDs, such as the multi-bi-layer structures of alternating inorganic/organic layers and inorganic-based nanolaminates systems. These initial TFEs, however, were complex and exhibited poor barrier and mechanical properties. Since recently, the use of high-tech deposition techniques based on CVD or ALD has enabled the achievement of superior TFEs with less than 100 nm thicknesses.

For flexible displays, it is important to prevent mechanical damage to the TFE. Bending stress can accelerate the growth of defects, which become diffusion paths for water vapor and oxygen. As OLEDs are already sufficiently flexible, improving the flexibility of the TFE will be the main issue with regard to the development of highly reliable rollable and foldable flexible displays. That is the aim of this review, which highlights the recent progress towards the realization of highly reliable flexible OLEDs using multibarrier approaches for advanced flexible TFE technologies. In particular, new methods of enhancing the flexibility of TFE are concentrated on, such as controlling the neutral axis (NA) with a buffer layer, employing a metal layer, and inserting a crack arrester in the TFE. This review is classified into two main categories: conventional encapsulation technologies and flexible TFE technologies.

2. Conventional encapsulation technologies

2.1. Types of encapsulation barrier

The encapsulation barrier technology is essential for preventing the degradation of flexible displays. Flexible substrates like plastic materials have very poor barrier properties. The design objectives of the encapsulation barrier depend on the required WVTR and lifetime of the device. For OLEDs in actual industrial products, the desired WVTR is within the range of $10^{-6}$ g/m²/day. Traditionally, three types of encapsulation barrier technology have been used for devices, as shown in Figure 1: glass lid encapsulation, barrier foil encapsulation, and TFE. This section provides a brief explanation of each of these technologies.

Glass lid encapsulation is known as the most secure encapsulation barrier [40]. In this approach, the device is fabricated on a glass substrate and then encapsulated by mounting another glass sheet on top of it, as illustrated in Figure 1(a). It is attractive in that it is not deformed even at a high temperature, is transparent and easy to handle, and has very low moisture and oxygen penetration rates. For these reasons, glass lid encapsulation is the most stable and reliable barrier technology, which is why it is widely used as a global reference for the encapsulation barrier.

Nevertheless, glass lid encapsulation has two main limitations: edge permeation and lack of flexibility. Edge permeation refers to permeation through the sealant between two glass slides that do not have enough barrier properties. To address this issue, edge sealing can be combined with a desiccant beneath the glass lid. In addition, a well-optimized design and advanced sealant materials can lower the WVTR of glass lid encapsulation to the range of $10^{-6}$ g/m²/day. Glass lid encapsulation, however, still cannot be applied to flexible devices because of its fragile and heavy properties.

The barrier foil lamination technology is a generally known alternative to glass lid encapsulation [41]. The device can be fabricated on a glass or flexible substrate and then encapsulated by laminating the top with barrier foil, as shown in Figure 1(b,c). Typically, the barrier foil is made of ultra-thin glass (under 50 μm thickness), metal foil, and graphene, and can be accomplished using a roll-to-roll process. By using such process, the barrier foil can be fabricated in advance or parallel to the organic devices. This can be a great advantage because organic materials are sensitive to temperature, radiation, and gases, which limits the types of encapsulation process that can be employed.
Figure 1. Types of encapsulation barriers and requirements: (a) glass lid encapsulation; (b) barrier foil encapsulation on a glass substrate; (c) barrier foil encapsulation on a flexible substrate; (d) TFE; and (e) WVTR and flexibility requirements for various applications.

At the same time, the barrier foil technology has disadvantages that remain technological challenges to large-area manufacturing, handling, and lamination. For example, the barrier foils are thin and sensitive to mechanical damage. When used for lamination, the barrier foil technology also needs a sealant, which can result in parasitic permeation issues similar to those in glass lid encapsulation. Also, as the barrier foils can be exposed to mechanical deformation, which is not an issue in glass lid encapsulation, the sealant might be thicker than that used for glass lid encapsulation, leading to higher oxygen and water vapor permeation.

