White paper on the characterisation of thin-film barrier layers for protection of organic Light-Emitting Diodes

Peter van de Weijer[a] and Ton van Mol[b]

[a]Philips Research, High Tech Campus 4, 5656 AE Eindhoven, The Netherlands
[b]Holst Centre, High Tech Campus 31, 5605 KN Eindhoven, The Netherlands

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Executive summary

As humanity becomes more and more aware of the often non-reversible effects it's causing on a global scale, a trend for sustainability and energy-efficiency has emerged in the past few years. Strict laws are being passed by environmentally-conscious governments that pose new challenges in otherwise traditional products and force the industry to look for new solutions to old problems. As almost 20% of the total generated electricity goes to lighting, the old-fashioned, loved but highly inefficient incandescent lamp will not be found anymore at the European supermarket shelves as early as 2012 while other light sources such as the halogen lamp are now under scrutiny.

Much research effort is currently taking place in the field of Organic electroluminescence, a lighting solution that promises to surpass in efficiency even the compact fluorescent lamps (CFL's). Apart from the energy efficiency factor, OLEDs are cold area sources, highly suitable not only for creating a lighting solution but a lighting solution with a well-being feeling. And as cost is always an important factor in any market, in this case cost-efficiency can be achieved if OLEDs were made on foil and manufactured using high speed roll-2-roll processing.

The Fast2light Integrated European project aims on just that: to set in place the technological platforms for R2Rmanufacturing of OLED lighting foils. One of the most challenging hurdles to overtake is the development of a suitable thin film barrier and much effort is dedicated on this subject around the world. With press-releases of success stories appearing but with disappointing results when actual testing is taking place, it soon became apparent to the Fast2light consortium that measuring of the properties of a barrier is very important and still not standardized. In this white paper, we aim to give our view on how to measure the properties of a thin film barrier and we invite discussions on standardizing this.

1. Introduction

For the last several years, organic light-emitting diodes (OLEDs) have been intensively studied because of their potential applicability to large-size flat panel displays, and more recently also solid-state lighting [1-4]. The use of thin plastic substrate foils can add device flexibility and reduced thickness, opening the possibility to R2R processing, and bendable applications [5-9]. However, an important issue in fabricating OLEDs on flexible substrate is how to protect them from moisture and oxygen [10, 11]. They must be protected on both sides, not only on the top-side like the OLEDs fabricated on glass OLEDs. The conventional solution for glass-based OLEDs has been to seal the OLED with a glass or metal lid using an epoxy based glue. A getter material such as CaO is often incorporated within the package to eliminate residual water and water penetrating through the glue.

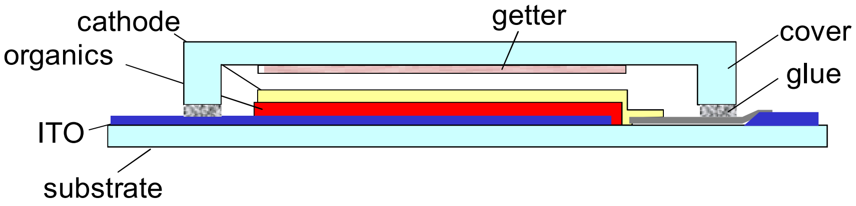

Figure 1. *Schematic diagram of an OLED device on a rigid substrate (glass) with conventional encapsulation based on a cover lid (metal or glass) applied by a glue edge. A getter is incorporated to remove residual water and water penetrating through the glue.*

However, this standard solution is insufficient or problematic for flexible OLEDs where the ability to conform or bend the device is essential. In the case of flexible OLEDs thin-film barrier layers consisting of inorganic and sometimes inorganic/organic multi-layers are usually used for protection on both sides (figure 2) [10,12]. The thin-film barrier layer on top of the cathode is usually referred to as thin-film encapsulation; the thin-film barrier layer on the foil is referred to as barrier layer.

