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Al$_2$O$_3$ [20 nm, atomic layer deposition (ALD)] and SiO films’ [25 nm, physical vacuum deposition (PVD)] single barriers as well as hybrid barriers of the Al$_2$O$_3$/SiO or SiO/Al$_2$O$_3$ have been deposited onto single 100 nm thick tris-(8-hydroxyquinoline) aluminum (AlQ$_3$) organic films made onto silicon wafers. The defects in the different barrier layers could be easily observed as nonfluorescent AlQ$_3$ black spots, under ultraviolet light on the different systems stored into accelerated aging conditions (85 °C/85% RH, ~2000 h). It has been observed that all devices containing an Al$_2$O$_3$ layer present a lag time $\tau$ from which defect densities of the different systems start to increase significantly. This is coherent with the supposed pinhole-free nature of fresh, ALD-deposited, Al$_2$O$_3$ films. For $t > \tau$, the number of defect grows linearly with storage time. For devices with the single Al$_2$O$_3$ barrier layer, $\tau$ has been estimated to be 64 h. For $t > \tau$, the defect occurrence rate has been calculated to be 0.268/cm$^2$/h. Then, a total failure of fluorescence of the AlQ$_3$ film appears between 520 and 670 h, indicating that the Al$_2$O$_3$ barrier has been totally degraded by the hot moisture. Interestingly, the device with the hybrid barrier SiO/Al$_2$O$_3$ shows the same characteristics as the device with the single Al$_2$O$_3$ barrier ($\tau = 59$ h; 0.246/cm$^2$/h for $t > \tau$), indicating that Al$_2$O$_3$ ALD is the factor that limits the performance of the barrier system when it is directly exposed to moisture condensation. At the end of the storage period (1410 h), the defect density for the system with the hybrid SiO/Al$_2$O$_3$ barrier is 120/cm$^2$. The best sequence has been obtained when Al$_2$O$_3$ is passivated by the SiO layer (Al$_2$O$_3$/SiO). In that case, a large lag time of 795 h and a very low defect growth rate of 0.032/cm$^2$/h ($t > \tau$) have been measured. At the end of the storage test (2003 h), the defect density remains very low, i.e., only 50/cm$^2$. On the other hand, the device with the single PVD-deposited SiO barrier layer shows no significant lag time ($\tau \approx 0$), and the number of defects grows linearly from initial time with a high occurrence rate of 0.517/cm$^2$/h. This is coherent with the pinhole-full nature of fresh, PVD-deposited, SiO films. At intermediate times, a second regime shows a lower defect occurrence rate of 0.062/cm$^2$/h. At a longer time span ($t > 1200$ h), the SiO barrier begins to degrade, and a localized crystallization onto the oxide surface, giving rise to new defects (occurrence rate 0.461/cm$^2$/h), could be observed. At the end of the test (2003 h), single SiO films show a very high defect density of 600/cm$^2$. Interestingly, the SiO surface in the Al$_2$O$_3$/SiO device does not appeared crystallized at a high time span, suggesting that the crystallization observed on the SiO surface in the AlQ$_3$/SiO device rather originates into the AlQ$_3$ layer, due to high humidity ingress on the organic layer through SiO pinholes. This has been confirmed by atomic force microscopy surface imaging of the AlQ$_3$/SiO surface showing a central hole in the crystallization zone with a 60 nm depth, deeper than SiO thickness (25 nm). Using the organic AlQ$_3$ sensor, the different observations made in this work give a quantitative comparison of defects’ occurrence and growth in ALD-deposited versus PVD-deposited oxide films, as well as in their combination PVD/ALD and ALD/PVD. © 2016 American Vacuum Society. [http://dx.doi.org/10.1116/1.4947289]

I. INTRODUCTION

The Holy Grail for encapsulation of fragile organic optoelectronic devices [organic light-emitting diodes (OLED), organic photovoltaics, and organic thin film transistors (OTFT)] consists in the addition of vacuum deposited thin mineral barrier such as oxides, nitrides, or oxinitrides layers directly onto the organic circuit. This technology is today’s so called thin-film encapsulation (TFE). The technology basics is somehow similar to the one encountered in the world of food packaging, where barrier materials such as Al, Al$_x$O$_y$, or SiO$_x$ are vacuum-deposited onto the plastic sheet surfaces, which act as barrier layers against moisture and oxygen. The main challenge today for organic optoelectronics is to achieve TFE with ultra-high barrier grade in order to allow a robust encapsulation with water vapor transmission rate (WVTR) $\approx 10^{-6}$ g/m$^2$/day necessary for OLED devices. Such achievements will open the way for the realization of lightweight, flexible OLED displays.

