Atomic Layer Deposition on Polymers for Ultralow Water Vapor Transmission Rates: The Ca Test

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ABSTRACT

Ultralow permeability gas diffusion barriers on polymers with water vapor transmission rates (WVTRs) as low as \(<10^4\) g/m²/day are required for organic electronic and thin film photovoltaic devices. The Ca test is the only technique with sufficient sensitivity to measure these ultralow WVTRs. WVTR values as low as \(5 \times 10^3\) g/m²/day have been measured for Al₂O₃ atomic layer deposition (ALD) films at 38°C/85 %RH using the Ca test with optical transmission probing (J. Appl. Phys. 106, 023533 (2009)). However, glass lid control experiments indicated that these WVTRs were limited by H₂O permeability through the epoxy seal. Several new implementations of the Ca test were explored to overcome the limitations caused by epoxy seals. In one design, the Al₂O₃ ALD barrier was deposited directly on the Ca test film and the electrical conductance method was used to monitor the Ca oxidation. This design allowed the direct observation of pinhole defects in the Al₂O₃ ALD barrier. However, the electrical conductance changed dramatically when the oxidized areas of Ca prevented electron conduction across the Ca film. A second design also measured the electrical conductance of Ca films in a test chamber that does not require epoxy seals. In this case, the polymer films were attached to the test apparatus using differential seals. All components in the apparatus were also baked in vacuum to remove any residual H₂O. This new test setup has yielded a baseline WVTR of \(\sim 1.0 \times 10^4\) g/m²/day that should enable accurate measurement of the WVTR of Al₂O₃ ALD ultrabarriers.

INTRODUCTION

Atomic Layer Deposition (ALD) has shown promise as a technique to deposit conformal, transparent gas diffusion barriers [1, 2]. These barriers can protect organic electronic or thin film solar devices from degradation by water and oxygen [3]. A water vapor transmission rate (WVTR) of \(<10^4\) g/m²/day and an oxygen transmission rate (OTR) at STP of \(<10^5\) cm³/m²/day are needed for organic based electronics to reach device lifetimes of 10,000 hrs [4]. These requirements arise from the sensitivity of the low work function metals (e.g. Ca, Li, Mg) in these devices. There is great interest in fabricating organic electronic devices on flexible polymer substrates. However, these polymer substrates must have a gas diffusion barrier because they have a WVTR on the order of 10-0.1 g/m²/day [4].

The development of gas diffusion barriers needs an accurate method for determining H₂O and O₂ permeation rates. In 2001, Nisato et. al described a testing method using calcium (Ca) metal for measuring low H₂O and O₂ permeation rates [5]. Their tests relied on using optical observations of the oxidation of metallic Ca to Ca(OH)₂ and CaO to determine calcium corrosion rates. Other groups have subsequently employed the Ca test with optical transmission probing to measure gas diffusion barriers [6]. A similar Ca test method was recently used by DuPont to evaluate Al₂O₃ ALD barriers on polymer substrates [2]. An illustration of the Ca test at DuPont is shown in Figure 1 [2]. The barrier film is adhered to the Ca test films on a glass substrate using an epoxy seal. The Ca test revealed that the Al₂O₃ ALD film was an excellent barrier and effective WVTR values of \(\sim 5 \times 10^4\) g/m²/day were obtained at 38°C/85 % relative humidity (RH) [7].

![Figure 1: Optical transmission test configuration.](image)

LIMITATIONS OF Ca TEST

There are some limitations of the optical implementation of the Ca test. In particular, the optical Ca test is limited by the epoxy edge seal that provides a path for H₂O and O₂ diffusion. Recent tests have revealed that Al₂O₃ ALD barriers on PEN were equivalent to the glass lid control [7]. The measured water vapor transmission rate (WVTR) for both the Al₂O₃ ALD film and the glass lid yielded effective WVTR values of \(\sim 1 \times 10^4\) g/m²/day [7]. This WVTR value was assigned to H₂O permeation through the epoxy edge seal [7]. With such a high baseline WVTR value, the Ca test can not easily be used to evaluate high quality, low permeability barriers.