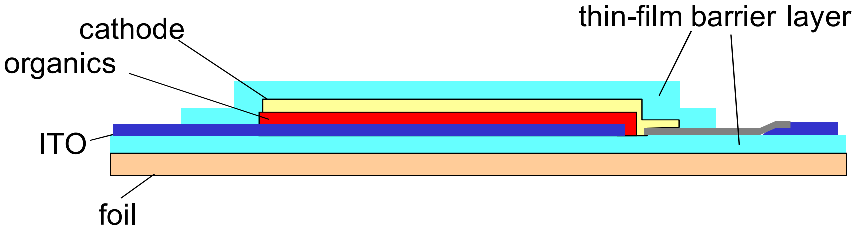

Figure 2. *Schematic diagram of a flexible OLED device that is protected by a thin-film barrier layer on both sides of the OLED device.*

This paper describes the requirements for thin-film barrier layers as applied on OLEDs. In Section 2 a description is presented of the degradation mechanism induced by exposure of OLEDs to moisture from the ambient atmosphere. The characterization of the applied barrier layer with respect to water vapor transmission rate (WVTR) and pinholes with the calcium-test is presented in section 3. The performance of encapsulation by a single barrier layer and with a stack of barrier-layers is presented in section 4 and 5, respectively. Finally section 6 discussed the relevance of the criteria for the encapsulation on an OLED device.

2. Interaction of organic LEDs with the ambient atmosphere

Exposure of OLEDs to the ambient atmosphere results in a reduction of the practical lifetime of the device. The most pronounced failure as a result of this interaction is the formation of black spots in electroluminescence (figure 3). A qualitative description of the mechanism of black spot formation in polymer OLEDs with a Ba/Al cathode is available in the literature [13, 14], and a short description of this is given here.

Figure 3. *Example of the formation of black spots in electroluminescence of a OLED as a result of storing the device at ambient conditions for a few days. The area of the picture is approximately 3 mm^2.*

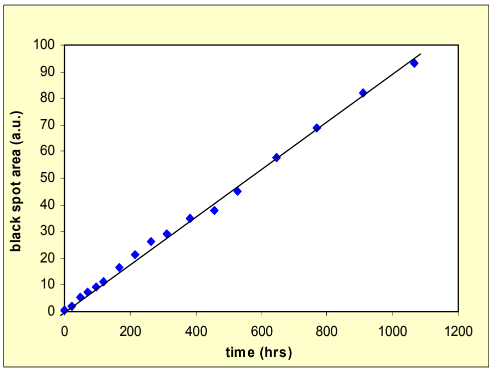

Figure 4. *Typical linear growth of the area of an individual black spot as a function of the time elapsed in a (shelf) test.*

The cathode in an OLED device most often consists of a thin (1-10 nm) layer of Ba (polymer LED) or LiF (small molecule OLED) covered with a relatively thick Al layer. Aluminum would be an excellent barrier against water if not for the fact that it contains pinholes. Water from the ambient atmosphere is penetrating through pinholes in the cathode layer. Oxidation of metal at the cathode-polymer interface prevents electron injection from the cathode into the polymer during operation of the device, thus introducing a local spot without emission, i.e. a black spot in the bright field of electroluminescence. The evolution of the black spots is determined by the diffusion rate of water from the pinhole. The area of the resulting circular shaped spots increases linearly with time. Black spot formation and growth is a shelf effect, *i.e.* no current or voltage is necessary to drive the process.

As Ba is responsible for electron injection from the cathode into the polymer in a non-degraded device, one might anticipate that local oxidation of Ba is responsible for the formation of black spots. However, both X-ray Photo-electron Spectrometry (XPS) and Secondary Ion Mass Spectrometry (SIMS) [15] demonstrated that excessive oxidation of Al is responsible for the formation of black spots.

For small molecule OLEDs the operation of the cathode and its lack of functionality in the black spots are less clear. For the mechanism of electron injection from the cathode several options have been proposed [16]. The presence of (a thin layer of) aluminum is essential. Application of silver on top of LiF for the sake of conductivity, as applied in transparent cathodes, is only possible when a layer of at least 1 nm Al is used between LiF and Ag. Application of SIMS revealed the nature of the black spots in OLEDs. In the black spots an increased oxidation of aluminum is observed. Apparently, the presence of aluminum on the LiF-layer is only effective for the functionality of the cathode when aluminum is present in its metallic state.

