# Gas Diffusion Barriers Using Atomic Layer Deposition: A New Calcium Test and Polymer Substrate Effects

by

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B.S., University of Redlands, 2005

PREVIEW

A thesis submitted to the

Faculty of the Graduate School of the

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A New Calcium Test and Polymer Substrate Effects

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Bertrand, Jacob Andrew (Ph.D., Chemistry)

Gas Diffusion Barriers Using Atomic Layer Deposition: A New Calcium Test and Polymer Substrate Effects

Thesis directed by Professor Steven M. George

## Abstract

The increasing demand on available energy resources has led to a desire for more energy efficient devices. The wide use of displays in consumer electronics, such as televisions, cell phones, cameras and computers makes them an ideal target for improvement. Organic light-emitting diodes (OLEDs) are a good candidate to replace traditional Si based devices. However, the low work function metals typically used as electrodes in OLEDs are very reactive with water and oxygen. Ultralow permeability gas diffusion barriers with water vapor transmission rates (WVTRs) as low as $<10^{-6}$ g/($m^2$*day) are required on the polymers used to fabricate organic electronic and thin film photovoltaic devices.

Atomic Layer Deposition (ALD) uses self-limiting surface reactions to deposit thin conformal films. ALD is capable of depositing thin, conformal, high quality barriers. WVTR values as low as $\leq 5 \times 10^{-5}$ g/($m^2$*day) have been measured for $Al_2O_3$ ALD films at 38°C/85% RH using the Ca test with optical transmission probing. The Ca test is a technique with very high sensitivity to measure ultralow WVTRs. This test relies on measuring the oxidation of a Ca metal film by monitoring the change in its optical or electrical properties. However, glass lid control experiments have indicated that the WVTRs measured by the Ca test are limited by $H_2O$ permeability through the epoxy seals. Varying results have been reported in the literature using the electrical conductance of Ca to measure permeation.

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In this work, two approaches were applied to overcome the epoxy edge seal limitations. The first approach was to deposit $Al_2O_3$ ALD barriers directly on Ca metal. While the $Al_2O_3$ ALD barriers were successfully deposited, the measurement of an accurate WVTR was limited by barrier pinholes. The presence of pinholes in the $Al_2O_3$ ALD barrier on Ca results in the localized oxidation of the Ca sensor. Heterogeneous degradation of the Ca causes inaccuracies in the conductance of the film. As oxidation regions merge, large percolation paths are severed without complete Ca oxidation. To solve this problem, a new apparatus was developed that measures the electrical conductance of Ca films. This new apparatus does not rely on epoxy seals and separates the Ca metal from the barrier. Unfortunately, the electrical conductance of the Ca film versus Ca oxidation was found to be extremely nonlinear. This nonlinearity severely complicates the usual analysis to obtain WVTR values from the Ca test.

The new apparatus was useful for the examination of PEN polymer substrates using the total lifetime of the Ca sensor. Polymer effects on the measurement of gas permeability for polymer/barrier systems have largely been ignored. Experiments were performed to determine the effect of the PEN polymer substrates on the WVTR measurement. The $H_2O$ permeation activation energy in the PEN polymer, the effect of water saturation of the PEN polymer and the dependence of the lifetime of the Ca sensor on the $H_2O$ flux on the PEN substrate were of particular interest. The experiments obtained $H_2O$ permeation activation energies in the PEN polymer of 12.4 kJ/mol. The Ca sensor lifetime was found to be linear with $H_2O$ flux. No difference in Ca sensor lifetime was observed between dry or $H_2O$-saturated PEN polymer substrates.

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# Dedication

I dedicate this work to my wife, Dr. Jenny M. Demos-Bertrand for her unfailing love and support before and throughout this work. I also dedicate it to my father, Capt. Lee S. Bertrand, for his dedication to his family, his example, and his constant encouragement without which I would not be the man I am.

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Foremost, I would like to acknowledge my Ph.D. advisor and mentor Dr. Steven M. George. He provided me with the resources, support, guidance and environment that allowed me to grow as a scientist. I cannot thank him enough his willingness discuss and explore new ideas.

