Thin-film Encapsulation of Organic Light-Emitting Diodes Using Single and Multilayer Structures of MgF_2, YF_3 and ZnS

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ABSTRACT—In this research, the lifetime of green organic light emitting diodes (OLEDs) is studied using four passivation layers. To encapsulate the OLEDs, MgF_2, YF_3, composed of alternating MgF_2/ZnS and YF_3/ZnS layers were grown by thermal vacuum deposition. Measurements show that the device lifetime is significantly improved by using YF_3 and ZnS as passivation layers. However, diodes encapsulated by MgF_2/ZnS and YF_3/ZnS nano-structures show a highly efficient gas diffusion barrier that results in a longer lifetime of the devices. The half lifetime of the green OLEDs reached 1200 minutes using YF_3/ZnS layers. The electroluminescence (EL) and current-voltage characteristics of the devices were also examined to compare the electrical and the emissivity properties of the devices before and after encapsulation. This simple and inexpensive thin-film encapsulation method would be potentially employed to capsulate top emitting OLEDs and flexible OLEDs due to their good performance and easy fabrication.

KEYWORDS: MgF_2, OLEDs, Thin-film encapsulation, YF_3, ZnS

I. INTRODUCTION

In 1990, a special interest was taken in organic emission pieces after the electroluminescence of organic thin films was observed [1]. Because of their advantages, in 1987, a team of Kodak worked on an organic device and produced a double-layer Organic Light Emitting Diode (OLED) with attractive luminance efficiency [2], [3]. After the first demonstration of an efficient OLED, this device was able to show its potential for displaying and lighting applications. OLED technology has a great potential for big flat panels and flexible displays. It is due to such technical traits of the device as thinness, light weight, low power consumption, fast switching, wide viewing angel, etc. [4]-[5]. Manufacturability and low cost have been considered as other advantages [6]. However, short operation lifetime limits the device potential for industrial applications. The device structure is very sensitive to oxygen and water vapor. These substances infiltrate into the organic structure of the device and make non-conducting dark spots on it. The dark spots reduce the efficiency and lifetime of OLED, which hinders large-scale OLED marketing [7], [8].

Therefore, doing encapsulation is important to improve the lifetime of OLED by blocking water vapor and ambient oxygen penetration. One of the most typical ways to capsulate OLEDs is to use metal and glass with UV-curable sealants, but that is not suitable for flexible OLEDs [9]. Another common way to capsulate OLEDs is to employ UV-cured epoxy seals as perimeter seals together with a strong desiccant inside the devices [10]. Desiccants are necessary to have a good moisture barrier, but they are opaque and block the emitting of light from the top of OLEDs [11], [12]. Hence, high-performance thin-film technology should be used for the encapsulation of OLEDs. This is a simple inexpensive technology that is suitable for flexible and top emitting OLEDs. Thin-film encapsulated devices are thin and light-weight

and have a lifetime comparable to that of glass-encapsulated devices [13].

In order to improve the lifetime of OLEDs, researchers have employed different inorganic materials such as Al_2O_3, SiO_2, and polymer (polyacrylic) or organic-inorganic hybrid composites for encapsulation [14]-[17]. Moreover, different methods such as physical and chemical vapor deposition, atomic layer deposition, and sputtering have been proposed [18]-[20]. Visible transmission, thermal effect, and number of layers used as passivation layers are some other parameters investigated by researchers [21]-[24].

In this paper, we report a low-cost and high-performance encapsulation method for OLED devices by using a simple thin-film technology and estimate the lifetime of diodes capsulated by different materials. The effects of transparent yttrium fluoride (YF_3), magnesium fluoride (MgF_2), and zinc sulfide (ZnS) as a protection layer were studied on metal electrodes to improve the lifetime of OLEDs. Green OLEDs with ITO/PEDOT: PSS/TPD/Alq_3/LiF/Al structures were fabricated. MgF_2 and YF_3, composed of alternating MgF_2/ZnS or YF_3/ZnS were also used as protection layers. Both fabrication and encapsulation lamination were completed in a thermal evaporation system. Then, the current voltage characteristics of the devices and their lifetime were determined.