Today, devices can be fabricated on nearly any substrate and then finally directly encapsulated with a thin film, as described in Figure 1(d). While the TFE technology has the disadvantages of potentially damaging the device through direct deposition and limited processing conditions, it has the advantage of not allowing moisture and oxygen to penetrate from the edge. When glass or barrier foil is used as an encapsulation film, adhesive is inevitably used, which can cause parasitic effects and contamination, but as TFE does not require the use of adhesive, it can avoid such results. Above all, TFE is the most promising encapsulation technology for displays because it is flexible and easy to apply to any device.

For flexible, rollable, and foldable displays, the required bending radii are 30R, 10R and 1R, respectively, as shown in Figure 1(e). Figure 2 and Table 1 summarize the recent progress in TFE towards highly reliable flexible OLEDs. As shown, TFE is mechanically robust without losing its barrier properties. The detailed features of TFE barriers are discussed in Chapter 3.

2.2. Measurements of barrier properties

As organic devices require a higher barrier performance than other devices, it is important to measure the WVTR when designing an encapsulation barrier. Various methods of evaluating the performance of barriers have been developed, including using a chemical reagent, direct
detection, electrical or optical change, weighing, mass spectrometry, and pressure measurements. For all measurements, controlling the permeation condition is most important to obtain an accurate WVTR or oxygen transmission rate (OTR). Depending on the measurement method, the test environments can be quite different. This section provides a brief description of the currently known technologies.

2.2.1. Gravimetric cup

The use of a gravimetric cup, known as ASTM D1653 or ASTM E96/E96M, is the most effective method of measuring the WVTR of a foil. The impermeable cup is filled with a desiccant or water and then covered with a foil to measure its inlet. When using a desiccant or water, the penetration into the cup or the permeation outside the cup is measured based on the mass change after a certain time interval. To close the entrance, it is usually sealed with materials like wax or asphalt. The WVTR can be calculated based on this mass change, and measured at up to 0.1 g/m²/day [60].

2.2.2. Coulometric devices

With a coulometric device, an inert carrier gas transports the permeated water to a sensor, and the sensor evaluates its value. The sensor uses phosphorus pentoxide ($P_4O_{10}$), known to be a strong desiccant, as the electrolyte between the two adjacent electrodes. The transported water is electrolyzed differently from $P_4O_{10}$, so current can flow between the electrodes, and the WVTR value is calculated based on this current. This method is also called 'MOCON test' because it was developed and commercialized by MOCON, Inc. Their AQUA-TRAN Model 3 is known to be able to measure up to $5 \times 10^{-5}$ g/m²/day.

2.2.3. Mass spectrometer

Using a mass spectrometer, it is possible to measure not only moisture but also all kinds of gas change. In the equipment, two gas cells are separated by a barrier for measurement. One cell consists of a high-pressure permeation gas, and the remaining cell is connected to a mass spectrometer in an ultra-high vacuum status. The amount of gas that permeates through the barrier is measured by the mass spectrometer [61]. There is a record of $1.9 \times 10^{-7}$ g/m²/day [62]. The mass spectrometer has the advantage of being able to measure various gases, but it has a disadvantage in that the equipment is complicated and difficult to use.

2.2.4. Direct pressure measurement

Direct pressure measurement is very similar to the mass spectrometric test. The vacuum vessel is divided into two chambers by a barrier film. Unlike the mass spectrometric test, this method is suitable for time lag diffusion through the barrier film because the time-dependent pressure increase is measured during the test. The direct pressure device is available as Deltaperm from Technolox Ltd., with a measurement limit of $10^{-4}$ g/m²/day. It has the advantage of measuring the outgassing from a barrier film, but it is difficult to use with a thin barrier film because the pressure may lead to the deformation of the barrier film.

