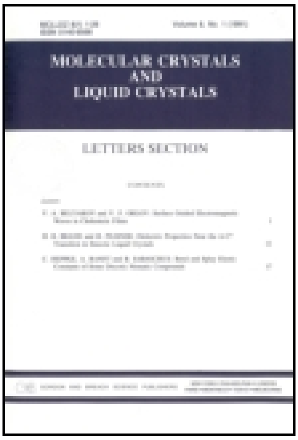

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Effects of Surface Roughness on Gas Barrier Property of Thin Film Passivation with Mg-Zn-F

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The thin film passivation is the key technology for the application of flexible organic light emitting diodes. We fabricated very effective gas barrier with Mg-Zn-F thin film using the RF magnetron sputter. In this study, we employed inorganic and organic buffer layers between Mg-Zn-F gas barrier and polyethylene naphthalate substrate to evaluate the effects of surface morphology. Organic layer had much lower surface roughness than that of inorganic layer. It is very effective to decrease water vapor transmission rate (WVTR). We showed that WVTR of gas barrier using organic layer and Mg-Zn-F film reached 4.5 × 10^{-4} g/(m^2·day) using calcium corrosion test.

Keywords Calcium corrosion test; gas barrier; organic light emitting diode; thin film passivation

Introduction

Organic light emitting diodes (OLEDs) have been highlighted as the next generation of flat-panel displays due to its advantages: thin, compact, light, low cost, high contrast, fast response, and wide viewing angle [1,2]. They are also expected to apply flexible display. Despite the potential advantages, the commercialization of OLEDs is hindered by their extreme sensitivity to water vapor and oxygen [3–5]. The limitation lies in their defects such as nano-scale pores and more seriously, by micron-scale pinhole defects [6]. Packaging methods for application of OLEDs are required with demonstrated water vapor transmission rates (WVTR) of $< 10^{-5}$ g/(m^2·day) at 25 °C and 40% relative humidity (RH) [7]. The encapsulation requirements are similar to other organic electronic applications, particularly those involving current injection.

In the previous report, we used MgF_2, which is a fluoride-group material with high optical transmittance, and Zn to manufacture a passivation thin film [8,9]. Compared with conventional materials (such as oxides or oxynitrides), fluoride materials have many advantages, such as low production cost, easy formation of both amorphous and multi-layer structures, and high optical transmittance. Also, when we evaluated the characteristics of the Mg-Zn-F thin films, the 200 nm single layer passivation of amorphous Mg-Zn-F on polyethylene naphthalate (PEN) had WVTR of 1.6 × 10^{-3} g/(m^2·day).

In this study, we report the improvement of barrier properties of Mg-Zn-F film and the effects of surface roughness of buffer layers. Inorganic thin film deposited by thermal

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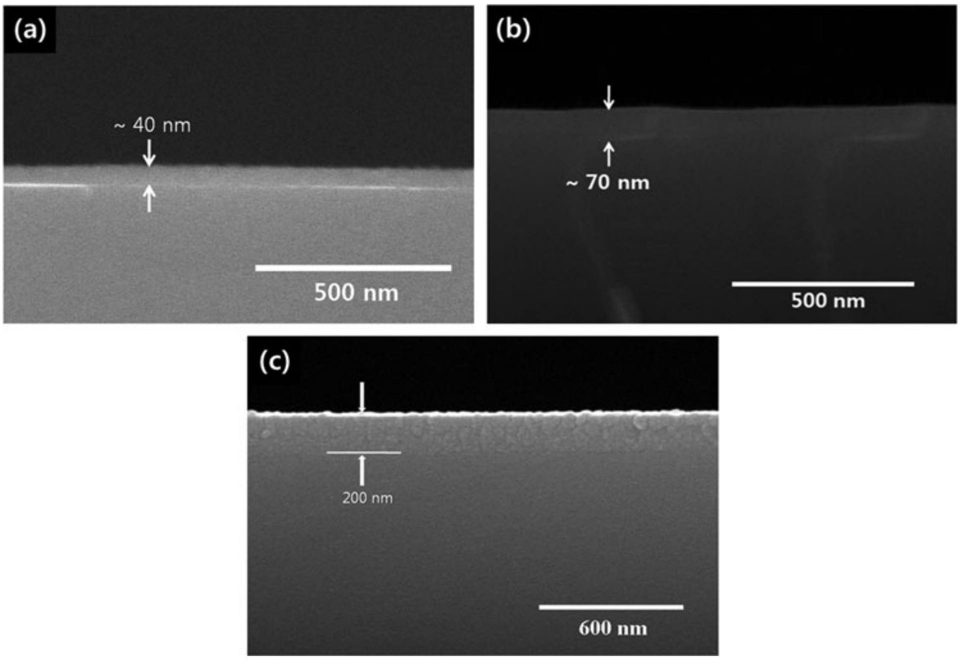