The atomic layer deposition (ALD) technology is highly suitable for making thin film barriers because it allows the deposition of pinhole-free and highly conformal, reproducible, oxide films at temperatures that are compatible with...
the limiting low glass transition temperature (typically 100 °C) of organic semiconductors that compose the devices. In particular, a couple of publications have demonstrated the capability of the Al2O3 ALD films to reach this high level of WVTR requirement \(^1\) as well as their applicability to encapsulate OLED.\(^2\) While being very good barriers against moisture at initial times (fresh films), these Al2O3 films suffer however from accelerated degradation, especially when they are exposed to high humidity content during storage tests. It is thus mandatory to shield the Al2O3 barrier films from moisture ingress with additional moisture-stable passivation layers. In a recent paper, we have proposed to passivate the Al2O3 ALD films by means of an ebeam-deposited SiO2 layer.\(^3\) The results have confirmed that the use of a SiO2 layer deposited on top of the Al2O3 barrier layer drastically decreases the level of defects into the raw Al2O3 layer (\(\sim 6\) times less defect).

Alternatively, silicon monoxide or SiO films deposited by physical vacuum deposition (PVD) (evaporation from resistive boats) have been extensively studied for decades and show better environmental barrier properties compared to SiO2.\(^4\) One of the first commercial exploitation of the oxide has been dedicated to the protection of Al and Ag metallic mirrors against corrosion and wear based on the work of Haas during World War II.\(^5\) Other applications involved SiO films, for instance, as antireflective coatings,\(^6\) thin-film capacitors,\(^7\) insulator in integrated circuits,\(^8\) and food packaging.\(^9\) Recently, SiO films have been introduced in OLED encapsulation architectures, as a buffer interlayer to protect OLED stack from plasma-based encapsulation of Al2O3 and SiNx, as well as an oxide layer in multilayer encapsulation for the protection of OTFT.\(^10\) An interesting recent paper from Suzuki et al. stated that the thermally evaporated SiO coatings can protect graphene from ozone and air up to 500 °C.\(^11\) The authors explained that the evaporation process is safe for the graphene material while the e-beam SiO2 process is detrimental to the graphene material because a buried graphene layer is severely damaged by the e-beam process itself. Finally, a publication even stated on the integration of a very thin SiO layer inside the OLED architecture to enhance the emission of the OLED.\(^12\)

While defect occurrence in the Al2O3 ALD films has been investigated recently using different methods, there are few studies on defect occurrence in the PVD-deposited SiO films,\(^13\) and to the best of our knowledge, no comparison between the occurrence and growth of defects in both types of barrier layers exists, at least based on the use of the same sensor to probe the defects. This is probably, in part, because (1) the use of ALD/PVD combination to achieve high environmental barrier quality is scarce and (2) the implementation of methods to visualize defects in the thin film barriers is not trivial. Regarding the latter, the pioneering works, based on the reactive ion etching in oxygen plasma of the barrier films deposited onto the plastic sheets followed by optical or electron-microscopic examination of the etched surface, have been developed by da Silva Soirinho and co-workers in the late 1990s for Si3N4 and SiO2 PECVD-deposited barrier films.\(^14\) Alternatively, one of the methods that allow the visualization of defects is the well-known calcium-test proposed first by Nisato in 2001.\(^15\) However, due to the high reactivity of calcium with water, fast and inhomogeneous corrosion of the calcium film arises,\(^16\) which may lead to flawed observations of the defects in the layer. Particularly with the PVD-deposited SiO, the evolution of the calcium film is very fast when the device is exposed to ambient conditions (21°C/50% RH) that it is impossible to get a clear interpretation of the defect evolution.\(^17\) As a corollary, this also means that a clear distinction between the pinhole-type defects and microstructural defects cannot be made.

