

Gas diffusion barriers on polymers using Al₂O₃ atomic layer deposition

M. D. Groner

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

S. M. George^{a)}

Department of Chemistry and Biochemistry and Dept. of Chemical and Biological Engineering, University of Colorado, Boulder, Colorado 80309

R. S. McLean and P. F. Garcia

DuPont Central Research & Development, Wilmington, Delaware 19803

(Received 6 July 2005; accepted 6 December 2005; published online 31 January 2006)

Thin films of Al₂O₃ grown by atomic layer deposition (ALD) were investigated as gas diffusion barriers on flexible polyethylene naphthalate and Kapton® polyimide substrates. Al₂O₃ ALD films with thicknesses of 1–26 nm were grown at 100–175 °C. For Al₂O₃ ALD films with thicknesses ≥ 5 nm, oxygen transmission rates were below the MOCON instrument test limit of $\sim 5 \times 10^{-3}$ cc/m²/day. Applying a more sensitive radioactive tracer method, H₂O-vapor transmission rates of $\sim 1 \times 10^{-3}$ g/m²/day were measured for single-sided Al₂O₃ ALD films with thicknesses of 26 nm on the polymers. Ultrathin gas diffusion barriers grown by Al₂O₃ ALD may enable organic displays and electronics on permeable, flexible polymer substrates. © 2006 American Institute of Physics. [DOI: 10.1063/1.2168489]

The development of organic light-emitting diode (OLED) devices may lead to efficient displays fabricated inexpensively on flexible substrates.¹ One obstacle to this development is the facile permeation of O₂ and H₂O through the flexible plastic substrates. For most polymers, the transmission rates are generally ≥ 1 cc/m²/day for O₂ and ≥ 1 g/m²/day for water.¹ The permeability of polymer substrates can be reduced by about two orders of magnitude using single-layer inorganic coatings.^{1–3} These levels of barrier improvement are sufficient for applications such as liquid crystal displays and food packaging. However, the requirements for reducing O₂ and H₂O permeability are orders of magnitude more demanding for OLEDs.^{1,2,4,5} Barrier improvements of 10⁵–10⁶ are needed to exclude O₂ and H₂O that can seriously degrade both the light-emitting polymer and the water-sensitive Ca or Ba metal cathode in OLEDs.¹

A defect-free, continuous thin-film coating of an inorganic material should ideally be impermeable to atmospheric gases. Unfortunately, most thin films have pinholes and defects caused by the deposition process or substrate imperfections that compromise the barrier properties. Grain boundaries in a barrier film can also present a pathway for facile permeation. Recent studies have recommended a multilayer structure as the only practical way to achieve “ultrabarrier” performance.^{1,5} Barriers with alternating inorganic/organic layers with as many as 12 individual layers reportedly approach the performance needed by OLEDs.⁵ However, more recent detailed measurements and modeling of these multilayer structures attribute the “apparent” low transmission rate for these multilayers to long lag times and not to reduction in steady state permeability.⁴ This recent study also highlights the need to deposit more perfect single-layer barrier films.

Atomic layer deposition (ALD) is a process that can deposit smooth, conformal, and pinhole-free films with a nearly featureless structure.^{6–8} The excellent dielectric properties

that have been measured for Al₂O₃ ALD films are consistent with defect-free films needed for superior permeation barriers.^{8,9} High quality Al₂O₃ films can be deposited by ALD at temperatures as low as 33 °C.⁹ These temperatures are compatible with most thermally fragile plastic substrates. In this work, Al₂O₃ ALD films grown directly on polyethylene naphthalate (PEN) and Kapton® substrates are investigated as water and oxygen permeation barriers. Earlier studies have measured water vapor transmission rates for Al₂O₃ ALD coated on polyethersulfone (PES) substrates.³

Al₂O₃ ALD was performed in a hot-wall ALD flow reactor using sequential, self-limiting exposures to trimethylaluminum (TMA) (Aldrich) and water (Fisher HPLC-grade).⁷ The reaction chamber was built to accommodate 4 in. square PEN and Kapton® substrates. This chamber was 3 in. tall and 6 in. diameter and was equipped with a loading port. Substrates were taped to 4-in. Si wafers to achieve single-sided ALD coatings. Multiple substrates could be coated simultaneously by stacking them in a cassette-like arrangement.