3. Characterization of the barrier layer with the calcium test

In order to measure the low water vapor transmission rate of the applied barrier layer that is relevant for a long lifetime of an OLED device, the calcium test has been developed within Philips Research. The principle of the method is shown in figure 5. A pattern of calcium of well-defined thickness is applied on a transparent substrate. The calcium is covered with a transparent encapsulant. The optical transmission of the calcium layer is measured with a lamp as a light source and a camera as detector. Calcium as a metal has a low transmission, but after reaction with water or oxygen the layer becomes transparent. Measurement of the optical transmission as a function of time provides information of the permeability of the encapsulant and substrate for water and oxygen. In practice, the reaction with water is the dominant with respect to that with oxygen. Though the formation of calcium hydroxide is considered to be more realistic from a chemical point of view, the reaction $Ca + H_2O \rightarrow CaO + H_2$ has been proven to provide accurate data on the water vapour transmission rate (WVTR) [18]. In our experiments we use a substrate without significant permeation for water and oxygen (glass). Therefore, the permeation of the encapsulant is measured. The detection limit of the calcium test is in the order of 10^{-6} g/m^2/day.

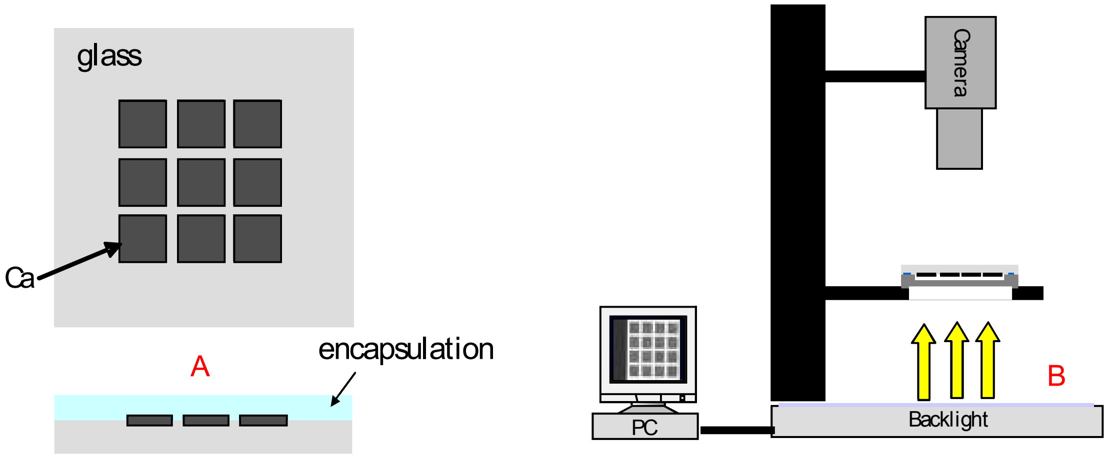

Figure 5. *Schematic diagram of the calcium test as used in this work. A layer of calcium is sandwiched between a glass substrate and the thin-film encapsulation layer (**A**). The optical transmission of the calcium-layer is measured with a lamp and a camera (**B**) as a function of time. The increase of the transmission provides quantitative information on the water vapor transmission rate of the encapsulation layer. A LabVIEW^{TM} program controls the measurements and data storage in a relational database.*

