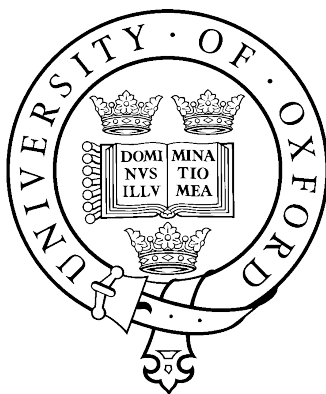


Roll-to-roll Deposition of Highly Flexible Organic-Inorganic Barrier Layers for Printed Electronics and Photovoltaics



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Abstract

This thesis investigates how to improve transparent flexible water vapour barriers by understanding how water permeates through them. The barriers consisted of a reactively sputtered aluminium oxide coating on an industrial-grade polypropylene substrate. Some also incorporated a di-acrylate smoothing layer.

Key deposition conditions were studied and optimised for permeation and visible-light transparency: sputtering power, thickness & sequential deposition rate. One of the main deposition conditions corresponded to increasing coating nitrogen content in order to induce barrier-water interaction. The final investigation consisted of including acrylate layers in different barrier stacking combinations.

It was found that thin, high sputter power coatings formed the best barriers to permeation. This was due to denser packing of the oxide and the inclusion of fewer macro-defects (large defects allowing unhindered permeation) and nano-defects (defects small enough to cause the permeant to interact with the coating).

No clear benefit to permeation was found from the inclusion of nitrogen, but refractive index was seen to increase and the oxynitride coatings mechanically failed at a greater force than the oxides. This case illustrated the importance of considering the role of permeation through nano-defects: although a high activation energy was achieved for the nitrogen containing films, possibly suggesting greater interaction between the water vapour and the barrier, the amount of permeation was not reduced as the nitrogen gave rise to increased permeation due to nano-defects, thus changing the processing and chemistry can affect both the macro-defect and nano-defect permeation.

Smoothing layers were found to reduce the permeation rate by covering large substrate features, thus allowing rough substrates to be used even for high barriers. Although a coating of acrylate on top of a barrier oxide showed no improvement, a 1-2-1-2 stack of smoothing layer (1) and oxide (2) was found to exhibit a large delay in the onset of permeation.

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List of Abbreviations

AFM	Atomic force microscope
ALD	Atomic layer deposition
AlO _x	Aluminium oxide
AlO _x N _y	Aluminium oxynitride
AO	Atomic oxygen
BE	Binding energy
BIF	Barrier improvement factor
CVD	Chemical vapour deposition
DA	Di-acrylate (see TRPGDA)
DC	Direct current
FT-IR	Fourier transform infrared spectroscopy
GO	Graphene oxide
IB	Ion beam
ILT	Ideal laminate theory
LBL	Layer by layer
LN ₂	Liquid nitrogen
MD	Machine direction
OLED	Organic light emitting diode
OPV	Organic photovoltaic
OTR	Oxygen transmission rate
PC	Polycarbonates
PECVD	Plasma-enhanced chemical vapour deposition
PEN	Polyethylene naphthalate
PES	Polyethersulfones
PET	Polyethylene terephthalate
PP	Polypropylene
RBS	Rutherford back scattering
RF	Radio-frequency
RH	Relative humidity
RIE	Reactive ion etch
Sccm	Standard cubic centimetres per minute
SEM	Scanning electron microscope
SiO _x	Silicon oxide
SiN	Silicon nitride
ToF SIMS	Time of flight secondary ion mass spectrometry
TD	Transverse direction
TRPGDA	Tri(propylene glycol) diacrylate
UV-Vis	Ultraviolet visible spectrometer
WVTR	Water vapour transmission rate
XPS	X-ray photo-electron spectroscopy

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1 Introduction and Context

1.1 Why Are Gas Barriers Required?

Flexible organic optoelectronics, e.g. organic light emitting diodes (OLEDs) and organic photovoltaics (OPV), are of great interest in the spheres of industry and government policy. Gustaffson [1] who fabricated the first flexible OLED on a polymer substrate, pointed immediately to the simplicity of their fabrication (in that case, solution processing) and the possibility of moving to mass-production, an advantage not shared by other LED technologies. Even though OPVs exhibit efficiencies around a factor of 3.4 lower than their leading solid state counterparts, they present a possible paradigm shift in energy generation due to the possibility of roll-to-roll production of solar cells [2]. The central problem with this burgeoning technology however is that un-encapsulated OLEDs have lifetimes of hours [3]. Exposure of OLEDs to moisture and oxygen has been found to cause organic/cathode delamination [4], [5].

In order for OLEDs and OPV to perform on timescales required for the economic manufacture of devices, estimates have suggested that encapsulation must provide a water permeation rate of $<1 \times 10^{-6}$ g/m²/day and an oxygen permeation rate $<1 \times 10^{-3}$ cm³/m²/day in order to sustain a 10,000 hour lifetime for an OLED device or a 3-5 year lifetime for OPV [6], [7].

Optical transparency is a key requirement of the encapsulant, with the benchmark set as >90% transmission in the visible region [8].

Polymers are an obvious choice for the substrates of OLEDs & OPV, but only provide an intrinsic barrier of ~ 0.1 -100 g/m²/day for water vapour and 10-1000 cm³/m²/day for oxygen [9]. Glass is the encapsulation method of choice for current, rigid technologies due to its stability and essentially impermeable barrier qualities, but it is brittle and unable to function successfully as a flexible substrate [6]. Thin oxides such as SiO_x, AlO_x and TiO_x have been used in the packaging industry to imbue polymers with high barrier qualities [3]. Their

optical transparency, hardness and flexibility make them of great interest for use as barriers for OLED and OPV applications.

1.2 The Aim of the Project

This project aims to investigate improvements to the method for producing transparent, flexible barriers as encapsulation for organic optoelectronics. The project will aim to develop a greater understanding of the influence of the substrate on the formation of the coatings. It will be seen how the nature of water permeation through different materials and under different process conditions influences barrier properties. This improved understanding will be applied to large area production on a new substrate, biaxially oriented polypropylene.

1.3 Substrate Considerations

1.3.1 Polymers

The choice of substrate polymer is important and there are many different types to be considered. Erlat [6] described how a key metric for substrates used for barrier oxides is glass transition temperature, T_g , which helps define an upper temperature for fabrication (see Section 2.1) as well as the important factor of whether or not the polymer is amorphous or semi-crystalline. The review explained that semi-crystalline films of Polyethylene naphthalate (PEN) and Polyethylene terephthalate (PET), with T_g 120 °C and 78 °C respectively, have a low coefficient of thermal expansion and good resistance to solvents but that the key strength of these polymers was their stiffness, with a Young's modulus a factor of 3 times higher than the amorphous polymers [6]. PET, PEN have a Young's modulus of 5.3 and 6.1 GPa respectively [7] compared to amorphous PP which is 1.4 GPa [10]. Most examples of barrier oxides in this literature review (Chapter 2) have PET substrates.

Erlat discusses the amorphous, high T_g Polyethersulfones (PES ~ 220 °C) and Polycarbonates (PC ~150-220 °C)[6], with Choi [9] explaining how their intrinsic water vapour transmission rate (WVTR) properties are an order of magnitude worse than PET/PEN, but that they exhibit superior surface smoothness. Choi stresses that surface roughness is very important as active

elements of OLEDs are ~100 nm thick and that 50 nm surface features are present even on high quality PEN [9]. The addition of a planarising smoothing layer can compensate for substrate roughness and is discussed in Section 2.4.2.2.

Deng's comparison of 12 μm thick (biaxially drawn) PET with 20 μm (co-extruded, two-layer, amorphous) PP, see Table 1, found that PP was a bad intrinsic OTR barrier, with PET performing 13 times better, but that PP was a better WVTR barrier by one order of magnitude [11].

Table 1. Reproduced from [11] showing the permeation rates for PET and PP.

Substrate	Thickness (μm)	OTR ($\text{cm}^3/\text{m}^2/\text{day}$)	WVTR ($\text{g}/\text{m}^2/\text{day}$)
PET	12	176	41
PP	20	2419	3.3

It is understood that the nature of the substrate's polymer surface affects the growth of the oxide by controlling nucleation [12]. Deng explained that uniform nucleation promoted a homogenous oxide structure with fewer nano-defects [11].

1.3.2 Substrates as a source of defects

Silica anti-block particles are approximately spherical and used in the fabrication of some substrates to avoid multiple layers of polymer sticking together on the roll. These particles can protrude from the surface, sometimes by a distance an order of magnitude greater than the thickness of the oxide. The ability of a thin layer to cover these relatively large features is questionable. Also, damage to the substrate can be manifested in the oxide layer, for example a series of scratches and chains of gouges (20-30 nm deep and 1-2 μm wide) present in a PET substrate produced deformation in a subsequently deposited oxide, emphasising the critical nature of substrate preparation [12].

2 Literature Review

2.1 Barrier Fabrication

The main processes for fabricating barrier oxides are **Chemical Vapour Deposition - CVD** (Section 2.1.1), **Atomic Layer Deposition -ALD** (Section 2.1.2), **evaporation** (Section 2.1.3) and **sputtering** (Sections 2.1.6 and 2.1.7). Their basic operation and advantages are outlined in this section. Other barrier technologies that do not incorporate inorganic layers are also briefly discussed, including **Layer-by-Layer Deposition** (Section 2.1.4) and the use of **Graphene Membranes** (Section 2.1.5). An approach to barrier fabrication that relies on the use of **nano-structures** (Section 2.4.2.1) will also be discussed.

2.1.1 Chemical Vapour Deposition

Figure 1, shows the basic function of Chemical Vapour Deposition (CVD).

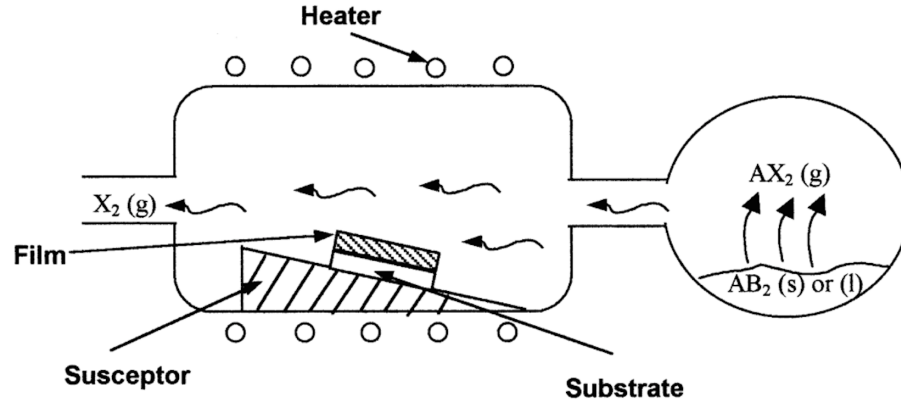


Figure 1. Schematic of CVD, gaseous reactants are activated and a thin film is deposited on a substrate, reproduced from [13].

Gas reactants are passed into the chamber and activated, either by a heated substrate or a plasma, with the products of the reaction causing a film to grow on the substrate [13]. Choy's study [13] gives a thorough review of the advantages/disadvantages of the method. The ability of the method to provide uniform coverage, with a deposition rate up to $\sim 170 \text{ nm/min}$ and at low-cost make this technique attractive, but the high operating temperatures

~1000°C (for SiC - depends on the reaction) and toxic/flammable precursors can be a drawback for many applications [13].

Plasma Enhanced Chemical Vapour Deposition (PECVD), a technique used by various groups to produce barrier layers [14]–[17], is an adaptation of CVD: it takes place under vacuum with a plasma discharge activating dissociation and heating the substrate [13]. It takes place at lower temperatures (at or around room temperature), while maintaining a high deposition rate [13].

Wuu [18] notes the lower barrier quality of a coating produced by low-temperature CVD, and suggests the use of a polymer such as PES (which can withstand a process temperature up to 180°C) to overcome this issue.

Choy pointed to a significant drawback of PECVD in the fabrication of oxides, that high purity was difficult to achieve due to the presence of unreacted precursors, which can negatively affect the mechanical and electrical properties of the films [13].

A study by Liu [19] found that the PECVD process damaged the operation of the OLED it was encapsulating. A sputtered ZnO interlayer prevented this damage, but that even this sputtered layer induced some damage in the OLED. A quantitative illustration of this can be seen in Figure 2 [19].

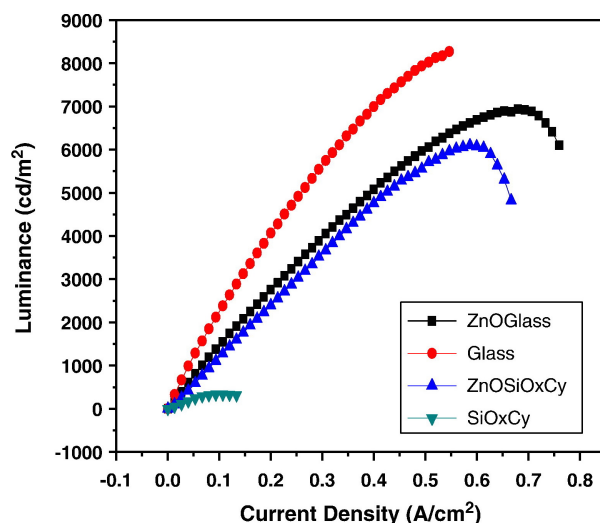


Figure 2. Luminance vs Current Density for a PEDOT:PSS OLED encapsulated by glass, RF sputtered ZnO and glass, ZnO and PECVD SiO_xC_y and just SiO_xC_y. From [19].