My work would not have been possible without the knowledge and help provided by all of the members of the George Group. I would like to specially thank David Goldstein, Andrew Cavanagh, Arrelaine Dameron, Dragos Seghete, Layton Baker, Stephen Davidson, Beau Burton, and Jarod McCormick. They were responsible for teaching me how to build, program and run ALD reactors. Furthermore, many of them acted as sounding boards for my ideas and were always willing to help refine and prioritize them. Shih-hui Jen has been invaluable for her help throughout many facets of my graduate studies. Thank you to Daniel Higgs, Tim Schiesswohl, Jennifer O'Patchen for their help in executing experiments presented in this work.

The members of the group that I have not mentioned have been just as valuable to me for their contributions to my experience. From my first day as part of the group they have made me feel at home and always been willing to lend a hand.

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# Chapter 1 Introduction

## *Atomic Layer Deposition*

Atomic Layer Deposition (ALD) is based on two sequential, self-limiting surface reactions that yield atomic level control of thin film growth.[1] Likewise, the self-limiting nature of the surface chemistry allows ALD to produce extremely conformal films on very high aspect ratio structure. The reactants are introduced to the surface in a sequential manner with a sufficiently long purge of carrier gas in between each reactant dose. Binary compounds lend themselves to this technique easily since the reaction can be split into two half reactions. The most studied of these materials is aluminum oxide or alumina ($Al_2O_3$). Alumina ALD is performed using trimethyl aluminum (TMA) and water following the scheme below.

(A) $AlOH^* + Al(CH_3)_3 \rightarrow AlOAl(CH_3)_2^* + CH_4$

(B) $AlCH_3^* + H_2O \rightarrow AlOH^* + CH_4$

The asterisks indicate the surface species.

The first reaction, (A), shows a dose of TMA reacting with a hydroxylated surface resulting in a methyl terminated surface. After a purge of inert carrier gas, typically nitrogen, water is dosed into the reaction chamber. This results in a return to a hydroxylated surface as shown in step (B). This sequence, ABABAB…, is repeated until the desired thickness is reached. In order for consistent growth per cycle, the doses of each reactant must be kept sufficiently large so as to saturate the surface and react with as all available surface sites. The repetition of these AB cycles results in an $Al_2O_3$ ALD growth of 1.1-1.2 Å per AB cycle.[2, 3] Previous studies have shown that $Al_2O_3$ ALD can be deposited over a very wide temperature range from 36-200 °C. $Al_2O_3$ ALD can also be deposited very effectively on a variety of polymers.[4]

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Since first developed in the late 1970's, ALD has come a long way in terms of the materials that can be deposited with the technique.[5-8] As the number of materials available for deposition with ALD has increased, so have the number of applications. One growing application is the use of ALD to create transparent diffusion barriers to protect organic light emitting diodes (OLEDs)[9] and other organic electronic devices[10, 11] from degradation by water and oxygen. The most rigorous barrier requirements exist for OLEDs (Figure 1.1)[12]. For organic based electronics to reach device lifetimes comparable to their silicon based counterparts (>10,000 hrs), they require a water vapor transmission rate (WVTR) of $<10^{-6}$ g/($m^2$*day) and an oxygen transmission rate (OTR) at STP of $<10^{-5}$ $cm^3/m^2$/day.[13-16] These requirements arise from the sensitivity of the low work function metals (Ca, Li, Mg, etc.) necessary to get efficient charge injection into the organic layers of electroluminescent devices.[13-15, 17] Current methods to protect these devices involve encapsulation of the entire device between glass plates. This leads to a longer device lifetime but is not necessarily suitable for all applications.[18] There is great interest in creating thinner, flexible, electronics based on organic molecules. This is made possible by creating the devices on a polymer substrate. However, polymers typically have a WVTR on the order of 10-0.1 g/($m^2$*day).[15] ALD provides an effective solution to this problem since ALD is capable of coating devices of any geometry with a conformal film of precisely controlled thickness.