Although pinholes in the encapsulant are not considered to be the main problem in the encapsulation process (see next section), they do hamper the measurement of the intrinsic water vapour transmission rate (WVTR) in the standard calcium test. *As the lateral averaged transmission is considered, the derived WVTR is larger than the intrinsic permeation rate of the barrier layer.* We adapted the software of the calcium test with the option to define the area of measurement in retrospect. In this way the white spots can be excluded from the considered area. Even then, the white spots hamper the determination of the permeation rate, as they tend to cover the complete active area. A precise determination of the WVTR on basis of *e.g.* a 50% transmission point is often not possible. The determination has to be performed on a time-scale in which the size of the white spots is still limited. A typical example is shown in figure 6 for a barrier layer of SiN on top of calcium. The increase in optical transmission is only a few percent in that case. On account of the precise calibration procedure as applied in the calcium test the increase in optical transmission can be measured with a precision of 5-10 %. Inclusion of the pinholes in the derivation of the WVTR results in numbers that are typically more than one order of magnitude larger. It should be noted that the pinhole diffusion is excluded from the derived WVTR as far as they lead to visible white spots. The WVTR might still contain a contribution of diffusion through (smaller) pinholes that did not lead yet to the formation of visible white spots.

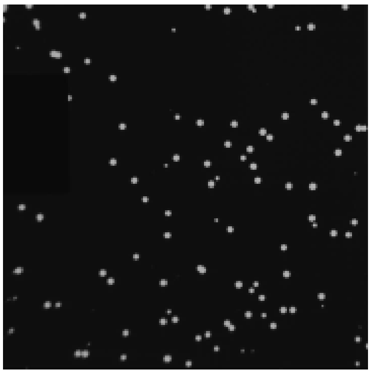

Figure 6. *Photograph of a calcium layer covered with 100 nm SiN (2x2 cm^2). The white spots correspond to a large transmission of the calcium layer. Pinholes in the SiN layer allow water to diffuse to the calcium layer where it reacts with calcium to form a transparent layer. Lateral diffusion of water results in growth of the white spots.*

4. Characterization of the barrier layer on top of an OLED

The major role of the thin-film encapsulant to be applied on top of the cathode (see figure 7) is to cover the particles that are responsible for the pinholes in the aluminium layer. In order to prevent water to penetrate into those pinholes it has to be a good diffusion barrier with a water vapour transmission rate (WVTR) in the order of 10^{-6} g/m^2/day. Any pinholes in the thin-film encapsulation layer itself are not catastrophic for its functionality as long as they do not coincide with the pinholes in the aluminium cathode.

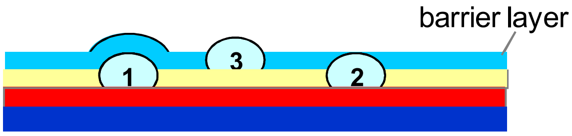

Figure 7. *Schematic diagram of the thin-film encapsulation of an OLED device. The organic stack (red) is covered with the cathode (yellow). Aluminium is a good water barrier. However, pinholes induced by particles (1 and 2) allow water to penetrate into the device. This results in black spots. The water barrier layer is able to cover many of those particles (1). Some particles are not covered (2) leaving pinholes for water diffusion. Any particles that create a pinhole in the barrier layer (3) are not harmful, as water penetrating through such a pinhole, is blocked by the aluminium layer.*

The specification of a WVTR of 10^{-6} g/m^2/day is often motivated [19] as the amount of water that is capable of oxidizing a 10 nm layer of metal at the cathode-organic interface during the specified lifetime of the devices (10 years). However, this suggests homogeneous degradation of the cathode, whereas the actual penetration of water is limited to the area of the pinholes in the cathode. Outside these pinholes the combination of the thin-film barrier and the aluminium layer prevents any water penetration into the device. Though the pinhole density in the cathode is high (typically 10^6 -10^8 /m^2) the small size of the pinholes, as determined by (dust) particles, results in an estimation of the total fractional area of the pinholes below 1 ppm. This would imply that 10^{-6} g/m^2/day results in black spots after 10 years of storage that are well below the detection limit of the naked eye. However, the formation of a black spot does not necessarily imply oxidation of 10 nm metal. ***A much thinner layer of oxidized metal might be responsible for the elimination of electron injection form the cathode into the organic stack.***