The only form of permeation test in Liu's paper was to expose the ZnO/SiO_xC_y encapsulated OLED to atmosphere, which was shown to have 70-80% of the total pixel area still operational after 24 hrs [19]. The paper of Liu shows the possibility to tailor hardness and hydrophobicity of films by altering their chemistry but also the considerations of damage from the barrier deposition methods. There is a lack of any quantifiable permeation testing, with the phrase "exposed to atmosphere" undefined in terms of RH or temperature. This compounds the issue in the field of a lack of standard other than the MOCON (see Section 2.2.1), with Choi lamenting the fact that different papers present wildly different temperatures and humidities, making comparison difficult [20].

A paper by Premkumar shows the ability of this technique to be scaled up. The 2010 paper describes the roll-to-roll PECVD fabrication of "SiO₂-like films" onto PEN using the same precursors, but with N₂ and air as reactant gases [21].

2.1.2 Atomic Layer Deposition

Atomic Layer Deposition (ALD), [22] is, as the name suggests, a method of growing thin films in steps of atomic monolayers [23], with the basic principle of operation outlined in Figure 3.

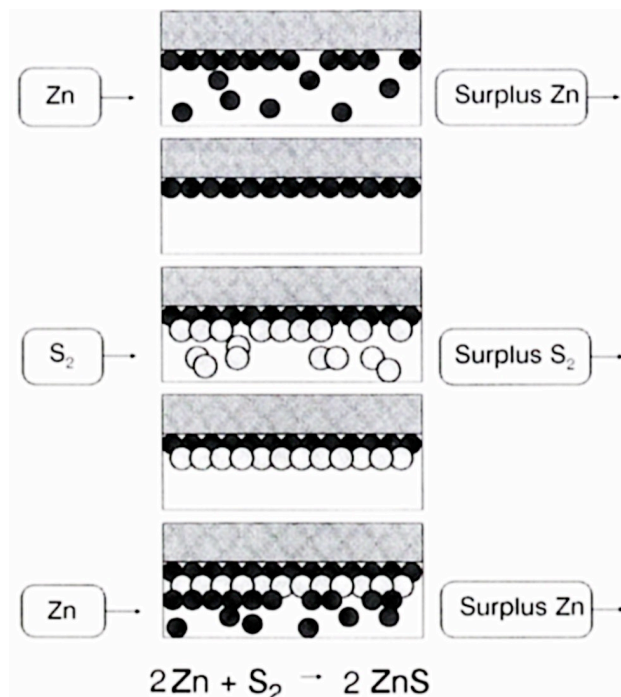


Figure 3. Reproduced from [23]: the principles of ALD, subsequent gaseous reactants deposit atomic monolayers.

The basic operation consists of the substrate being exposed in turn to the elements of which the desired compound is to be formed, with the growth limited by the availability of sites for the reaction, thus forming monolayers, with the excess reactants purged from the system [24].

ALD was used by Kim to produce AlO_x , but with a deposition rate of 0.5 nm/min [25], compared to 17 nm/min for sputtered AlO_x using the Oxford Webcoater, it is a comparatively slow process (factor of 34 slower). It was also stated that the ALD process took place at 110°C [25], which when considering Wuu gives the maximum process temperature of PET as 120° C [18], can be problematic for many polymer substrates. A low temperature ALD production method showed that AlO_x could be fabricated at 33°C but that the density (found using quartz microbalance crystal sensors) of the film was much lower (2.5 g/cm³) when compared to those produced at 177° C (3 g/cm³) [26].

2.1.3 Evaporation

Evaporation is a method with a high deposition rate and one that is used extensively in the packaging industry. Metals are heated up in a crucible, vaporized and condensed onto a substrate. A variation of this method, and the one used by Roberts [27], is electron beam evaporation, where the material to be evaporated is heated through irradiation from an electron beam gun: see Figure 4 for an example of this.

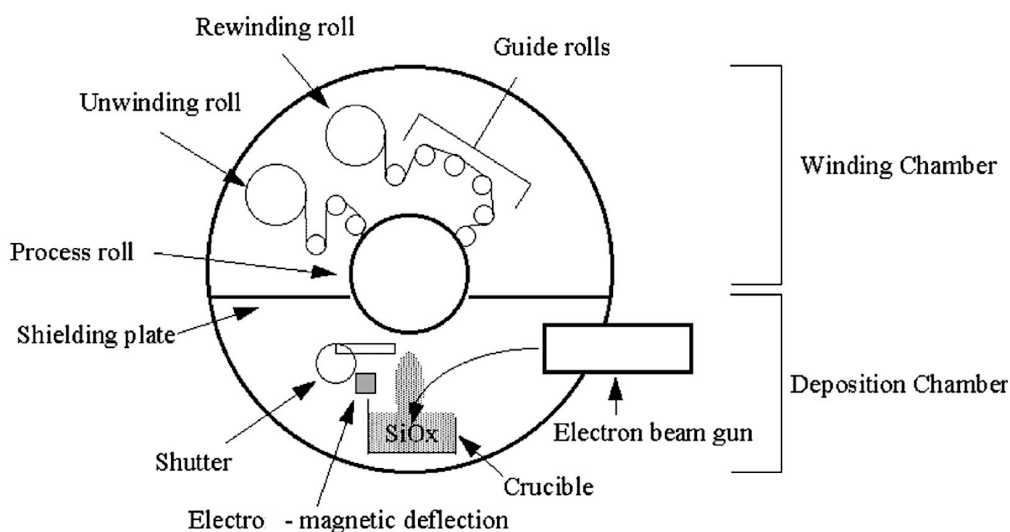


Figure 4. Reproduced from [27], a schematic of a roll-to-roll electron-beam evaporation set up.

Suntola, in his ALD patent, contrasted his technique to that of evaporation by stating that the relatively poor control of the stoichiometry of films produced by evaporation was an impetus for the development of ALD; it is also suggested that sputtering provides the best (pre-ALD) stoichiometric films [24]. Affinito's study showed sputtered AlO_x outperformed evaporated layers when both were deposited on a smoothing layer [28].

Ludwig reports evaporation of 25 nm thick AlO_x on 12 μm PET in a roll-to-roll setup at web-speeds of ~ 700 m/min, exhibiting WVTR of 1 g/m²/day (a BIF of 20 over the substrate) [29].

Struller reported roll-to-roll reactive evaporated AlO_x (10 nm) on PP (20 μm), which recorded OTR of 27 cm³/(m² d) (at 23°C, BIF= 77) and WVTR of 4.7 g/m²/day (37.8 °C, BIF=

1.4, see Section 2.3.1) [30]. Struller points out that PP is a cheaper material, and used widely in packaging, but that PET performs better as a barrier substrate.

2.1.4 Layer by Layer Deposition

Layer by layer (LBL) deposition differs from many other coating techniques in that it is a mainly polymeric and all-organic process (see Figure 5). It consists of 4 steps 1) polyanion adsorption 2) wash 3) polycation absorption 4) wash, then repeat as necessary [31].

The Figure originally presented here cannot be made freely available via ORA because permission could not be secured for adaptation of the image. The Figure was sourced at <http://science.sciencemag.org/content/277/5330/1232>

Figure 5. The 4 steps of layer-by-layer assembly. The anionic polymer is adsorbed to the substrate, then the system is washed, then the cationic polymer is adsorbed and the system is washed again, from [31].

An All-Polymer Barrier

Yang reported an all-polymer gas barrier in 2011. Polyethylenimine (PEI) and poly(acrylic acid) (PAA) are used as polyelectrolytes [32]. These two polymers interpenetrate following LbL deposition which causes exponential film thickening with increasing numbers of layers [32]. The degree to which they thicken can be controlled by the pH of the PEI/PAA with the

smallest growth at 7/7 and the largest at 10/4 [32]. The much-reduced free volume of the interpenetrated polymers, due to the strong electrostatic attraction between them, is the cause of the high barrier properties of the assembly [32]. The thickest (10/4) barriers were shown to have the best OTR ($<5 \times 10^{-3} \text{ cm}^3/(\text{m}^2 \text{ day atm})$ - 10 bi-layers, 1.08 μm thick) with the other pH layers recording the same OTR as the 175 μm PET substrate [32]. As was noted by Yang and Priolo, the barrier properties of these LbL assemblies degrade under humid conditions [32], [33], which goes to explain why only OTR are quoted with no WVTR. Yang suggests that these barriers could be used to encapsulate flexible electronics, however this seems unlikely due to their water sensitivity. Yang reports that the cross-linking of the layers using Glutaraldehyde (GA) improves the layers barrier properties under 100% humidity but limits the exponential thickening previously observed [32].

Clay-Polymer Barrier

Priolo's technique (similar to that of Yang), introduces clay nanoparticles to further lower permeation (see Figure 6). The difference with Yang's technique is that one of the anionic polyelectrolyte layers is replaced with an anionic montmorillonite clay (MMT) [33].

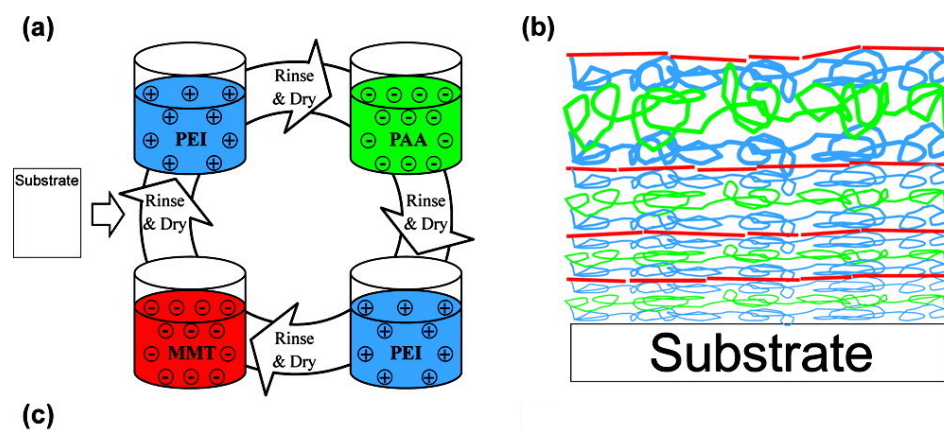


Figure 6 reprinted with permission from M. A. Priolo, D. Gamboa, K. M. Holder, and J. C. Grunlan, "Super Gas Barrier of Transparent Polymer - Clay Multilayer Ultrathin Films," *Nano Lett.*, pp. 4970–4974, 2010 Copyright 2010 American Chemical Society.

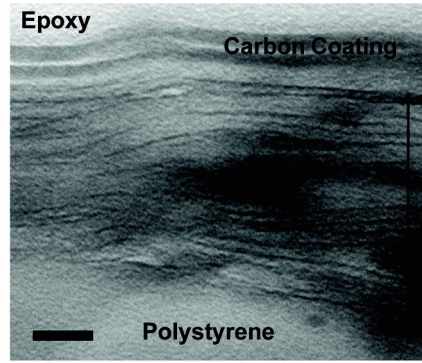


Figure 6. a) the 8-stage LbL process, anionic PAA is adsorbed, washed, cationic PEI is adsorbed, washed, anionic MMT adsorbed, washed, PEI adsorbed and washed. (b) Schematic of the layers, showing the layers of clay nanoparticles between the polymers. (c) TEM cross-section of the layers, with the dark lines of the clay layers clearly visible. From [33].

The key finding is that only four quad-layers (QL - one full LbL process as shown in Figure 6 (a)) of thickness 50.9 nm are needed to lower the OTR to below the measurable MOCON limit $< 5 \times 10^{-3} \text{ cm}^3/(\text{m}^2 \text{ day atm})$ at 0% RH [33]. However, the barrier properties of these films degraded in 100% RH, with a 7 QL film only providing an OTR of $0.14 \text{ cm}^3/(\text{m}^2 \text{ day atm})$, but that cross-linking of the polymer layers helped decrease the rate to $0.09 \text{ cm}^3/(\text{m}^2 \text{ day atm})$ [33].

Nolte's study found that the polyelectrolyte layers of LbL films swell and become plasticized in the presence of water [34].

Polymer-Graphene Oxide Barrier

Yang's 2013 paper developed a bilayer LbL barrier that composed of cationic PEI and anionic graphene oxide (GO). However, the polymer/GO nanobrick structure has questionably low transparency (optical inspection only) and a 30 bilayer system only provides an OTR of $0.27 \text{ cm}^3/(\text{m}^2 \text{ day atm})$ [35].

2.1.5 Graphene Single Membranes

The concept of a single membrane of graphene as a barrier layer is worthy of brief mention.

In the paper by Bunch, a square micro-chamber (4.75 μm x 4.75 μm) is covered by a graphene membrane 1-75 graphene layers thick, with the chamber sealed by the van der Waals forces

between it and the membrane [36]. This can be seen in Figure 7a) [36].

Figure 7 is reproduced from J. S. Bunch, , "Impermeable atomic membranes from graphene sheets," *Nano Lett.*, vol. 8, no. 8, pp. 2458–2462, 2008. Copyright 2008 American Chemical Society.