2.2.5. Radioactive isotopes

As tritiated water is generally used for testing most radioactive isotopes, it is also called 'tritium test.' During the tritium test, there are two gas cells separated by a barrier. One cell has 100% relative humidity including tritiated water (HTO-enriched water) while the detection cell purges the permeated HTO with a nonreactive

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Table 1. Summary of the properties of various flexible TFEs.

| Structure | WVTR (w/o bending) | Bending radius | Strain | Bending cycle | WVTR (w/ bending) | Remark |
|-----------|--------------------|----------------|--------|---------------|------------------|--------|
| 1 MgO//S–H nanocomposite | $4.9 \times 10^{-5}$ | N/A | N/A | N/A | N/A | [42] |
| 2 MgO//S–H nanocomposite | $4.33 \times 10^{-6}$ | N/A | N/A | N/A | N/A | [43] |
| 3 Al₂O₃//S–H nanocomposite | $1.26 \times 10^{-5}$ | 30 mm | 0.26% | 100 | $1.76 \times 10^{-5}$ | [44] |
| 4 Al₂O₃//silamer | $3.11 \times 10^{-6}$ | 10 mm | 0.75% | 100 | $7.65 \times 10^{-4}$ | [45] |
| 5 Al₂O₃/graphene | $2.62 \times 10^{-4}$ | 7 mm | 0.89% | 1000 | $7.65 \times 10^{-4}$ | [46] |
| 6 Al₂O₃//PP | $3.1 \times 10^{-4}$ | 5 mm | 1.16% | 10,000 | $3.65 \times 10^{-4}$ | [47] |
| 7 Si₃N₄//PMMA | $9.2 \times 10^{-5}$ | 5 mm | 0.89% | 500 | $1.11 \times 10^{-4}$ | [48] |
| 8 Al₂O₃//SAOLs | $3.47 \times 10^{-4}$ | 10 mm | N/A | 1000 | $1.0 \times 10^{-4}$ | [49] |
| 9 SiO₂//Al₂O₃//resin | $3.79 \times 10^{-5}$ | 10 mm | 0.75% | 1000 | $1.64 \times 10^{-3}$ | [50] |
| 10 MgO//ZnO//Al₂O₃ | $1.58 \times 10^{-5}$ | N/A | N/A | N/A | N/A | [51] |
| 11 MgO//ZnO//Al₂O₃//Ag | $9.2 \times 10^{-5}$ | 30 mm | 0.41% | 1000 | $4.46 \times 10^{-5}$ | [52] |
| 12 Al₂O₃//S–H nanocomposite//Ag | $8.70 \times 10^{-6}$ | 10 mm | 0.63% | 1000 | $8.2 \times 10^{-5}$ | [53] |
| 13 Al₂O₃//S–H nanocomposite//hybrimer | $4.4 \times 10^{-5}$ | 30 mm | 0.21% | 1000 | $4.05 \times 10^{-5}$ | [55] |
| 14 Al₂O₃//ZnO//S–H nanocomposite | $1.91 \times 10^{-5}$ | 10 mm | 0.63% | 1000 | $7.78 \times 10^{-5}$ | [56] |
| 15 Al₂O₃//ZnO//S–H nanocomposite | $7.87 \times 10^{-6}$ | 5 mm | 1.25% | N/A | $4.39 \times 10^{-4}$ | [57] |
| 16 ZnO//Al₂O₃//MgO//S–H nanocomposite | $2.44 \times 10^{-6}$ | 10 mm | 0.63% | 100 | $7.7 \times 10^{-4}$ | [58] |
| 17 ZnO//Al₂O₃//MgO//silamer | $5.94 \times 10^{-5}$ | 3 mm | N/A | 1000 | N/A | [59] |
and nonradioactive carrier gas that transports it to the detector. Theoretically, it can measure up to $2 \times 10^{-7}$ g/m²/day, but atomic tritium also permeates through the barrier due to the proton exchange reaction, which can result in overvaluation [63,64].

### 2.2.6. Organic devices

As an organic device is itself a good sensor of water and oxygen, one possible method of measuring the WVTR is using the organic device itself. This is attractive because it takes into account all the factors affecting the device. This method and the research on it, however, have not been well publicized, and it is not easy to calculate the exact transmissivity using such method [65]. In addition, the method has a disadvantage in that it is difficult to distinguish whether the phenomenon is due to deterioration from external permeation or deterioration due to light emission.