Figure 1. SEM image of (a) LiF, (b) organic layer, and (c) Mg-Zn-F film.

evaporator and organic thin film coated by spin-coating method were employed as buffer layer. Additionally, in order to measure WVTR under 1.0×10^{-3} g/(m^2·day), which is the limitation of Modern Controls (MOCON) system, we utilized calcium corrosion test (Ca test). Ca test is based on the corrosion of thin Ca films [10]. It involves the observation of the optical change as Ca converts to a transparent Ca salt by the water vapor permeation through the barrier film.

Experimental

Fabrication of Thin Film Passivation

The Mg-Zn-F thin film, which had an amorphous phase, was deposited at 1.5×10^{-2} Torr with 100 W forward sputtering power by the radio frequency (RF) magnetron sputter system. The target of 2-inch radius for sputter was made by using MgF_2 and Zn with weight ratio of 4 : 6. To produce a thin film that had the amorphous structure, we fused two materials by heating them to the temperatures above their melting points. A Q65 Teonex PEN film manufactured by Teijin Dupont (gas permeability 8.0×10^{-1} g/(m^2·day), thickness 200 μm) was used as the substrate.

As shown in Fig. 1, 40 nm film of lithium fluoride (LiF), which was deposited by thermal evaporator, was employed for inorganic multilayer thin film passivation. Moreover, organic layer for hybrid multilayer thin film passivation was spin-coated at 3,000 rpm for 1 min, and then dried. The thickness of organic layer was about 70 nm. Mg-Zn-F thin films of 200 nm thickness were sputtered on the LiF film and organic layer, and then WVTRs of multilayer passivation films were evaluated.

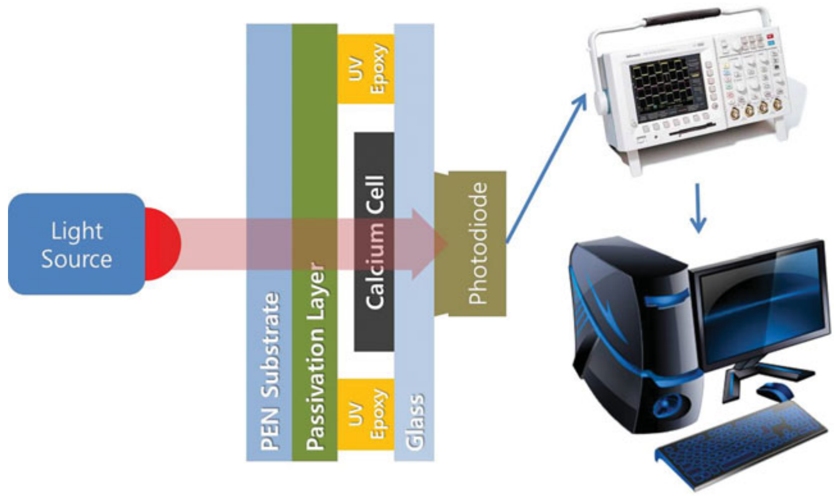

Figure 2. Schematic of Ca test System.

Measurements

The thicknesses of the passivation films were analyzed by field emission scanning electron microscopy (FE-SEM, S-4300, HITACHI). The contact mode-AFM (NanoScope III, Digital Instruments) was employed to measure surface roughnesses of passivation films. Images in this report were obtained at a scan rate of 3 Hz in the rage of 2 μm × 2 μm.

The WVTR was measured by using two kinds of equipment-the Permatran W 3/31 (Modern controls, Inc.) and the L80-5000L (PBI Dansensir) model at 38 °C, 90∼100% RH. The limitations of them were 1×10^{-3} g/(m^2·day). The Ca test was performed to measure WVTR below 1×10^{-3} g/(m^2·day).

The Ca degradation time was measured by using home-made measurement system, as shown in Fig. 2. Ca was deposited on the glass substrate to fabricate a Ca cell (18 × 18 mm^2, 300 nm) by using a thermal evaporator. Base vacuum pressure before the deposition was less than 10^{-5} Torr. The ultraviolet curable epoxy was dispensed on the edge of the glass, and was attached to a PEN coated with Mg-Zn-F passivation film. The variation of light through the Ca cell was measured in the ambient conditions by a photodiode mounted on an oscilloscope. The program for the measurement was home-designed and based on LabView graphic programming language. It provided a real time monitor of light variation.

