Fluorescence tag-based inspection of barrier coatings for organic light emitting diodes and polymer packages

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1. Introduction

Barrier coatings are essential to protect organic light emitting diodes (OLED) and other polymer packaged components from moisture- and oxygen-aided deterioration. One such coating technology is atomic layer deposition (ALD), which can be used to grow a nano-thickness, pin-hole free, and uniform alumina layer on a polymer substrate even at temperatures as low as 33 °C [1]. The water vapor permeability for ALD alumina can be lower than 0.0001 gram/m^2/day, which is 10,000X better than that of a typical polymer [2, 3]. Such improvement may enable flexible polymer packaging for flexible displays, OLED, and other chemically sensitive electronics.

To limit defects and cracks in the barrier coating, which allow the leakage of reactive species, is very important to barrier quality. Gas (oxygen or helium) or water vapor transmission are often used to characterize the barrier coating [4]. The "Mocon" test is commonly used for measuring the oxygen and water vapor transmission rate (WVTR). But, as its sensitivity cannot satisfy barrier transmission specification for the OLED application, the Calcium [5], and HTO tests [6] have been recently used to evaluate ALD barrier coating quality. However, these tests are time-consuming and not easy to implement, and therefore not suitable for rapid quality evaluation expected in a manufacturing environment. It is well known that the measurable permeability is attributed to the defects in the coating, such as pinholes or cracks, which allow the leakage of reactive species [7, 8]. The quality of the barrier coating is directly related to the defect density in the coating. Table1 compares the defect densities between various state-of-the-art barrier coatings. The defect densities are estimated based on the WVTR and oxygen transmission rate (OTR) data using the model described in [7]. For easy comparison, we used the nominal defect size of 0.6 μm as demonstrated in [7]. The ALD barrier coating is of much better quality than the conventional coatings, attributed to the lack of pin-hole defects.

As no barrier coating technology is perfect, coating-related defects have to be inspected and controlled to assure high-yield manufacturing. However, the characteristics of ALD barrier coatings, such as nanoscale thickness, transparency, and smooth surface, make it formidable to inspect the defects directly using common microscopy-enabled methods. In the past, researchers have used O_2 plasma etching or aching to undercut and enlarge defects or cracks [7, 9], which can require extensive sample preparation. In support of fast defect inspection, we have developed novel fluorescent tags which are capable of identifying nanometer-scaled defects. This approach allows rapid quality inspection of ALD alumina barrier coating on polymer substrates used for OLED encapsulation.

The fluorescent tag molecule has a particularly designed lipophilic moeity that facilitates selective binding to defect sites, based on the surface adhesion characteristics of the material system. As shown in Fig. 1, the tag binds solely to the polymer substrate, based on its greater hydrophobicity. The tag molecules bear a fluorescent moiety, allowing for their identification at specific wavelengths. In addition, the tag has been designed to bear a relatively small molecule size, i.e. molecular weight of ~300, allowing the tag molecule to easily enter into nanometer-scale defects.

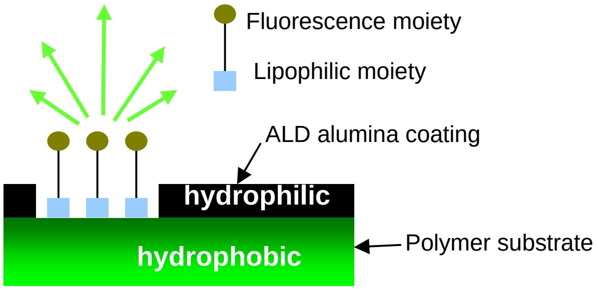

Figure 1. Fluorescent tag labeling mechanism, in which the tag binds solely to the polymer substrate, based on its greater hydrophobicity

2. Mechanical cracks visualization

To demonstrate the tagging application, 25 nm thick ALD alumina barrier films were deposited onto Polyethylene Naphthalate (PEN) substrates. The coated specimens, some of which were mechanically manipulated in order to intentionally generate defects, were then soaked in a fluorescent tag solution for 5 min. Then solvent solution containing 70% ethanol and 30% water was used to wash away the excess tag that was not specifically attached to the film. The sample was then dried using clean dry air and maintained in an ultraviolet-safe environment. The tag can be excited by many commonly used excitation sources, yielding a bright fluorescent signal. A LSM 510 confocal microscope (Carl Zeiss, Inc.) was specifically used for the tag inspection. A 488nm laser source was used to excite the tag and the fluorescent emission (maximum at 515 nm) was measured with a 505-530 nm band pass filter.

We tested a PEN substrate with an ALD alumina coating, and an identically coated PEN substrate bearing intentionally-made scratches, respectively. As shown in Figure2 (a), the fluorescent tag does not attach to the ALD alumina, which consists of an all dark field. For the scratched ALD alumina coating, the tag attached only to the exposed PEN, as shown in Figure2 (b). Figure 2 demonstrates that the tag will selectively attach to the polymer substrate, where it is exposed in the PEN/alumina materials system.

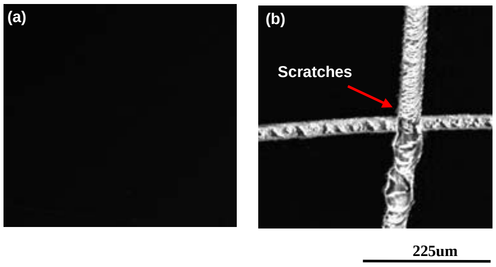

Figure 2 Fluorescence enabled imaging, demonstrating the tag molecules do not adhere to PEN substrate coated with ALD alumina (left); but adhere selectively to scratches introduced to ALD alumina coating (right).