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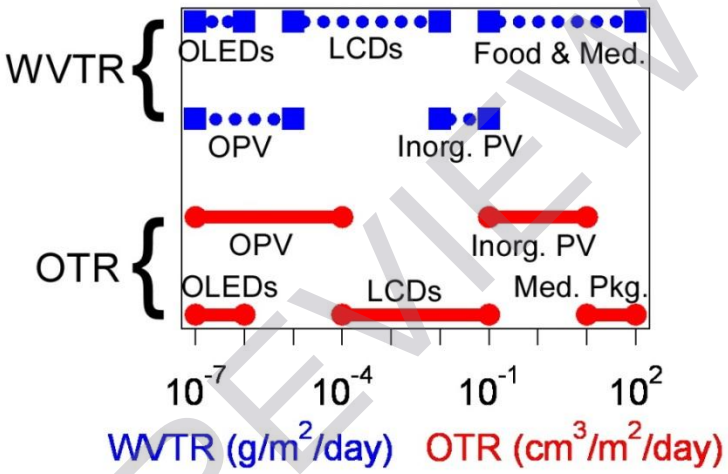



Figure 1.1 Barrier Requirements

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$Al_2O_3$ ALD films of ~12nm are capable of providing diffusion barriers with a WVTR (~$10^{-3}$ g/(m2*day)) that is a great improvement over the polymer substrates themselves.[9, 11, 13] However, these barriers do not meet the requirements discussed earlier. The films still possess some pinhole defects that limit their effectiveness as barriers.[14, 16, 19] Making the barrier layer thicker will lower the probability of having a defect through the entire layer but results in a film that is more likely to fracture during processing and handling. Inorganic-organic multilayer structures have been used to overcome this problem. However, they do not show the decrease in permeability expected from standard laminate theory, where the total permeation rate can be obtained by addition of the reciprocals of the permeation rates for each layer (Equation 1).[14, 20]

$$(1) \qquad \frac{1}{P_T} = \frac{1}{P_1} + \frac{1}{P_2} + \cdots + \frac{1}{P_i}$$

Multilayer barriers were first introduced in 1994 and were created using layers of aluminum metal and acrylate polymer.[14] The polymer interlayer provides flexibility as well as decoupling of defects in the metal or oxide films. This increases the path length of permeants through the material and decreases the permeation rate for the multilayer[14, 16]. Multilayer structures occur in nature and have been shown to the capable of creating extraordinarily mechanically robust super lattices based on inorganic platelets separated by a polymer interlayer.[21, 22]

Multi layering of inorganic and organic materials can be problematic. There can be low adhesion[23] between the layers and decreasing flexibility with increasing thicknesses of individual layers or the total film.[12] Low adhesion can be addressed through the use of

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molecular layer deposition (MLD). Recent work within our group has shown that it is possible to deposit polymers using MLD.[24, 25] This technique uses the same sequential approach as described for ALD but deposits an organic molecular fragment during one or both of the steps in the reaction cycle. One class of materials that can be deposited in this manner is poly(aluminum alkoxides) or alucones which will be discussed briefly later.[26] The precursors used in MLD are compatible with those used to deposit inorganic materials with ALD which should lead to good adhesion between the layers. The level of control provided by ALD and MLD techniques also makes it possible to create graded interfaces between the layers to increase adhesion. Little has been done to explore the mechanical properties of these barriers.[9, 12] If they are to maintain their integrity while in use on flexible devices, then more work is needed to understand the behavior of multilayer barriers during flexing. The mechanical characteristics of the individual layers are particularly important.

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## *Mechanical Testing*

When a material is flexed, the surface farthest from the center of curvature is put into tensile strain and the inner surface undergoes compressive strain (Figure 1.3 and Figure 1.2).[27] This results in the formation of a neutral plane within the material. If the material is uniform, i.e. an uncoated polymer, the neutral plane exists in the center of the material. As coatings are applied, the neutral plane moves away from the center of curvature. In the case of ALD films, the coatings are three orders of magnitude thinner and the neutral plane remains relatively unchanged. Linear tensile strain is described by $= \frac{\Delta L}{L}$, where L is the samples original length. Due to the gradient that exists when a sample undergoes a bending, the strain is obtained through $\varepsilon = \frac{y}{R}$, where *y* is the distance from the neutral plane and R is the radius of

curvature.[12] The strain at the surface of the substrate is taken to be the strain through the ALD coating since any gradient that exists within the coating would be negligible. This relationship leads to the strain applied to an ALD film being $\varepsilon = \frac{h_s}{2R}$ , $h_s$ being the thickness of the substrate.[27]