Results and Discussion

In the previous report, we confirmed that 200 nm Mg-Zn-F film on PEN substrate by RF magnetron sputter had WVTR of 1.6×10^{-3} g/(m^2·day). Compared to other fabrication methods of barrier films, if RF magnetron sputtering was used, thin films could be formed in nano-defect or lattice-defect shape to structurally minimize moisture and oxygen permeation. Also, because of the amorphous structure formed by RF magnetron sputter, it had a merit in minimizing gas permeability between the lattices that could be generated from the crystals [11].

WVTRs of LiF film and organic layer were approximately 0.6 g/(m^2·day) and 0.3 g/(m^2·day), respectively. Compared to the result that WVTR of PEN substrate was

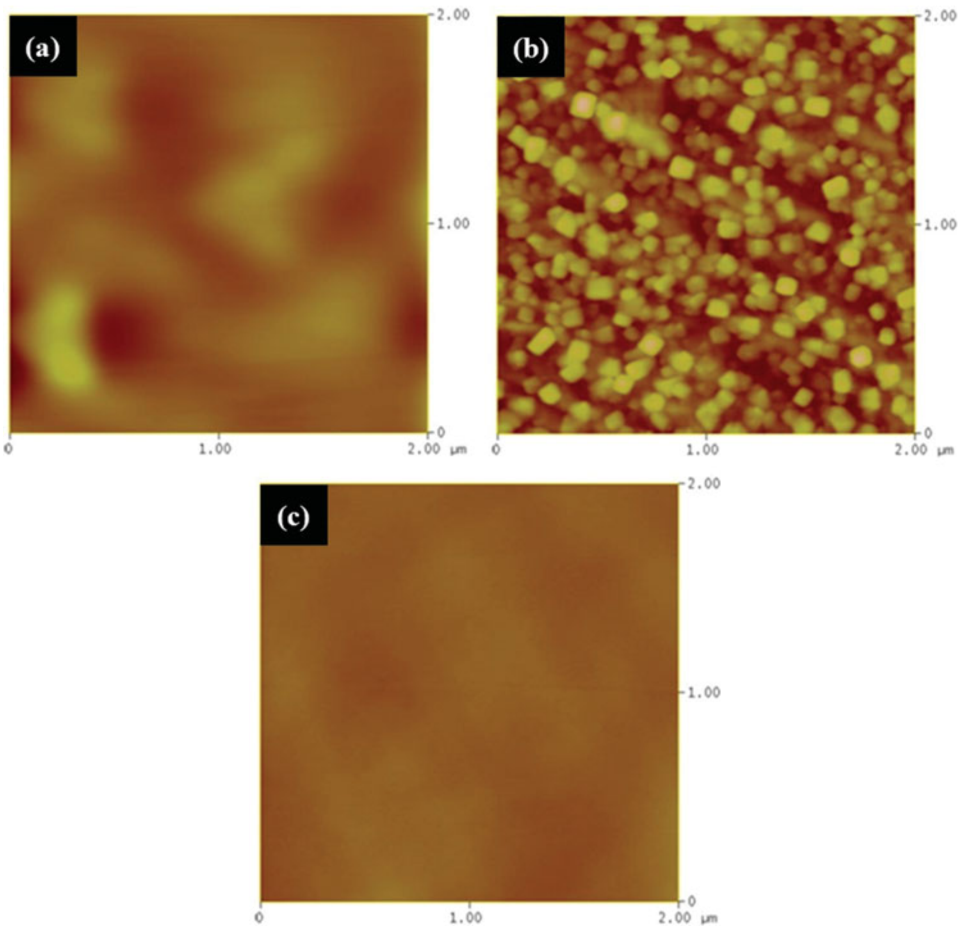

Figure 3. AFM image of (a) PEN substrate, (b) LiF film, and (c) organic layer.

0.8 g/(m^2·day), WVTRs of LiF film and organic layer on PEN substrates decreased slightly. However, these results were too high to protect OLEDs from water vapor.

WVTR of LiF/Mg-Zn-F on PEN substrate was about 0.165 g/(m^2·day). It showed that in spite of the increase from 200 nm to 240 nm in the total thickness of passivation film, LiF/Mg-Zn-F passivation could not block water vapor effectively. In comparison, WVTR of organic layer/Mg-Zn-F on PEN substrate reached the limitation of MOCON equipment.