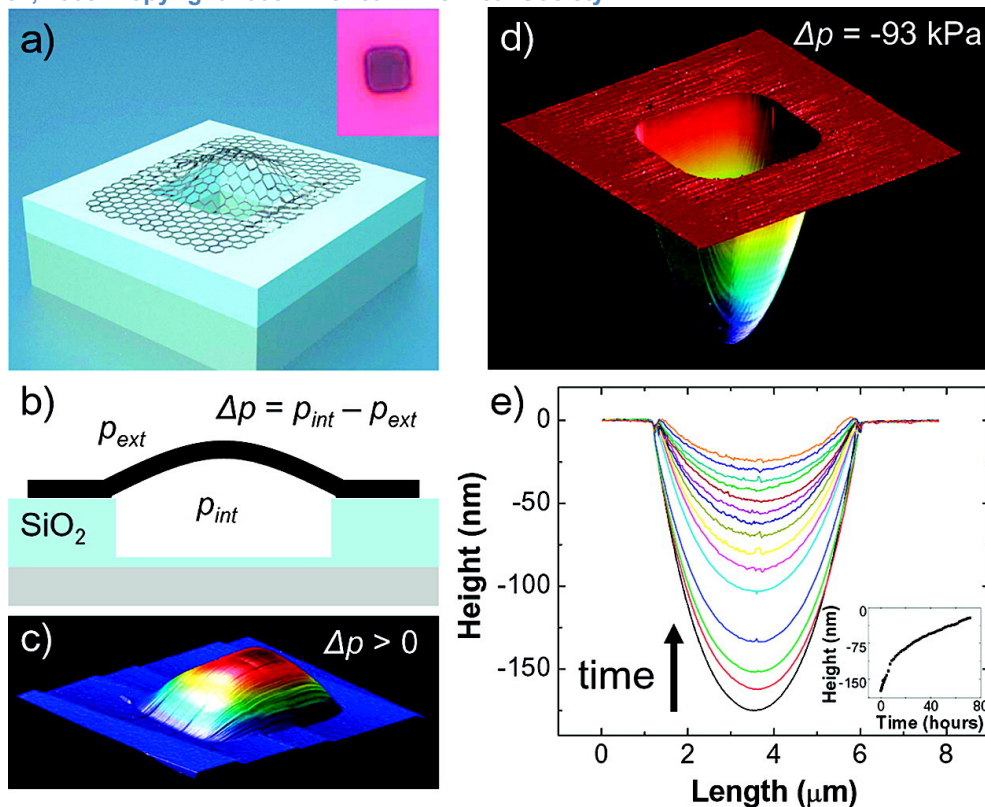


Figure 7. a) Microchamber (4.75 μm x 4.75 μm) sealed with a graphene membrane, b) a schematic of the pressure gradient set up across the membrane, c) a tapping-mode AFM of a chamber sealed with a 9 nm graphene stack with a pressure gradient deforming it, d) AFM of the sealed microchamber with -93 kPa gradient across it, e) AFM line traces through the centre of the 9 nm graphene membrane over 71 hours as the membrane “deflates”. From [36].

A pressure gradient is set across the membrane by filling the chamber with different types of gas at differing pressures, then translating the system to a vacuum to create a positive gradient [36]. It can be seen from Figure 7 e) that the pressure gradient normalises over time [36]. It was reported that the leak rate for the different gases was independent of the thickness of the graphene layer, leading them to the conclusion that the gases were escaping through the walls of the chamber or the seal between the chamber and the membrane, rather

than passing through the membrane itself [36]. This was reinforced by calculations of helium egress through a solitary graphene vacancy as being much higher than the leak rates observed [36]. The paper concludes that the graphene membrane is impermeable to argon, air and even helium [36].

This paper shows a possible route for development in barrier technology albeit one in its infancy. The areas in question are small ($22.6 \mu\text{m}^2$ in this example) and there is no possibility in the short to medium term of this being used for the applications discussed throughout this paper.

2.1.6 Radio Frequency Reactive Magnetron Sputtering

Sputtering is an important industrial technique that can produce high quality barriers. In order for a material to be sputtered, argon ions generated in a plasma are accelerated and are incident on a target cathode, emitting material from the target that is deposited on a substrate. Secondary electrons, also emitted from the target, contribute to the maintenance of the plasma [13]. An elliptical array of magnets behind the target trap the secondary electrons, keeping them close to the target which increases the plasma ionization and subsequent target-bombardment [13]. These secondary electrons, being magnetically trapped, do not contribute to substrate heating and the damage that this can cause [37].

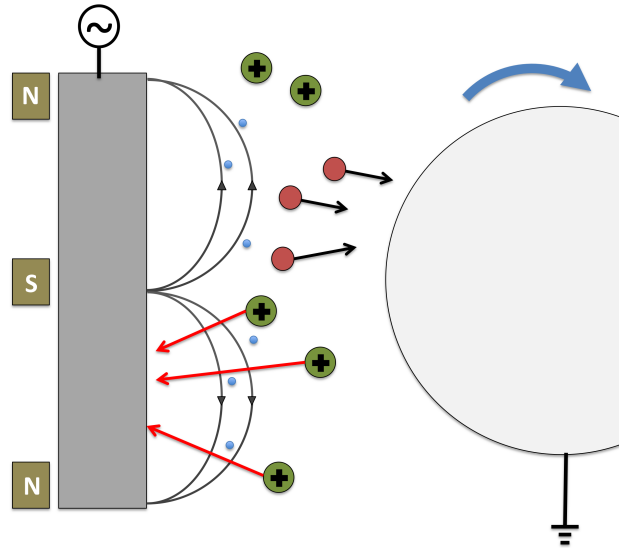


Figure 8. Schematic showing RF magnetron sputtering of metal. Red circles represent metal atoms, green circles represent the positively charged argon ions and the small blue dots are secondary electrons. Adaptation based on a figure from [38].

A characteristic “race track” of liberated material marks the target after prolonged use. The wearing away of only part of the cathode reduces its lifetime [39].

In the case of reactive sputtering, a reactive gas, e.g. oxygen and/or nitrogen, is added to the plasma, which reacts with the emitted material, e.g. a metal, to produce an oxide or nitride. A problem with reactive sputtering from a metal target is that the reaction product, so desirable on the substrate, can also form on the target itself, which insulates it and causes charge build up and subsequent arcing, leading to damage of the deposited films [40]. This process exhibits hysteresis, with the reactive gas needing to be reduced far below the poisoning flow rate before the oxide is sputtered away [41]. Figure 9 shows how the hysteresis of reactive sputtering of AlO_x can be observed in the applied voltage.

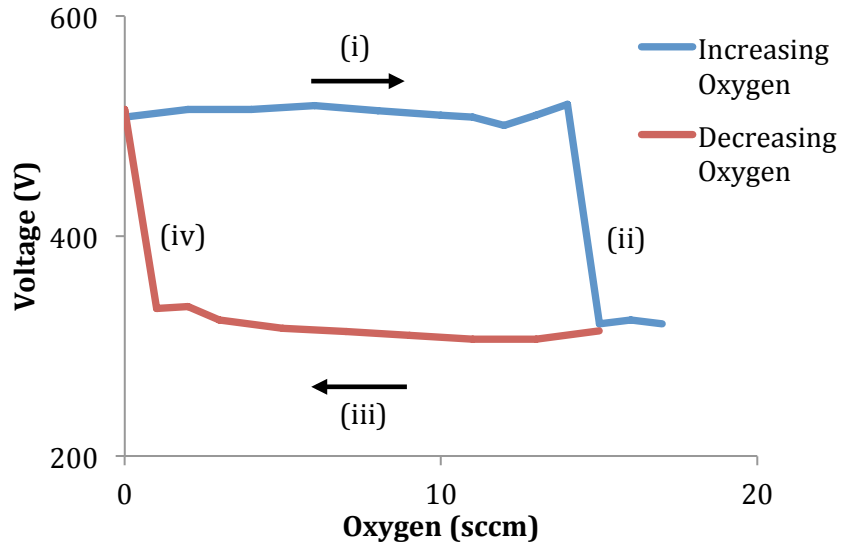


Figure 9. Hysteresis of RF Reactive Sputtering with oxygen as the reactive gas.

The power supply is in constant power mode. Any fluctuations in current are compensated automatically through a change of voltage at the cathodes. Consider Figure 9, stage (i). The reactive gas flow is slowly increased, with little visible effect on the voltage due to its reaction with sputtered metal [42], [43]. This continues to a critical value, (ii), where there is a “runaway” build up of reaction products at the cathode and the target poisons [42]. As the current of the system is the sum of process gas ions and secondary electrons [43], and the secondary electron coefficient of the AlO_x is greater than the Al, there is a drop in voltage to compensate for the sharp increase in current that occurs [37]. When the reactive gas is reduced (iii), the system does not recover until the flow rate is much lower (iv) due to the lower sputter yield of the AlO_x compared to the Al [43]. After (iv), the system returns to the original voltage, and continues to sputter in metal mode [42].

A useful model for understanding hysteresis and sputtering was outlined by Berg and Nyberg. Equation 1 describes the balance between the build up and sputtering away of insulating species [43].

$$\frac{J}{q} Y_c \theta_t = \alpha 2F(1 - \theta_t)$$

Equation 1

where J is the ion current density, q is the elemental charge, Y_c is the sputter yield of the compound, θ is the area fraction of the target covered in compound, α is the sticking coefficient and F is the number of molecules of reactive gas impinging on the target/unit area/unit time. The right hand side of Equation 1 describes the rate at which the reactive gas forms a layer of compound on the target metal, with the factor of 2 included to account for the diatomic nature of the gas [43]. The left hand side describes the rate at which the compound (oxide or nitride) is sputtered away [43]. The two sides are in dynamic equilibrium for all reactive gas flow rates, except for when the target poisons and there is a “runaway” effect of compound formation [41], [43], [44]. The difference in the ratio of sputter yields for the metal and the compound was shown by Berg to increase the width of the hysteresis region [43].

There is further discussion of sputtering yield, sticking coefficient and how these values change with reactive gas type in Section 5.1.1.

Target wear affects hysteresis. As the target becomes more worn, the operating voltage decreases and the target poisons at a lower reactive gas flow rate [45].

Choi pointed to the difficulties in changing stoichiometry, large area coverage and the expense of the vacuum systems as drawbacks for sputtering systems in general [13]. Another shortcoming, Kelly points out, is that “RF sputtering can produce high-quality films, but deposition rates are very low (typically in the μ/hr range)”[40].

2.1.7 Direct Current Sputtering

Direct current sputtering is generally used to produce conducting films, but can be used in a reactive sputtering set-up to produce oxides [46]. The difficulty of reactive sputtering with a DC power supply arises from the fact that when an insulating oxide forms at the metal target, positive charge builds up and disrupts the sputtering process [39] and arcs occur [47]. RF reactive sputtering overcomes this issue due to the repeatedly reversing polarity between the

cathode and anode, which dissipates the charge build up. This also allows RF to sputter not just from metal but from insulating targets [48].

Kelly notes that producing dense, defect free oxides with DC reactive sputtering is difficult due to multiple arcing events and low deposition rates [40].

Pulsed Magnetron Sputtering is a DC-method which overcomes the charge build up that causes arcing by interrupting the power supply at radio-frequency intervals, allowing the plasma to dissipate the charge [40].

Suttle, in a study of AlO_x on PEN, found that DC sputtered films (thickness 145 nm) exhibited BIF of 1.01 over the uncoated substrate (measured at 30°C), whereas the RF sputtered coating (of thickness 116 nm, 20% thinner than the DC film) showed an improvement of a factor of 28.3 over PEN [38]. The activation energy of permeation (explained in Section 2.3.2 on page 28) of the DC film was shown to be identical to that of the substrate whereas the RF sputtered film showed an increase of 26 kJ/mol.

2.2 Barrier Characterisation

There are two main ways of determining the gas transmission for barrier oxides: **MOCON permeation testing** (Section 2.2.1) and **the calcium test** (Section 2.2.2).

2.2.1 Steady-State Permeation

The basic principle of the MOCON permeation measurement of water vapour is that the oxide/polymer forms a barrier between two chambers, one of saturated water vapour and the other of a dry carrier gas (nitrogen), with the permeant gas passing from the former to the latter and being detected [11]. A schematic is shown in Figure 10.

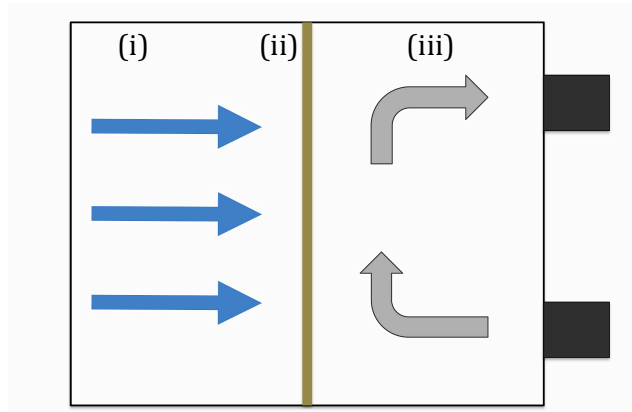


Figure 10. Schematic of a steady state water permeation testing device, adapted from [6]. The device is partitioned into two halves with the (i) water vapour saturated cell separated by the (ii) barrier from the (iii) “dry” cell, with permeating water carried to the detector [6].

The sample is first conditioned until steady-state (i.e. constant) permeation is achieved (generally 24 - 48 hours) at a constant temperature [11]. The same is done for oxygen permeation but the test gas is oxygen and the carrier gas is N₂ with 4% Hydrogen [11]. The test area for the samples is 50 cm² [38] but smaller samples can be measured with a metal collar fitted.

