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P. F. Carcia, R. S. McLean, and M. H. Reilly

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Permeation measurements and modeling of highly defective Al₂O₃ thin films grown by atomic layer deposition on polymers

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

DuPont Research and Development, Experimental Station, Wilmington, Delaware 19880-0400, USA

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We measured the thickness and temperature dependence of moisture permeation in highly defective (10–20 at. % hydrogen) Al_2O_3 thin films grown by atomic layer deposition on polymer substrates. We found that when films were grown at higher temperature or were thicker, independent of growth temperature, they were better moisture barriers. We determined the threshold thickness for measurement-limited barrier performance to be 7.5 nm for growth at 100 °C compared to 9.6 nm at 50 °C. We explained the permeability of these highly defective films with a new model, which relates moisture permeability to a critical density of defects and not due to pinholes. © 2010 American Institute of Physics. [doi:10.1063/1.3519476]

Organic electronic devices are emerging as attractive alternatives for lighting¹ (organic light emitting diodes, OLEDs) and power generation² (organic photovoltaics). Fabricating these devices on flexible polymers further provides a portable, lighter weight, and more robust product. However, a deficiency of organic devices is that they are not always stable in atmospheric conditions.^{3,4} Recently, Al₂O₃ thin films, grown by atomic layer deposition (ALD), have been shown to provide superior protection⁵⁻¹⁰ from moisture degradation even for the most sensitive organic devices (OLEDs). Since organic devices and polymeric substrates are also temperature-sensitive, a lower ALD growth temperature is preferred to avoid damaging them, and thinner layers are preferred for cost reasons. However, thin films grown by ALD at low temperature are highly defective.^{11,12} Specifically, Al_2O_3 films grown by thermal¹¹ or oxygen-plasma ALD (Ref. 12) contain 10-20 at. % hydrogen, when ALD growth is in the range of 50-100 °C. However, it is unknown how these chemical defects affect gas permeation. Current models^{13–15} ascribe permeation through inorganic thin films to pinholes in the film, and no connection is made to chemical defects. The pinhole model poses a particular paradox for films grown by ALD because they have been shown to be pinhole free.¹⁶

In this letter, we present new data for water vapor permeation in Al_2O_3 thin films (5–25 nm thick) grown by ALD on polyethylene terephthalate (PET) polymeric substrates at 50, 75, and 100 °C. Until now, there has been no systematic study of the effect of temperature *and* thickness on ALD barrier properties. The temperature range of 50–100 °C also maps the space for ALD growth of Al_2O_3 thin films with high defect content. We present a model to describe gas permeation through highly defective ALD Al_2O_3 films. Permeation is postulated to be by a chemical exchange reaction with H₂O along OH-defect clusters that percolate the thickness of the ALD coating, not by pinholes. This model is analogous to models used to explain the electrical breakdown in insulating thin film oxides.^{17–20}

Thin films of Al_2O_3 were grown in a Cambridge Nanotech (Cambridge, MA) Savannah 200 ALD reactor. The substrate was PET and only *one side* was coated with Al_2O_3 at

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

50, 75, and 100 °C. The precursors were trimethyl aluminum and water, and purge times were adjusted at each temperature to ensure an ALD growth process. The deposition rates, determined optically from 250 cycle thick films, were 0.926 Å/cycle (100 °C), 0.86 Å/cycle (75 °C), and 0.85 Å/cycle (50 °C).

Water vapor transmission rate (WVTR) was determined by the optical Ca-method^{7,10} and measured directly with a commercial instrument, the MOCON (Minneapolis, MN) Aquatran 1, which uses a coulometric sensor and NISTtraceable calibration standards. The commercial instrument has a sensitivity of 0.5 mg H₂O/m² day at 38 °C/85% relative humidity (RH). In the Ca-test, optical changes in thin (~50 nm), moisture-sensitive Ca films, protected by and epoxy-sealed to a PET lid coated with an ALD Al₂O₃ barrier film, are periodically monitored in ambient after aging at 38 and 60 °C/85% RH. The Ca-method relates the changes in optical transmission to WVTR and has about one order of magnitude better sensitivity at 38 °C/85% RH (~5 ×10⁻⁵ g/m² day, corresponding to a glass-lid control sample).