In this work, we have studied the defect occurrence and growth mechanisms of the Al2O3 ALD and SiO PVD barrier layers, as well as a combination of both SiO/Al2O3 and Al2O3/SiO. For this purpose, we have used the AlQ3-based fluorescence test described in previous publications.\(^3\) In Ref. 21, we showed that a very simple structure of Si/AlQ3/Al2O3 allows the visualization of defects in the Al2O3 barrier layer, which are revealed by the observation, under ultraviolet (UV) light, of nonfluorescent black spots in the AlQ3 layer beneath, when the device is stored under harsh conditions. The method has been applied here for the observation of defects in single barrier layers by making devices of Si/AlQ3/SiO and Si/AlQ3/Al2O3 and, concomitantly, hybrid devices of Si/AlQ3/SiO/Al2O3 and Si/AlQ3/Al2O3/SiO. The details of the four devices that will be investigated in this work have been listed in Table I.

II. EXPERIMENT
A. Thin-film deposition

AlQ3 films have been deposited onto the 200 mm silicon wafers by vacuum deposition. The whole process took place in a clean room environment, and the evaporation tool was a cluster tool Sunicell Plus 200 from Sunic Systems. The clean silicon wafers have been used as received. Once introduced inside the cluster tool, the silicon wafers were Ar-plasma treated (60 W, 60 s). The base pressure in the deposition chamber was 1.33 × 10⁻⁵ Pa. The evaporation rate of the AlQ3 molecule was ~0.1 Å/s. The deposition has been performed through a shadow mask to allow 135 pads of the organic molecule (~9 × 5mm² each) to be deposited independently onto the silicon wafer. The organic layer thickness was controlled by a quartz monitor and was cross-checked by ex situ profilometer measurement. The silicon wafers with the organic pads were stored into a N₂ filled glove box from MBraun (UniLab model) directly connected to the Sunicell system and then transferred to a Savannah 200 ALD system from Ultratech/Cambridge Nanotech, hermetically embedded in another UniLab glove box system. The whole process took place in an inert atmosphere using the particle-controlled transfer inert boxes. The ALD process has been performed at 85 °C from trimethylaluminum/H₂O precursors at a GPC of 0.85 Å/cycle. Prior to deposition, the silicon wafer with organic pads onto it has been allowed to degas for 1800 s inside the ALD chamber. The first precursor to be pulsed during the ALD run was H₂O. The SiO films have been deposited in the same cluster tool by thermal
evaporation from dedicated sources with chimney design which eliminate spitting from the SiO to the substrate. After deposition of Al$_2$O$_3$, device B2 has been quickly (couple of minutes) exposed to air during its reloading into the Sunicell Plus 200 tool for the final deposition of SiO coating. The substrate temperature was 20°C, and the deposition rate was optimized at 0.1 å/s to further decrease spitting phenomenon. Two kinds of silicon monoxide compounds have been purchased at Umicore with two different grain sizes, 3.5–5 mm and 0.2–0.7 mm (purity 99.99%). They were mixed together into the dedicated crucible before loading into the vacuum chamber. SiO films have been made under secondary vacuum (1×10$^{-5}$ Pa).

B. Thin-film characterization

1. Ellipsometry

The spectroscopic ellipsometry (SE) analyses were performed using a Woollam M2000 rotating compensator ellipsometer, which features automated variable angle of incidence capability (VASE), 193–1700 nm spectral range, and a spot size in the millimeter range. First, the analysis was limited to a spectral region where the layer is optically transparent (600–1700 nm) to determine its thickness and refractive index in this limited range, using a Cauchy model. Then, at a fixed thickness, the refractive index has been calculated at each wavelength of the investigated spectral range. Finally, based on this mathematical approximation, an oscillator-based model (Tauc Lorentz), Kramers-Kronig consistent, was built to fully describe the optical dispersion of the layer, including the position and shape of the absorption peak in the UV range.

