Gas Diffusion Barriers on Polymers Using Al_2O_3 Atomic Layer Deposition

M.D. Groner and S.M. George, Dept. of Chemistry and Biochemistry,
University of Colorado, Boulder, CO; and R.S McLean and P.F Carcia,
DuPont Central Research & Development, Wilmington, DE

Key Words: Permeation barrier coatings; Atomic layer deposition; Polymer substrates; Moisture permeation

ABSTRACT

Polymer substrates are needed for flexible organic devices such as organic light-emitting diodes (OLEDs). However, gas permeability in polymers is high and gas diffusion barriers are required to reduce H_2O and O_2 permeability. Inorganic films such as SiO_2 and Al_2O_3, can have extremely low gas diffusion rates and may be excellent gas diffusion barriers if they are continuous and pinhole-free. Low temperature Al_2O_3 atomic layer deposition (ALD) has been investigated on PEN and polyimide films. Al_2O_3 ALD films were deposited on these polymer substrates at temperatures between 100-175°C with thicknesses between 1-25 nm. MOCON measurements yielded O_2 permeation rates below the MOCON test limit of 5 x 10^{-3} cc/m^2/day for Al_2O_3 ALD films ≥ 5 nm thick. A sensitive new testing method has been employed to measure the extremely low H_2O permeation rates obtained after Al_2O_3 ALD. This test has measured water permeation rates of ~1 x 10^{-3} g/m^2/day for 26 nm thick Al_2O_3 ALD films on these polymers. Results are presented for the dependence of the H_2O permeation rate on Al_2O_3 ALD film thickness and for single-sided and double-sided Al_2O_3 ALD films on the polymers.

INTRODUCTION

The deposition of excellent permeation barriers on polymer substrates is a key requirement for the development of flexible OLED displays. The extreme sensitivity of OLEDs to oxygen and water demands diffusion barriers far better than the performance of conventional single layer barrier films [1]. Multilayer inorganic/organic barrier structures have been developed in an attempt to achieve lower permeation rates [2]. However, the apparently low permeation rates reported for these multilayer structures have recently been attributed to lag time effects [3]. The modeling of water and oxygen permeation through pinholes and defects in these multilayer structures indicates the need to deposit more perfect single-layer barrier films [3].

The deposition of barrier films by atomic layer deposition (ALD) is a promising approach because ALD is well known for depositing smooth, conformal, and pinhole-free films [4]. The excellent dielectric properties that have been measured for Al_2O_3 ALD films [5] suggest that they may also be superior permeation barriers. We have shown that high quality Al_2O_3 films can be deposited by ALD at temperatures as low as 33ºC [6]. Al_2O_3 is one of only a few ALD systems suitable for thermally fragile polymer substrates.

Al_2O_3 ATOMIC LAYER DEPOSITION ON POLYMERS

Al_2O_3 ALD was performed in a hot-wall ALD flow reactor using trimethylaluminum (TMA) (Aldrich) and water (Fisher HPLC-grade) [6,7]. A diagram of this reactor is shown in Figure 1. Growth temperatures ranged from 100-175ºC. Nitrogen gas flowed through the reactor at 100 sccm and produced a pressure of ~1 Torr. A typical ALD cycle at 120ºC consisted of a 0.1 s TMA exposure, a 30 s purge, a 0.15 s water exposure, and another 30 purge. A larger reaction chamber (3" tall, 6" diameter, with load lock) was built to accommodate 4" PEN and Kapton® substrates. Some substrates were taped to 4" Si wafers to achieve single-sided ALD coatings. Other substrates were suspended such that the polymer substrates were coated on both sides. Multiple substrates could be coated simultaneously by stacking them in a cassette-like arrangement. Polymer films were rinsed and loaded into the reactor in class 100 cleanroom conditions to minimize contamination of the polymer substrate prior to ALD.