As a coated sample is bent, the strain continues to increase until such point that the coating will fracture. The strain at which this occurs is known as the critical strain ($\varepsilon_c$) and is proportional to the reciprocal square root of the film thickness. Initial cracks will lengthen and additional fractures will occur if the increase in strain continues until the number of fractures reaches saturation.[28] The failure mechanism for thin brittle layers is different from that of bulk materials. In bulk materials, a crack, once initiated, will propagate the full width across the material. For thin films, cracks initiate at point defects and propagate to a finite length for a given strain. As strain increases, the crack length will increase proportionally until either the maximum stable crack length ( $l_p$) or critical crack propagation strain ($\varepsilon_p$) is reached. Once one of these conditions is met the crack will propagate to the full width of the film.[29]

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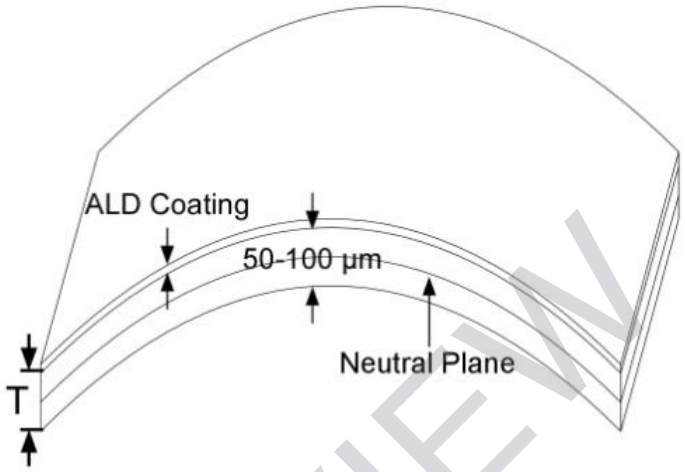



Figure 1.3 Flexed ALD Coated Polymer

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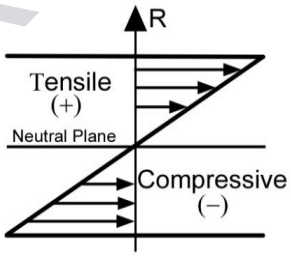



Figure 1.2 Bent Polymer Cross-sectiion

In order to explore these properties of a thin film it is necessary to have a sensitive technique to monitor changes in the film's behavior. The changes that occur in film may, initially, be very small in comparison to the original film. To determine an accurate measurement of the critical strain, we must be able to detect these minute changes as soon as they occur during testing. Depending on the properties of the film, i.e. conductivity, there are few methods that can be used. Indium tin oxide (ITO) is the most studied thin film. As a conducting oxide it is easily monitored with sensitive resistance measurements.[27, 30, 31] Typical diffusion barriers, are not conducting oxides ($Al_2O_3$) and are not capable of such characterization.

Zinc oxide ALD provides us with a useful analog to explore the mechanical properties since it is a conductive film. A four-point probe can be used to determine a critical strain. We can then compare the accuracy of other methods that can be used on non-conductive films.

## *Barrier Testing*

Atomic Layer Deposition (ALD) has shown promise as a technique to deposit conformal, transparent gas diffusion barriers .[9, 13] These barriers can protect organic electronic or thin film solar cell devices from degradation by water and oxygen.[10] For organic based electronics to reach device lifetimes of 10,000 hrs, they require a water vapor transmission rate (WVTR) of $<10^{-6}$ g/($m^2$*day)and an oxygen transmission rate (OTR) at STP of $<10^{-5}$ $cm^3/m^2$/day.[15] 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 require a gas diffusion barrier because they typically have a WVTR on the order of 10-0.1 g/(m2*day).[15]