These two considerations hamper an *a priori* estimation of the specification of the WVTR of the barrier. Instead we defined our specification in an empirical way. Figure 8 shows the electroluminescence of part of OLED device after storage during half a year under ambient conditions. The device is encapsulated with a SiN layer with a WVTR of 10^{-5} g/m^2/day. Most apparent are the large black spots that correspond to uncovered pinholes in the cathode (particles 2 in figure 2.2). However, a lot of tiny black spots are visible between the large ones in this microscope photograph. For the naked eye they are below the visibility limit. These spots correspond to pinholes that are covered by the SiN layer (particles 1 in figure 7). The formation of these spots is limited by the WVTR of the SiN layer. Based on the linear growth of these spots, we estimate that it will take another half year before these spots become visible for the naked eye. So at 10^{-5} g/m^2/day the samples remain free from these spots. This means that for a SiN barrier with WVTR of 10^{-6} g/m^2/day that covers all pinholes, indeed no black spots are visible for 10 years, which corresponds to the generally accepted WVTR requirement albeit from a different perspective.

Figure 8. *Electroluminescence from an OLED device (2x1.5 mm^2) encapsulated with a SiN-layer after exposure to the ambient atmosphere for one year. The large black spots correspond to pinholes that are not covered by the SiN layer. The tiny ones correspond to pinholes that are covered by SiN. The growth of the tiny spots is limited by the WVTR of the SiN layer (10^{-5} g/m^2/day)*

5. Stacking of barrier layers

The need for encapsulation of OLED devices is related to the occurrence of particle induced pinholes in the cathode. A single SiN layer is able to cover 90-99% of the pinholes. The remaining number of pinhole induced black spots is still in the order of 10^5 m^{-2}. This is many orders of magnitude larger than acceptable for devices in any application. Our problem, therefore, still concerns pinholes. *We want to emphasize here, that the pinhole problem is not the occurrence of pinholes on the SiN layer (particle 3 in figure 7) that can be measured with the calcium test, but pinholes in the cathode that are not covered by the SiN layer.*

Reduction of the number of black spots, *i.e.* the number of uncovered pinholes by increasing the layer thickness of SiN does not provide a solution within practical boundary conditions of the processing as pinholes tend to grow while depositing more material. A small factor is possible, but a reduction of several orders of magnitude cannot be obtained in the sub-µm range.

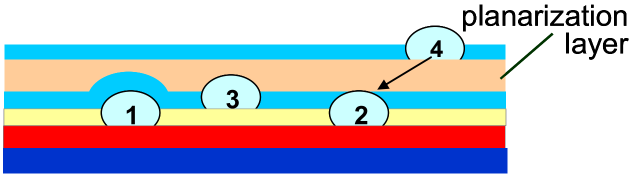

Figure 9. *In order to eliminate black spot formation as a result of uncovered particles in the cathode-SiN layer (particle 2) an intermediate layer is applied for the purpose of planarization. The presence of particles (4) in the second SiN, is harmful due to lateral diffusion of water in the intermediate layer. Eventually, black pots will become visible around particle 2. The obtained time delay of black spot formation should match the requirement for the OLED device in its application.*

A widely used approach to suppress the black spots in thin-film encapsulated OLED devices is the application of a stack of layers. In such a stacked layer, a combination of an inorganic layer and an organic layer is often chosen (figure 9). The inorganic layer serves as a water barrier; the organic layer is intended to planarize all particles that protrude the cathode-SiN layer. As the organic layer has poor barrier properties for water, possible pinholes in second SiN layer will destroy the water barrier quality of the layer eventually. Penetration of water through the inorganic layer, followed by lateral diffusion in the organic layer will result in a black spot around the particle that remained uncovered by the first inorganic layer. It should be emphasized that pinholes in the first SiN layer (on top of the cathode) are not considered to be relevant, whereas pinholes in the second SiN layer are relevant. The latter ones determine the water penetration in to the planarization layer and result in the occurrence of black spots. A time-delay in the black spot growth is expected (please note that the application of the stack does not reduce the number of black spots). Obviously, this time delay should match the specification of the device in an application with respect to lifetime. Figure 10 shows a comparison of the growth of individual black spots in an OLED device encapsulated with a single SiN layer and that in an OLED device encapsulated with a SiN-org-SiN stack. The size of the black spots in the latter device is three orders of magnitude smaller than that in the former one. Obviously, a further suppression of the black spots is necessary to prevent visible black spots over a period of years.

