

Ca test of Al₂O₃ gas diffusion barriers grown by atomic layer deposition on polymers

P. F. Garcia,^{a)} R. S. McLean, and M. H. Reilly

DuPont Research and Development, Experimental Station, Wilmington, Delaware 19880-0356

M. D. Groner

Department of Chemistry and Biochemistry, University of Colorado, Boulder, Colorado 80309

S. M. George

Department of Chemistry and Biochemistry, University of Colorado, Boulder, Colorado 80309

and Department of Chemical and Biological Engineering, University of Colorado, Boulder, Colorado 80309

(Received 6 March 2006; accepted 25 May 2006; published online 19 July 2006)

Quantitative Ca tests were used to determine the water vapor transmission rate (WVTR) through 25 nm thick Al₂O₃ gas diffusion barriers grown on plastic by atomic layer deposition (ALD). The measured WVTRs were 1.7×10^{-5} g/m² day at 38 °C and 6.5×10^{-5} g/m² day at 60 °C. Based on the apparent activation energy, the WVTR at 23 °C is estimated to be only 6×10^{-6} g/m² day. The WVTR values for the Al₂O₃ ALD film are very similar to the WVTR value for the glass control. These Ca tests indicate that Al₂O₃ ALD gas diffusion barriers should enable display and lighting applications of highly moisture sensitive organic light-emitting diodes on plastic. © 2006 American Institute of Physics. [DOI: 10.1063/1.2221912]

Future application of organic light-emitting diodes¹ (OLEDs) may be for general lighting use.² While OLEDs are already an emerging technology for displays, white light-emitting OLEDs (Ref. 2) manufactured economically on flexible plastic substrates offer unlimited possibilities for residential lighting panels. Unfortunately, H₂O and O₂ readily permeate plastic³ and degrade sensitive organic electronic materials. OLEDs present the greatest challenge and require a low water permeability of $<10^{-5}$ g/m² day.⁴ Only complex multilayer barrier films consisting of five to six pairs of polymer and inorganic layers currently show promise for meeting these requirements.⁵

The measurable permeation in single layer, inorganic barrier film is attributed to defects or pinholes in the film caused by the deposition process or by substrate imperfections.^{6,7} Not surprisingly, the deposition process has a significant influence on barrier properties of thin inorganic films.⁸ Atomic layer deposition (ALD) is a process known for growing thin, conformal, pinhole-free films with featureless microstructure and low stress.⁹ ALD should be ideal for producing excellent gas diffusion barriers.

We previously reported very low oxygen transmission rates (OTRs) of $<5 \times 10^{-3}$ cm³ O₂/m² day at 23 °C and 50% relative humidity (RH) through ultrathin <25 nm thick Al₂O₃ and HfO₂ films grown by ALD on plastic substrates.¹⁰ These OTR results were at the limit of the commercial (MOCON OX-Tran-2/21) testing equipment. Our group also recently reported a water vapor transmission rate (WVTR) of $\sim 1 \times 10^{-3}$ g/m² day for 25 nm thick Al₂O₃ ALD films grown on polymer surfaces at 120 °C.¹¹ These films were measured by a radioactive tritium method. In related barrier work, Park *et al.*¹² measured a WVTR of 0.03 g/m² day at 38 °C/100% RH for an Al₂O₃ ALD barrier that was 30 nm thick and grown on both sides of a poly(ethersulfone) (PES) substrate. Ghosh *et al.*¹³ also reported that encapsulating an

OLED device with a 180 nm thick ALD Al₂O₃ film and other layers increases the device lifetime.

While the previous results are encouraging, they do not demonstrate the WVTR $<10^{-5}$ g/m² day needed for OLEDs on plastic substrates. In this letter, we show that ultrathin Al₂O₃ barrier films grown by ALD on polyethylene naphthalate (PEN) substrates can have a WVTR $<10^{-5}$ g H₂O/m² day. Details of our ALD film deposition process have been published earlier.¹¹ Briefly, Al₂O₃ barrier thin films with a thickness of 25 nm were deposited in a hot-wall ALD flow reactor at 120 °C using sequential, self-limiting exposures to trimethylaluminum (TMA) (Aldrich) and water [Fisher high performance liquid chromatography (HPLC)-grade] with intermediate nitrogen gas purging steps.¹¹ The plastic substrates were 125 μm thick heat-stabilized PEN (Teonix® Q65, DuPont-Teijin Films). These substrates were rinsed and loaded into the reactor residing in a laminar-flow hood operated at class 100 cleanroom conditions. The substrate cleanliness and surface chemistry of the polymer were critical for achieving thin, defect-free films with ultralow permeability.