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A second implementation of the Ca test has also been developed that relies on measuring the electrical conductance of a Ca film during oxidation [8]. Other groups have employed electrical conductance to monitor Ca oxidation [9]. In this version of the Ca test, samples can be prepared by depositing Ca metal on a polymer substrate. A schematic of a possible experimental configuration adapted from Ref. 8 is shown in Figure 2. Silver contacts were evaporated and the sample was covered with a glass lid using an epoxy seal. One problem for the Ca test using conductance probing is again the epoxy seal that can lead to a high baseline WVTR as mentioned above.

These metals form crystalline alloys with Ca at temperatures where the permeation tests are conducted [10, 11]. This alloy formation leads to changes in the conductance measurement that cannot be accounted for and increases the uncertainty in the measurements. Other metals besides silver and gold must be employed to avoid this difficulty.

**Al2O3 ALD BARRIERS DEPOSITED DIRECTLY ON Ca METAL**

Faced with a realization of all of the difficulties with the Ca test using the conventional methods of optical or conductance probing, a new implementation of the Ca test was developed to improve the accuracy of the Ca test. To perform all aspects of the Ca test within our laboratory, an apparatus was built consisting of a physical vapor deposition (PVD) chamber, a N2 glovebox and an attached ALD reactor. This apparatus is shown in Figure 3. Calcium pads were deposited on glass substrates with Au or Cr contacts in the PVD chamber. The samples were then transferred into the N2 glovebox where the samples could be directly placed into the ALD reactor. The desired Al2O3 ALD barrier were then all deposited at 120-125°C using trimethylaluminum (Al(CH3)3) and H2O [12, 13].

In an attempt to overcome epoxy edge sealing problems, the Al2O3 ALD barriers were deposited directly on the Ca metal. After the desired barrier thickness was deposited, the Al2O3 ALD-coated Ca metal samples were removed from the ALD reactor and N2 glovebox. The samples were then placed into an oven set at 70°C. The oven contained a saturated MgCl2 solution that set the relative humidity within the oven at ~28%. This method of setting relative humidity is widely used to calibrate humidity sensors [14, 15]. The oven has electrical feedthroughs and a viewport.

The electrical conductance of the sample was monitored with a Keithley 2400 digital multi-meter connected to a computer. A custom Labview program was used to record the sample conductance four times in every one second. The measurements were then averaged to attenuate any electrical noise present in the signal. A USB camera was also positioned at the oven viewport to monitor the sample visually. Image capture software, Flix by Nimisis, was used to record a sample image every five minutes for the duration of the sample test. The
software was then used to compress the photos into a video to provide a time lapse video of the sample. This video has proved valuable in evaluating the evolution of sample oxidation.

This method of obtaining both the electrical conductance and the optical image simultaneously is also very useful in evaluating the defects in a given barrier. The optical image is a direct measure of the defect density of the barrier. Knowing the defect density and correlating the permeation rate with the defect density allows for the determination of an average defect size [6]. This information is critical for understanding defects in large area barriers needed for organic photovoltaics.

The effect of the visible oxidation regions resulting from defects on sample conductance can be determined by correlating the sample images to the conductance. The images show that there are changes in sample conductance while there is no visible oxidation. In the initial minutes of the test, these changes can be attributed to the Ca metal undergoing a change in its conductance due to temperature equilibration. Some of the initial changes are also due to oxidation of Ca at the edge of the metal contacts where the crystalline Au-Ca alloy may have disrupted the barrier if Au was used as the electrical contact.

Visual images of the Ca film versus time are shown in Figure 4. The Ca film shows the presence of a few pinhole defects in the Al₂O₃ ALD barrier after 23 hours at 70°C/28 % RH. The oxidized Ca regions appear as circular areas that grow in size versus time. This behavior argues strongly for the existence of pinhole defects in the Al₂O₃ ALD coating on the Ca film. After some time has passed at 37.5 hours, a “bloom” of oxidized Ca areas appears. At this point, the conductance decreases very rapidly. From this point onwards, only photographic observations are useful to assess the WVTR of the Al₂O₃ ALD barriers.