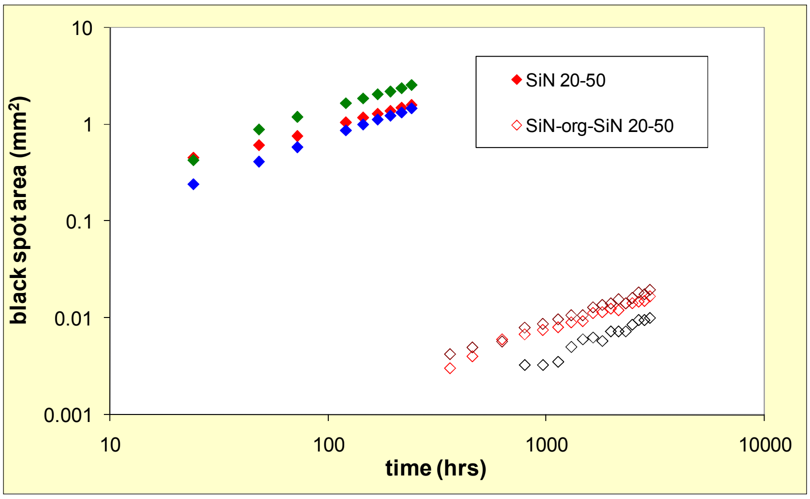

Figure 10. *Comparison of the growth of individual black spots in OLED devices encapsulated with SiN only and SiN-org-SiN during storage under ambient conditions. The giant step forward in the reduction of the black spot problem is obvious.*

6. Quality of the thin-film encapsulation layers.

The quality of the thin-film encapsulation concept is based on a barrier layer with a low WVTR (< 10^{-6} g/m^2/day). The WVTR can be measured with the calcium test. Pinholes are excluded in this measurement. It should be mentioned that pinholes are excluded only if they are so large that their presence results in a white spot in the calcium test. Most likely, micro-cracks are still contributing to the WVTR that is derived from calcium degradation outside the (visible) white spots. The intrinsic WVTR of stoïchometric Si_3N_4 is orders of magnitude lower than the SiN that is applied as our barrier layer.

A low WVTR (< 10^{-6} g/m^2/day) is a prerequisite for a high-quality thin-film encapsulant. It would even be sufficient to prohibit black spot formation in OLED devices if all pinholes in the cathode would be covered properly by the barrier layer. Unfortunately, this is not the case. With our SiN barrier layer we obtained a pinhole coverage of 99% only. The remaining pinholes density and the related black spot density is orders of magnitudes too high.

The pinhole density in the barrier layer, *as applied directly on top of the cathode,* is not relevant for the black spot formation and growth in SiN-only encapsulated devices. This pinhole density might be related to the pinhole density as observed in the calcium test in a glass-Ca-SiN stack, but this number is not related to the quality of the barrier layer as applied on an OLED device.

In order to improve the quality of the encapsulation, a stack of layers is applied where an organic planarization layer is sandwiched between two inorganic barrier layers (SiN-org-SiN). The size of the black spots can be reduced by three orders of magnitude. In this stack the water penetration into the device is dominated by the pinhole density in the upper SiN layer. These pinholes are not visible directly in an OLED device, as we can only observe the black spots, *i.e.* pinholes in the cathode that are not covered properly by the first SiN layer. The delay in black spot formation by application of a stack is determined by the average distance between a pinhole in the upper SiN and a pinhole in the cathode that is not covered properly by the first SiN layer. Therefore, it is essential to reduce the pinhole density in both layers as much as possible.