The WVTR for the Al₂O₃ ALD-coated PEN was measured using the Ca-test method.¹⁴ This test tracks optical transmission changes that occur in a thin Ca layer resulting from the reactivity of Ca with moist air. This test is particularly relevant to OLEDs because Ca is commonly the cathode electrode and this test structure mimics the OLED device. Briefly, an array of 16 Ca squares was thermally evaporated on 2 × 2 in.² Corning 7059, alkali-free glass. Using a quartz crystal microbalance, the Ca thickness was controlled to obtain a semitransparent film.

The Ca squares on glass were then epoxy sealed with a plastic lid that had the Al₂O₃ ALD barrier layer. The Al₂O₃ ALD barrier film was usually oriented toward the Ca on the inner side of the test cell. The test cell is shown schematically in Fig. 1. All operations to fabricate this test cell were carried out in a nitrogen-atmosphere glove box. The test cell was subsequently placed in an environmental chamber at

^{a)}Electronic mail: peter.f.garcia@usa.dupont.com

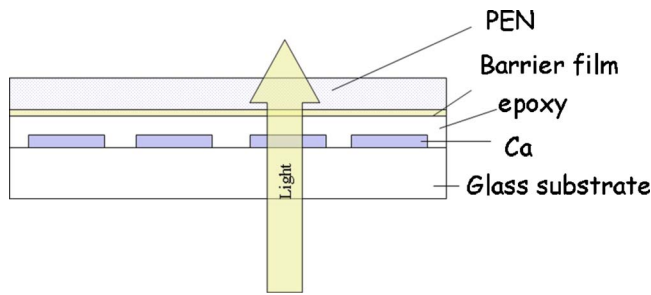
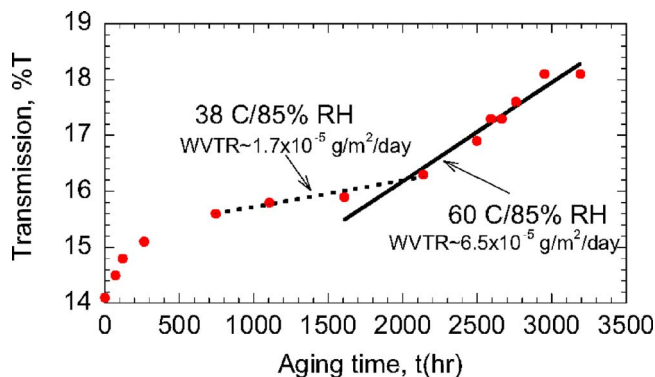


FIG. 1. (Color online) Cross section of a Ca-test cell consisting of 16 semi-transparent Ca squares, $5 \times 5 \text{ mm}^2$, evaporated on a glass substrate, epoxied to a plastic (PEN) lid coated on one side with a thin-film barrier material.

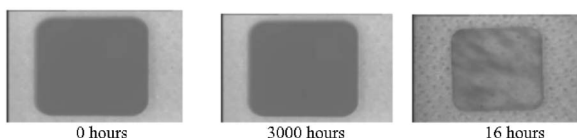
controlled temperature and humidity. Changes in optical transmission through the test cell were periodically recorded in ambient with aging at 38 or 60 °C and 85% RH.

The multilayer test cell stack was modeled with optical simulation software (n&k Corp., San Jose, CA). The transmission at 600 nm increased because of the formation of a CaO or Ca(OH)₂ layer that consumed the Ca thin film. The optical modeling determined that the initial Ca metal thickness prior to aging was 50–60 nm thick. This thickness agreed well with the thickness determined by the quartz crystal microbalance used to control the Ca deposition. The WVTR was determined from the simulated Ca-oxide thickness. This implementation of the Ca test is similar to “method A” described by Nisato *et al.*¹⁴

Optical aging at 38 °C/85% RH and 60 °C/85% RH for a 25 nm Al₂O₃ ALD barrier on PEN is shown in Fig. 2. There was a small initial increase in %T followed by a slower, constant steady-state change. When the aging temperature was increased from 38 to 60 °C, the optical transmission abruptly changed to a higher steady-state rate. The initial change in %T was attributed to outgassing of residual



(a)



(b)

FIG. 2. (a) (Color online) Change in optical transmission with aging for a representative Ca thin-film square in a test cell where the lid was PEN, coated with 25 nm thick Al₂O₃, grown by atomic layer deposition. Aging was at 38 °C (85% RH) and 60 °C (85% RH). (b) Optical images of Ca, protected by ALD Al₂O₃ barrier before and after aging for over 3000 h, and after ~16 h in ambient for a plastic lid without a barrier.