3. Tag molecules-enabled visualization of mechanical "channel-cracks"

The failure mode of "channel cracking" is commonly encountered when a brittle inorganic coating is subjected to mechanical strain or thermal cycling. However, a series of such cracks is not readily observed in transparent films. To demonstrate the use of the fluorescent tag, an external tensile loading was applied to PEN substrates coated with 25 nm of ALD alumina. The fluorescent tag was then applied to these specimens according the previously described procedure. Figure 3 (a) shows cracks identified across the gage section of a specimen that was elongated to 5% strain. Such cracks, which propagated in the direction orthogonal to the applied load, are common when the stress in brittle films exceeds their critical threshold limit.

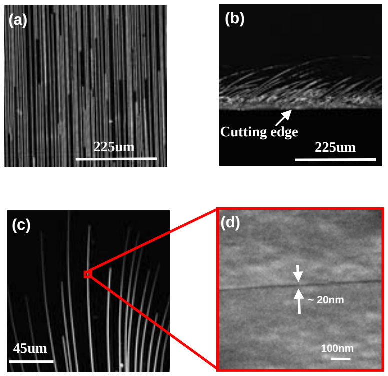

Figure 3 Cracks in the ALD alumina coating rendered visible by the fluorescent tag: (a) series of channel cracks generated at the specimen's interior after a 5% externally applied strain, (b) cracks at edge of specimen resulting from shearing during sample preparation, (c) the fully-developed region of the shear cracks, (d) FESEM image demonstrating the true size of a single shear crack

The cracks in Figure 3 (a) may be distinguished from those at the edges of the specimen, shown in Figure 3 (b), which were generated during the sample preparation. Specifically, these cracks were generated in shear when the specimen was cut to size prior to testing. Figure 3 (b) identifies the unique characteristics of the shear cracks, which quickly arrest near the edge of the specimen. Excellent image contrast was obtained in all of the confocal measurements, allowing cracks to be readily identified despite minimal sample preparation. At the fully formed region of the shear cracks Figure 3(c), the crack opening is observed to be ~20nm using a JSM-7401F field emission scanning electron microscope (FESEM, JEOL Limited), Figure 3(d). In comparison, the standard fracture mechanics solution predicts the crack opening displacement of 28 nm for the alumina coating [10]. Importantly, the true minimum feature size is identified using the FESEM. Disparity in the size (width) of the cracks between the fluorescence and FESEM measurements may be explained according to the point spread distribution of the combined specimen/microscope system. Compared with SEM observation, however, the tagging offers the advantage of continuous observation at low magnification, allowing a large field size to be examined.

4. Visualization of individual defects and particles

In contrast to mechanical cracks, individual defects are generally caused by particulate contamination and/or the substrate surface roughness. In the absence of mechanical cracks, tiny individual defects become the critical features limiting barrier permeation. Fig. 4(b), obtained from the fluorescent tag, shows a defect rich region in 25 nm thick ALD alumina coating deposited on PEN. Prescribed marker features were made on the ALD coating as the white arrows indicated in Fig. 4(b) to facilitate defect location during imaging. Sites #1 and #2, shown in Fig. 4(a) and (c), respectively, were subsequently observed using the FESEM in order to more accurately determine the size of the individual defects. For sites #1 and #2, the diameters of ~200nm and ~1.2um were determined, as indicated in Fig. 4(a) and (c). In addition to site #1, defects smaller than 200nm were also rendered by the tag during continued inspection. This indicates that the minimum detectable defect size for the tag is below 200nm. Fig. 4 also provides information about the morphology of the individual defects. From Fig. 4(a), the oval shaped defect bears a tiny crack at its top end. Concerning the origin of the defect, it could have been generated by a particle contained within on impressed into the specimen. The tag, however, does not necessarily distinguish between contamination occurring before or after coating and the sources of contamination are currently being investigated. Regardless of the origin of the defect, its interaction with alumina coating resulted in crack formation, perhaps based on residual stress or alternately through abrasion. Fig. 4(a) identifies that individual defects serve as the crack initiation sources during the coating processing and subsequent handling. The defect in Fig. 4(c) is explained as a contaminated region, to which alumina was not able to form the chemical bond required for ALD. Information, including the size and morphology of defects, is essential to the improvement of barrier quality. However, defect inspection becomes very cumbersome for transparent and nanoscale-thick coatings using SEM or atomic force microscopy (AFM), because the general defect-locations as well as the defect density cannot be determined at low magnification, whereas examination at high magnification (subject to a small field size) is not very efficient.

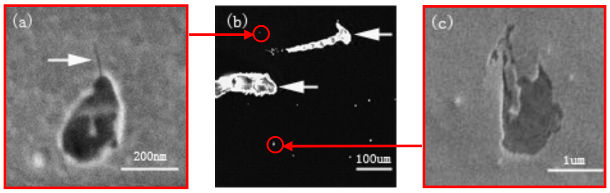

Fig. 4: Individual defects in/on the ALD alumina coating rendered visible by the fluorescent tag: (b) the defect density and location is rendered at low magnification using confocal microscopy, allowing the details of size and morphology to be indentified in high magnification FESEM images, insets (a) and (c).

5. Conclusion and application

A fluorescent tag molecules-enabled visualization technique is developed for rapid inspection and evaluation of the quality of barrier coatings. Excellent selectivity was demonstrated for the material system consisting of a PEN substrate coated with ALD alumina. The tag readily identified channel cracks ~20 nanometers in width and individual defects as small as 200 nanometers in diameter. The excellent image contrast for the taggant advantageously allows the defect location and density to be determined at low magnification, whereupon additional details can be determined at high magnification. This novel method can be applied to barrier quality inspection in research and manufacturing of OLED, polymer packages and other organic components or systems.

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