2. Storage test into climatic chamber

The storage of wafers has been done in a climatic test chamber from Votsch. The conditions have been fixed to 85°C/85% RH during the entire test. The samples have been extracted from the climatic chamber directly to the laboratory atmosphere (21°C/50% RH) for each measurement. Fluorescent imaging of AlQ$_3$ films in the different devices has been performed by using a UV-vis broadband Hg lamp (350 mW/cm$^2$ at the wafer surface) connected to an Olympus BX 51 optical microscope (mounted with an Infinity 2 CCD camera from Lumenera), which allows the excitation of the AlQ$_3$ films with only the UV part of the lamp and the large band observation in the visible (fluorescence of the AlQ$_3$ film is green). The observations have been performed onto middle pads to avoid dispersion due to the AlQ$_3$ thickness variation onto the whole 200 mm silicon wafer. Ten to fifteen AlQ$_3$ pads have been randomly chosen each time to ensure a good statistical characterization. All samples have been blown with a particle filtered N$_2$ gun before each observation sequence. The black spot defects have been counted manually from the picture taken using a high resolution camera. Their size distribution of defects onto device A1 has been calculated using IMAGEM software analyze particle module with a suitable thresholding of the image, as well as a size calibration of the image surface.

3. Surface imaging

AFM measurements have been performed with an AFM Dimension 3100 (Nanoscope IIIA controller) from Veeco. The contact mode has been employed for that purpose together with a precalibration of the probe onto the calibrated Au grids. The AFM tool has been used to image defects onto the sample surfaces. SEM imaging has been performed with a scanning electron microscope Ultra + 55 from Zeiss.

III. RESULTS AND DISCUSSION

A. Characterization of single films SiO and Al$_2$O$_3$

Figure 1 shows the optical index $n$ of the PVD-deposited SiO films and ALD-deposited Al$_2$O$_3$ films in the visible part of the electromagnetic spectrum.

![Fig. 1. Optical index $n$ of 25 nm thick PVD-deposited SiO (full line) and 50 nm ALD-deposited Al$_2$O$_3$ (dashed line).](image-url)

The
Al₂O₃ film (50 nm) has an optical index of 1.62 at 555 nm in accordance with literature values for this low temperature-deposited, water-oxidized, oxide film. A particular attention has been given for the deposition of SiO films. It is known that the SiO material can easily spith from the crucible during sublimation. Spitting refers to the scattering of particles or cluster of materials onto the substrate. These particles cause defects and pinholes in the growing film. As a consequence, the lowest deposition rate (0.1 Å/s) has been chosen for all experiments in order to deposit a SiO layer with the lowest defect density. Usually, these very low deposition rates imply that the stoichiometry should be rather toward SiO₂ because, at a low deposition rate, a large fraction of SiO in the film is sublimated. However, as the degree of oxidation depends on the partial pressure of oxygen, a very low partial pressure in our case (10⁻³ Pa vs 6 × 10⁻²² in Ref. 24) ensures that the SiO is not further oxidized into SiO₂ even at extremely low deposition rates, as confirmed by optical measurements made on our SiO films. Then, we investigated their use as a passivation layer onto the water-sensitive Al₂O₃ ALD barrier films, as an alternative to the e-beam deposited SiO₂ barrier films that we have already discussed in Ref. 3. Some internal experiments (unpublished) made on the raw e-beam deposited SiO₂ and vacuum-evaporated SiO films onto the Si wafers have led to the conclusion that the SiO₂ films show an advanced degradation under hot humidity, compared to the SiO ones, confirming that the SiO₂ films are much sensitive to water, as described in Ref. 25. This observation was the main motivation to replace SiO₂ material by SiO in this work, as a moisture stable passivation layer for Al₂O₃.

**B. Characterization of devices A1 and A2 (single barrier layers)**

Devices A1 and A2 are described in Table I. Figures 2 and 3 describe the defect density evolution versus storage time for device A1 and device A2, respectively. It has been observed that the black spot occurrence rates can be decomposed into different regimes (numbered 1, 2, and 3 in different figures). The defect occurrence rates are represented by the slope of the linear fits of the defect density evolution versus time. They have been named \( z_i \), \( i = 1,2,3 \) representing each regime zone.

The defect occurrence rates, as well as \( \beta \) and \( \tau \) parameters that represent the intercept on y axis at \( t = 0 \) (from regression curve in regime 1 only) and the lag time, are listed in Table II, respectively.