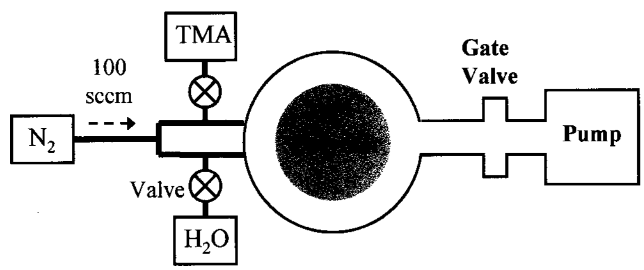

Figure 1. Diagram of the ALD reactor for depositing Al_2O_3 on polymer films.

Al_2O_3 ALD film thicknesses on polymer films were determined using an n&k 1280 Analyzer metrology system that was able to determine film thicknesses on transparent substrates using transmittance and reflectance measurements. These results agreed well with the 1.2-1.3 Å/cycle growth rates for Al_2O_3 ALD measured on Si wafers. This agreement indicates a rapid nucleation of Al_2O_3 on PEN and Kapton®. Rapid nucleation of Al_2O_3 ALD has also been demonstrated on other polymers [8, 9].

48th Annual Technical Conference Proceedings (2005) ISSN 0737-5921

OXYGEN PERMEATION

Oxygen transmission rates (OTR) were measured using a MOCON OX-TRAN 2/21 instrument with a sensitivity of 5 x 10^{-3} cc/m^2/day. OTR measurements were performed on a series of Al_2O_3 ALD films with thicknesses of 1, 5, 10, and 26 nm. Growth temperatures were 100 and 125ºC on PEN, and 125, 150 and 175ºC on Kapton®. OTR measurements of 1 nm thick Al_2O_3 ALD-coated polymers yielded no improvement over uncoated polymer films that displayed an OTR of ~1 cc/m^2/day. Al_2O_3 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 < 5 x 10^{-3} cc/m^2/day have never been achieved before for such thin single-layer coatings on polymers [1]. These OTR results also indicate a very low critical thickness of < 5 nm. Unfortunately, the MOCON OTR test is not sensitive enough to characterize the effects of film thickness, single versus double-sided coatings, and growth temperature.

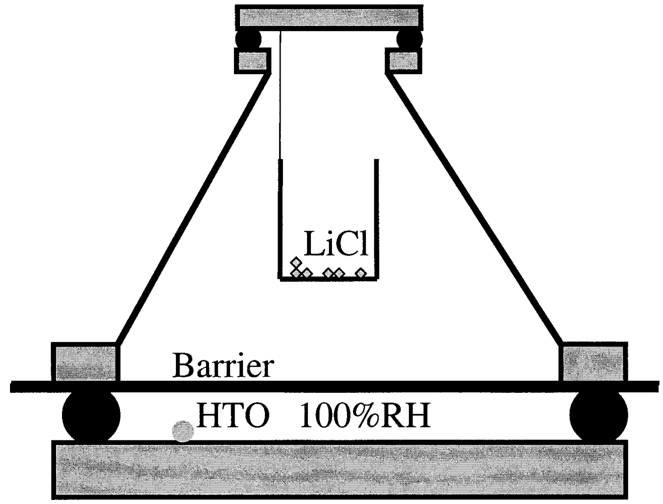

Figure 2. Tritiated Water Test. LiCl absorbs H_2O and HTO that permeates through the ALD-coated polymer film.

WATER VAPOR PERMEATION

Tritiated Water Test

More sensitive water vapor transmission rates (WVTR) were obtained using a tritiated water (HTO) test. The HTO test chamber is shown in Figure 2. A droplet of HTO (Perkin Elmer, 1 mCi/ml) is placed on the bottom flange. This tritiated water creates a 100% RH environment on the upstream side of the Al_2O_3-coated polymer film. The barrier film to be tested is clamped between a Viton o-ring and a reducing flange. A scintillation vial containing ~ 20 grains of LiCl is suspended in the top part of the chamber on the downstream side. The LiCl collects the HTO and water permeating through the film and the background water in the chamber. After a time period the vial is taken out and replaced with a new vial. The LiCl containing HTO is dissolved in 1 ml of water and 3 ml of Perkin Elmer Ultima Gold LLT scintillation cocktail. A Packard 1600TR scintillation counter was then used to count the tritium decays and calculate permeation rates. Measurements were taken usually once per day for several weeks until the permeation rate stabilized.