The pinhole density in the SiN layer on top of the planarization layer can be quantified with the calcium test in a glass-Ca-org-SiN stack. It should be realized that this calcium test provides the pinhole density but the time delay of the white spot formation is not the same as the time delay of the black spot formation in an OLED device. This is mainly related to the amount of material that is necessary to from a black spot (inhibit electron injection) and the amount of material that has to be oxidized to form a white spot (optical transmission). In case of the black spot formation in an OLED device we do not know the exact amount of material of the oxidized layer that is responsible for the inhibition of the electron injection when operating a device. It could be as low as a monolayer. ***In case of the calcium test we apply a layer thickness of 50 nm that is fully oxidized in a white spot. Obviously, the sensitivity of the calcium test can be enhanced by application of a thinner calcium layer***. However, processing of a glass-calcium-barrier stack involves transfer of the glass-calcium sample to the PECVD reactor for deposition of the barrier layer. Even the transport in a glovebox system induces partly oxidation of the calcium layer. Therefore, calcium layer of a few nm is not practical. In case of the application of the cathode such a practical problem does not occur. The low-workfunction material is covered by aluminium in the same vacuum system (thermal evaporator).

In our experience an OLED device is two orders of magnitude more sensitive to water than a calcium test. Therefore, the calcium test cannot be used directly to qualify the encapsulation stack in term of black spot formation. Reports of barrier layers that survive a standard test of 500 hours at 60/90 (60 °C and 90 % relative humidity) are irrelevant, as this would correspond to a few hours only without black spots if this barrier layer is applied on an OLED device.

The one-and-only test that is relevant in the qualification of an encapsulant is a test on an OLED device. Black spots should not become visible for the naked eye within the specified period during a shelf test. Depending on the application this period can be as long as 10 years.

Obviously, any test on the quality of the thin-film encapsulation should be performed on an active area that is relevant for the aimed OLED product. For large-area light sources this would imply an active area that is impractical for a carrier device. The current amount of pinholes in the cathode-barrier that we observe for Al-SiN combination is typically 10^5 m^{-2}. Therefore, a device with an active area of 10 cm^2 (we use three devices of 4 cm^2 each) would lead to a statistically relevant number of possible black spots.

For a practical test period we recommend a test at 60/90 for three weeks. The acceleration factor with respect to 20/50 depends on the mechanism of water penetration into the devices (different for SiN and SiN-org-SiN). For our encapsulants this acceleration factor is between 10 and 100.

We propose to express the quality of a thin-film encapsulation stack as the fraction of 10 cm^2 devices that do not show any black spots after shelf test at 60/90 for three weeks. Black spots smaller than 0.01 mm^2 are considered to be invisible for the naked eye.

Finally, it should be mentioned that all considerations from above apply not only to thin-film encapsulants but also on thin-film barrier layers. Obviously, for a flexible OLED device water can penetrate from both cathode and anode side into the device.

7. Conclusions & Recommendations

- A barrier layer with low WVTR ($< 10^{-6}$ g/m^2/day) is a prerequisite for a functional thin-film encapsulant of an OLED device.
- For encapsulation with a single inorganic barrier layer the intrinsic pinhole density is irrelevant. The layer should cover particles/pinholes in the cathode.
- A single inorganic barrier layer will not provide black spot free devices over a relevant period of time.
- With a hybrid stack where a planarization layer is sandwiched between two inorganic barrier layers an enormous improvement can be achieved.
- Intrinsic pinholes in the upper inorganic barrier layer are domination water penetration into the device. Their number can be derived from a calcium test in the geometry glass-calcium-org-barrier
- *The sensitivity of the calcium test for water from the ambient atmosphere is much lower than the sensitivity of an OLED device and therefore it cannot be used for the qualification of barrier stack.*
- **To our view qualification of a thin-film encapsulation stack can only be performed on an OLED device. Its active area should enable the observation of a statically relevant number of (possible) black spots.**
- **We propose to express the quality of a thin-film encapsulation stack as the fraction of 10 cm^2 devices that do not show any black spots after shelf test at 60°C/90%RH for three weeks. Black spots smaller than 0.01 mm^2 are considered to be invisible for the naked eye.**

Comments and suggestions on the contents of this white paper can be made through www.fast2light.eu

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