II. Experimental Procedures

The experimental procedures consist of two parts: fabrication and encapsulation of OLED's. Poly-3,4-ethyl-enedioxy-thiophene/ polystyrene-sulphonate (PEDOT:PSS), N, N0-bis(3-methylphenyl)-N, N0-diphenylbenzidine (TPD), tris(8-hydroxyquinoline) aluminum (Alq_3) and lithium fluoride (LiF) with 99.9% purity were purchased from Sigma Aldrich. ITO glass with a sheet resistance of 14Ω/sq was also used. A three-millimeter-wide ITO strip line was made by etching with diluted hydrochloric acid (HCl) for 15-20 minutes at room temperature. Then, the patterned ITO had to be cleaned. As a matter of fact, since cleaning is typically of great importance in such a process, the glass was cleaned sequentially in a detergent solution of propanol, acetone, and de-ionized water by ultra-sonication for 15 minutes. Then, the substrate was dried in a pure N_2 gas stream. At first, PEDOT:PSS, as a hole injection layer, was spin-coated onto the ITO for 60 seconds at 3000 ram/s and then dried in an oven at 110°C for 30 minutes. The thickness of PEDOT:PSS was between 80-100 nm. The fabrication of OLED continued by sequentially depositing the following organic layers: TPD (40 nm) as a hole-transport layer, Alq_3 (50 nm) as a light-emitting and electron transport layer, LiF (5 nm) as an electron injection layer, and Al (120 nm) as a cathode. These were evaporated in a thermal evaporation system at room temperature. During depositing, the pressure in the vacuum chamber was 1×10^{-3} Pa. The evaporation rate was around 0.1 nm/s for the organic materials and 0.5 nm/s for LiF and Al. The thickness of the deposited layer was determined by a quartz crystal thickness-measuring device. The active area of the OLED was $1\times0.6\,cm^2$. Fig.1 shows the schematic diagram and the bound structure of the ITO/PEDOT:PSS/TPD/Alq_3/LiF/Al devices.

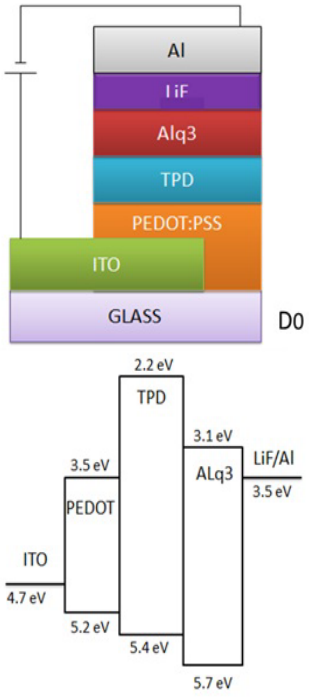

Fig. 1. Schematic diagram and bound structure of device D_0.

Four groups of identical OLED samples which were differently encapsulated were tested as follows:

D0: glass/ITO/PEDOT:PSS/TPD/Alq_3/LiF/Al (reference sample)
D1: lass/ITO/PEDOT:PSS/TPD/Alq_3/LiF/Al/ MgF_2(100 nm)
D2: glass/ITO/PEDOT:PSS/TPD/Alq_3/LiF/Al/ YF3(100 nm)
D3: glass/ITO/PEDOT:PSS/TPD/Alq_3/LiF/Al/ MgF_2(100 nm)/ZnS(50 nm)
D4: glass/ITO/PEDOT:PSS/TPD/Alq_3/LiF/Al/ YF_3(100 nm)/ZnS(50 nm)

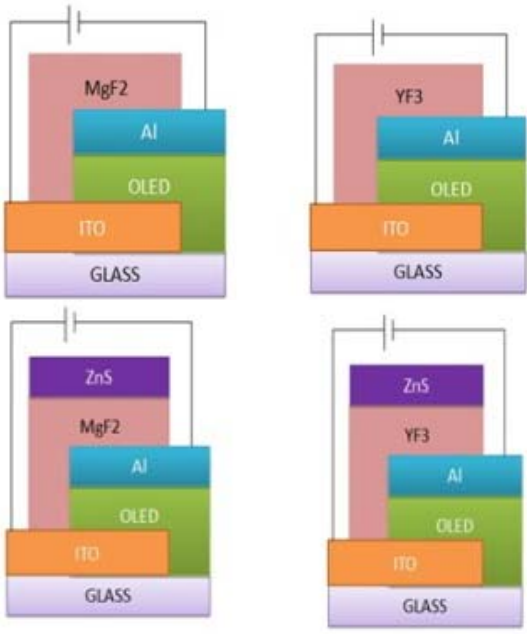

Fig. 2. Schematic diagram of capsulated devices D_1-D_4 from left to right.