The AFM analysis results of PEN substrate, LiF film, and organic layer were given in Fig. 3. Surface roughnesses of PEN substrate, LiF film, and organic layer on PEN substrate were approximately 2.452 nm, 5.559 nm, and 0.150 nm respectively. It was well known that the gas barrier properties of thin films depended on morphology of substrate [12,13]. The most important factor was the surface roughness. Affinito et al [14,15]. suggested that smoothing the surface by the pre-deposition of a layer of a thin film led to an improvement of the gas barrier property of the thin film passivation on polymer substrate. Similarly, according to the results, the roughness of organic layer was much lower than that of LiF film. It was believed that the good water vapor barrier properties originated from decreasing surface roughness.

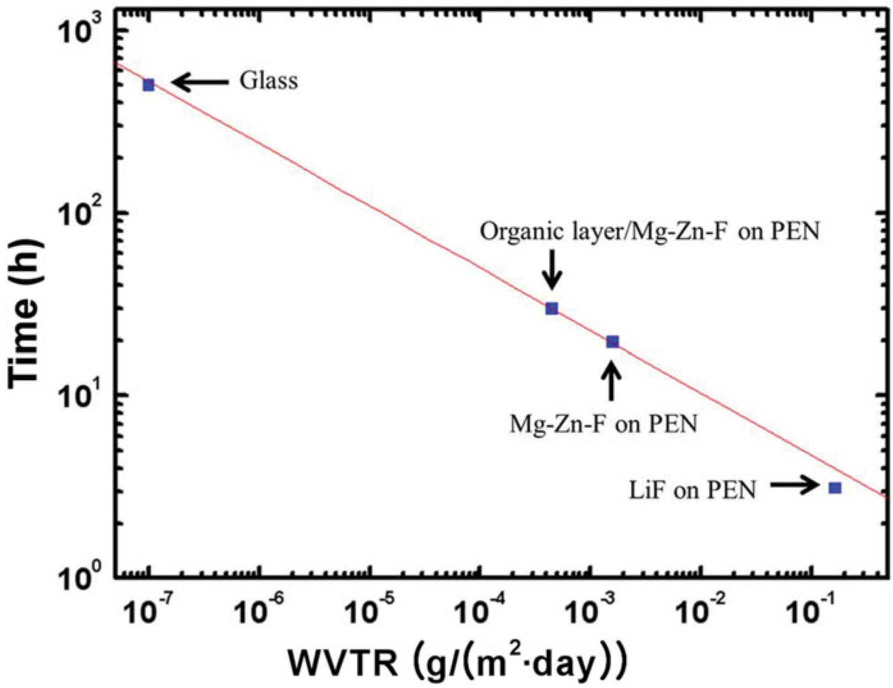

Figure 4. Ca test results of thin film passivations on PEN and glass cap.

Additionally, we already showed that organic layer could contribute to the enhancement of OLEDs performance [9]. During the fabrication of Mg-Zn-F film using RF magnetron sputter, OLEDs could be damaged by ion bombardment. As a result, some cracks appeared on the cathode after sputtering. However, OLEDs could be protected by organic layer.

We measured the time required for optical transmittance to be reduced by half through the Ca cell. The detection limitation by edge-sealing effects using a glass cap was 5.0×10^2 hours, as established by Ca test, which corresponded to the WVTR of approximately 10^{-7} g/(m^2·day) [16]. By utilizing the WVTR results of the MOCON test, we obtained the best-fitting line, as shown in Fig. 3. The WVTR results for PEN substrates coated with Mg-Zn-F and organic layer/Mg-Zn-F were measured approximately 1.6×10^{-3} g/(m^2·day) and 4.5×10^{-4} g/(m^2·day), respectively, as shown in Fig. 4.

Conclusions

We have fabricated thin film passivation of Mg-Zn-F on PEN substrate, LiF film, and Organic layer. Through the AFM analysis, gas barrier property of Mg-Zn-F thin film passivation was improved by decreasing the surface roughness of substrate. The Ca test was conducted to measure the WVTR below the limitation of MOCON test. Additionally, we showed that the WVTR of organic layer/Mg-Zn-F passivation film on PEN was approximately 4.5×10^{-4} g/(m^2·day) using the Ca test. We believe that the gas barrier properties can be further improved by stacking multi-layer. This work can be a next promising gas barrier for the OLEDs using polymer substrates.

Acknowledgment

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