Polymer films were rinsed and loaded into the reactor in a laminar flow hood operating at class 100 cleanroom conditions to minimize particle contamination. Al₂O₃ ALD growth temperatures ranged from 100–175 °C. Nitrogen gas flowed through the reactor at 100 sccm and produced a pressure of ~ 1 Torr. A typical ALD cycle at 120 °C consisted of a 0.1 s TMA exposure, a 30 s purge, a 0.15 s water exposure, and another 30 s purge. The substrates were PEN and Kapton® polyimide with glass transition temperatures of $T_g = 126$ °C and $T_g \sim 300$ °C, respectively.

Al₂O₃ ALD film thicknesses on the polymer films were determined using an n&k 1280 Analyzer metrology system. This instrument is able to determine film thicknesses on transparent substrates using transmittance and reflectance measurements. These results agreed with growth rates for Al₂O₃ ALD of 1.2–1.3 Å/cycle that were measured on Si wafers.^{7–9} This agreement indicates a rapid nucleation of Al₂O₃ on PEN and Kapton®. Rapid nucleation of Al₂O₃

^{a)}Electronic mail: steven.george@colorado.edu

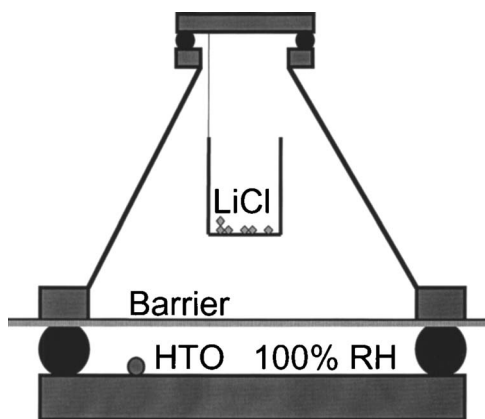


FIG. 1. Schematic of the HTO water test to measure the water vapor transmission rate. LiCl absorbs the HTO that permeates through the ALD-coated polymer film.

ALD has also been demonstrated on other polymers.^{10,11}

Oxygen transmission rates (OTRs) were measured using a commercial MOCON OX-TRAN 2/21 instrument with a detection limit of $\sim 5 \times 10^{-3}$ cc/m²/day. OTR measurements at 23 °C and 50% relative humidity were performed on a series of Al₂O₃ ALD films with thicknesses of 1, 5, 10, and 26 nm. Growth temperatures were 100 and 125 °C on PEN, and 125, 150, and 175 °C on Kapton®. OTR measurements of polymers with an Al₂O₃ ALD thickness of 1 nm yielded no improvement over uncoated polymer films with an OTR of ~ 1 cc/m²/day. Al₂O₃ ALD films with thicknesses of 5, 10, and 26 nm achieved OTR values below the MOCON test limit on both PEN and Kapton® at all growth temperatures.

OTR values of $< 5 \times 10^{-3}$ cc/m²/day have never been reported for such thin single-layer coatings on polymers.¹ These OTR results indicate a very low critical thickness of between 1 and 5 nm for the onset of useful barrier properties. In comparison, SiO₂ barrier films grown by plasma-enhanced chemical vapor deposition (PECVD) on polyethylene terephthalate (PET) have a corresponding critical thickness of 15 nm and a OTR of ~ 0.4 cc/m²/day for thick films > 100 nm.¹² Unfortunately, the MOCON OTR test is not sensitive enough to measure these low OTR values or to characterize the effect of parameters such as film thickness and growth temperature.

More sensitive water vapor transmission rates (WVTRs) were obtained using tritiated water (HTO) as a radioactive tracer.^{13,14} The HTO test chamber is shown in Fig. 1. A droplet of HTO (Perkin Elmer, 1 mCi/ml) was placed on the bottom flange. This tritiated water with 0.6 parts per million HTO created a 100% relative humidity environment on the upstream side of the Al₂O₃-coated polymer film. The barrier film to be tested was clamped between a Viton® o-ring and a reducing flange. The Al₂O₃ ALD film was on the downstream side of the polymer film. A scintillation vial containing ~ 20 grains of LiCl was suspended in the top part of the chamber on the downstream side. The hygroscopic LiCl absorbs the HTO and water permeating through the polymer film as well as the background water in the chamber.