Stevens highlighted a number of key sources of error for the MOCON Permatran. Leakage into the testing-side of the system from the ambient was shown to have a large effect on results with a leak of 1 ppm of moisture corresponding to 0.01 g/m²/day [49]. Uncertainty in the temperature was also reported to be problematic, with the received wisdom being that a 1°C change produces a 10% change in permeability [49].

This method and the widely used devices developed by MOCON to carry them out (Oxtran and Permatran) are reliable and reproducible but limited by a maximum sensitivity of around 5×10^{-3} g/m²/day (water vapour) and 5×10^{-3} cm³/m²/day (oxygen) [50] which does not measure down to the requisite permeation level outlined in Section 1.1.

Graff introduces the concept of “lag time” to permeation. His study points out that there is an initial, lower permeation rate, before permeation reaches dynamic equilibrium, and this initial lower rate is often quoted [3]. The conditioning period for simple films can ensure that

the system is in equilibrium before the WVTR is recorded, but the lag time for multilayer films can be of the order of months and years [3]. This will be discussed further in Chapter 6.

2.2.2 The Calcium Test and Qualitative Permeation

The calcium test is based on the sensitivity of calcium to water vapour [6] and was initially proposed by Nisato (as cited by Erlat in [6]). The calcium test uses the difference between calcium (opaque, conducting) and calcium hydroxide (transparent, insulating) to determine the amount of water passing through a barrier [51]. Cros' study showed that oxygen does not react with calcium at room temperature, with all calcium degradation being due to a reaction with water vapour [52].

There are two main approaches to the calcium test. Schematics of these can be seen in Figure 11.

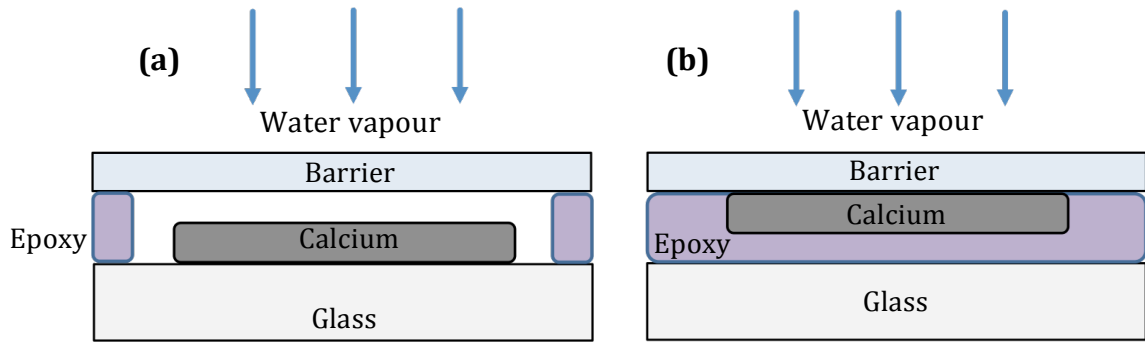


Figure 11. Schematic of the (a) “total rate” calcium test and the (b) “defect imaging” calcium test, adapted from [6].

The “total rate” test [6], [53], is shown in Figure 11 (a). In this set up, the calcium is evaporated onto glass (assumed impermeable), with the barrier sealed on top with epoxy around the edges [53]. Due to the gap, water permeating inward through the barrier will degrade the calcium uniformly, with the transition to transparent hydroxide recorded by interposing the sample between a light source and photodiode detector [6]. From this the WVTR is calculated as being a function of the change in optical density of the calcium [53].

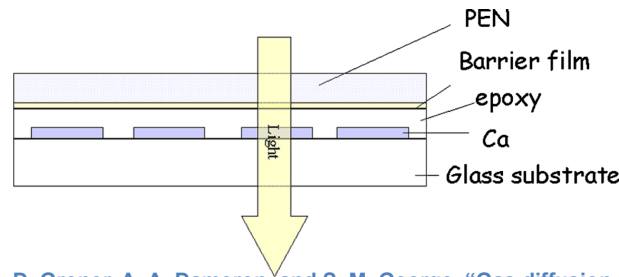
Nisato reported the sensitivity possible with this technique as $3 \times 10^{-7} \text{ g/m}^2/\text{day}$ (as cited by Lewis [50]), but Erlat pointed to the issues surrounding reproducibility of results with this method, chiefly due to the differing methods of encapsulation and preparation [6].

One issue with the calcium test is that the atmosphere in the testing region (the calcium spots) is not actively controlled (as it is for the MOCON test) with Graff commenting that due to moisture accumulation within the encapsulated set up the calcium test cannot be considered to provide equilibrium permeation [3].

A variation on the total rate test is based on measuring the changing resistivity of the calcium, rather than the optical transmission. Paetzold’s technique includes silver contacts deposited on the calcium, which are used to measure the change in resistance with time [54]. As the thickness of calcium metal is inversely proportional to the resistance, the permeation rate is calculated [54]. The best arrangement for this resistivity-dependent technique is Figure 11 (a) in order to ensure homogeneous degradation of the calcium [51].

The “defect imaging” test [6], [55] uses the arrangement in Figure 11 (b). It allows local information about permeation that is not possible in the total rate test [6], as the calcium degrades in the local area around defects in the barrier layer, hence showing local areas of permeation. This is the method used later in this report and it gives qualitative information on the distribution of water permeation, which it is not possible to ascertain from a WVTR value.

There is another calcium test architecture that is of some use. It is illustrated in Figure 12 and used by Carcia [56].



Reprinted from P. F. Carcia, R. S. McLean, M. D. Groner, A. A. Dameron, and S. M. George, “Gas diffusion ultrabarriers on polymer substrates using Al₂O₃ atomic layer deposition and SiN plasma-enhanced chemical vapor deposition Gas diffusion ultrabarriers on polymer substrates using Al₂O₃ atomic layer deposition and SiN plasma-enhanced chemi,” J. Appl. Phys., vol. 106, no. 2009, p. 23533, 2009. with the permission of AIP Publishing. Figure 12. Calcium test set up of Carcia – from [56].

If it is assumed that there is no permeation through the glass, there are two routes of ingress: through the side of the seal, and through the barrier film. Ingress through the side-seal (between the epoxy and the glass) is an issue that has been discussed by others, and it forms the measurable limit of the test [4], [55], this is discussed further in Section 3.3.3. In this setup however (Figure 12), any permeation occurring through the barrier also has to pass through a layer of epoxy. As permeation through multiple layers follows a series resistance relation [57] (discussed further in Section 2.3.1), thus considering Equation 2:

$$\frac{1}{WVTR_T} = \frac{1}{WVTR_E} + \frac{1}{WVTR_B}$$

Equation 2 from [57]

where $WVTR_T$ is the overall WVTR, $WVTR_E$ is the WVTR of the epoxy, and $WVTR_B$ is the WVTR of the barrier. Any measured WVTR results are the sum of barrier performance of the barrier and the epoxy, but the overall $WVTR_{Total} \approx WVTR_b$ only when $WVTR_{barrier} \ll WVTR_{epoxy}$.

The issue of water corrosion of AlO_x is described in many cases [8], [56], [58], and is clearly an issue to consider, although all the aforementioned papers dealt with ALD-formed AlO_x , and in Carcia [59] it is described how permeation takes place through OH defect clusters present throughout the ALD film. It is not known how greatly this affects sputtered AlO_x barriers. Choi mentions the degradation of AlO_x sputtered films, but does not go into any further detail [20]. Ghosh deals with the issue of corrosion by coating his ALD with parylene so bulk water cannot form on it [8]. Coating with an organic spacer layer would deal with many of these issues, but the effect of polymer deposition on the barrier would need to be investigated.

Many papers use the calcium test as even the most advanced model of MOCON instrument, the Aquatran, can only measure down to $5 \times 10^{-4} \text{ g/m}^2/\text{day}$, although Bertrand points out that there is evidence to suggest that the relationship between conductance and oxidation may not be linear [58]. Our MOCON “Permatran” device can measure to $5 \times 10^{-3} \text{ g/m}^2/\text{day}$.

2.2.3 Topography

Barrier morphology is characterized through a number of standard techniques, with examples in this review of atomic force microscopy (AFM) [11], [12], [14], [27], [46], [60], [61], transmission electron microscopy (TEM) [14], [15], [60], scanning electron microscopy (SEM) [46], [60] and white light interferometry [38], [46], which are used to characterize barrier quality upon comparison with gas transmission rates.

2.2.4 Elemental Composition and Chemical Bonding

X-ray photoelectron spectroscopy (XPS) is a valuable method used to determine the elemental composition and bonding environment within barrier coatings whereby a sample is irradiated with X-ray radiation of a fixed energy causing photoemission of electrons [62]. The kinetic energy of the photoelectrons is measured, and by using Equation 3 the corresponding binding energies can be calculated [63].

$$E_{kin} = \hbar\omega - \phi - E_{bind}$$

Equation 3 Using the kinetic energy of emitted electrons, binding energy can be calculated (from [63]).

where E_{kin} is the kinetic energy of the photoelectron, $\hbar\omega$ is the energy of the X-rays, ϕ is the work function and E_{bind} is the binding energy. Peaks in the spectra correspond to ionization energy of core electrons and reveal the elemental species that make up the sample [62]. The short mean free path of electrons in solid materials limits XPS to probing the sample surface ($\sim 0.5\text{-}2\text{ nm}$) [63]. The technique is sensitive to the chemical state of elements present, with different peaks, for example, visible for a metal and its oxide [62].

Argon ion etching (or Ion Bombardment - IB) of surfaces allows the removal of adsorbed carbonaceous contaminants [64]. If IB etching is alternated with XPS, a depth profile can be built up, overcoming the surface-only nature of the technique and discovering the bulk characteristics of the sample [65]. Care must be taken however as an argon signal can be observed in XPS spectra following an IB etch due to argon ion implantation [66]. The IB etch can also induce chemical changes in films: one study found that as the argon IB energy increased, etched polyimide exhibited a decreasing amount of oxygen and nitrogen (compared to theoretical values) [67].

Bertoti also observed the preferential removal of nitrogen under argon ion bombardment of TiN [68]. For materials like AlO_x and AlO_xN_y , the argon implantation can be ignored, but these chemical changes as a result of the etching will add to the uncertainty in XPS measurements. It is assumed, particularly for the AlO_xN_y films (Chapter 5), that there will be a level of underrepresentation in the nitrogen content.

Fourier Transform Infrared Spectroscopy (FTIR) is a technique that produces an absorbance spectrum for materials using infrared radiation. FT-IR can be used to identify molecules and even functional groups based on the vibrational and rotational modes excited by the incident radiation [69].

2.2.5 Mechanical Testing

The ability of the barriers to be mechanically flexed, during the fabrication process or in device implementation, without failing as barriers, and the way the oxides react under stress are important to understand [70]. When optimising barrier structures and composition, the mechanical properties need to be studied, as a high quality barrier that is extremely brittle will be of limited applicability. Studies by Yanaka found that the onset of cracks under uniaxial strain took place at a larger initial strain for thinner films, but that these films show a larger crack density under higher strains, and that these are related to the interfacial shear stress of the polymer acting on the coating [70].

Other key mechanical techniques which study the bending of barrier systems (the collapsing radius test and the x, y, θ test) are introduced by Lewis [46].

Another important form of mechanical testing is the Nano-scratch test. An initial topographical scan sets the baseline, then a stylus is scratched across the sample surface with a user-defined load profile. This is followed by a post-scratch topographical scan to assess the nature of the damage [71]. Nano-scratch testing can be used to find the load at which a film fails, as well as the strength of its adhesion to the substrate [72].

2.3 Introduction to Permeation

The rate of gas permeation through inorganic barrier films is controlled by transport through macro-defects, nano-defects and, in the case of water vapour, chemical interaction with the oxide [60].

2.3.1 Permeability

Water vapour transmission rate (WVTR) and oxygen transmission rate (OTR) describe the amount of permeant passing through the barrier per unit area per unit time. It is the absolute amount passing through a film. A useful concept [11], when comparing different types of barriers at different thicknesses is permeability

$$P = \frac{\Pi \times t}{\Delta p}$$

Equation 4 from [11].

where P is permeability, Π is gas transmission rate, Δp is the pressure difference across the film and t is thickness.

For an ideal system of a defect free coating on a polymer substrate, Ideal Laminate Theory can be used to differentiate the component contributions to the overall permeation:

$$P_{ILT} = \left(\frac{\phi_p}{P_p} + \frac{\phi_g}{P_g} \right)^{-1}$$

Equation 5 from [46]

Such that $\phi_p = d_p/d$, $\phi_g = d_g/d$, and $d = d_p + d_g$, $\phi_g + \phi_p = 1$, where ϕ_p and ϕ_g are the volume fractions of the polymer and the glass respectively, d_p and d_g are the thickness of the polymer and glass layers respectively, and P_p and P_g are the permeability of the polymer and glass respectively.

Chatham [73] observed that the transport of gas through materials could take place through two mechanisms, (1) solubility-diffusion flow, where the permeant is absorbed onto the surface, becomes soluble and diffuses through the material, or (2) flow through macro or nano-defects, but that for high barriers mechanism (2) may make a much greater contribution.

The permeation of water is more complicated due to the chemical interaction of the water with the oxide [11], this will be discussed further in Section 2.6.3.

Barrier improvement factor (BIF) is defined as the WVTR of the polymer substrate alone divided by the WVTR of the barrier system (coating + polymer) [17], [73].