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 detection limit of < 1 x 10^{-6} g/m^2/day. This HTO test detection limit is over 1000 times more sensitive than the commercially available MOCON test for WVTR.

Water Vapor Permeation Through ALD Coatings

WVTR measurements were performed on a series of Al_2O_3 ALD films with thicknesses of 2.5, 5, 10, and 26 nm. Growth temperatures were 100 and 120ºC on PEN, and 100, 120, 150 and 175ºC on Kapton®. WVTR measurements of 2.5 nm thick Al_2O_3 ALD-coated polymers yielded no improvement over uncoated polymer films that had a WVTR of ~1 g/m2/day. Al_2O_3 ALD films with thicknesses of 5 nm yielded rates about an order of magnitude lower than the uncoated polymers. 10 nm thick Al_2O_3 ALD films achieved a WVTR of ~ 2 x 10^{-3} g/m^2/day. 26 nm Al_2O_3 ALD films averaged permeation rates of ~ 1 x 10^{-3} g/m^2/day on both PEN and Kapton® at all growth temperatures. A summary of these WVTR measurements versus Al_2O_3 ALD thickness is shown in Figure 3. These are excellent water vapor permeation rates for single layer barrier films.

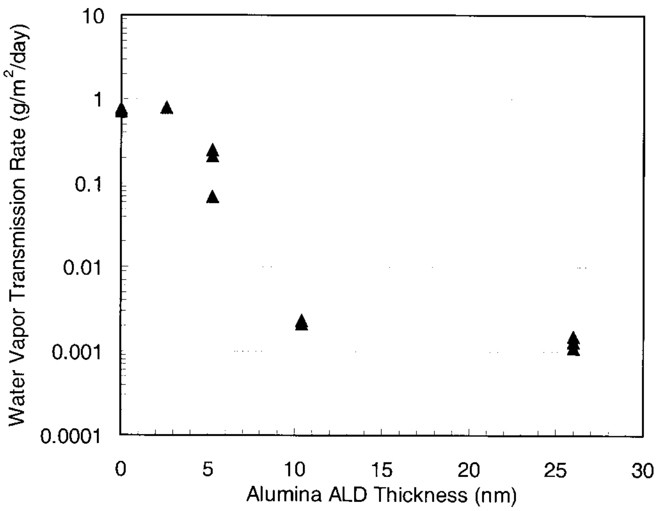

Figure 3. Water vapor permeation rates versus thickness of Al_2O_3 ALD films grown at 120°C on PEN and Kapton®.

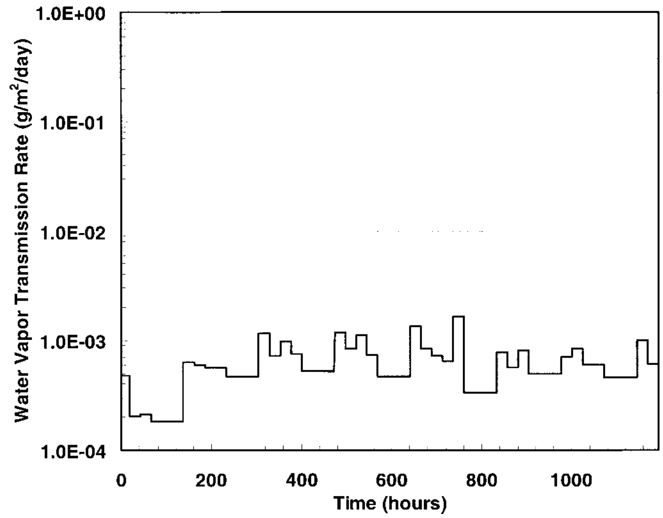

Figure 4. Water vapor permeation rate data for a Kapton® film with a double-sided 26 nm Al_2O_3 ALD coating. The WVTR averaged ~ 7 x 10^{-4} g/m^2/day over the last five weeks of the test.