The value of \( \beta \) represents the residual black spot density of the fresh samples. The lag time \( \tau \) is defined as the time for the number of defects to grow significantly (slope > 0) and has been assessed by the intercept of linear regression of plots in regimes 1 and 2. Both \( \beta \) and \( \tau \) have been defined on the inset of Fig. 3 for clarity.

The hatched pattern in Fig. 3 indicates that the fluorescence of device A2 totally failed during this time window. This might be the signature of the total failure of the Al₂O₃ barrier layer due to the great quantity of water in air at 85 °C/85% RH. As a consequence, the Al₂O₃ films were completely exposed to hot moisture and degrade very quickly as we have previously observed for Si/AlQ₃ (100 nm) devices in 65 °C/85% RH storage conditions. This total failure occurs at a time which stands in between 520 and 670 h. This behavior is similar to what Park et al. have observed: a total degradation of OLED encapsulated by a single Al₂O₃ ALD layer after \( \sim500h \), in 60 °C/90% RH storage conditions. At the end of the storage test, the defect densities have been estimated to be 600/cm² (2003 h) for device A1.

**Table II. Description of different parameters \( z_i, \beta, \) and \( \tau \) calculated from the different regimes of defect density evolution vs time in Figs. 2, 3, 9, and 10.**

<table>
<thead>
<tr>
<th>Sample</th>
<th>( z_1 ) (cm²/h)</th>
<th>( z_2 ) (cm²/h)</th>
<th>( z_3 ) (cm²/h)</th>
<th>( \beta ) (cm²)</th>
<th>( \tau ) (h)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A1</td>
<td>0.517</td>
<td>0.062</td>
<td>0.461</td>
<td>3.40</td>
<td>0</td>
</tr>
<tr>
<td>A2</td>
<td>0.005</td>
<td>0.268</td>
<td>0.005</td>
<td>2.71</td>
<td>64</td>
</tr>
<tr>
<td>B1</td>
<td>0.002</td>
<td>0.246</td>
<td>0.005</td>
<td>1.11</td>
<td>59</td>
</tr>
<tr>
<td>B2</td>
<td>0.001</td>
<td>0.032</td>
<td>0.001</td>
<td>1.82</td>
<td>764</td>
</tr>
</tbody>
</table>

\( ^a \)Regime 3 nonexistent for A2 because of device total failure in the time window 551–663 h.

\( ^b \)Regime 3 not reached for B2 on this time scale.
Figure 4 shows the optical images of device A1 and A2 surfaces at the end of the storage.

It can be seen on the device A1 surface that the size distribution of the black spot defects is quite large with minimum detectable defect sizes of few microns in diameter and large defect sizes of several hundreds of microns in diameter. We noticed that big (typically $>100 \, \mu m$), nongeometrical, black spots are related to the presence of a particle in the middle (with an observed density of $<5/cm^2$). We infer that small (typically $<100 \, \mu m$), perfectly round-shaped, black spots are rather related to a pinhole in the SiO coating. We often also noticed some clusters of defects in random area on the different samples (see the arrow in Fig. 4, device A1). The origin of such clusters is not understood. The huge defect density of device A1 is in accordance with pinhole-rich nature of the SiO films obtained by thermal evaporation. Besides, we noticed at the end of the test another type of defects on the device A1 surface. These defects have been observed only at the end of regime 2, and their exact occurrence time is undefined. They do not exist onto other devices. They have been described in Fig. 5 from optical and AFM images.

A detailed investigation shows dendritic features on the SiO films surface, spreading from a central black spot (see optical photograph). From the AFM image, it can be seen that the central black spot correlates with a pinhole (diameter $<5 \, \mu m$) whose depth has been estimated to be $\sim 60 \, nm$ (Fig. 6).

The hole therefore is extending through the whole 25 nm thick SiO film deep into the AlQ3 layer, suggesting that the crystallization originates rather from the organic film AlQ3. The sudden increase in defect occurrence in regime

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**Fig. 4.** (Color online) Optical images of devices (a) A1, (b) A2, (c) B1, and (d) B2 at the end of storage test (see Table I); the full area of each image corresponds to $6 \times 4 \, mm^2$. The white arrow on A1 shows a localized cluster of black spots.
3 correlates with these new features. Figure 7 depicts the black spot mean diameter evolution versus storage time, for device A1, as calculated from the binarized images using IMAGEJ software.

