Organic Electronics 53 (2018) 256–264

Contents lists available at ScienceDirect

Organic Electronics

journal homepage: www.elsevier.com/locate/orgel

Side leakage into the organic interlayer of unstructured hybrid thin-film encapsulation stacks and lifetime implications for roll-to-roll produced organic light-emitting diodes

Peter van de Weijer[a,*], Hylke B. Akkerman[a], Piet C.P. Bouten[a], Pradeep Panditha[a], Pieter J.M. Klaassen[b], Ahmed Salem[a]

[a] Holst Centre, High Tech Campus 31, 5656AE, Eindhoven, The Netherlands
[b] Reliability Lab, Philips Innovation Labs, High Tech Campus 7, 5656AE, Eindhoven, The Netherlands

ARTICLE INFO

Keywords:
Side leakage
Lifetime
Roll-to-roll
Thin-film encapsulation
OLED
Diffusion coefficient

ABSTRACT

Side leakage experiments have been performed on the organic interlayer, so-called organic coating for planarization (OCP), in a hybrid thin-film encapsulation (TFE) stack based on two silicon nitride (SiN) barrier layers that was developed for organic light-emitting diodes (OLED). To measure the side leakage into OCP, a metallic Ca thin-film monitor can be used. However, the water uptake capacity of the Ca monitor affects the measurements. Here, we eliminated the contribution of the Ca layer from the measurement by variation of the Ca thickness and by measuring the side leakage until it reaches the Ca layer. For OCP with a water getter inside (5% CaO) the side leakage can be monitored by the loss of scattering of the CaO when it reacts with water to $Ca(OH)_2$. This work describes measurements of the rate of side leakage into the OCP layer of the TFE stack, both for plain OCP and for OCP with CaO getter inside. The side leakage curves are used to derive diffusion coefficients. Performing measurements at various climates provides acceleration factors that are relevant for the performance quantification of the TFE stack. The limiting factors on the performance of an unstructured TFE stack as produced in a roll-to-roll (R2R) process are presented. For small OLED devices side leakage would drastically reduce the shelf lifetime but for larger devices the permeation properties of the TFE stack determine the shelf lifetime.

1. Introduction

Since the introduction of the organic light-emitting diodes (OLEDs) by Tang and VanSlyke [1] much progress has been made in their performance. This enables the exploitation of their intrinsic advantages like low-cost and the possibility to create mechanically flexible devices. Both efficacy and operational lifetime have improved significantly [2,3]. Further, encapsulation methods have been developed to prevent black spot formation as a result of exposure to water and oxygen from the ambient atmosphere. Conventional encapsulation with a glass or metal cover lid [4] is expensive, limits upscaling of device area, and inhibits the possibility for flexible devices. Thin-film encapsulation (TFE) of OLED devices [5] overcomes these disadvantages. It opens the possibility of flexible OLEDs and enables low-cost manufacturing in a roll-to-roll (R2R) process. Even when applied on rigid substrates it contributes significantly to cost reduction of the device. Recently, we reported on a hybrid thin-film encapsulation stack consisting of two SiN barrier layers with an organic interlayer [6]. The relatively thick interlayers, so-called organic coating for planarization (OCP), results in decoupling of the pinholes in the two barrier layers and enables large getter capacity on basis of CaO nanoparticles that are incorporated in the OCP layer. In combination with good quality SiN barrier layers (low water vapor transmission rate and low pinhole density) the stack enables black spot free devices during many decennia when exposed to the ambient atmosphere [6].

