Enhancement of PLED lifetime using thin film passivation with amorphous Mg-Zn-F

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Abstract

In this study, a new thin films passivation technique using Zn with high electronegativity and MgF_2, a fluorine material with better optical transmittance than the sealing film materials that have thus far been reported was proposed. Targets with various ratios of MgF_2 to Zn (5:5, 4:6 and 3:7) were fabricated to control the amount of Zn in the passivation films. The Mg-Zn-F films were deposited onto the substrates and Zn was located in the gap between the lattices of MgF_2 without chemical metathesis in the Mg-Zn-F films. The thickness and optical transmittance of the deposited passivation films were approximately 200 nm and 80%, respectively. It was confirmed via electron dispersive spectroscopy (EDS) analysis that the Zn content of the film that was sputtered using a 4:6 ratio target was 9.84 wt%. The Zn contents of the films made from the 5:5 and 3:7 ratio targets were 2.07 and 5.01 wt%, respectively. The water vapor transmission rate (WVTR) was determined to be 38℃, RH 90-100%. The WVTR of the Mg-Zn-F film that was deposited with a 4:6 ratio target nearly reached the limit of the equipment, 1×10^{-3} g/m^2·day. As the Zn portion increased, the packing density also increased, and it was found that the passivation films effectively prevented the permeation by either oxygen or water vapor. To measure the characteristics of gas barrier, the film was applied to the emitting device to evaluate their lifetime. The lifetime of the applied device with passivation was increased to 25 times that of the PLED device, which was non-passivated.

Keywords: PLED, passivation, fluoride, WVTR

1. Introduction

Organic light emitting diodes (OLEDs), which are among the next-generation displays, are currently the subject of vigorous research due to their advantages in weight, thickness, viewing angle, and operation voltage etc. They are classified, based on their molecular structure and weight, into small molecular OLEDs and polymer OLEDs (PLEDs). They have advantages in production cost and rate due to their simple production process compared with that of the existing display elements, although they show differences in the processes and methods of defining the device patterns [1-4]. They use organic materials, however, and the resulting lifetime deterioration by the atmospheric oxygen and water vapor poses a significant threat to their commercialization. The current passivation technologies for fabricated devices use metal and glass caps, which disturb the advantages of the OLED elements. New technologies are thus being developed to extend the OLEDs' lifetime by creating thin films, via vapor deposition, on the fabricated devices to prevent the infiltration of oxygen and water vapor [4-7]. The sealing film materials with low water vapor transmission rate (WVTR) that are currently being researched on include organics like polyimide, parylene, and acryl, and inorganics like as SiO_x and SiO_xN_y [8]. They are effective in reducing the WVTR when fabricated with a multilayer thin film structure. In the case of the laminated structure that requires high optical transmittance within the cathode range, however, it has low optical transmittance within the

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range of the visible rays and thus may result in the deteriorated emitting efficiency of the elements. Besides, it must be deposited with a thickness of at least 1 ㎛ to provide the extremely low water and oxygen transmission rate required for commercialization (i.e. 10^{-6} g/(m^2·day) and 10^{-3} g/(m^2·day), respectively). Such thickness can hardly be applied to flexible displays requiring 200 nm or thinner passivation films.

Therefore, in this study, new thin films were fabricated using Zn with high electronegativity and MgF_2, a fluorine material with better optical transmittance than the sealing film materials that have thus far been reported. The performance of the sealing film with a structure where Zn occupies the pores in MgF_2 was improved by forming a film with a sputter on a target mixed with Zn so that the packing density can be raised compared with that of the single inorganic film of MgF_2. Its structure, physical characteristics, packing density, WVTR, and optical transmittance were then evaluated to verify its feasibility as a new sealing technology applicable to flexible displays. We also applied the film to emitting unit elements to evaluate their lifetime.

2. Experimental Method

2.1 Fabrication of the thin Film passivation

In this study, targets for sputtering were fabricated by mixing MgF_2 and Zn after heating each of them above the melting point, to create thin films where MgF_2 and Zn are physically mixed in an amorphous structure. The targets were fabricated in various composition ratios by varying the mix ratio of MgF_2 and Zn to 3:7, 4:6 and 5:5, to observe the variation of the Zn ratio by the composition of the ratio of MgF_2 and Zn [9]. Every target had a 2 inch radius and 0.125 inch thickness. A thin film was deposited in the atmosphere of Ar while maintaining the distance of 11 cm from the target using an RF magnetron sputter. Then a 200 nm thick passivation layer was formed, as shown in table 1, with the thickness limit of the flexible and bendable display.