D0 was a bare device. Devices D1, D2 , D3, and D4 were sequentially encapsulated with an MgF_2 film a YF_3 film, an MgF_2/ZnS film, and a YF_3/ZnS film respectively. For comparison purposes, the thickness of the encapsulation thin film was decided to be 100 nm for MgF_2 and YF_3 and 50 nm for ZnS in all the experiments. Moreover, the capsulated layers were deposited in the same condition by a thermal evaporation system. Fig. 2 shows the schematic diagram of the four different encapsulation devices.

III. Results and Discussion

A. *Current-voltage characteristics*

A Keithley 2400 source and an HR400 (Ocean Optic) spectrometer were used to record the current-voltage and the electroluminescence characteristics of the devices simultaneously. The current-voltage characteristics of the five devises are shown in Fig. 3. As the figure shows, the diode behavior is nearly an Ohmic behavior at lower voltages, and the current dramatically increases at higher voltages. At the beginning, no significant difference was observed in the I-V behavior between the bare device and the capsulated devices. Based on luminance intensity and current-voltage the device's efficiencies at the beginning were calculated and are shown in Table 1. The temporal evolution of current–voltage in each device was recorded, and the data were then compared to one another. It was found that, for all the devices, the current density at a given voltage would decrease with time. The lifetime of OLED could be estimated based on the temporal evolution of the current–voltage of the device [25].

Table 1. Efficiency of bare and capsulated devices (D_0-D_4) at the first minute.

Device	D0	D1	D2	D3	D4
Efficiency	0.34	0.34	0.33	0.32	0.31

B. *Electroluminescence spectra*

The electroluminescence (EL) spectra of the bare device and those of the encapsulated devices at 2500 mA are depicted in Fig. 4. The main emission is observed at 540 nm. It indicates a green light emitted from Alq_3 as an emitting layer. The EL spectra of all the devices were recorded for a long time duration to compare their electrical behavior before and after forming the capsulated layers. It is obvious that time can strongly influence the device EL intensity. As it can be seen, the colors of the devices coordinate, or are almost identical, before and after capsulation.

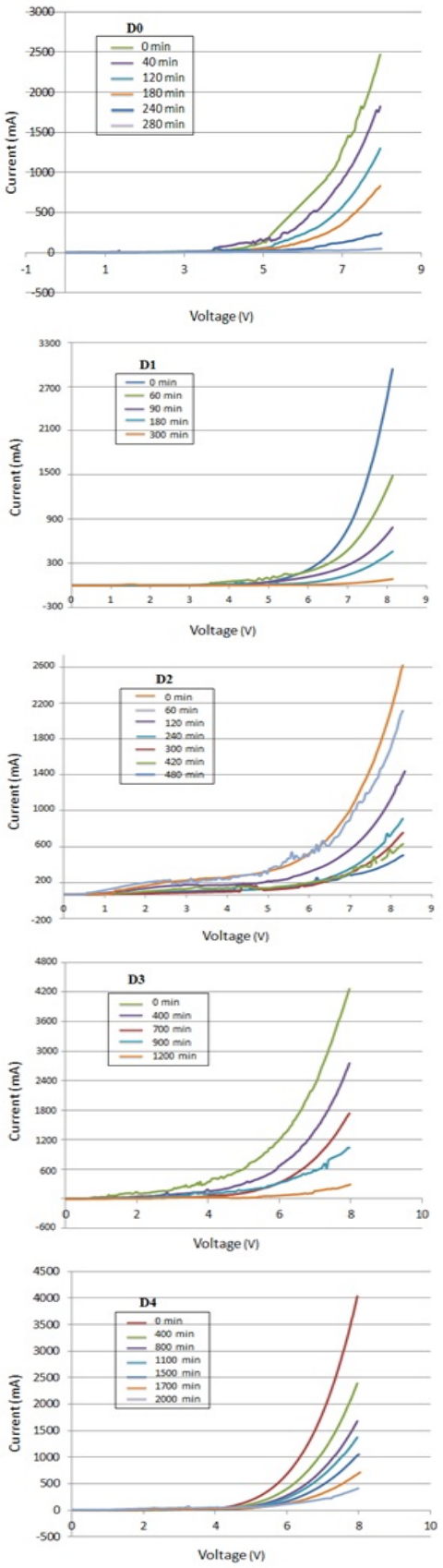

Fig. 3. Current-voltage characteristics at different times for the bare device (D_0) and the capsulated devices by MgF_2 (D_1), YF_3 (D_3), MgF_2/ZnS (D_4), and YF_3/ZnS (D_5).