The growth rate has been calculated to be 0.04 \( \mu \text{m/h} \) between initial time and \( \approx 630 \) h. Then, the lateral expansion becomes zero between \( \approx 630 \) h and the end of storage, suggesting that water diffusion is impeded by the crystallization of the AlQ\(_3\) organic film underneath the SiO barrier layer. We infer that the lateral expansion of the dark spot may also depend on the initial size of the pinhole in the SiO layer. Figure 8 depicts a SEM image of device A1 and device A2 surfaces at the end of storage, 2003 and 670 h, respectively. The particles on the surface are presumably residual dust particles coming from the storage in the climatic chamber. They have been used in order to image the device surface easily during SEM imaging process. The SEM images clearly indicate a smooth surface of the SiO layer in device A1 and a rough surface of the Al\(_2\)O\(_3\) layer in device A2. The circular defect on device A1 surface is presumably corresponding to a black-spot type defect, with a diameter of approximately 14 \( \mu \text{m} \). Interestingly, it shows a wrinkly surface inside the circular zone, suggesting a probable delamination at the AlQ\(_3\)/SiO interface. Outside the defect zone, the SiO layer turns out to be very smooth, attesting the high stability of this layer against hot humid environments. The rough surface of the Al\(_2\)O\(_3\) film in device A2 is, on the contrary, the proof of the high reactivity of the ALD-deposited aluminum oxide in hot humid environments.

C. Characterization of devices B1 and B2 (hybrid barrier layers)

The hybrid barrier films have been constructed onto the AlQ\(_3\) organic layer, as described in Table I, leading to devices B1 and B2 whose barrier films’ deposition sequences are PVD/ALD and ALD/PVD, respectively. The evolution of defect densities has been depicted in Figs. 9 and 10 for devices B1 and B2, respectively. For device B1, the slope in regime 1 is very low, \( a_1 = 0.002/\text{cm}^2/\text{h} \), and the lag time is \( \tau = 59 \) h (see Fig. 9 inset for clarity), similar to the lag time...
value obtained for device A2. The slope in regime 2, from 55 to 520 h, drastically increases to $a_2 = 0.246/cm^2/h$, a value which is very close to that of device A2, suggesting that Al$_2$O$_3$ ALD is the factor that limits the performance of the barrier system when it is exposed directly to the atmosphere. The slope in regime 3, from 520 to 1410 h, is $a_3 = 0.005/cm^2/h$.

For device B2, the slope in regime 1 is $a_1 = 0.001/cm^2/h$, and the lag time is very high, $\tau = 795 h$, $\sim 13$ times the mean lag time values measured on devices A2 and B1. The slope in regime 2, from 795 to 2003 h, is $a_2 = 0.032/cm^2/h$. The slope in the regime 3 could not be assessed because on the time scale of the study, regime 3 is nonexistent for this device. At the end of the storage test, the defect densities have been estimated to be 120/cm$^2$ (1410 h) for device B1 and 50/cm$^2$ (2003 h) for device B2. These low defect densities surfaces could be seen in Fig. 4 showing the surfaces of devices B1 and B2 under UV light. Contrary to device A1, device B2 does not show any crystallized features on the SiO surface at a long storage time.

D. Discussion

The first observation made from the results described above is that all devices having an Al$_2$O$_3$ layer in their structure show a lag time feature $\tau$, defined here as the time when defects' density starts to significantly increase for devices A2, B1, and B2. Only device A1 with the single SiO layer does not show any significant lag time ($\tau \sim 0$). The PVD-deposited SiO films have been extensively studied in the food packaging industry. These barrier coatings have been used instead of SiO$_2$ ones because they are presumably better moisture barrier candidates with a high stability against moisture. In this work, it is clear that the barrier layer in device A1 showed a very high stability against storage, up to 2000 h: at the end of the test, the AlQ$_3$ films are still fluorescent despite the numerous black defects, and the SiO surface is still smooth (at least compared to the Al$_2$O$_3$ surface imaged by SEM onto device A2). The three different regimes in device A1 probably reflect a large distribution of pinhole sizes in the film, each zone representing a mean pore diameter. Transition from one regime to another is probably driven by the different diffusion rates of water molecules inside the different pore sizes. At the end of the storage test, the defect density has been calculated to be $\sim 600/cm^2$. It is noteworthy that the defect density of the SiO film produced by thermal evaporation in this work is relatively low. da Silva Sobrinho et al. have, for instance, measured the defect densities of the PECVD-deposited SiO$_2$ and SiNx barrier films to be 8000/cm$^2$,[16] which are 13 times higher than the defect density of our SiO coating. Their process was however not taking place in clean room conditions; therefore,
a strong particle contamination is expected, leading to a high particle level contamination. The benefit of the clean room deposition as well as the care that has been taken for the optimization of the deposition rate of the SiO films is therefore undeniable in this work.