### 2.2.7. Calcium test

The calcium corrosion test, also known as the Ca test, is the most widely used method for measuring the simplest and the highest WVTR. Calcium is deposited in the form of a pad, and then shielded by a barrier film to examine the oxidation reaction. Although calcium is easily oxidized by oxygen as well as moisture, oxidation by moisture is considered much more dominant and effective than oxygen [66]. A method of calculating the WVTR using the calcium oxidation phenomena over time has also been studied. It is assumed that all the water passing through the barrier film will cause an oxidation reaction with calcium. Measurement can be done using the optical or electrical characteristics of the calcium pad.

The optical calcium test calculates the WVTR using the principle that opaque calcium becomes transparent with oxidation. The transmittance of light passing through the calcium film is measured based on the Lambert–Beer law, as follows:

$$I = I_0 e^{-\alpha h},$$

where $I$ is the light intensity passing through the layer, $I_0$ is the light intensity reaching the layer, $\alpha$ is the absorption coefficient of the layer material, and $h$ is the homogeneous height of the calcium layer.

Nisato, in 2001, calculated the WVTR using the transmitted light, based on the height of the remaining calcium. Another optical method that excludes the cavity between calcium and the barrier was reported. In this approach, the reaction takes place in an inhomogeneous form, where the calcium film is oxidized due to the positions of the defects in the barrier. At this time, the WVTR is calculated based on the rate of growth of a corroded calcium circle, but this is used more for defect imaging [67].

Figure 3 shows a schematic of the calcium test using the electrical characteristics. Calcium oxide (CaO, Ca(OH)$_2$) has an insulator property while a typical calcium thin film has about $4 \times 10^{-6}$ Ω·cm resistivity. A type of electrical calcium test that exploited this property was studied by Pätzold [68]. When two electrodes are connected to calcium, the resistance increases with time depending on the progress of the oxidation reaction. When the WVTR is calculated using this method, the following formula is used [69,70]:

$$\text{WVTR} = -n \frac{M(H_2O)}{M(Ca)} \delta \rho \frac{l}{b} \frac{d(1/R)}{dt},$$

where $n$ is the number of water molecules per calcium atom, $M$ is the molar mass, $\delta$ is the calcium density, $\rho$ is the calcium resistivity, $l$ is the length of the calcium layer, $b$ is the width of the calcium layer, $R$ is the resistance of the calcium layer, and $t$ is the time.

### 3. Advanced flexible thin-film encapsulation technologies

#### 3.1. Multilayer thin-film encapsulation technology (multibarrier)

Single-layer TFE has been attractive because it has a simple fabrication process compared to other encapsulation methods. It has limited performance, however, because of the growth of nodular defects and the fact that the defect density increases with the thickness. These defects act as pathways for water vapor and oxygen to permeate through the encapsulation barrier, which deteriorates the WVTR. In addition, other factors should be considered...
for the encapsulation of OLEDs such as moisture stability, thermal stability, mechanical stability, ultraviolet (UV) stability, and the optical properties. As organic materials are sensitive, their continuous exposure to UV and to temperatures above 100°C can result in their degradation over time. The optical properties of the encapsulation directly affect the light transmitted from the OLEDs through the encapsulation.

Multilayer technologies address the aforementioned issues by inserting an interlayer. This can improve the WVTR by increasing the lag time. The flexibility can also be improved by the newly inserted layer. A nanolaminate barrier, which is entirely composed of inorganic nano-scale-thickness layers, has been reported. This type of barrier has the advantage of being easy to fabricate because it can be prepared using the same equipment. The lag time of the nanolaminate barrier is higher than that of a single-layer TFE with the same thickness because several inorganic layers are used. Although the nanolaminate barrier can improve the WVTR, its brittleness makes flexibility a tough challenge.