The performance of our SiN-OCP-SiN was evaluated on top of rigid OLEDs with glass substrates. These devices require top encapsulation only as the bottom is protected by glass. For flexible devices on plastic substrates a bottom barrier is also needed as the water vapor transmission rate (WVTR) of plastic foils is orders of magnitude larger than the required transmission rate for OLEDs (WVTR $< 10^{-6}$ $g/m^2/day$) [7]. For top encapsulation the TFE stack is applied after completion of the OLED processing. The OCP layer covers the complete active area of the device. The SiN layer extends the OCP area resulting in a double SiN stack outside the OCP area. This prohibits side leakage into the OCP layer that would bypass the protection of the upper SiN layer. To show

* Corresponding author.
E-mail address: peter.vandeweijer@tno.nl (P. van de Weijer).

https://doi.org/10.1016/j.orgel.2017.11.019
Received 28 September 2017; Received in revised form 9 November 2017; Accepted 18 November 2017
Available online 21 November 2017

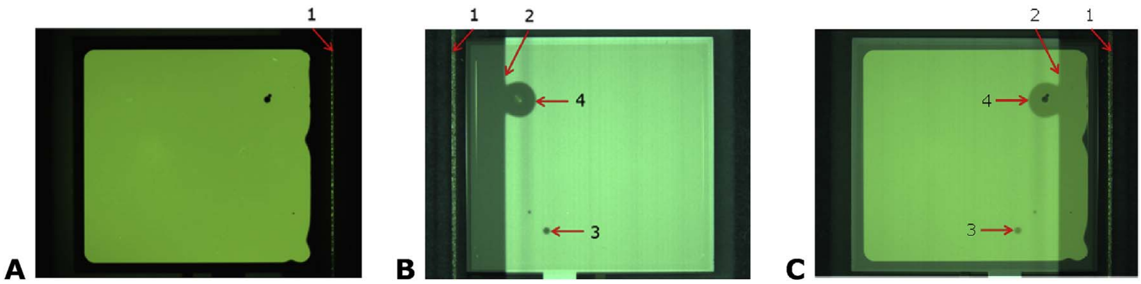

Fig. 1. Pictures of a 5 cm^2 smOLED encapsulated with SiN-OCP-SiN with 5% CaO getter in the OCP layer after exposure to 60°C/90% RH for 1000 h. A laser slit (1) is made in the SiN-OCP-SiN 2 mm from the edge of the active area of the OLED. A: Electroluminescence from the bottom side of the OLED. B: Optical photograph of the scattering of the CaO particles in the barrier on top of the OLED showing the saturation front (2) and two saturated spots (3,4). C: Overlay of B on A after horizontal flip of B. It shows that the saturation front has proceeded much further than the black spot formation at the edge of the cathode as a result of water ingress through the pinhole in the cathode in the saturated getter area. This aspect is similar to water ingress through pinholes in the upper SiN. Saturated spot 3 does not show a black spot yet, but the larger spot (4) does show a black spot (in fact 2 spots). The area of the black spot is much smaller than the area of getter saturation.

what happens when the edge of OCP is not protected by SiN, we made a laser slit in the SiN-OCP-SiN layer on top of a bottom emitting OLED at a distance of approximately 2 mm from the active area. Fig. 1 shows photographs of the OLED device after 1000 h exposure to a climate of 60°C/90% relative humidity (hereafter denoted as 60/90). Fig. 1A is the electroluminescence of the OLED, Fig. 1B is the optical photograph of the light scattering of the CaO nanoparticles in the SiN-OCP-SiN barrier on top of the cathode and Fig. 1C is an overlay of Fig. 1B (after horizontal flip) on Fig. 1A. The getter OCP has a milky white appearance due to the optical scattering effect of the CaO getter in the OCP. Formation of a darker area from the edge in these photographs corresponds to saturation of CaO in OCP as a result of water ingress, thereby creating a locally non-scattering area with $Ca(OH)_2$, referred to as saturated spots [6].

Both the saturated spots as a result of water penetration through pinholes in the upper SiN and the front of side leakage into the OCP with 5% CaO are clearly visible by the loss of scattering when CaO is converted into $Ca(OH)_2$. In the area of saturated CaO black spots will grow in time. Their formation is delayed with respect to getter saturation. Fig. 1 shows that the black spot in the area of getter saturation by water ingress through a pinhole in the upper SiN is much smaller than the saturated spot. In a similar way the front of getter saturation by side leakage through the laser slit has proceeded much further than the front of black spot formation at the edge of the cathode as can be seen from the emission profile.