A **critical thickness** has been observed for many thin-film coatings. This is the empirically observed phenomena of permeation decreasing with coating thickness until reaching a

minimum value, continuing to plateau, and then increasing again [6], [74]–[76]. It is an important concept as permeability is related to barrier thickness, so past the critical thickness, permeability sharply increases [76].

A seminal investigation by Felts of PE-CVD SiO_x on PET, found that OTR decreased with increasing thickness but then reached a point of inflection at ~ 100 nm and worsened again [74]. Felts suggested this behaviour could be due to “internal stresses of the SiO_x coating and/or thermal degradation of the PET and SiO_x ” [74].

Suttle’s report of sputtered AlO_x on PEN [38], did not observe a critical thickness, but it was posited that this was due to the layer-after-layer type deposition produced by fixed substrates undergoing multiple passes of the sputter cathode.

Howells et al. also did not observe a critical thickness for WVTR in his study of PE-CVD SiO_x on PEN and PET, but produced the required thicknesses in multiple passes of the deposition area (200 nm - 2 passes, 400 nm – 4 passes, 1000 nm – 6 passes)[77]. For that study the WVTR only improved with increasing thickness.

Erlat’s study of sputtered AlO_xN_y on PET observes a critical thickness for water permeation at 60 nm, but the experimental set up deposited the coating in a single layer [12], as opposed to the multiple-pass architecture of Suttle and Howells.

Sobrinho [15] used PECVD to produce SiO_x and SiN coatings on PET, with the SiO_x exhibiting a critical thickness for OTR at 15 nm and WVTR at 25 nm, but for SiN the optimal thickness was found at 8 nm for both OTR and WVTR. From Table 2 it can be seen that the oxygen permeability of SiN shows a BIF of 5, allowing a 40% reduction in OTR at 53% of the SiO_x thickness. It can be seen in Table 2 that there is an increase of water vapour permeability from $0.7 \mu\text{m g/m}^2/\text{day}$ for SiO_x , to $0.8 \mu\text{m g/m}^2/\text{day}$ [12], [15], but this is much less significant than the change in OTR. Sobrinho also noted that the performance of SiN barriers is less sensitive than SiO_x to PECVD deposition conditions.

Table 2. Reproduced from [12] with data compiled from references in the table, all oxides are at their critical thicknesses.

Material	OTR (cm³/m²/day.at m)	P(O₂) (μm cm³/m²/day.atm)	WVTR (g/m² /day)	P(H₂O) (μm g/m²/day)
AlO_xN_y	1.41	0.070	0.11	0.006
Al [78]	0.02	0.001	0.05	0.002
AlO_x [60]	1.69	0.050	0.42	0.014
SiO_x [15]	1.00	0.020	0.28	0.007
SiN [15]	0.60	0.004	1.06	0.008

Figure 13 shows the water vapour permeation rate for AlO_xN_y coatings, which drops sharply with increasing coating thickness until some critical minimum value is reached, demonstrating an optimum barrier thickness [16].

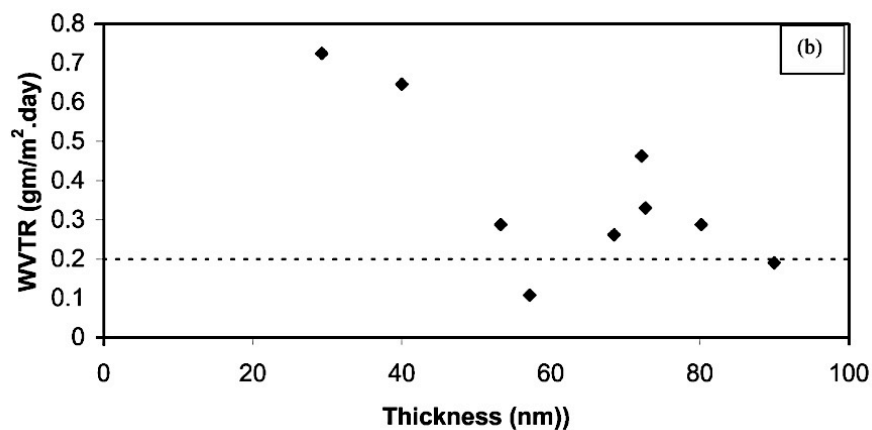


Figure 13. Reproduced from [12] WVTR with thickness for AlO_xN_y, showing a minimum at 60 nm.

An extremely useful comparison of the main thin film barriers, at their critical thicknesses, is presented in Table 2. For AlO_xN_y this is around 60 nm which is thicker than the critical thickness calculated for AlO_x (30-33 nm) [12]. Erlat notes, that a larger critical thickness

could be a drawback in industrial applications as nearly twice the amount of material (in the example) is to be used for an optimum barrier, but the advantage is that when the higher WVTR permeability (a measure of the barrier quality) is considered, the AlO_xN_y is a better barrier than all the other reported materials, except the Al barrier [12]. As Al is opaque, this is strong evidence supporting the use of AlO_xN_y as a barrier for an optoelectronics device.

It is clear that AlO_xN_y is not as good an oxygen barrier, and the SiN of [15] has a barrier an order of magnitude better at a thickness of only 8 nm. AlO_xN_y functions as a competitive O_2 barrier, with a marginally lower permeation rate than AlO_x , but this arises mainly from its greater thickness [12].

2.3.2 Activated Rate Theory

The activation energy of permeation is the energy required for a permeant molecule to pass through the barrier material [79]. This might be thought of in terms of local deformation of the structure [79], or by the making and breaking of chemical interactions between the permeant and the barrier matrix [27][61][80]. Activation energy is one of the key metrics in the study of gas permeation through oxide barriers, as the general tendency is that an increase in activation energy is associated with a lower permeation rate [27] and it gives an indication of changes in the mechanism of permeation.

Transport of ideal gases through oxides and polymers is temperature dependent and is described by the Arrhenius equation [46]

$$P = P_0 e^{-\frac{\Delta E}{RT}}$$

Equation 6 from [46].

where ΔE is the activation energy for permeation, R is the gas constant, T is the absolute temperature, P is the permeability and P_0 is the pre-exponential factor. Transmission rate can be used in place of P to find the activation energy [11].

2.3.3 Defect Definition

The definition of what constitutes a macro or nano-defect differs between authors, which confuses a qualitative description. Roberts [27] defined a macro-defect as having a size >1 nm and a nano-defect 0.3-1 nm, justified by the argument that the macro-defect is approximately 3-4 times larger than the permeant radius, enabling un-hindered transport, whereas the nano-defect is of comparable dimensions with the permeant, so restricted passage occurs. Roberts noted, however, that barrier coating defects can be smaller or larger than 1 nm and pointed to a study by Erlat [14] which used TEM to identify intrinsic barrier defects of average size 4-6 nm in poor barriers, but in the best barriers they were smaller than 1 nm, the resolution limit of the technique. Roberts' study also considered the possibility of diffusion through amorphous lattice interstices of order 0.2-0.3 nm [27]. Erlat defined the defects by their source, that the larger macro-defects are products of dust, inclusions in the substrate, or handling damage, and the nano-defects are intrinsic to the barrier and controlled by nucleation and growth [12]. Anti-block particles are of the order of 1 μm and are believed to cause the majority of macro-defects in the barriers deposited on them [46]. Other sources of macro-defects include those induced by stress relaxation or post-deposition handling [11].

The definition used in *this* report is that a nano-defect is one small enough to cause an increase in activation energy of permeation from that measured for the bare substrate, whereas a macro-defect does not. The definition of Roberts, of the permeant size defining the nano-defect, will form the lower limit for this report's definition of the nano-defect size. But there is also the possibility of interaction of water with the barrier [14], [61] but it is not known at what (upper) defect-size this ceases to influence activation. It is not possible to separate the chemical and physical contributions from the activation energy, so they will be taken together.

2.4 Macro-Defects

Macro-defects are caused by the substrate (as described in Section 1.3.2 on page 3) and by the deposition conditions, for example micro-arcing in sputtering [61], and allow unhindered gas transport through the barrier [27]. This sub-section will deal with the investigation, imaging and removal of these defects.

2.4.1 Identifying Macro-defects

2.4.1.1 Reactive Ion Etching

Reactive Ion Etching (RIE) is a useful tool for visualising macro-defects. Henry described exposing a barrier/polymer system to a plasma of atomic oxygen (AO), which destroys the underlying polymer, while leaving the oxide unaffected, this lateral “undercutting” of the defects increases their radius (in the polymer), allowing easier identification with SEM [46] and even optical microscopy [15]. Increased exposure results in deeper and wider etches [15]. The initial oxide defect size is calculated by a simple relation from the size of the undercutting after different amounts of exposure to AO [16]. This technique helps in the determination of micro-defect density and in determining whether a thin (~ 8 nm) layer is defect-rich or island-like [15]. Figure 14 shows an RIE pinhole.

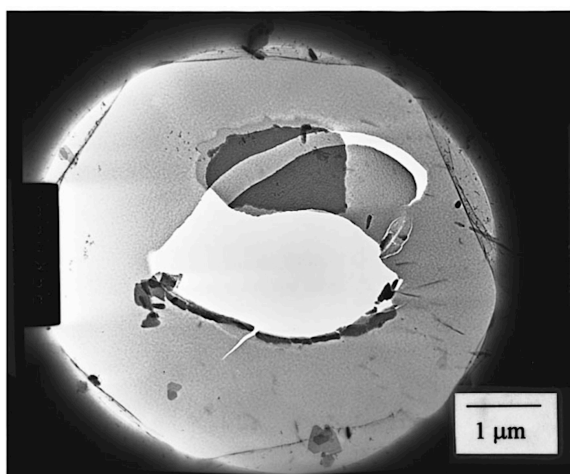


Figure 14. Reproduced from [15], a TEM image of a pinhole in SiO_x on PET after RIE, the smaller hole in the oxide visible in the centre, with the wider hole of undercut polymer behind.

Reprinted with permission from a. S. da Silva Sobrinho, “Transparent barrier coatings on polyethylene terephthalate by single- and dual-frequency plasma-enhanced chemical vapor deposition,” *J. Vac. Sci. Technol. A Vacuum, Surfaces, Film.*, vol. 16, no. 1998, p. 3190, 1998.. Copyright 1998, American Vacuum Society

The strength of this technique (apart from the ability to use optical microscopy for identification) over white-light interferometry is that the undercutting confirms that a hole propagates through the whole thickness of the barrier into the polymer, which would allow unhindered flow of gas. Holes identified with interferometry could be “pits” i.e. terminated holes or gouges which reduce the thickness, but not affecting permeation in as significant a way as a true pinhole.

Although used for pinholes of the order of a micron, Sobrinho describes how the technique can be applied for defects down to 50 nm in diameter [16].

2.4.1.2 SEM and AFM

In a study of DC reactive sputtering of ITO and AlO_x on PET, SEM found an absence of defects $>1\text{ }\mu\text{m}$ in the ITO barriers, but a density of 10^3 defects/ mm^2 in the AlO_x [46]. The oxygen permeability of the AlO_x is independent of oxide thickness and is in the range $0.023\text{--}0.036\text{ }\mu\text{m}/\text{cm}^3/\text{day}$, whereas the ITO oxygen permeability decreases with oxide thickness, with the best barrier of $0.007\text{ }\mu\text{m}/\text{cm}^3/\text{day}$ at 5 nm [46]. Henry argues that the better OTR displayed by the ITO is due to the absence of the high density of macro-defects present in the AlO_x [46].

Erlat’s study of 72 nm sputtered AlO_xN_y used large area AFM (0.1 mm^2) analysis and found a defect density of $600/\text{mm}^2$ for macro-defects of size $>500\text{ nm}$, which amounted to 0.05% of the total area [12]. Large ($1\text{--}2\text{ }\mu\text{m}$ wide, 30 nm deep) substrate features were also identified and found to have propagated through to the coating [12].

2.4.2 Reduction of Macro-defects

In order to reduce permeation it is necessary to minimise the density of these macro-defects. This can be achieved by careful process control e.g. the reduction of arcing or by choice of substrate. Additional approaches are considered in the following sub-sections.

2.4.2.1 The Use of Nano-structures

A patent by Ramadas describes an interesting approach to barrier technology. A 50 nm metal-oxide is RF sputtered onto a polycarbonate substrate, and it is assumed that the barrier contains numerous defects (see Figure 15 a) [81].

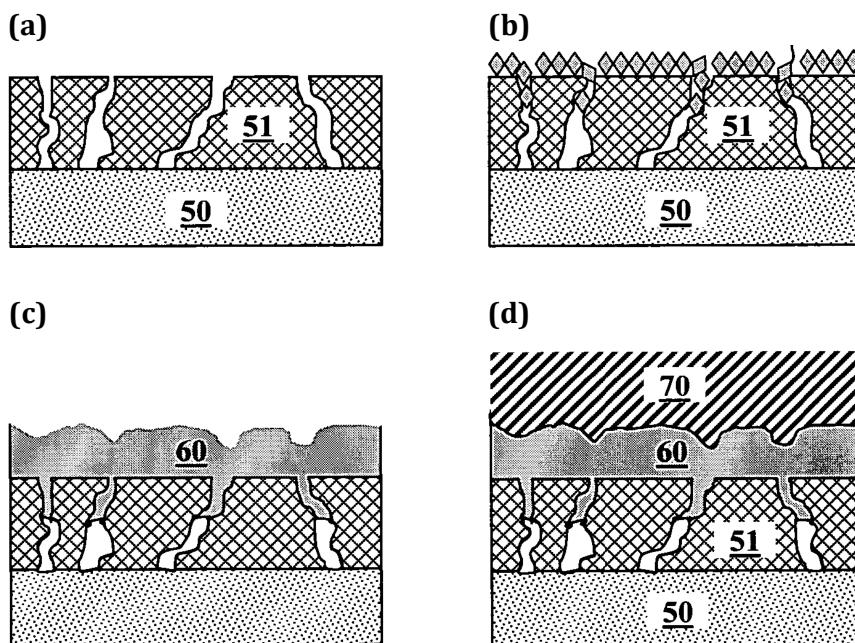


Figure 15. The four main stages of the barrier fabrication in the Ramadas patent: From [81].