However, the luminance intensity of the capsulated devices decreases overtime. Although the luminance intensity of the bare device decreases too, this value takes more time for the capsulated devices to reach 50% of its maximum intensity.

C. *Lifetime study*

The lifetime of a diode could be estimated based on the temporal evolution of its luminance [6]. As it was stated before, five types of devices were fabricated as D0, D1, D2, D3, and D4. The temporal evolution of luminance of the devices D0–D4 are depicted in Fig. 5. The device D0 was monitored over 300 minutes, and its lifetime was estimated to be around 190 minutes. The devices D1 and D2 were monitored over 700 minutes, and their lifetimes were estimated about 300 and 500 minutes, respectively. The devices D3 and D4 were examined over 2000 minutes, and their lifetime were estimated 750 and 1200 minutes respectively. All the measurements were performed in the same conditions. In Fig. 6, the lifetimes of identical OLEDs that have been differently encapsulated are compared. It can be seen that the lifetime of the encapsulated devices has been improved significantly as compared to non-capsulated devices. Both MgF_2 and YF_3 show strong adhesion to the cathode, and MgF_2 is a rugged and hard material that can function as the hydrophobic materials reported in a previous study [26]. However, YF_3 shows a better resistance to oxygen and water vapor as compared to MgF_2. As it can be seen in Fig. 6, a composition of alternating magnesium fluoride (MgF_2) and zinc sulfide (ZnS) layers and yttrium fluoride (YF3) and zinc sulfide (ZnS) as passivation layers significantly improves the lifetime of OLEDs. It can be concluded that the use of these encapsulation layers can enhance the effective barrier action against moisture and oxygen permeation. Moreover, these multilayer systems influence thermal stress as reported earlier [26]. Therefore, YF_3 and MgF_2, used as a first layer, may initiate a good adhesion, and then ZnS layer improves the gas diffusion barriers for OLEDs.

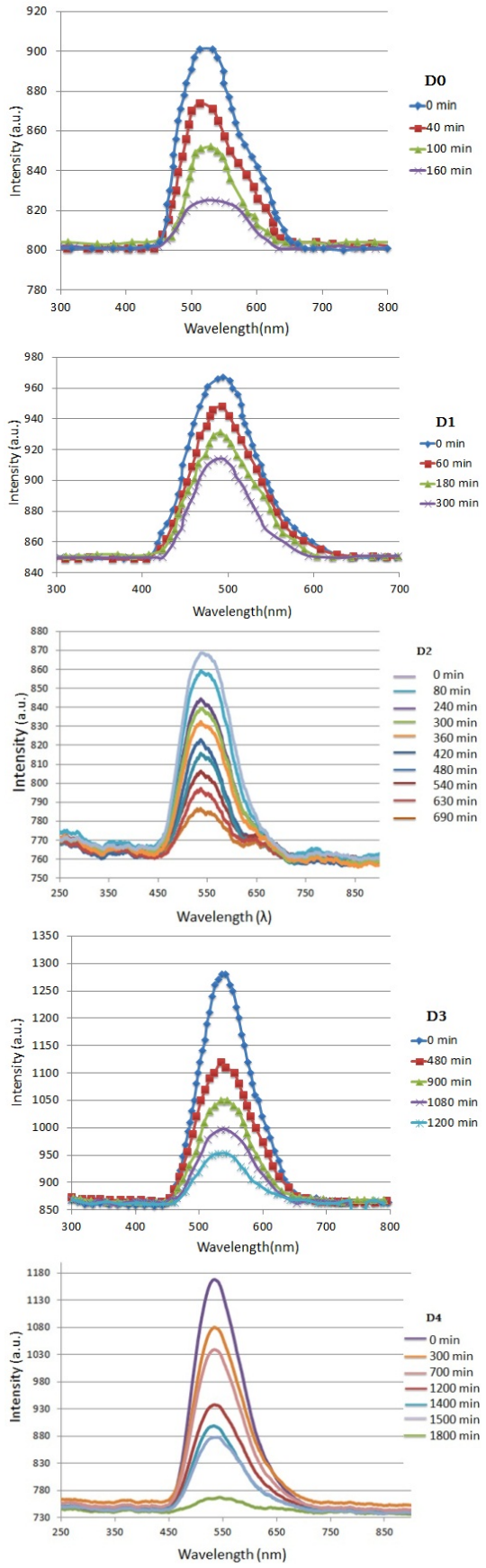

Fig. 4. Comparison of the operating characteristics of bare device (D_0) and capsulated devices by MgF_2 (D_1), YF_3 (D_2), MgF_2/ZnS (D_3), and YF_3/ZnS (D_4) at different times at 2500 Ma.