Table 1. Sputtering conditions used to fabricate the Mg-Zn-F passivation films

Parameter	Condition
Target-substrate distance	11 cm
Sputtering pressure	6.26×10^{-1} Pa
Gas flow rate	50 sccm
RF Power	100 W
Sputtering time	20 min

2.2 Fabrication of the OLED device

A PLED unit device consisting of glass/ITO/PEDOT:PSS/EML/LiF/Al was fabricated to evaluate the characteristics of the passivation thin films. The patterned ITO that was used as the anode was 150 nm thick and had a surface resistance of 12 ohm/square. For the hole injection layer, PEDOT:PSS (VP AI 4083, Baytron) was used to form approximately 40 nm thickness by spin-coating at 3000 rpm for 60 sec and annealing at 150℃ for 10 min. For the emissive layer, emitting copolymer with PL 528 nm (ADS233YE, American Dye Source, U.S.A) was formed by spin-coating at 3000 rpm for 100 seconds. Finally, Al of a 150 nm thick was deposited after depositing 0.5 nm thick LiF via thermal evaporation.

3. Experiment Results

3.1 Evaluation of the thin film passivation

The composition and bind of the fabricated thin films were analyzed by using the Al Kα X-ray with 1486.6 eV energy of X-ray photoelectron spectroscopy (XPS), and with a 90° take-off angle. The key spectra were analyzed with the energy gap of 20 eV for the binding energy from 0 eV to 1,100 eV. The lattice structure of MgF_2 varies greatly if chemical reactions or metatheses occur while deposition is being performed using an MgF_2-Zn target mixture. Thus, physically mixed thin films should be formed to fill the porosity of MgF_2. Therefore, XPS measurements were performed to confirm the physical state of the thin film.

Figure 1 shows the measurement results and confirms that the Mg, F and Zn components can be found inside the thin film formed by sputtering with the mixed target. To find out more about the state of each component in the mixed target, the components were compared with the binding energies of MgF_2 and Zn. When MgF_2 was formed from the binding of Mg and F, the characteristic binding energies of Mg and F were 51 eV and 684.9 eV, respectively. Similarly, the binding energies of the elements in the thin film, obtained via XPS measurements, were 50.5 eV for Mg and 685 eV for F. The characteristic binding energy of Zn is 1021.8 eV, and the value that was obtained was 1021 eV [9]. It was found from the measurement results that without chemical metathesis, Zn physically forms a thin film between the gaps of the MgF_2 film.

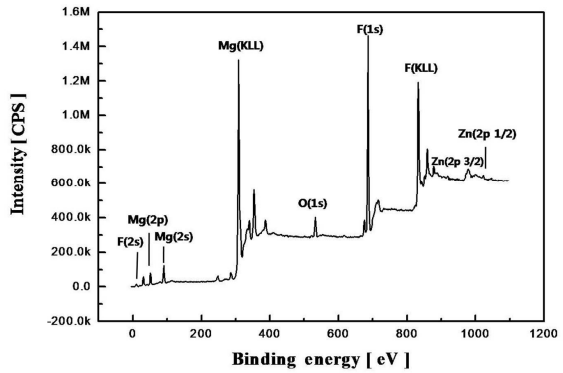

Fig. 1. XPS results for the Mg-Zn-F films deposited on a bare Si wafer.

The packing density, which shows the porosity of the thin films, is closely related to the refractive-index value of the deposited thin films, or the bulk state. Based on the assumption that the pores within the films are accessible to the molecules present in the ambient atmosphere, the refractive index of the pores in an ambient atmosphere is 1. Thus, the packing density can be calculated using the following equation:

$$n_f = p \cdot n_s + (1 - p) \cdot n_v \qquad (1)$$

where p, n_f, n_s, and n_v are the packing density, the index of the film, the index of the solid part of the film, and the index of the pores in the film (n_v=1), respectively [10]. As the refractive index increases, the packing density also increases. It thus effectively prevents the permeation of either oxygen or water vapor.

To confirm the increase in packing density, the refractive indices of the thin films were measured. The refractive index of the thermally deposited MgF_2 thin film was 1.38, and those of the sputtered amorphous MgF_2 and Mg-Zn-F thin films were 1.43 and 1.45, respectively. The packing density was calculated using equation (1), and it was found to be 54, 61 and 64% for the thermally deposited MgF_2, the sputtered amorphous MgF_2 and the Mg-Zn-F thin films, respectively. Therefore, the packing density of the amorphous MgF_2 film was superior to that of the crystalline MgF_2. Moreover, the injection of Zn into the MgF_2 film increased the packing density by 3%. The gas barrier characteristics improved due to the Zn atoms co-deposited in the thin film.

As shown in figure 2, the WVTR of the fabricated thin films was measured using the L80-5000 system (PBI Dansensor Inc., Denmark) and Permatran W 3/33 (Modern Controls, Inc., U.S.A). The insertion of Zn into the MgF_2 film increased the packing density of the thin film and enhanced its gas barrier characteristics. Thus, the 3:7 and 5:5 targets showed WVTR values of 1.1×10^{-2} g/(m^2·day) and 1.6×10^{-2} g/(m^2·day), respectively. The 4:6 target had the highest Zn portion and showed a remarkably low value compared to the WVTR for the other composition ratios. It nearly reached the measurement limit of the equipment [1×10^{-3} g/(m^2·day)].

The optical transmittance of the films was measured with a UV-visible spectrophotometer (UV-1601, Shimadzu, Japan) and it was found to be at least 80%, as shown in figure 3. The available value, which has no out-coupling problem, was considered.