ZnO seeds (20-50 nm in diameter) are spin-coated on the barrier (Figure 15 (b)), which cover the surface and fill defects (to block O_2 and H_2O permeation), a solvent- thermal approach is used to grow these into ZnO nanorods, forming the nanostructured layer in Figure 15 (c) [81]. Finally a UV-cured smoothing layer is deposited which has carbon nano-tubes (CNTs) dispersed within (as a desiccant, due to capillary action) as well as TiO_2 nanoparticles (to physically block permeants), all whilst smoothing the nanostructured layer below [81]. Ramadas notes, that the addition of these nanoparticles to the smoothing layer causes some diffusion of incident light, and that this would be useful for OPV (by increasing the path length of the light and aiding absorption) [81].

The addition of desiccant to the smoothing layer is a novel approach to decreasing barrier permeation and increasing the lag time. However the issue of light diffusion, although indeed useful for OPV, would be detrimental to OLED applications - lowering display resolution.

Another drawback to this technique is the solvent-thermal step, which complicates its adaptation to mass-production. Also, the 20-30 nm ZnO seeds would likely have little success with defects ~ 1 nm, as well as those many times larger (~ 2 μm).

2.4.2.2 *Smoothing Layer*

Affinito [28], [82] proposed a flash-evaporated acrylic smoothing layer added onto substrates in order to decouple substrate defects and features from the subsequently deposited oxides. Figure 16 shows comparisons of the topography of smoothed and unsmoothed substrate and oxide.

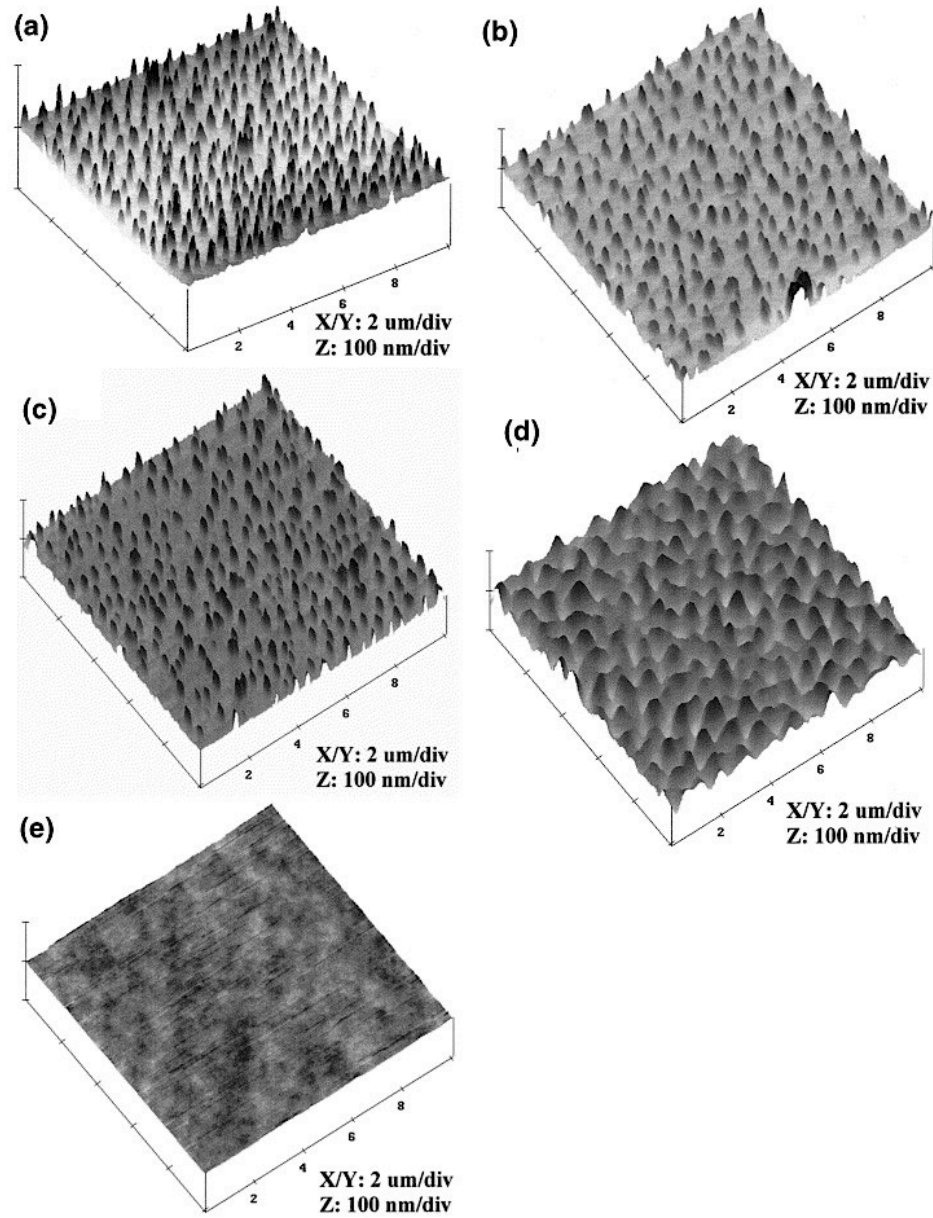


Figure 16. Reproduced from [28], AFM images of a) uncoated PET substrate, b) e-beam evaporated AlO_x (20 nm) on PET, c) reactively sputtered AlO_x (20 nm) on PET, d) reactively sputtered AlO_x (20 nm) on e-beam cured acrylate on PET, e) reactively sputtered AlO_x (20 nm) on UV cured acrylate on PET.

The native substrate, Figure 16 a) is shown to be very rough, and deposition of AlO_x , either by evaporation b) or by sputtering c) is shown to maintain the substrate roughness [28]. It was explained that methods that deposit films atomistically tend to reproduce the surface roughness and features as well as introducing other sources of disorder from the formation of grain boundaries [82]. Acrylate evaporation was shown to be different, as the monomer condenses onto the film as a *liquid*, with Affinito using the analogy of the rocky bottom of a

pond filling with water to leave a smooth, unbroken surface. The irradiation of the liquid polymer with either UV or e-beam then activates cross-linking to form the solid polymer [82]. As an aside, the “curing” of this smoothing layer is an important factor, with Affinito showing that partial curing of the acrylate, identifiable with Fourier Transform Infrared Spectroscopy FTIR, produces not fully smoothed surfaces with inferior barrier properties [28].

In Figure 16 d) sputtered AlO_x on e-beam cured polymer is shown, which has a large, altered surface roughness, but AlO_x deposited on the UV cured smoothing layer in Figure 16 e) is shown to be much smoother [28].

Figure 17 shows a comparison of the permeation rates for different smoothing/oxide combinations.

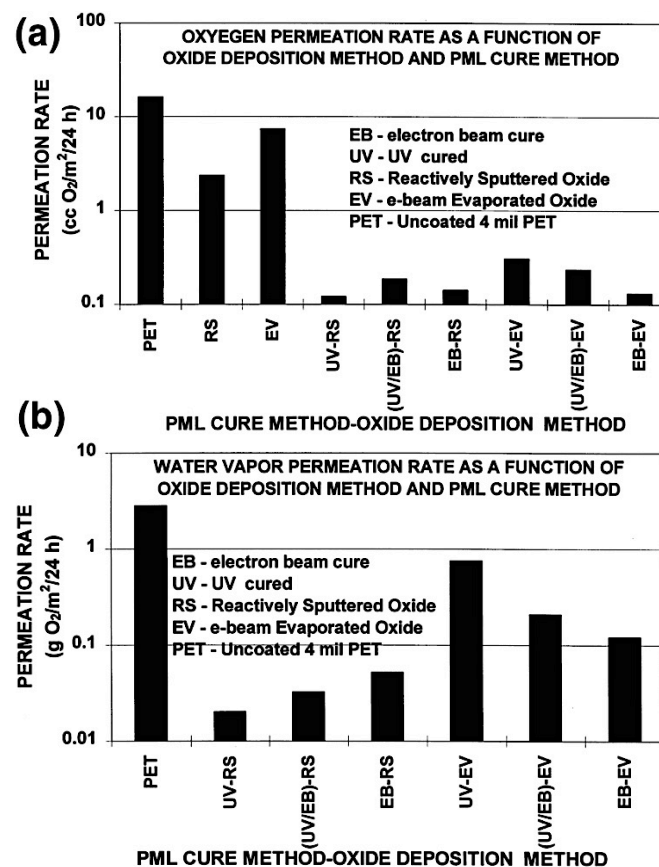


Figure 17. Comparing oxygen (a) and water (b) permeation rates for barriers produced with different smoothing layer cure methods. From [28].

The study showed that the barrier with the lowest WVTR (~ 0.04 g/m²/day) and OTR (0.2 cc/m²/day) was sputtered AlO_x on UV cured acrylate, with the study showing on the whole

that the inclusion of a smoothing layer improved the oxygen permeation rate of an oxide by an order of magnitude, this on top of the order-of-magnitude-improvement of the oxide over the bare substrate [28]. A WVTR improvement of 2 orders of magnitude is observed for sputtered oxide/smoothing layer structure over the native polymer. A structure of *only* PET/Smoothing layer was described to have a barrier improvement of only a few percent, showing that the decrease in permeation is from the oxide.

2.4.2.3 Atomic Layer Deposition

A multi-layered study by Lee [83] compared coverage of micron sized defects by different deposition techniques. Figure 18 from the paper shows the 45° tilted SEM of the dyad system, with (a) showing co-sputtered $\text{Al}_2\text{O}_3/\text{ZrO}_2$ followed by ALD SiO_2 , and (b) showing the reverse order.

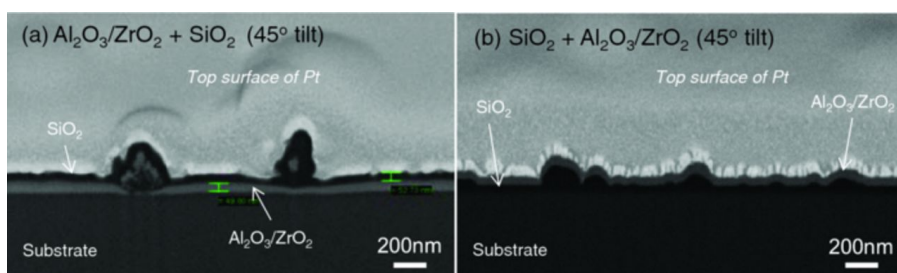


Figure 18. SEM of bi-layer (a) co-sputtered $\text{Al}_2\text{O}_3/\text{ZrO}_2$ - ALD SiO_2 (b) ALD SiO_2 - co-sputtered $\text{Al}_2\text{O}_3/\text{ZrO}_2$ from [84].

Lee observed that the sputtered layer did not coat silica particles scattered on the substrate, but the ALD deposited layer did. With identical amounts of material deposited, the order was shown to be pivotal, with (b) seeing an improvement in WVTR of a factor of over 3 [84]. Lee points to the shadowing effect for the sputtered layers, pointing to these regions around the particles as being possible permeation routes, being closed out in Figure 18 (b) [84]. Covering of surface features is shown again to be of great importance to barrier technology.

Unfortunately, Lee's study, like others [85] [86] report WVTR values using steady-state permeation devices (i.e. MOCON Permatran) but do not report activation energy. In the case

of Figure 18 it would be interesting to know if there was a significant change in activation energy, as would be expected with the closing of macro defects.

2.4.3 “Macro-Pores”

In the reactive-sputtered AlO_xN_y barrier coating produced by Erlat in 2004, dark features were visible, (circled in Figure 20), which were suggested to be nano-pathways leading from the oxide surface to the substrate and but that form with smaller radii for denser coatings [61]. Similar features were observed by Henry as “sub-micron pores” of 35 nm wide and 3 nm deep in AlO_x [60]. The DC-sputtered ITO films of Henry displayed “macro-pores” posited to extend into the layer [46]. Earlier in 2001, Erlat identified “micro-channels” (see Figure 19 on page 38) in his RF-sputtered AlO_xN_y films, which it was suggested also went deep into the oxide [12].

Non-standard nomenclature aside, the importance of these will be related to the thickness of the barrier, and as the agglomerate size (see Section 2.5.1) approaches the barrier thickness their significance will increase. On consideration of Figure 19, the “micro-channel” is seen to taper to a point tens of nm wide, but only 5 nm deep in an oxide 60 nm thick. It is not possible with AFM (reported as the tips having a radius of 10 nm), to confirm whether or not this feature propagates through the full depth of the oxide, directly or circuitously or at all. It is necessary to look at the activation energy, as discussed in Section 2.6.

2.5 Nano-defects

Once the macro-defects have been eliminated from the coating, to the extent that they no longer dominate the permeation, the contribution from the nano-defects can be investigated. This section specifically looks at the morphology and nucleation of the barrier oxide growth as a source of nano-defects, discussing a few different materials examples.