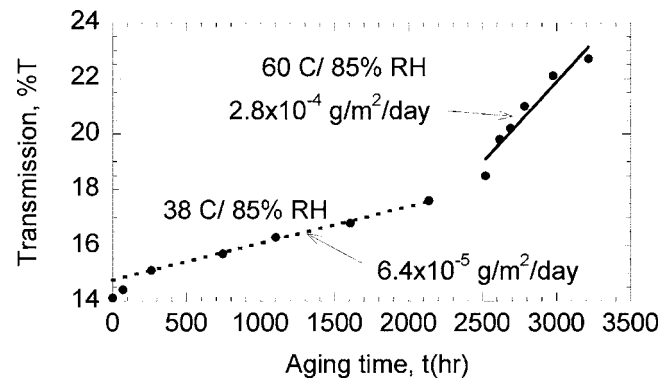


FIG. 3. Change in optical transmission with aging for a representative Ca thin-film square in a test-cell control where the lid was glass. Aging was at 38 °C (85% RH) and 60 °C (85% RH).

H₂O or air in the epoxy that reacted with the Ca film.

From the steady-state change in %T at 38 °C/85% RH, the WVTR was $1.7 \times 10^{-5} \text{ g/m}^2 \text{ day}$. From the steady-state change in %T at 60 °C/85% RH, the WVTR was $6.5 \times 10^{-5} \text{ g/m}^2 \text{ day}$. These measurements were both for single Al₂O₃ ALD barriers. A WVTR of $6.2 \times 10^{-5} \text{ g/m}^2 \text{ day}$ was also measured at 60 °C/85% RH for a bilayer barrier of a 100 nm SiN_x film together with a 25 nm Al₂O₃ ALD film. The SiN_x film was deposited by plasma-enhanced chemical vapor deposition (PECVD) on PEN.

At 38 °C, the WVTR for the single layer Al₂O₃ ALD film corresponded to a permeability of $P = 7.33 \times 10^{-19} \text{ g H}_2\text{O/cm s atm}$. Using the solubility for sputtered Al₂O₃ of $S = 0.029 \text{ g/cm}^3 \text{ atm}$,⁵ the diffusion coefficient was calculated to be $D = P/S = 2.5 \times 10^{-17} \text{ cm}^2/\text{s}$. This diffusion coefficient is equivalent to a defect concentration that consists of a single 10 nm diameter pinhole per square millimeter of coated barrier film.⁵ As a comparison, Graff *et al.*⁵ determined that $D = 1.4 \times 10^{-13} \text{ cm}^2/\text{s}$ for diffusion through a sputtered Al₂O₃ barrier thin film that was 37 nm thick in a multilayer structure with a polymer smoothing layer and a polymer overcoat.

Optical images of the reflective Ca squares protected with an Al₂O₃ ALD barrier before and after aging for over 3000 h are also shown in Fig. 2. No visual change in Ca film reflectivity or any localized degradation was observed on the Ca squares. In contrast, the thin Ca became fully transparent at ambient conditions in a few hours for a plastic lid without the Al₂O₃ ALD barrier.

The control for experimental measurement was a glass lid that was epoxy sealed on glass. The optical aging data for this glass control lid is shown in Fig. 3. The general features for the plastic lid with an Al₂O₃ ALD barrier and the glass control are the same. The WVTR for the glass control was slightly higher at $\sim 6.4 \times 10^{-5} \text{ g/m}^2 \text{ day}$ at 38 °C and 85% RH and $\sim 2.8 \times 10^{-4} \text{ g/m}^2 \text{ day}$ at 60 °C and 85% RH. The glass control consistently had slightly higher WVTR than the test cell with an Al₂O₃ ALD barrier film. This higher WVTR for the glass control does not yet have an explanation.

Using the apparent activation energy¹⁵ E_a from the WVTR data at 38 and 60 °C, a WVTR was determined at 23 °C. E_a was 52 kJ/mole for a single 25 nm thick Al₂O₃ ALD barrier. E_a was 58 kJ/mole for the glass control. These apparent activation energies yield a WVTR at 23 °C of $6 \times 10^{-6} \text{ g/m}^2 \text{ day}$ for the 25 nm Al₂O₃ ALD film and $2.1 \times 10^{-5} \text{ g/m}^2 \text{ day}$ for the glass control. Assuming that E_a

~ 50 kJ/mole for the bilayer, the estimated WVTR for the bilayer at 23 °C was $\sim 6.4 \times 10^{-6}$ g/m² day.