Another type of organic–inorganic hybrid polymer layer was studied by the Fraunhofer POLO group, using lacquer [65]. The polymer layer has a very flat surface because it is deposited in a liquid state. This method is limited, however, because it is impossible to use in the vacuum process and because a large amount of water is generated. VITEX Technologies Inc. developed a multilayer TFE called ‘BARIX barrier’ based on this technology [71]. The BARIX barrier is deposited on the OLED substrate by evaporating an acrylate precursor, followed by UV curing. Sputtered Al2O3 or SiO2 is used as the inorganic material. The resulting organic–inorganic multibarrier improved the WVTR and increased the flexibility as the organic material provides both flexibility and a more complicated diffusion path.

For these reasons, multibarriers based on this form have been continuously studied. The inorganic layers in the multibarrier were deposited using physical vapor deposition (PVD), CVD, or ALD. The PVD films, however, exhibited relatively low film quality, with many defects and pinholes in the film, and the CVD films were difficult to directly apply to the OLEDs because of plasma damage and high process temperature. In contrast, ALD enables the thin film to be stably deposited at a low temperature in a vacuum chamber, and to be almost defect-free. ALD studies have been actively employed of late to improve the performance of impermeable multibarriers.

Han et al. and Kim et al. investigated the differences between PVD and ALD using magnesium oxide (MgO) [42,43]. 100-nm-thick PVD-MgO was deposited using an electron beam (E-beam) evaporator at 2 × 10−6 Torr and 60°C while 40-nm-thick ALD-MgO was deposited using bis(ethyl cyclopentadienyl)magnesium (Mg(CpEt)2) and H2O at 70°C. As expected, ALD-MgO (7.13 × 10−2 g/m²/day) exhibited much less WVTR than PVD-MgO (0.46 g/m²/day) despite being thinner. To satisfy the WVTR requirement for OLEDs, the number of inorganic/organic dyads was optimized at 6 dyads for PVD-MgO (Figure 4(a,b)) and at 4.5 dyads for ALD-MgO (Figure 4(d,e)). With these PVD-MgO and ALD-MgO multibarriers, the lifetime of thin-film-encapsulated OLEDs was found to be comparable to that of glass-lid-encapsulated OLEDs (Figure 4(c,f)).

The multibarrier based on MgO, however, still has limited flexibility because the deposited MgO layer is crystalline [72]. The grain boundaries in the crystalline structure expand and provide a diffusion path for water vapor and oxygen with applied bending stress. On the other hand, the ALD-deposited aluminum oxide (ALD-Al2O3) film can be simply fabricated, and almost defect-free, under a relatively low temperature and with an amorphous structure. As the amorphous-structured ALD-Al2O3 film has too few grain boundaries to act as a defect channel, ALD-Al2O3 is suitable as a flexible TFE barrier.

Using this approach, Han et al. and Kwon et al. tried to fabricate flexible multibarriers based on ALD-Al2O3 [44,45]. 30- and 60-nm-thick ALD-Al2O3 was deposited using trimethylaluminum (TMA) and H2O at 70°C. As the WVTR of the single ALD-Al2O3 layer is insufficient for OLEDs (7.94 × 10−4 g/m²/day for 30 nm and 8.06 × 10−5 g/m²/day for 60 nm), a 190-nm-thick S–H nanocomposite (hybrimer) layer and a 2-μm-thick silamer layer were used as the organic layers of the multibarrier, respectively. A 3.5-dyad multibarrier is suitable for a 30-nm-thick ALD-Al2O3 layer (Figure 4(g)), and a 3-dyad multibarrier is suitable for a 60-nm-thick ALD-Al2O3 layer. The WVTR was measured after 100 iterations of the bending test. While the single ALD-Al2O3 layer lost its barrier properties (Figure 4(j)), the WVTR of each multibarrier retained their properties (Figure 4(h,k)). The encapsulated OLEDs were as stable as the glass-lid-encapsulated OLEDs (Figure 4(i,l)).