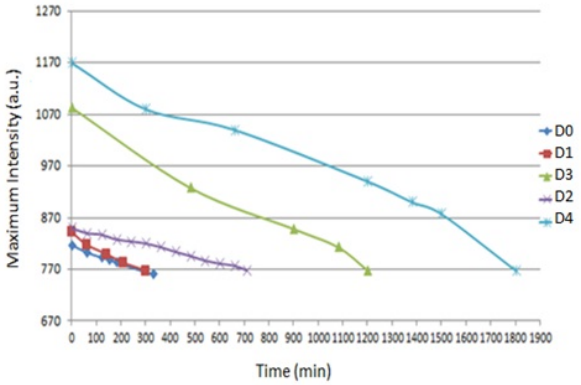

Fig. 5. Temporal evolution of luminance of bare device D_0 and capsulated devices by MgF_2 (D_1), YF_3 (D_2), MgF_2/ZnS (D_3) and YF_3/ZnS (D_4).

Since ZnS has excellent physical properties such as wide energy band gap, high refraction index, and high transmittance in the visible range, it can be used for top-emitting OLEDs [9, 24]. Furthermore, MgF_2 and YF_3 are transparent, so the multiple capsulations are also suitable for encapsulating top-emitting OLEDs. The evolution curve of luminance for the devices D3 and D4 was almost consistent at the first stage, about 100 minutes, but it ceased to be consistent afterwards. This indicates the formation of a dark spot that resulted from the permeation of moisture and oxygen, particularly after a long-term operation. Because of hydrophobic nature of passivation layers, oxygen and water vapor molecules could hardly react with organic materials; however, by an increase in pinholes with time, a pathway opened for the oxygen and water molecules to pass through the passivation layer, and this led to the degradation of OLEDs. The pinholes formed in the barrier film by accumulated Joule heat during the device operation. The slower decreasing rate of D4 curve as compared to D3 shows a slower change over time. Figure 6 shows a good trend in the lifetime of OLEDs. The devices encapsulated with a composition of YF_3/ZnS films showed a substantial improvement in lifetime as compared to the devices encapsulated with a composition of MgF_2/ZnS thin films. The half lifetime of the green OLEDs reached 1200 minutes by using YF3/ZnS as an encapsulation layer.

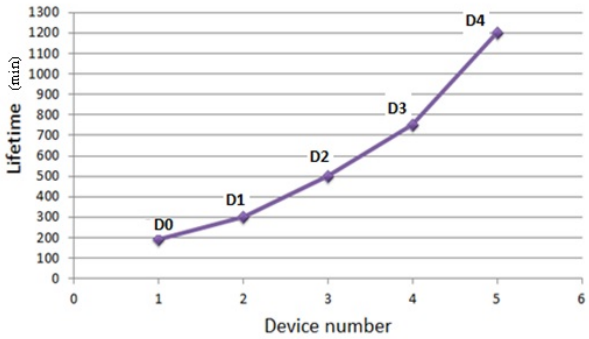

Fig. 6. The lifetime of encapsulated devices compared with the bare device (D_0).

IV. CONCLUSION

In conclusion, we fabricated and capsulated green OLEDs and studied the aging of these devices. We compared four passivation layers and demonstrated that YF_3 shows a better gas barrier behavior as compared to MgF_2. Also, we compared films of MgF_2/ZnS composition with single-layer MgF_2, as well as films of YF_3/ ZnS composition with single-layer YF_3 used as encapsulation thin films. It was shown that multi-layer encapsulated OLEDs gain a substantial improvement in their lifetime and have a good water vapor and oxygen barrier capability. Finally, an enhanced performance was observed for the OLEDs encapsulated by YF_3/ZnS. The lifetime of the fabricated green OLEDs reached 1200 minutes by using YF3/ZnS as an encapsulation layer. Due to its good performance and easy fabrication, this transparent and smooth thin film can be potentially employed to capsulate top emitting OLEDs and flexible OLEDs.

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