These data indicate that WVTR $< 10^{-5}$ g/m² day at room temperature can be achieved using a single thin Al₂O₃ ALD barrier layer on plastic. Since the WVTR for the impermeable glass control lid is $\sim 1 \times 10^{-5}$ g/m² day, edge diffusion of water vapor through the epoxy seal apparently limits the measurement sensitivity. In support of this interpretation, the calculated activation energy for permeability was $E_p \sim 10$ kJ/mole for the glass control. This activation energy is close to $E_p = 4.5$ kJ/mole reported for moisture permeation in epoxy and epoxy-glass composites.¹⁶

The WVTR of other barrier films prepared by other deposition techniques were also measured using the same Ca test. These measurements were performed to corroborate that Al₂O₃ ALD barriers dramatically reduce the WVTR as deduced by the Ca tests. In addition, these tests ruled out the self-limiting degradation of the Ca film by formation of a reaction layer. One film was 100 nm of Al₂O₃ deposited by electron beam evaporation on PEN. Another film was 100 nm of SiN_x grown by PECVD. At 38 °C/85% RH, the optical transmission of the Al₂O₃ e-beam evaporated barrier increased rapidly corresponding to WVTR ~ 0.1 g/m² day. The PECVD SiN_x film was a better barrier with WVTR ~ 0.02 g/m² day at 60 °C/85% RH. However, this WVTR was still about 500 times larger than the WVTR for a single layer ALD Al₂O₃ barrier.

In conclusion, an Al₂O₃ barrier film grown by ALD can have a WVTR $< 10^{-5}$ g/m² day at room temperature. This low WVTR should be adequate to enable fabrication of air-sensitive OLEDs for displays and lighting on flexible poly-

mer substrates. Combining Al₂O₃ ALD layers with other layers or multiple ALD layers may further improve barrier performance. This possibility could not be verified because the WVTR of a single thin Al₂O₃ ALD layer was near the limit of the Ca-test method.

¹C. W. Tang and S. A. Van Slyke, Appl. Phys. Lett. **51**, 913 (1987).

²R. F. Service, Science **310**, 1762 (2005).

³*Polymer Permeability*, edited by J. Comyn (Elsevier, London, 1985).

⁴J. S. Lewis and M. S. Weaver, IEEE J. Sel. Top. Quantum Electron. **10**, 45 (2004).

⁵G. L. Graff, R. E. Williford, and P. E. Burrows, J. Appl. Phys. **96**, 1840 (2004).

⁶G. Rossi and M. Nulman, J. Appl. Phys. **74**, 5471 (1993).

⁷A. S. D. Sobrinho, G. Czeremuszkin, M. Latreche, and M. R. Wertheimer, J. Vac. Sci. Technol. A **18**, 149 (2000).

⁸H. Chatham, Surf. Coat. Technol. **78**, 1 (1996).

⁹M. Ritala and M. Leskela, in *Handbook of Thin Film Materials*, edited by H. S. Nawla (Academic, San Diego, 2001), Vol. 1, p. 103.

¹⁰R. S. McLean, P. F. Carcia, S. G. Park, and Y. Senzaki, Proceedings of the ALD 2003 Conference, American Vacuum Society Topical Conference, San Jose, August 2003.

¹¹M. D. Groner, S. M. George, R. S. McLean, and P. F. Carcia, Appl. Phys. Lett. **88**, 051907 (2006).

¹²S. H. K. Park, J. Oh, C. S. Hwang, J. I. Lee, Y. S. Yang, and H. Y. Chu, Electrochem. Solid-State Lett. **8**, H21 (2005).

¹³A. P. Ghosh, L. J. Gerenser, C. M. Jarman, and J. E. Fornalik, Appl. Phys. Lett. **86**, 223503 (2005).

¹⁴G. Nisato, P. Bouten, P. J. Slikkerveer, W. Bennett, G. Graff, N. Rutherford, and L. Wiese, *21st International Asia Display/8th International Display Workshop, Nagoya, Japan, 2001* (Society for Information Display, San Jose, CA, 2001), p. 1465.

¹⁵Y. G. Tropsha and N. G. Harvey, J. Phys. Chem. B **101**, 2259 (1997).

¹⁶L. L. Marsh, R. Lasky, D. P. Seraphim, and G. S. Springer, IBM J. Res. Dev. **28**, 655 (1984).