For Al2O3, the existence of a lag time is coherent with previous works. In the work of Bertrand and George, they measured a blooming time of 32 h for an 18.7 nm thick Al2O3 film deposited onto a Ca sensor. These authors explained that the blooming phenomenon may be due to water molecules traveling through hydroxyl defects in the oxide layer, during a mean 37 h traveling time before reacting with the Ca in its metallic state. In the 0–37 h period of time, the residual defect density (∼1/cm², calculated from the paper data) are due to pinholes coming from extrinsic particles present on the Ca surface at the initial time. In our study, the lag time we described is analogous to the blooming time because from this very time the defect occurrence rate increases suddenly for devices A2, B1, and B2. The mean lag time we measured for devices A2 and B1 (those for which Al2O3 is directly exposed to hot moisture) is 61.5 ± 3.5 h, almost double the value measured by Bertrand et al. This difference could not be easily explained by considering only the difference of water content in air between 70°C/28% RH (Bertrand et al.) and 85°C/85% RH (this work). Indeed in the first storage conditions, the amount of water in air has been calculated to be ∼65 g/kg while it is ∼590 g/kg (calculation not detailed here) for the second one. Therefore, assuming that water diffusivity in the barrier layer is proportional to water concentration, we should have calculated a lag time at least ∼9 times (590/65) lower than 37 h, for almost the same Al2O3 thickness (18.7 vs 20 nm). On the contrary, the value is almost doubled compared to the work of Bertrand et al. The oxide layer composition should not be so different compared to Bertrand et al. because the ALD layer growth has been made from the same precursors, both at rather low temperature (120°C vs 85°C). We tested internally (unpublished results) the evolution of Si/Ca (100 nm)/SiO (25 nm) samples. In that configuration, the evolution of the Ca film was so quick at the laboratory ambient that it was impossible to extract a clear interpretation of evolution of the Ca. In the case of Si/Al2O3, we have observed that a homogeneous degradation of the Ca film was not possible because of localized degradation that flaws the monotonous evolution of the conductance G so that the general relation KVTR ∝ f(dG/dt) is not easily applicable. In order to circumvent this issue, we previously proposed to use a buffer layer, which allows a homogeneous surface oxidation of Ca, in order to assess the KVTR of ALD Al2O3 barrier layer from Ca-test conductance measurement [from the general relation KVTR ∝ f(dG/dt)]. It is clear that the reaction of Ca with water, even small quantities, could be detrimental to the barrier layers because of the outgassing H2 gas and volume expansion of the Ca(OH)2 compound. On the contrary, the reaction of the AlQ3 organic molecule with water does not give any outgassing as described in Ref. 27. A small volume expansion should also be expected due to the presumed crystallization of the AlQ3 layer as described previously, so that for small quantity of water reaching the sensor, the change in the AlQ3 layer underneath are supposed to be too small to be detectable with optical microscopy.