Figure 1 presents quantitative and visual results for Ca-testing after aging test structures for ~ 1200 h at 38 °C/85% RH. The data in this figure are arranged in in-



FIG. 1. Results of Ca-testing at 38 °C/85% RH of Al_2O_3 barrier films grown on PET by ALD at 50, 75, and 100 °C corresponding to 75, 125, and 250 ALD cycles at each growth temperature. The corresponding thickness can be calculated from the individual ALD deposition rates: 0.926 Å/cycle (100 °C), 0.86 Å/cycle (75 °C), and 0.85 Å/cycle (50 °C).

dividual cells. Each cell represents barrier performance for a specific ALD growth temperature (50, 75, or 100 °C) and thickness, i.e., number of ALD cycles (N=75, 125, or 250). In these transmitted-light images, the white spots are regions where metallic Ca fully oxidized to optically transparent Ca(OH)₂. The recorded aging time (in days), when these oxidation defects *first* appeared, is indicated in an individual cell. For ALD growth conditions, for which the Ca-pixels retained a featureless, defect-free metallic appearance⁷ (no apparent defects), and damp heat aging only produced a very thin, uniform surface oxidation layer, we report only the value of WVTR in that cell.

The key observations were the following. (1) For all thicknesses: 75, 125, and 250 cycles, films grown at 100 °C had a WVTR equal to the glass control limit ($<5 \times 10^{-5}$ g/m² day at 38 °C/85% RH). (2) When ALD films were thick (250 cycles), independent of growth temperature, they also had WVTR at the glass control limit. (3) For the intermediate thickness, corresponding to 125 cycles, *most* Ca-pixels developed oxidation defects after 51 days, except for the isolated Ca-pixels, without oxidation defects. WVTR determined from pixels without defects was also at the measurement limit. Finally, (4) for the thinnest film (75 cycles), Ca-pixels became fully transparent in only 7 days, corresponding to the first measurement, for growth at 50 °C, while Ca-pixels developed defects sooner (34 days) than thicker films for growth at 75 °C.

After an additional ~500 h at 60 °C/85% RH, ALD films grown at 100 °C for all thicknesses and thick Al₂O₃ films (250 cycles) grown at all temperatures continued to show no visible oxidation defects and maintained a WVTR equal to the glass control sample (~ 3×10^{-4} g/m² day at 60 °C/85% RH). After 12 days at 60 °C/85% RH, the 75 cycle film grown at 75 °C now also became fully oxidized. Moreover, for 125 cycles, Ca-pixels protected with a barrier made at 50 °C showed more degradation—greater pixel shrinkage—compared to a 125 cycle film made at 75 °C. *These data support that growing* barrier films at higher temperature or that are thicker reduces moisture permeation.

In comparison with the Ca results, we measured WVTR at 38 °C/85% RH, using the MOCON Aquatran-1, versus the thickness of ALD Al₂O₃ films grown at 50, 75, and 100 °C. The results are summarized in Fig. 2 with the published instrument sensitivity limit, 0.5 mg H_2O/m^2 day, indicated as a horizontal dotted line. For all growth temperatures, the WVTR falls as the ALD film thickness increases. For growth at 100 °C, a dashed line fitting these data intersects the instrument measurement limit at \sim 7.5 nm (81 cycles). We define this thickness as the "threshold" thickness.¹⁴ It is the thickness below which permeation increases rapidly and above which permeation is at the limit of the measurement technique. Because of the scatter of the data for ALD growth at 50 and 75 °C, we fitted these combined data with a single dashed line and assigned one threshold thickness for the two temperatures, ~ 9.6 nm (113) cycles).

To explain these results for water vapor permeation in ALD thin films, we propose a new model that does not rely on pinholes in our ALD films, which we contend are pinhole-free. In our model, gas permeation proceeds along chains of chemical defect clusters that percolate the thickness of the This a film. This is related to models ^{17–20}/₁₀ of electrical breakdown in sub-



FIG. 2. (Color online) WVTR measured with commercial instrument at 38 °C/85% RH for Al_2O_3 barrier films grown on PET by ALD at 50, 75, and 100 °C vs the Al_2O_3 thickness. The horizontal dotted line corresponds to the published instrument measurement limit of 0.5 mg H_2O/m^2 day.

oxide thin films. In ALD Al_2O_3 films, the defects are H-atoms that form OH bonds to Al, whereas in electrical breakdown the defects are charge traps. At ALD growth temperature of 50 °C, the H-defect concentration is quite large,¹¹ ~21 at. % or 2.5×10^{22} H atoms/cm³, decreasing as the ALD growth temperature increases. We postulate that water permeates the film by an exchange mechanism, such as described by the reaction: $AIO(OH)+H_2O \rightarrow AI(OH)_3$. For any ALD Al₂O₃ film thickness, there is a corresponding critical defect density, at which the onset of water permeation occurs. Below this threshold thickness, permeation is facile.