Polymer films coated on both sides with Al_2O_3 ALD films were also tested with the tritium test. WVTR rates on double-sided Al_2O_3 ALD-coated Kapton® films were generally about a factor of two lower than single-sided coated films. Figure 4 shows the HTO test data for a Kapton® film coated on both sides with 26 nm ALD film. An average WVTR of ~ 7 x 10^{-4} g/m^2/day was measured over the last five weeks of this HTO test. Although this improvement is not dramatic, this factor of ~ 2 decrease is consistent with recent data analysis and modeling of multilayer barrier systems [3]. This modeling also predicted significant increases in lag time with each additional barrier layer. This prediction is also in good agreement with our observations. The lag time is the time required to obtain steady state permeation rates. Our lag time increased from ~ 1 day to ~ 4-5 days when going from single to double-sided coatings.

CONCLUSIONS

We have achieved excellent permeation barriers with WVTR ~ 1 x 10^{-3} g/m^2/day using thin Al_2O_3 ALD coatings on PEN and Kapton©. Even lower rates were measured for double-sided Al_2O_3 ALD coatings. Although these Al_2O_3 ALD films have yielded some of the best diffusion barriers reported for single layer films, these diffusion barriers are still not sufficient for protecting OLEDs. Ongoing research is dedicated towards lowering water and oxygen permeation rates even further to achieve this goal.

REFERENCES

1. J.S. Lewis and M.S. Weaver, "Thin-film permeation-barrier technology for flexible organic light-emitting devices," *Ieee Journal of Selected Topics in Quantum Electronics*, 10 (1), 45, 2004.

2. M.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, "Organic light-emitting devices with extended operating lifetimes on plastic substrates," *Applied Physics Letters*, 81 (16), 2929, 2002.

3. G.L. Graff, R.E. Williford and P.E. Burrows, "Mechanisms of vapor permeation through multilayer barrier films: Lag time versus equilibrium permeation," *Journal of Applied Physics*, 96 (4), 1840, 2004.

4. M. Ritala and M. Leskela, Atomic Layer Deposition, *In Handbook of Thin Film Materials*, ed. H. S. Nawla. Academic Press, San Diego, CA, 2001.

5. M.D. Groner, J.W. Elam, F.H. Fabreguette and S.M. George, "Electrical characterization of thin Al_2O_3 films grown by atomic layer deposition on silicon and various metal substrates," *Thin Solid Films*, 413 (1-2), 186, 2002.

6. M.D. Groner, F.H. Fabreguette, J.W. Elam and S.M. George, "Low-temperature Al_2O_3 atomic layer deposition," *Chemistry of Materials*, 16 (4), 639, 2004.

7. J.W. Elam, M.D. Groner and S.M. George, "Atomic Layer Deposition Viscous Flow Reactor with in situ Quartz Microbalance," *Rev. Sci. Instrum.*, 73 (8), 2981, 2002.

8. J.W. Elam, C.A. Wilson, M. Schuisky, Z.A. Sechrist and S.M. George, "Improved nucleation of TiN atomic layer deposition films on SILK low-k polymer dielectric using an Al_2O_3 atomic layer deposition adhesion layer," *Journal of Vacuum Science & Technology* B, 21 (3), 1099, 2003.

9. J.D. Ferguson, A.W. Weimer and S.M. George, "Atomic layer deposition of Al_2O_3 films on polyethylene particles," *Chemistry of Materials*, 16 (26), 5602, 2004.