3.2. Neutral-axis engineering for flexible TFEs

So far, this review has introduced studies about permeation barrier properties and the simple flexibility of inorganic/organic-based multibarriers. Although a low WVTR is the main purpose of the TFE technology, optimizing the bending characteristics is also important for achieving flexible TFEs. When OLEDs are prepared on flexible substrates like polyethylene terephthalate (PET), and encapsulated with flexible multibarriers, some components of the multibarrier are still vulnerable.
to mechanical strain. In particular, the flexibility of the entire device is limited by the physical properties of the inorganic materials, including the tensile strength and fracture toughness, despite their nano-scale thickness. To eliminate the restrictions of the materials, a composite beam theory was introduced for analyzing nano-scale multilayer systems, and has been getting a large amount of attention [73]. With the development of the composite beam theory, it is possible to design flexible OLEDs while considering their structural aspects, such as their bending stress distribution.

Han et al. particularly aimed to enhance the mechanical robustness of flexible OLEDs encapsulated with a multibarrier to resist repetitive bending stress [54]. Although the multibarriers achieved better WVTR values by increasing the number of dyads, their flexibility became worse because of their thickness. To establish an NA position with almost zero bending stress, a hybrimer
was utilized as a buffer layer. The mechanical stress in the 3.5-dyad multibarrier (Al₂O₃/S–H nanocomposite) produced by the repetitive bending stress was optimized using a theoretical prediction of NA behavior using the finite-element method (FEM) with ANSYS 16.0 (Figure 5(a)). The thickness of the buffer layer needed to locate NA at around the center of the multibarrier was calculated considering Young’s modulus. When the NA was located near the center of the multibarrier, the bending stress was effectively reduced. The multibarrier with the buffer layer maintained its WVTR (8.2 × 10⁻⁵ g/m²/day) after 1000 iterations of 0.63% bending strain (10 mm bending radius). The WVTR before bending was 4.4 × 10⁻⁵ g/m²/day (Figure 5(b)).

As the bending stress is linearly proportional to the distance from the NA, locating the encapsulated flexible OLEDs near the region adjacent to the NA can suppress the dark spots caused by the cracks in the TFE. By using NA engineering (Figure 5(c)), the flexible OLEDs were successfully encapsulated and continued to operate stably after the bending test. The active area of the encapsulated flexible OLEDs with a buffer layer maintained its initial state for 30 days even after the bending test. The encapsulated flexible OLEDs without a buffer layer suffered device failure after the bending test (Figure 5(d)). While the insertion of the thickness-optimized buffer layer does make the TFE process more complex, due to its additional steps, it can be employed to design an entire flexible display system because it takes into account all the subsequent panel processes, such as those using a polarizer, a touch screen panel, and a module.

### 3.3. Metal-containing flexible TFE

As a metal layer has high ductility and thermal conductivity, inserting a metal film can offer some flexibility to the TFE, and can improve the heat dissipation. A metal layer, however, is also electrically conductive and highly opaque. To solve this problem, the concept of a dielectric–metal–dielectric (DMD) structure, where a semi-transparent metal film is embedded between dielectric layers, was introduced [74–77]. By adjusting the thickness of the dielectric layer, high transmittance in the visible region can be obtained by using an anti-reflection coating. The thickness of the inner metal layer is another critical factor when applying the DMD structure to a flexible TFE, because a parasitic electrical path can be generated between the TFE and the electrode. To qualify as a transparent and flexible TFE, the thickness of each of the inner layers should be optimized.

Based on the aforementioned technique, Kwon et al. tried to develop a metal-containing flexible TFE using a DMD structure with a 15-nm-thick Ag thin film inserted between Al₂O₃ films. The Ag thin film was selected because of its high thermal conductivity and good flexibility (Figure 6(a)) [53]. The flexible TFE with
Figure 6. (a) Schematic of a DMD-based TFE barrier. (b) Results of the Ca test for the TFE samples before and after the bending tests. (c) Optical transmittance (simulation and experiment) of the TFE samples. (d) Schematic of a MAZO-based TFE barrier. (e) Results of the Ca test for the TFE samples under damp conditions. (a–c) Reproduced with permission [53]. Copyright 2017, American Chemical Society. (d–e) Reproduced with permission [52]. Copyright 2018, American Chemical Society.