The vial was periodically removed and replaced with a new vial. The LiCl-containing HTO was dissolved in 1 ml of water and 3 ml of PerkinElmer Ultima Gold LLT scintillation cocktail. A Packard 1600TR scintillation counter was then used to count the tritium decays and to calculate the HTO transmission rates. Measurements were taken usually

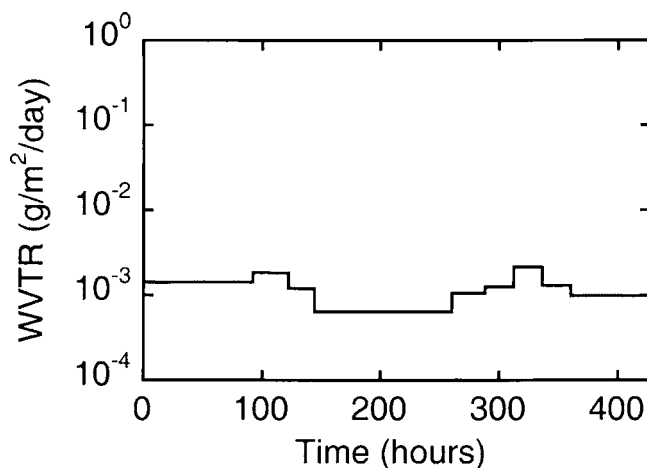


FIG. 2. Water vapor transmission rate (WVTR) data for a PEN film with a 26 nm Al₂O₃ ALD coating. The WVTR averaged 1.1×10^{-3} g/m²/day.

once per day for several weeks until the transmission rate stabilized at a constant value.

The detection limit of the HTO test was confirmed by testing an impermeable aluminum foil. The resulting tritium decay counts were at the background level for the scintillation counter. These results were consistent with a WVTR detection limit of $\sim 1 \times 10^{-6}$ g/m²/day. This HTO test detection limit is over 1000 times more sensitive than the detection limit of the MOCON PERMATRAN-W instrument.

WVTR measurements were performed on a series of Al₂O₃ ALD films with thicknesses of 2.5, 5, 10, and 26 nm. Growth temperatures were 100 and 120 °C on PEN, and 100, 120, 150, and 175 °C on Kapton®. WVTR measurements of Al₂O₃ ALD-coated polymers with a thickness of 2.5 nm yielded no improvement over uncoated polymer films that had a WVTR of ~ 1 g/m²/day. Al₂O₃ ALD films with thicknesses of 5 nm yielded rates about an order of magnitude lower than the uncoated polymers. Al₂O₃ ALD films with a thickness of 10 nm achieved a WVTR of $\sim 2 \times 10^{-3}$ g/m²/day. Al₂O₃ ALD films with a thickness of 26 nm obtained transmission rates of $\sim 1 \times 10^{-3}$ g/m²/day on both PEN and Kapton® at all growth temperatures.

A plot of the water vapor transmission rate versus time for a 26 nm thick Al₂O₃ film is shown in Fig. 2. Each horizontal line represents the average WVTR over the time period covered by the line. The time periods varied from approximately one to four days. The average WVTR for this film is 1.1×10^{-3} g/m²/day. A summary of all the WVTR measurements versus Al₂O₃ ALD thickness is shown in Fig. 3.

Comparing these results to SiO₂ PECVD barriers on PET,¹² the critical thickness was 5 nm for Al₂O₃ ALD versus 25 nm for SiO₂ PECVD. The thick film WVTR was $\sim 1 \times 10^{-3}$ g/m²/day at 26 nm for Al₂O₃ ALD versus 0.2 g/m²/day at > 100 nm for SiO₂ PECVD. The results are far superior for the Al₂O₃ ALD films. Recently, another study measured a WVTR of $\sim 6 \times 10^{-2}$ g/m²/day for 30 nm thick Al₂O₃ ALD films coated on both sides of a PES substrate.³ The WVTR values for the single Al₂O₃ ALD films with thicknesses of 10 and 26 nm in this study are over an order of magnitude lower than the reported WVTR values on PES.

The barrier properties of an Al₂O₃ ALD film with a thickness of 10 nm were also evaluated using the “Ca

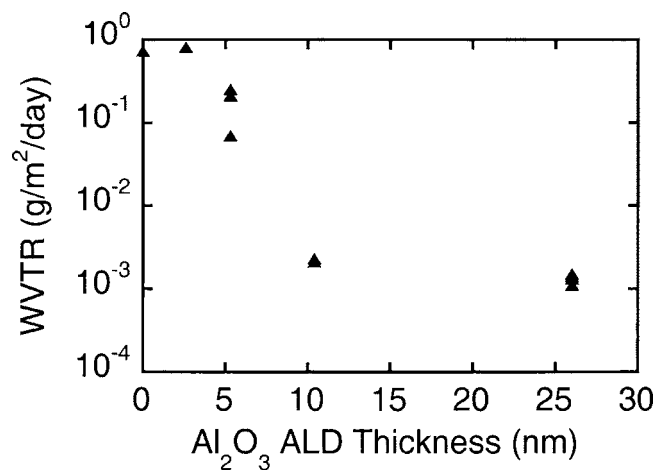


FIG. 3. Water vapor transmission rates versus thickness of the Al₂O₃ ALD films grown at 120 °C on PEN.