For bottom encapsulation of flexible OLEDs the TFE stack is applied before processing of the OLED. It would be most cost-effective to produce a Roll-to-Roll (R2R) barrier without pre-structuring of the barrier [8]. By defining a smaller width of the OCP layer than the SiN layers side leakage is prevented perpendicular to the roll direction. However, if the roll is cut into dimensions that meet the size of the intended OLED side leakage into the OCP layer is possible.

This paper describes measurements of the rate of side leakage into the OCP layer of the TFE stack, both for plain OCP and OCP with a CaO getter inside. Shelf life time experiments performed at ambient conditions do not provide long term predictions on a reasonable time scale and therefore the experiments were performed at accelerated climate conditions as well, *e.g.* 60/90 or 85/85.

To perform measurements on plain OCP a water ingress monitor has to be added. A local metallic Ca layer (a Ca pad) can be used for this purpose [9,10]. The reduction of the size of the non-transparent metallic layer when it is converted into a transparent $Ca(OH)_2$ layer, provides the rate of side leakage. However, the water uptake capacity of the Ca layer is included in this rate. Thickness variation of the Ca layer and extrapolation to the absence of Ca (zero thickness) provides the intrinsic rate of side leakage of the plain OCP layer. Alternatively, we tested a different approach. The basic idea is to vary the distance of the position of water ingress to the locally applied Ca layer and measure the time needed for the on-set of Ca oxidation. This value is independent of the Ca getter capacity and is supposed to provide the internal property of plain OCP.

Experimentally, side leakage into getter OCP is most straightforward. The scattering of the getter particles and the loss thereof upon the reaction with water, can be used as an internal monitor of the progress of the water front. The emphasis of this work is on the side leakage into getter OCP as the application of this material in SiN-OCP-SiN on top of the OLED results in superior performance with respect to the same stack on basis of plain OCP [6].

2. Experimental

A schematic diagram of the three different side leakage measurements in two geometries is shown in Fig. 2. All measurements are based on the hybrid thin-film encapsulation stack as described previously [6]. The inorganic barrier layer SiN (150 nm) is applied by plasma enhanced chemical vapor deposition (PECVD) in a parallel plate radio frequency plasma reactor (Oxford Instruments) or a microwave plasma reactor (AK800, Meyer Burger). The water vapor transmission rate is low (WVTR $< 10^{-6}$ g/m^2/day) and the number of pinholes when applied on the organic interlayer is in the order of 1 cm^{-2}.

The organic coating for planarization material (OCP) is a UV-curable acrylate supplied by Rolic Technologies. The plain formulation is applied by spin coating and the formulation containing 5% CaO by weight is applied by ink jet printing. The default thickness of the resulting OCP layer is 7 μm and 16 μm, respectively. Spin coating results in a more homogeneous layer than ink-jet printing. Ink-jet printing is used for structuring the OCP.

The substrate can be either glass or PEN foil. When many pinholes are present in the upper SiN (glass substrate) or in both SiN layers (PEN foil), ingress of water through pinholes can interfere with the side leakage measurements. In case of glass substrates (Fig. 2A and B) the effect of pinholes on the quality of the Ca layer was eliminated by reinforcement of the SiN layer above the Ca pad with an OCP-SiN dyad (not shown in Fig. 2). In case of PEN foils such reinforcement would be necessary on two sides. This would complicate the processing to such an extent that this reinforcement was not applied. As a consequence some samples were not suitable for analysis by the presence of saturated spots in the area of side leakage observation.

In method A and B we used a 6-inch glass substrate with nine square Ca pads in a 3 × 3 matrix applied by thermal evaporation. The default thickness of the 18 × 18 mm Ca layer is 40 nm. The individual Ca pads are separated by 25 mm from their nearest neighbors. The OCP layer is applied by spin coating. The default thickness is 7 μm. Variation of the layer thickness is obtained by adjusting the rotation speed. The SiN layers are applied without mask. A slit in the TFE stack is created with a CO_2 laser (Trotec Speedy 300) at two edges of the Ca pads. The slit width is typically 100–150 μm. This slit defines the location of water ingress into the OCP.