The most striking point in this work is obtained when we compare device A2 and B1 to device B2. Device B2 shows a large lag time of 795 h, almost 13 times higher compared to device A2 and B1. This result is in perfect accordance with our previous study, in an effort to protect the Al2O3 films from moisture ingress by employing a 25 nm-thick, e-beam deposited, SiO2. The data point from Ref. 3 has been added to Fig. 10 (open square). It can be seen that the defect density level is higher with SiO2 compared to SiO in the same device architecture B2, for the same storage conditions. The interesting point regarding device B2 is that regime 3 does not exist on this time scale. Regime 3 for device B2 will probably occur at a time >2003 h. This behavior clearly demonstrates that a minimum amount of water is responsible for the sudden occurrence, or blooming, of defects in the thin Al2O3 layer. If we assume a KVTRAl2O3 of 2 × 10⁻⁵ g/m²/day for a 20 nm thick Al2O3 layer in 85°C/85% RH conditions, as we have presented the calculation in Ref. 26, using a modified calcium-test with a buffer layer to ensure a homogeneous oxidation of the calcium film, it is easy to estimate KVTRAl2O3/SiO for the hybrid barrier Al2O3/SiO in device B2. For device A2, the minimum water quantity Q, for the defects to appear, per surface area, could be calculated from the lag time, which can be seen as a measure of the time it takes for the permeant gas front to reach the AlQ3 sensor, for a given barrier. It is

\[ Q = KVTR_{Al2O3} \times \tau_{Al2O3}, \]

which gives numerically \[ Q = 1.3 \times 10^{-3} \text{ g/m}^2 \] with \[ \tau_{Al2O3} = 64 \text{ h} \]. Assuming that the same quantity of water has diffused through the Al2O3/SiO barrier in device B2, with a lag time of 795 h, KVTRAl2O3/SiO could be therefore estimated from

\[ KVTR_{Al2O3/SiO} = \frac{Q}{\tau_{Al2O3/SiO}}. \]

The numerical calculation gives KVTRAl2O3/SiO = 1.6 × 10⁻⁶ g/m²/day. This value corresponds to the KVTR of the Al2O3/SiO barrier coating.

Alternatively for device B1, for which the lag time is identical to device A2, the KVTR is no less than 2.2 × 10⁻⁵ g/m²/day showing that the SiO/Al2O3 layout is no more effective as moisture barrier compared to single Al2O3 in device A2. Regardless of the KVTR value, this is contradictory to what has been observed by Yun et al. when a single Al2O3 barrier film is compared to a SiO/Al2O3 barrier film, both deposited onto a PEN sheet. The authors measured a 2.3 times decrease in the KVTR value of SiO/Al2O3 (3.3 × 10⁻³ g/m²/day) compared to Al2O3 (7.6 × 10⁻³ g/m²/day). However, in this publication, there is no mention of how the measurement has been made, in particular, if the Al2O3 film has been exposed directly to the moisture flow inside the permeameter, or reversely, if it has been measured...
opposite to the moisture flow, which may literally change the results according to Ref. 28.

This result obtained on device B2 is comforted by the work of Bulusu et al. who described the passivation of Al2O3 ALD films by means of a thin TiO2 capping layer, either by ALD (7 nm) or e-beam deposition (5 nm) in order to protect the Al2O3 film from degradation in aqueous environment (full immersion in deionized water).29 The authors reported that the Al2O3/oxide passivated system shows remarkable stability after ten days of immersion while the reference device without the extra capping layer degrades quickly.

IV. SUMMARY AND CONCLUSIONS

In summary, by using the AlQ3 organic film as a fluorescent sensor to probe defects in barrier layers, it has been shown that the passivation of ALD-deposited Al2O3 (20 nm) by means of a simple SiO layer (25 nm), deposited by thermal vacuum deposition under controlled conditions, is highly efficient because it preserves Al2O3 from moisture ingress and subsequent premature degradation. A very high lag time of 795 h has been calculated for the Al2O3/SiO barrier film, which is a 13 times improvement factor compared to a single Al2O3. In the meantime, it has been seen that the SiO layer itself shows a high density of pinholes that act as entry paths for water molecules. The SiO material is however highly stable under water vapor and acts consequently as a stable passivation layer for the ALD-deposited oxide, impeding condensation of moisture on the ALD-deposited film. We estimated a high WVTR for the Al2O3/SiO barrier layer, equal to $1.6 \times 10^{-6}$ g/m²/day in 85°C/85% RH conditions. We finally discussed the importance of having a stable sensor to sense the penetration of water through the barrier films. The AlQ3 organic film, which allows the observation of defects as black spots under UV light, turns out to be a good alternative to the metallic Ca films that may prematurely degrade the barrier because of H2 outgassing as well as volume expansion upon reaction with permeant water molecules.

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19Unpublished results.