2.5.1 Barrier Morphology

Studies of barrier morphology are important as boundaries between coating features have been suggested a source of nano-defects (with some large enough to be considered macro-defects) [27].

In studies of SiO_x barriers, columnar growth was observed on PET [14], [27], [57], with growth proceeding upward and around isolated nucleation points [27]. This form of growth, with defects propagating linearly down to the polymer substrate, is considered to be an important route for permeation. The absence of macro-pores, yet the continued, albeit low, permeation, lead to the conclusion that permeation was controlled by nano-defects [14]. The study [14] also noted that as the OTR decreased, so did the WVTR, showing that barrier quality, i.e smaller nano-defects, decrease permeation for both ambient gases.

Erlat [12] reports the production of AlO_xN_y thin films on PET using reactive sputtering, with the oxide coating formed of 30-40 nm spherical grains, with surface roughness of 1.4 nm (PET substrate 1.3 nm), see Figure 19.

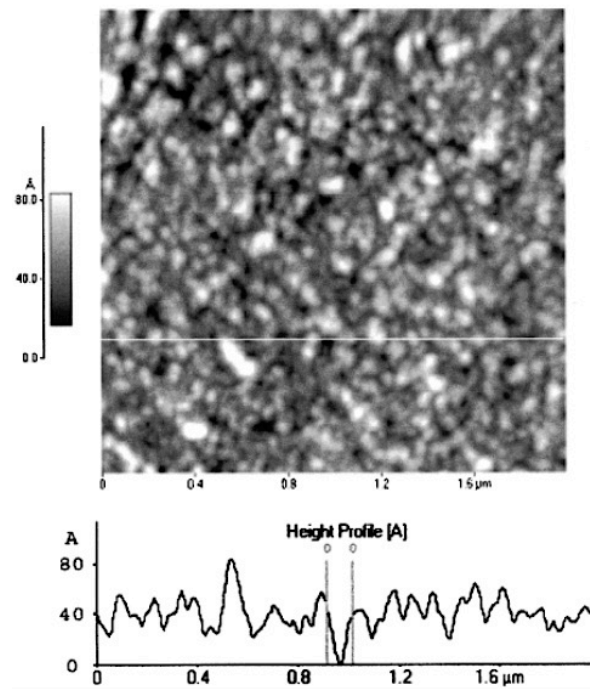


Figure 19. Reproduced from [12], AFM image of the AlO_xN_y surface with a line scan (white line) the profile reproduced beneath it.

Due to the close correlation of surface roughness between the oxide and the substrate, the uniform nucleation and growth of AlO_xN_y on the substrate was suggested [12].

A later paper by Erlat (also reactive sputtered AlO_xN_y on PET) investigated the variation of sputtering parameters and their effect on barrier morphology and permeance [61]. It was shown that as sputter chamber pressure decreased, WVTR of the barriers produced decreased, which was suggested to be as a result of the density of the films increasing. The OTR stayed largely the same with decreasing pressure. Through the AFM images (see Figure 20) Erlat stated that the lower pressure films had smaller grain size [61].

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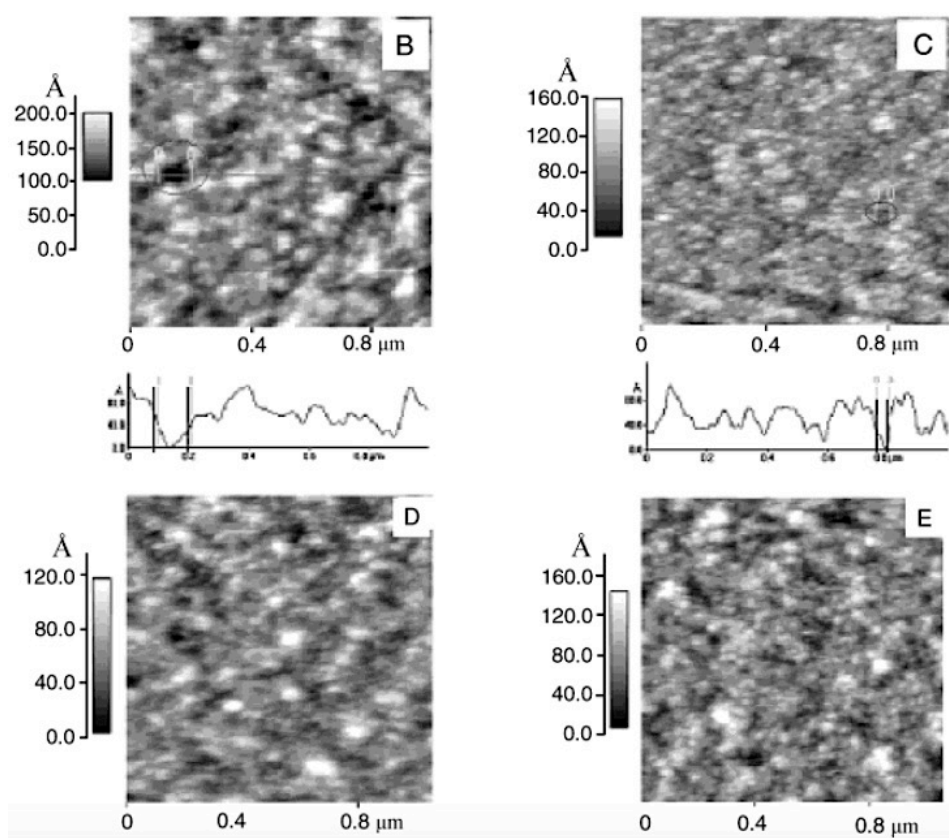


Figure 20. Reproduced from [61], AFM of sputtered AlO_xN_y films B (P: 850 W, $p=0.36$ Pa), C (P: 850W, 0.30 Pa), D (P =850 W, $p=0.28$ Pa), E (P 550 W, $p= 0.28$ Pa), with line profiles showing pores.

Two 30 nm thick AlO_xN_y barriers were produced, with one using sputter power of 850 W and the other of 550 W (D and E in Figure 20), and there was a concomitant increase in permeation from 0.6 to 1.6 $\text{g}/\text{m}^2/\text{day}$. The AFM images of these two films exhibit a finer scale morphology in the lower power coating [61].

Erlat suggested that the *density of the barrier had increased*, but it is not clear what is meant by this. It was not elaborated whether the suggested increased density was due to grains themselves being denser; this would imply that the reduction in permeation was due to a significant proportion of the flux having passed through the continuous oxide matrix. But in a model of gas permeation that is dominated by macro and nano-defects [11] this seems unlikely. Erlat pointed to Cuff's report, which showed that increased deposition power meant an increased ratio of Al to O in reactively sputtered AlO_x [87], which could be the cause of better barrier quality. Visual inspection of the morphology of Figure 20 C and D reveals that the decrease in pressure seems to cause an *increase* in grain size. These observations were contradicted by the paper, with Figure 20 C and D presented as the smallest grain barriers.

The morphology alone cannot explain why AlO_xN_y is a better water vapour barrier than AlO_x : further discussion of the transmission mechanisms (see Section 2.6 on page 40) and the interaction of water with the oxide (see Section 2.6.3 on page 45) will give the whole picture.

A thorough explanation of the relationship between deposition conditions and the morphology of sputtered barriers was supplied by Wasa and Hayakawa. It was explained that as sputtered material is deposited on the substrate, there is an initial period of surface mobility. The greater the surface mobility of the adsorbed species, the greater the size of the agglomerations formed [39]. Increased mobility was reported to be proportional to substrate temperature, kinetic energy of incident species (i.e. to sputter voltage), deposition rate and sticking coefficient [39]. Wasa also pointed out that "*the adhesion of the films is better for higher values of kinetic energy of the incident species*" [39].

2.6 Activated Rate Theory

Activated rate studies, introduced in Section 2.3.2, offer an insight into the nature of permeation.

2.6.1 Variation of Permeant Size

The thorough and elucidating study of Roberts [27] explored the activation energy of different permeants, He, Ne, Ar, O₂ and H₂O (see Table 3), through SiO_x on PET, and the inferences that can be made about the oxide structure. The main body of the work focused on the inert gases as it was assumed they had no chemical interaction with the oxide. Roberts explained how, in an ideal laminate system, a perfect macro-defect-free barrier would be expected to have the O₂ activation energy of silica glass (100 kJ/mol [88]), but an otherwise impermeable SiO_x barrier with macro-defects would exhibit an activation energy matching the polymer (42 kJ/mol [46]). It was stressed that the permeation energy of a barrier/substrate system was *not* the sum of the activation energies, but that as the oxide or macro-defect mechanism dominated, so the activation energy would reflect that process, exhibiting an activation close to that of the underlying substrate [27]. When permeation is dominated by nano-defects, the activation energy observed will tend to that of the transport through the nano-defects (greater than that of the polymer), and for regimes between the two, the activation energy will come somewhere between; as Roberts [27] says:

"In between these limiting cases (defect or oxide dominated) the barrier does not have a true activation energy, but over a small temperature range it will show an apparent activation energy between the two limits $\Delta E_p < \Delta E_b < \Delta E_g$ (if $\Delta E_p < \Delta E_g$)." [27]

It was shown how, in materials of known pore diameter (Zeolite, annealed silicon oxide), the activation energy increased with increasing permeant diameter (see Table 4), so for He through soda lime glass (pore size ~0.27 nm), $\Delta E = 46$ kJ/mol, but for He through microporous glass (~0.6 nm), it dropped drastically to 0.5 kJ/mol [27].

Table 3. Reproduced from ([89] cited in [27]), table of permeant gas diameters.

Gas	Diameter (nm)
He	0.2
Ne	0.24
Ar	0.32
O₂	0.32
H₂O	0.33

Table 4. Reproduced from [27] with data from [90], showing the affect of permeant radius on activation energy.

Annealed Silicon Oxide 0.27nm pores		
Gas	Permeability (10⁻¹⁸/cm s atm)	Activation Energy (kJ/mol)
He	1.7 × 10 ⁴	22
Ne	4.0 × 10 ¹	38
Ar	2.2 × 10 ⁰	105

Figure 21 shows conceptually how pore size/permeant diameter affects activation energy.

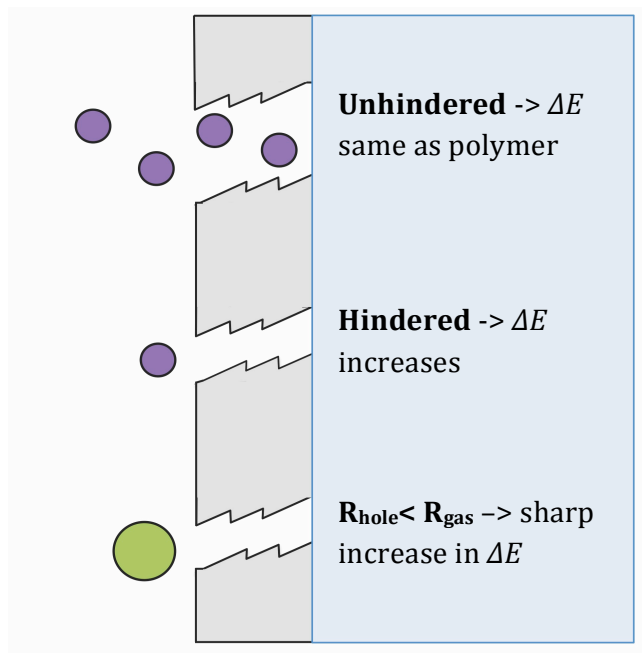


Figure 21. Conceptual understanding of activation energy, adapted from diagrams and concepts in [27] and [61].

2.6.2 Non-Ideal Permeation

Tropsha noted that single layers of SiO_x on PET, decreased the permeation on average by a factor of 161 over uncoated PET, but that the activation energy was identical to PET as the polymer provided the rate limiting barrier [57]. This means that the kinetics of the permeation was limited by the PET, with the energy required in order for permeation to occur defined by the polymer. The permeation decreased as gases had to make their way through tortuous paths of defects, which reduced the rate of transmission due to the reduced area through which the gas could pass, in effect reducing the flux of the permeant but not the mechanism with which it permeates [57]. Roberts showed how, when the defects were near the size of the permeants, the activation energy increased dramatically (see Table 4) as a larger amount of energy was required in order to force the argon (0.32 nm) through the pores (0.27 nm), the energy required was larger than that needed for permeation through the polymer, thus the pore diameter became the rate limiting factor for argon [27].

Tropsha found that even when two layers of SiO_x were deposited successively on the PET substrate, the activation energy remained identical, reinforcing the idea of a reduced flux (permeation) but an identical mechanism [57].

When the polymer was coated on *both* sides by SiO_x the activation energy increased from 29.7 kJ/mol (PET) to 84.1 kJ/mol, suggesting a different mechanism. The explanation given, related to that outlined in Section 2.6.1 (that activation energy is related to the dominant permeation mechanism) and described schematically in Figure 22.

Reproduced with permission from Y. G. Tropsha and N. G. Harvey, "Activated Rate Theory Treatment of Oxygen and Water Transport through Silicon Oxide I," J. Phys. Chem. B, vol. 101, no. 13, pp. 2259–2266, 1997. Copyright 1997 American Chemical Society.