To quantitatively describe defect related permeation, we use the analytical expression of Sune¹⁹ for analyzing electrical breakdown in oxide films,

$$N = \frac{d}{a_o^3} \left(\frac{a_o^2}{A} \right)^{a_o/d}.$$
 (1)

Applied to our permeation case, $N(1/cm^2)$ is the critical surface H- or OH-defect concentration responsible for permeation through the thickness d, which corresponds to the threshold Al₂O₃ thickness for permeation, along defect clusters with dimension a_o and sample reference area A. With $a_o = 1.25$ nm, an efficiency factor^{18,19} of 1/200 that an individual percolating chain of defects contributes to permeation, and the reference area A=1 cm², Fig. 3 plots N versus d. Superimposed on this graph are points for the H-defect concentration¹¹ measured for Al₂O₃ films grown by thermal ALD at 50 and 100 °C, plotted at the corresponding threshold thickness, determined in this work to be 9.6 and 7.5 nm, respectively. At d=7.5 nm, the model predicts a critical defect concentration of $N=0.75\times10^{22}$ cm⁻³ about half of 1.47×10^{22} cm⁻³, the H-defect concentration measured in ALD films grown at 100 °C, and for d=9.6 nm N=6.2 $\times 10^{22}$ cm⁻³, which is larger than 2.5×10^{22} cm⁻³, the measured H-defect concentration in ALD Al₂O₃ grown at 50 °C. In general, the model predicts the observed trend that a film with lower defect density, corresponding to a higher ALD Al₂O₃ growth temperature, will have a lower threshold thickness for permeation. Moreover, the predicted values of Nagree reasonably well with the measured H-defect content d to IP



FIG. 3. (Color online) Plot of calculated [Eq. (1)] critical defect density (*N*) in ALD Al₂O₃ films vs the corresponding threshold thickness (*d*) for the onset of permeation. Points correspond to the measured H-defect concentrations plotted vs threshold thick, determined from direct WVTR measurement on ALD Al₂O₃ films grown at 50 and 100 °C.

The model also implies that growing the barrier film thicker by Δd above the threshold will proportionally raise the critical defect density by ΔN . Then permeation will not occur in the thicker film before exposure conditions of temperature and humidity generate additional defects by an amount ΔN . This is consistent with the low, measurement-limited WVTR for ALD Al₂O₃ barrier films with thick ALD layers (250 cycles), even though they were grown at lower temperature (50 and 75 °C), where the defect density is relatively high.

Finally, this model, which we have adapted to gas permeation, can be used to qualitatively explain the timedependent onset of permeation, i.e., the sudden appearance of Ca-oxidation defects in *near threshold thickness* films. In the case of electrical breakdown, the time dependence to breakdown is exponentially related to the enthalpy or activation energy for new defect generation,²¹

$$\ln t \propto \frac{\Delta H_o}{kT}.$$
(2)

For permeation, a reasonable estimate of ΔH_o may be the replacement or exchange energy of water in aqueous solution (or vapor) with metal-oxide bound water.²² For insulating molecular oxides, ΔH_o is in the range of ~10–120 kJ/mole (0.1–1.25 eV),²² which leads to permeation "breakthrough" times²³ of ~1 to >10⁸ s. A high initial concentration of H-defects and the presence of oxygen vacancy defects²⁴ could favor the activation energy at the lower end of this range of ΔH_o . Thus, for a barrier grown at low temperature and with thickness near the threshold, an abrupt increase in

permeation, corresponding to the sudden appearance of Caoxidation defects, could occur after only days or weeks of exposure at 38 °C/85% RH. However, for a barrier layer grown at high temperature with low initial defect density, ΔH_o could be at the high end of its range so that generation of new defects would be imperceptible even on the timescale of years.

In summary, we have measured the thickness dependence of WVTR for Al_2O_3 barrier films grown by ALD on PET polymeric substrates at 50, 75, and 100 °C, where films grow with high defect content. We proposed the framework of a new model to explain the moisture permeation of these highly defective films.

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