The thickness-optimized metal demonstrated a WVTR of $8.70 \times 10^{-6}$ g/m²/day, and good mechanical reliability at a 0.41% bending strain (Figure 6(b)) as well as more than 60% transmittance (Figure 6(c)). As the multibarrier was composed of inorganic/organic layers with low thermal conductivity, heat dissipation from the TFE was not expected. The metal-containing flexible TFE, however, facilitated heat dissipation from the OLEDs.

A Mg- and Al-doped zinc oxide (MAZO) layer deposited at a low temperature was reported to improve the moisture resistance and the electrical and optical properties of a pure ZnO film (Figure 6(d)) [52]. The periodic insertions of MgO and Al₂O₃ dopants in the ZnO film caused the doped ZnO to become blue-shifted and electrically conductive. Using a MAZO/Ag/MAZO multilayer, it achieved $5.60 \Omega/sq$ sheet resistance (which could make it work as an electrode), an average transmittance of 89.72% in the visible range, and a WVTR of $10^{-5}$ g/m²/day (Figure 6(e)). Although the current metal-containing flexible TFE did not show a significant improvement in OLED lifetime, its high potential suggested a new direction for improving the flexibility and lifetime of flexible OLEDs.

### 3.4. Flexible TFE with a crack arrester included

In the previous sections, techniques that modified the TFE’s structural form to increase its flexibility by adding a layer that was not related to the barrier properties were introduced. As water vapor and oxygen permeation occurs through the cracks in the TFE, it is important to understand crack propagation in the inner inorganic materials in relation to bending stress, to ensure mechanically robust flexible TFEs. An approach involving the addition of a buffer layer to flexible OLEDs was previously introduced, which increased the flexibility with NA positioning, but it required extra processes as well as additional time and resources. A simple way of improving the mechanical properties and WVTR of internal inorganic layers is required for a flexible TFE structure.

To fabricate a highly impermeable inorganic-based barrier, ALD nanolaminate structures that alternately stack ultra-thin sublayers have been proposed of late. This configuration suppresses the formation of both microscopic voids and nanocrystals, which are statistical defects that open permeation paths in the barrier structure. The ALD process allows the deposition of few-nanometers-thick, uniform ultra-thin layers with thickness control at the angstrom level. Starting...
with Al₂O₃/SiO₂ bilayers, various nanolaminate barriers, including Al₂O₃/ZrO₂, Al₂O₃/ZnO, Al₂O₃/HfO₂, and Al₂O₃/TiO₂, have been proposed [64,78–80]. The proposed nanolaminate structures have shown improved barrier performance compared to a single layer. As nanolaminate structures are composed of various inorganic materials, their mechanical properties can also be enhanced by utilizing Griffith’s crack model.

Griffith’s crack model, proposed by Griffith, is a theory of brittle fracture that highlights bending stress phenomena [81]. The model explains that the fracture strength of the material becomes lower due to stress focusing, which originates in the microscopic flaws. As a result, fracture strength is strongly dependent on cracks, especially on their edge tip size. This approach provides a clear explanation of an ambiguous paradox: the difference between the stress needed to fracture and the theoretical value [82]. Based on this observation, highly reliable flexible OLEDs can be designed by interpreting the mechanical behavior of the materials under bending stress, and its effects.

A hybrid nano-stratified moisture barrier, which replaced a single inorganic layer in a multibarrier with a nanolaminate structure with the same thickness, was proposed by Jeong et al. [55,56,59]. As shown in Figure 7(a,b), a dyad in the nano-stratified barrier is composed of five pairs of Al₂O₃/ZnO nano-stratified layers and an organic layer. To deposit the nano-stratified layer, TMA...
and H2O were used for the ALD-Al2O3 and diethylzinc (DEZ), and H2O was used for the ALD-ZnO at 70°C. In this paper, the concept of a defect suppression mechanism caused by Zn etching with TMA is introduced, and is shown in Figure 7(c). Following the Griffith crack model, as the crack arrester acts like a microcrack in the microcrack toughening model (Figure 7(d)), the bending stress of the nano-stratified barrier is released. The bending stress concentration is reduced by the enlarging crack edge. The propagation of the crack is graphically shown in Figure 7(e).