As the oxidation areas begin to merge, the electrical measurements no longer give an accurate WVTR. Shortly after this portion of the test, the conductance of the samples drops to zero. No conduction paths remain even though there is metallic Ca still present on the glass substrate. Since the slope of the conductance curve is used to determine the WVTR, this loss of conduction paths leads to an artificially high WVTR. The loss of conduction paths may explain differences in WVTR values measured by the Ca test with optical or conductance measurements.

An additional problem is that oxidation of the Ca metal itself may disrupt the Al₂O₃ ALD barriers. The reaction of water with Ca metal to form Ca(OH)₂ results in a 27 % increase in volume. Calcium hydroxide can also readily react with CO₂ to form calcium carbonate. This reaction results in a further increase in volume to a total of 42 % above the original Ca volume. The CO₂ reaction is likely to occur given the long duration of the WVTR test.

To circumvent the influence of defect distributions on conductance measurements, the WVTR values were also obtained from the photographic observations. This determination of the WVTR values was accomplished using ImageJ software to convert color images from the USB camera to black and white images. ImageJ was then able to provide an accurate measurement of the oxidized areas (white areas). Similar approaches have been employed to measure the amount of oxidized Ca using optical microscopy [16-18]. In some instances, poor resolution and sample lighting led to inaccuracies in the converted photos, i.e. shiny metal areas appearing as oxide areas. Through careful observation and use of ImageJ, these errors could be avoided.

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The amount of Ca oxidized over a given time frame could be calculated using the thickness of Ca deposited and the time that the image was recorded. Some error is present in these measurements due to the photographic errors mentioned earlier and an unknown amount of Ca metal that was oxidized during the formation of the Al₂O₃ ALD film. However, there was fairly good agreement between the photographic WVTR determinations and the electrical WVTR measurements obtained at the middle time segments of the Ca test.

NEW Ca TEST APPARATUS

A change in methodology was needed after evaluating the lessons learned from depositing Al₂O₃ ALD barriers directly on the Ca film. A method was also desired that could measure Al₂O₃ ALD barriers on polymer substrates. Consequently, a new apparatus was developed that again did not use an epoxy adhesive to seal the polymer substrate to the Ca test pad. A schematic of this new apparatus is shown in Figure 5. This apparatus uses the conductance method to measure Ca oxidation. A differential seal is used to attach the polymer substrate and isolate the internal volume of the Ca test apparatus from the outside. This differential seal prevents H₂O ingress and allows the samples to be removed after the Ca test.

![Cross Section](image)

*Figure 5: Updated Ca test setup.*

This new apparatus can measure very low WVTR values. However, obtaining low WVTR values requires that residual H₂O is removed from the components and surface area in the Ca test apparatus. The main source of residual H₂O is the Viton differential seals. Fortunately, H₂O can be outgassed from the Viton by baking in vacuum for more than 72 hours [19]. After removing the residual H₂O, this apparatus has reached WVTR values of 3-5x10⁻⁶ g/m²/day at room temperature with a metal lid. Conductance values that yield an effective WVTR of ~4.3x10⁻⁶ are shown in Figure 6. This WVTR value is lower than the baseline of the best commercial instruments by two orders of magnitude.

![Figure 6: New Ca test baseline data.](image)

Other virtues of this new Ca test apparatus are that the Ca film can be replaced without destroying the polymer substrate. Retesting the same barrier with different Ca films can narrow the experimental uncertainty in the WVTR measurement. The apparatus is still being evaluated and is nearly ready to test Al₂O₃ ALD barrier films on polymers. Current tests are evaluating uncoated polymer substrates. The WVTR values from these uncoated polymers appear to show a large lagtime resulting from H₂O equilibration in the polymer substrate prior to transmission into the Ca test apparatus. The effect of this lagtime on H₂O %RH is significant.

CONCLUSIONS

In summary, there are problems with the existing implementations of the Ca test. Several new implementations of the Ca test method were developed that overcome many of the shortcomings of previous Ca tests. Using these new implementation schemes should facilitate accurate measurements of water and oxygen permeation through ALD barriers on polymer substrates. These new Ca test schemes should become valuable tools for characterizing ALD gas diffusion barriers that have surpassed the limits of current measurement techniques.

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REFERENCES