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The development of gas diffusion barriers requires an accurate method for determining $H_2O$ and $O_2$ permeation rates. The only commercial systems available for WVTR measurement are produced by MOCON.[9] Their detection limit of ~$10^{-3}$ g/($m^2$*day) is insufficient for testing ultra-barriers deposited with ALD. In response to this lack of characterization methods, two primary techniques have been developed to characterize ultra-low steady state permeation through barriers: the "calcium test" and "HTO tracer method".[9, 13]

The HTO tracer method involves placing the films in the apparatus shown in Figure 1.4. A small amount of 1mCi/g HTO is placed in the vessel base. The barrier coated polymer sample is enclosed within the vessel with rubber O-rings and a vial containing LiCl is suspended from the vessels cap. As HTO permeates the polymer/barrier it is absorbed by the hygroscopic salt. Once the salt vial is removed it is dissolved in a small amount of ultrapure water and a scintillation cocktail is added. The salt vials are changed roughly every twenty-four hours for the period of the test, usually 200-300 hours. The results from the scintillation counter can then be used to determine the WVTR through the sample.[9] The downside to this is that only measurement of the tritium concentration is measured. The assumption is that the tritium concentration is representative of the water concentration. However, there is evidence that atomic tritium can diffuse through the barrier with the aid of a proton exchange reaction, leading an over estimate in the WVTR.[32]

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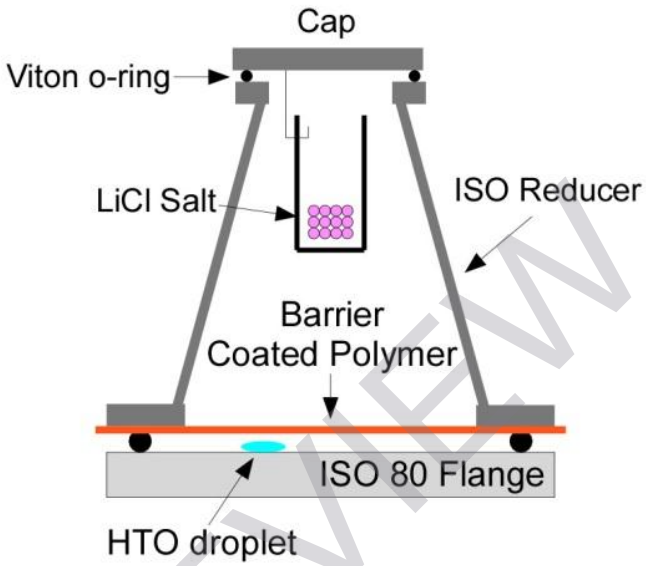



Figure 1.4 HTO Apparatus

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*Calcium Test*

The calcium test uses a thin, metallic, calcium layer as a sensor for water and oxygen permeation.[9, 12, 13, 16] There are two versions of the Calcium test, both of which rely on measuring the oxidation of Ca metal.[33, 34] The main difference in the methods is how the Ca oxidation is measured. As oxygen or water permeate the barrier, they react with Ca to form calcium oxide [CaO] or calcium hydroxide [$Ca(OH)_2$], both of which are transparent to visible light and electrically insulating

In 2001, Nisato et. al described a testing method using calcium (Ca) metal for measuring low $H_2O$ and $O_2$ permeation rates.[33] Their tests relied on using optical observations of the oxidation of metallic Ca to $Ca(OH)_2$ and CaO to determine calcium corrosion rates. A CCD camera was used to monitor the reflection from Ca pad. From the images obtained they measured the area growth of local oxidation regions. Once the growth rate of these areas becomes linear they use that rate to determine WVTR. These measurements allow the calculation of the overall degradation rate of the calcium layer and the permeation rate for the barrier. The WVTR and OTR cannot be easily separated by this method. Further small error is introduced by the difference in optical constants between the CaO and $Ca(OH)_2$ products. However, this method is useful to get a baseline measurement of the barrier performance. . The % transmittance of the sample can also be followed as a function of time. However, the development of localized oxidation regions will result in sudden increases in the transmittance. The non-uniformity of the Ca degradation can lead to errors in the determination of a WVTR.

Other groups have subsequently employed the Ca test with optical transmission probing to measure gas diffusion barriers.[35] A similar Ca test method was recently used by

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