test.^{5,15} The test structure consisted of a PEN substrate coated by Al₂O₃ ALD on one side with a film thickness of 10 nm. This structure was then edge-sealed in an inert atmosphere with epoxy to a glass plate coated with Ca with a thickness of 150 nm. The change in optical transmission of the Ca film was monitored for over six months in ambient. The combined O₂ and H₂O vapor transmission rate through the ALD barrier film could be deduced from these optical measurements. In good agreement with the tritiated water results shown in Fig. 3, the effective WVTR was determined to be $\sim 1.5 \times 10^{-3}$ g/m²/day.

The ability of barrier films to perform after bending is critically important for flexible electronics and display applications.⁵ A Kapton® substrate coated with Al₂O₃ ALD with a thickness of 25 nm was repeatedly ($\sim 5 \times$) flexed back and forth to a radius of curvature of ~ 2 cm before performing an HTO test. The WVTR of $\sim 1.0 \times 10^{-3}$ g/m²/day measured after flexing this film was equal to the WVTR of other Al₂O₃ ALD films tested without flex-

ing. This lack of degradation in barrier performance indicates that the Al₂O₃ ALD films have not cracked after bending.

In summary, flexible gas diffusion barriers with a WVTR of $\sim 1 \times 10^{-3}$ g/m²/day were achieved using ultrathin Al₂O₃ ALD coatings with thicknesses of 26 nm on PEN and Kapton® substrates. These results are exceptional for such thin barrier layers. This Al₂O₃ ALD barrier technology is an important step forward to enable a broad class of flexible organic electronics on polymers.

¹J. S. Lewis and M. S. Weaver, IEEE J. Sel. Top. Quantum Electron. **10**, 45 (2004).

²H. Chatham, Surf. Coat. Technol. **78**, 1 (1996).

³S. 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).

⁴G. L. Graff, R. E. Williford, and P. E. Burrows, J. Appl. Phys. **96**, 1840 (2004).

⁵M. S. Weaver, L. A. Michalski, K. Rajan, M. A. Rothman, J. A. Silvernail, J. J. Brown, P. E. Burrows, G. L. Graff, M. E. Gross, P. M. Martin, M. Hall, E. Mast, C. Bonham, W. Bennett, and M. Zumhoff, Appl. Phys. Lett. **81**, 2929 (2002).

⁶M. Ritala and M. Leskela, in *Handbook of Thin Film Materials*, edited by H. S. Nawla (Academic, San Diego, 2001), Vol. 1, p. 103.

⁷J. W. Elam, M. D. Groner, and S. M. George, Rev. Sci. Instrum. **73**, 2981 (2002).

⁸M. D. Groner, J. W. Elam, F. H. Fabreguette, and S. M. George, Thin Solid Films **413**, 186 (2002).

⁹M. D. Groner, F. H. Fabreguette, J. W. Elam, and S. M. George, Chem. Mater. **16**, 639 (2004).

¹⁰J. W. Elam, C. A. Wilson, M. Schuisky, Z. A. Sechrist, and S. M. George, J. Vac. Sci. Technol. B **21**, 1099 (2003).

¹¹J. D. Ferguson, A. W. Weimer, and S. M. George, Chem. Mater. **16**, 5602 (2004).

¹²A. S. D. Sobrinho, M. Latreche, G. Czeremuszkin, J. E. Klemberg-Sapieha, and M. R. Wertheimer, J. Vac. Sci. Technol. A **16**, 3190 (1998).

¹³C. M. Hansen and L. Just, Prog. Org. Coat. **44**, 259 (2002).

¹⁴A. R. Coulter, R. A. Deeken, and G. M. Zentner, J. Membr. Sci. **65**, 269 (1992).

¹⁵G. Nisato, P. Bouten, S. P. W. Bennett, G. Graff, N. Rutherford, and L. Wiese, in *21th International Asia Display/8th International Display Workshop*, Society for Information Display, San Jose, CA, Nagoya, Japan, 2001, pp. 1465.