The barrier properties were verified by the Ca test and transmission electron microscopy (TEM) analysis, as shown in Figure 7(f–h). The WVTR of the nano-stratified barrier was 7.87 × 10^{-6} g/m²/day, which increased to 7.78 × 10^{-5} g/m²/day under 0.63% strain bending stress (1000 iterations with a 10 mm bending radius). Meanwhile, the Al2O3-based multibarrier lost its barrier property (1.77 × 10^{-5} g/m²/day) during the bending test (1.35 × 10^{-2} g/m²/day). As the nano-stratified layer has a more complicated diffusion path than a single inorganic layer, the WVTR before the bending test was also superior to that of the Al2O3-based multibarrier. Encapsulated flexible OLEDs were successfully demonstrated before and after the bending test, and the approach boosted the reliability, as shown in Figure 7(i–k). The luminance of the flexible OLEDs remained at 52.37% after 2000 h even when they were subjected to bending tests, with results comparable to those of glass lid encapsulation (55.96%).

Kwon et al. tried to optimize the more complex nanolaminate structures through structural and material design, to fabricate highly impermeable and flexible TFEs using ALD-ZnO, ALD-Al2O3, and ALD-MgO (Figure 7(l)) [57]. The ALD-Al2O3 sublayers produced a chemical reaction at the respective interfaces with the ALD-ZnO and ALD-MgO sublayers. The resulting ZnO/Al2O3/MgO (ZAM) nanolaminate demonstrated excellent gas barrier properties through material design, which confirmed that the WVTR changes depended on the total ZAM thickness as well as the thickness of each constituent sublayer. As a result, the ZAM film achieved a WVTR of 10^{-5} g/m²/day with 1-nm-thick sublayers, and at a total thickness of around 50 nm. A 1.5-dyad TFE with a ZAM/organic layer/ZAM structure was fabricated, which resulted in an extremely low WVTR of 2.04 × 10^{-6} g/m²/day (Figure 7(m)) and a mechanical reliability level that endured close to 1% tensile strain (Figure 7(n)).

In summary, NA engineering was less helpful to WVTR because the materials suitable for the buffer layer usually have bad barrier properties, although they are very helpful for flexibility. An additional process that is not related to the barrier properties is highly needed for this technique, to make it applicable to flexible displays and all their components. As the metal layers are ductile and have better properties, the metal-containing TFEs can benefit both the WVTR and the flexibility. Introducing a crack arrester is very helpful to the WVTR because its complicated diffusion path and increased flexibility can prevent stress concentration. In addition, this method does not require additional processes and can be used for various applications, such as for transparent, wearable, and washable TFEs, by utilizing the chemical reaction between its layers. Ultimately, given the various pros and cons of the method, a combination of various techniques is likely required to optimize highly reliable flexible OLEDs that are suitable for rollable and foldable displays.

4. Conclusion

As the demand for flexible, rollable, and foldable displays continues to grow, realizing highly reliable and flexible organic light-emitting diodes (OLEDs) still requires further advances. Thin-film encapsulation (TFE), in particular, is considered a crucial core technology because it is concerned with both reliability and flexibility. As the TFE technology advances from brittle glass lid encapsulation, the primary focus is on improving the barrier performance by increasing the number of pairs of organic/inorganic layers or increasing the thickness of each layer.

With the movement from flexible and rollable displays to foldable displays, however, the required flexibility also greatly increases, such as from 30R to 1R. This review has discussed the technical issues of flexible TFEs as well as the efforts to realize reliable flexible OLEDs, and has highlighted various technical efforts to solve such issues. Considerable efforts are underway to maximize the potential advantages of TFEs and to compensate for their aforementioned limitations. The approaches that have been developed include the use of neutral-axis (NA) engineering, metal-based TFEs, and crack arresters. There is optimism that these technologies will help realize true next-generation flexible displays. Finally, rather than focusing on developing individual components for flexible displays, emphasis should be placed on integrating a unified flexible display system.

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