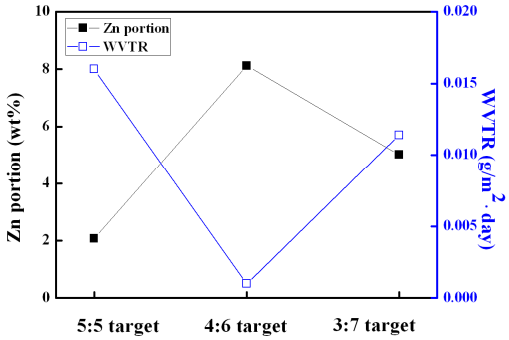

Fig. 2. WVTR and Zn portion data of the Mg-Zn-F thin films passivation deposited at 200 nm thickness according to various targets.

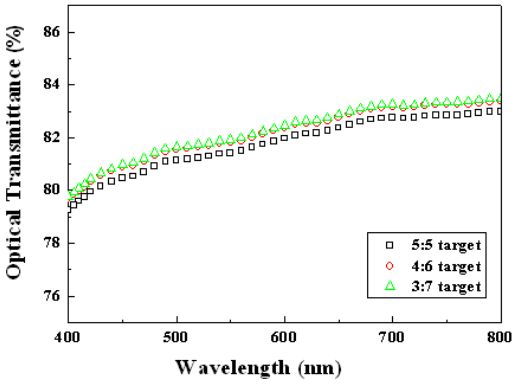

Fig. 3. Optical transmittances of thin film passivation deposited with various targets.

3.2 Evaluation of the PLED device lifetime

As shown in figure 4, a 200 nm thick passivation thin film was deposited on the fabricated PLED device. Then the lifetime of the emitting device was evaluated by defining the lifetime as half luminance.

To evaluate the characteristics of passivation, a PLED device with thin film passivation was fabricated. The turn-on voltage of the fabricated device was 5.5 V, its maximum luminance was about 8,200 cd/m^2 and its efficiency was 1.2 cd/A. Based on the results shown in figure 5, it was confirmed that lifetime of the non-passivation film device was 800 sec at half the maximum luminance, but that of the passivation film device was 20,000 sec under the same condition. Therefore, the passivation film device with the lowest WVTR can more effectively prevent moisture and oxygen and its lifetime can be 25 times that of the non-passivation device. As previously mentioned, the correlation between thin film passivation and the device lifetime was confirmed. The aforementioned result shows that the device has short lifetime expectancy, and it is considered that the device's thermal degradation can shorten the device's lifetime. In a future study, for the fabrication of a high-performance device, a specific evaluation scheme for thin film passivation will already be available.

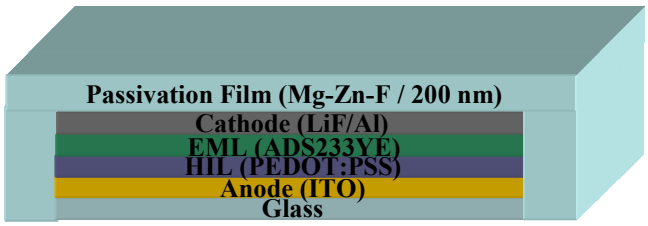

Fig. 4. Schematic diagram of the PLED element deposited with thin film passivation.

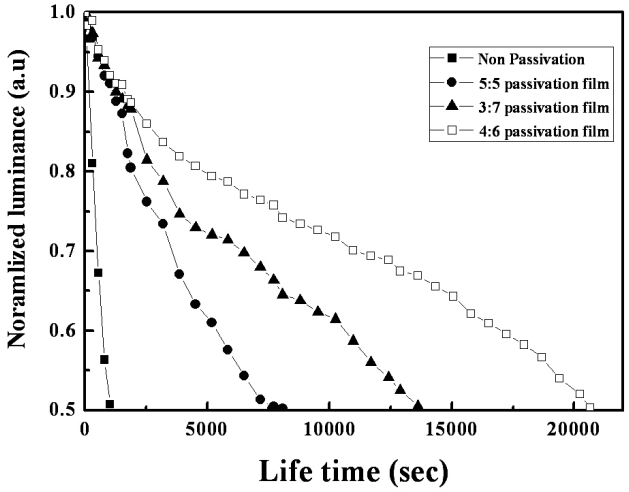

Fig. 5. Result of PLED lifetime by applying the thin film passivation

4. Conclusion

In this study, a novel thin film passivation for gas barrier was manufactured using inorganic Mg-Zn-F. The passivation film was formed designed to be 200 nm thick, which is the thickness of the flexible display. Among the fabricated thin films, MgF_2 and Zn with a 4:6 ratio showed below 10^{-3} g/(m^2·day) WVTR which is the measurement limit of the instrument. The optical transmittance of the fabricated thin films was 80%, which confirmed the possibility of their application to the display. When applied to PLED device, its lifetime was increased to 25 times that of the PLED device, which was non-passivated.

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