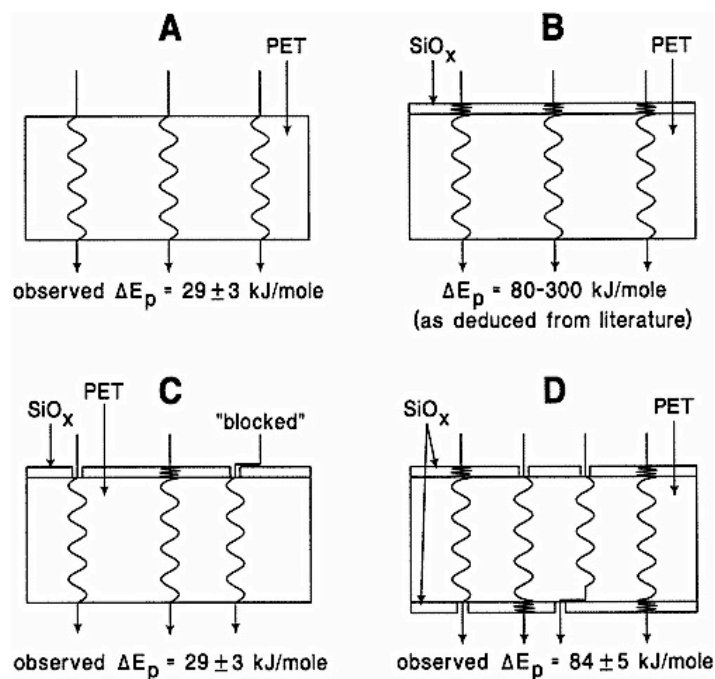


Figure 22. Reproduced from [57], showing permeation through A) uncoated PET, B) continuous SiO_x on PET, C) defect-containing SiO_x /PET, D) “sandwich” of SiO_x coatings on both sides of the PET

The limits of permeation, either through the defect free oxide (Figure 22 B) or the PET (Figure 22 A) with activation energy dictated by either mechanism were shown. In Figure 22 C, it was shown that although permeation can occur by both mechanisms, the dominant and thus rate-limiting process was through the macro-defects (with the associated activation energy of the polymer) [57]. In the case of the “sandwich” in Figure 22 D), there were 4 routes possible, with only one being solely through PET, the others through the oxide, due to the decoupled nature of the defects in the layers, which produced an increased activation energy with a contribution due to transport through the oxide [57].

2.6.3 Interaction of Permeants with Barrier Oxides

Water, unlike oxygen and the inert gases described in Section 2.6.1 on page 41, tends to chemically interact with the oxide layer affecting the activation energy, provided permeation is not dominated by macro-defects. This provides an opportunity to alter the chemical structure of barriers to increase the activation energy and minimise permeation [12].

Tropsha described how water interacts strongly with defect-containing SiO_x and PET and that the addition of *identical* SiO_x layers to three different polymer substrates produces the *same* activation energy for water (within error) [57], which confirms Roberts analysis (Section 2.6.1) that the limiting transport mechanism determines the activation energy, as the polymer substrates in question have differences of up to 18 kJ/mol in intrinsic activation energy.

Erlat [14] showed how the activation energy of oxygen permeation stayed constant even as the quality of the barriers increased (lower oxygen permeation), but that the activation energy of water permeation increased, see Figure 23.

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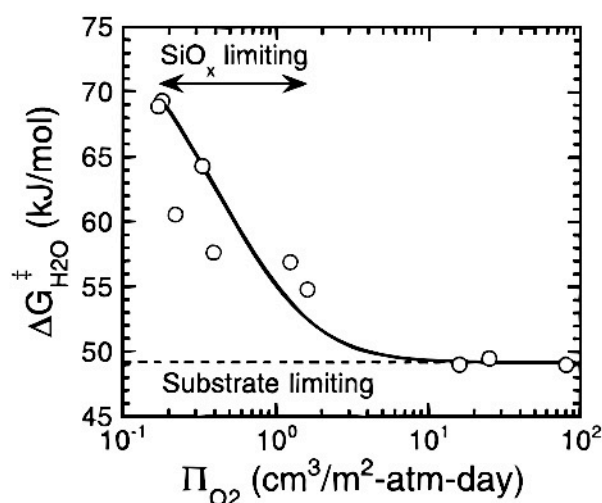


Figure 23. Reproduced from [14], activation energy of water (ΔG in this figure) as a function of OTR (Π_{O_2}) for SiO_x .

The two possible physical bases presented by Erlat for this increase in activation for water, was that the smaller size nano-defects, associated with improved oxygen barrier, allowed

hindered water vapour transport, and/or that water chemically interacted with the PECVD SiO_x structure. Erlat observes that as the activation energy for oxygen is constant there must be significant oxygen flow through macro-defects. The change in nano-defect size is shown to affect the activation energy of water but not oxygen.

It was suggested that in the case of silica, dangling bonds (Si-O- , Si-) react with water to form SiOH (Doremus cited in [14]). Erlat concludes that the increase in activation energy for water permeation is connected to the energy required to remove adsorbed water molecules from nano-defect walls [14]. The report conceded that a hindered-transport mechanism may also contribute.

Inter-diffusion

Secondary Ion Mass Spectrometry (SIMS) was used to analyse the depth distribution of elements in ITO and AlO_x on PET [46]. A uniform distribution of indium and tin was evident in the ITO layer, but the Rutherford Back Scattering (RBS) analysis suggested that inter-diffusion of the oxides with the polymer substrate had occurred. This effect, furthermore, present in AlO_x sputtered on PET, was not present if the AlO_x was deposited by electron beam evaporation. Henry suggested that the highly energetic species deposited with sputtering allowed inter-diffusion [46].

2.6.4 Barrier Chemistry

Looking at the barrier chemistry of AlO_xN_y coatings is a key focus of this project. The study of Liu in 2010 is analogous. PECVD was used to produce thick ($1\text{ }\mu\text{m}$) layers of SiO_xC_y with the ratios controlled by the ratio of N_2O to Argon. High O_2 content is shown to produce a hard, silica-like barrier [91], which is hydrophilic, with low O_2 barriers exhibiting elasticity and hydrophobicity [19]. The changes in chemistry, exhibited at three different ratios, was

identified using FTIR and the refractive index was found to decrease with increasing oxygen content [19]. However, no WVTR or OTR data were reported.

Addition of Nitrogen

One of the first examples of an AlO_xN_y film for optoelectronics was presented by Dehuang in 1990 [92]. Reactive sputtering was used, with a controlled ratio of oxygen and nitrogen, but it was found that this ratio didn't exactly correspond to the elemental ratio in the film which was explained as being due to residual oxygen in the vacuum chamber, an effect also observed by Erlat [12], who in addition observed trace impurities of Fe, Mn and Si which were divined to be from the target assembly.

Erlat [12], who fabricated AlO_xN_y films in a similar way to Dehuang, found a large increase in water vapour activation energy, 79.9 kJ/mol (for 72 nm AlO_xN_y) and 64.1 kJ/mol (for 57 nm AlO_xN_y), over the PET substrate (40.6 kJ/mol). The increase in activation energy for thicker coatings, even though a critical thickness of ~60 nm was evident, was suggested as being due to the removal of permeation paths or by a change in mechanism. This can be understood by consideration of Figure 22 on page 44, in that it would be possible that reduction of permeant paths would force greater permeation through the oxynitride layer, but also the activation energy, in part affected by adsorption of the water molecules onto the oxide in pore walls, could be different for different coating chemistries, as is suggested in the same study [12] (as in Section 2.6.3) and that of a later study [61]. It is not clear which mechanism dominates.

Erlat's study of 2004 is instructive regarding the nature of AlO_xN_y barriers and their relation with AlO_x and Al. In varying AlO_xN_y deposition parameters, it is noted that the permeation for oxygen is similar and the activation energy for oxygen is identical, pointing to oxygen permeation through macro-defects and not through nano-defects, so it is presented that changing the chemistry and microstructure would not alter permeation [61].

The addition of a smoothing layer in the study of Erlat reinforces the findings observed by Affinito as outlined in Section 2.4.2.2, chiefly (1) the addition of *only* a smoothing layer to the substrate gives no significant barrier improvement and (2) interposing a smoothing layer between substrate and oxide decreases the permeation rate significantly [61]. A comparison of three oxides, AlO_x , AlO_xN_y and TiO_xN_y and the effect of a diacrylate smoothing layer is shown in Figure 24.

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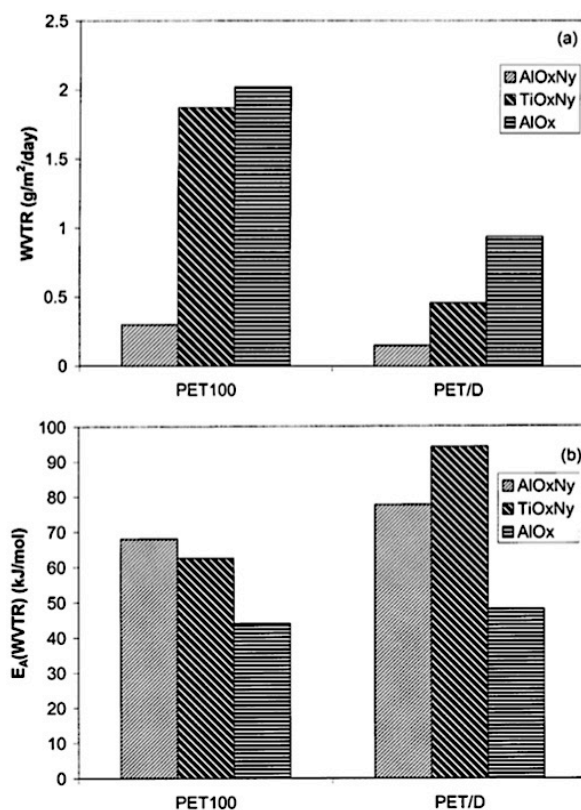


Figure 24. Reproduced from [61], where "PET 100" signifies that the layer has been deposited on 100 μm thick PET and "PET/D" means that the layer has been deposited on a 1 μm thick diacrylate layer on top of a 100 μm PET substrate.

It can be seen from Figure 24, that AlO_xN_y has the lowest rate of WVTR, and for un-smoothed samples, the highest activation energy, some 20 kJ/mol higher than AlO_x (which has the same activation energy as uncoated PET) [61]. The addition of the smoothing layer lead to a significant increase in the activation energy for the oxynitrides (TiO_xN_y and AlO_xN_y), this is suggested to mean that without the acrylate, a large portion of the gas flow was unhindered through the macro-defects, and that the closing of these paths due to the presence of the

acrylate lead to chemical and physical interactions of the permeant with the coating, dominating the activation energy [61]. The smoothing layer did not seem to affect AlO_x in the same way, leading to a further affirmation by the author that N species in the coatings are the main sites for chemical interactions [61] adding to the evidence from other sections in this review.

Another key finding was that WVTR tended to decrease for increasing Al/N ratio [61], although the concomitant effect on transparency is not discussed. It was suggested that the presence of some minimum nitrogen content increases the activation energy and barrier quality, but that excessive nitrogen degrades the function of an AlO_xN_y barrier. Erlat suggests that the excessive adsorption on nitrogen sites could lead to condensation and liquid transport along the walls pointing to a study of alumina by Cooper [93], which describes this process and states that the effect is significant at pore sizes ~ 2 nm.

SIMS Analysis of Water Transport

SIMS analysis of Erlat [61] is pivotal in explaining the nature of water transport through AlO_xN_y . Three identical, 43 nm thick AlO_xN_y /PET barriers were produced, and for each one the permeation (for 50 hrs) of a different isotopic form of water was carried out. The depth analysis is reproduced in Figure 25.

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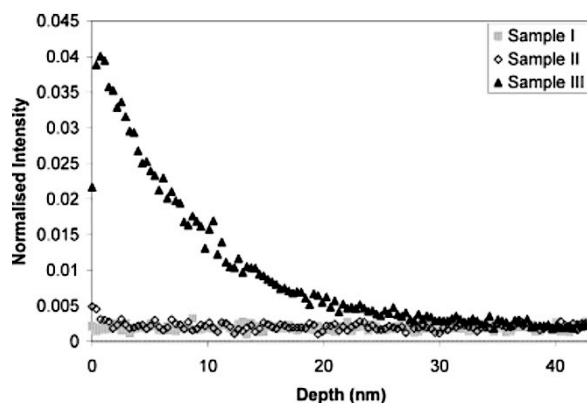


Figure 25. Reproduced from [61], depth profiles for mass 18, where Sample I is normal water vapour, Sample II is D₂O and Sample III is ¹⁸O rich water.

The three samples demonstrated a WVTR value of 0.3 g/m²/day with Sample I displaying a high activation energy of 68 kJ/mol (PET - 40.2 kJ/mol) [61]. Figure 25, normalised to the signal from sample I, shows an accumulation of ¹⁸O in the barrier, tailing off with increasing barrier depth [61]. Erlat suggested this was due to trapping of ¹⁸O as the H₂¹⁸O passed through the barrier, giving evidence for a chemical interaction of water with the barrier [61]. The dissociation of water during permeation through AlO_xN_y was suggested as an explanation for the aforementioned SIMS evidence. The same process was repeated for an AlO_x layer, see Figure 26.

Reprinted with permission from A. G. Erlat, B. Henry, C. Grovenor, A. Briggs, R. Chater, and Y. Tsukahara, "Mechanism of Water Vapor Transport through PET/AlO_xN_y Gas Barrier Films," J. Phys. Chem. B, vol. 108, no. 100, pp. 883–890, 2004. Copyright 2004 American Chemical Society.

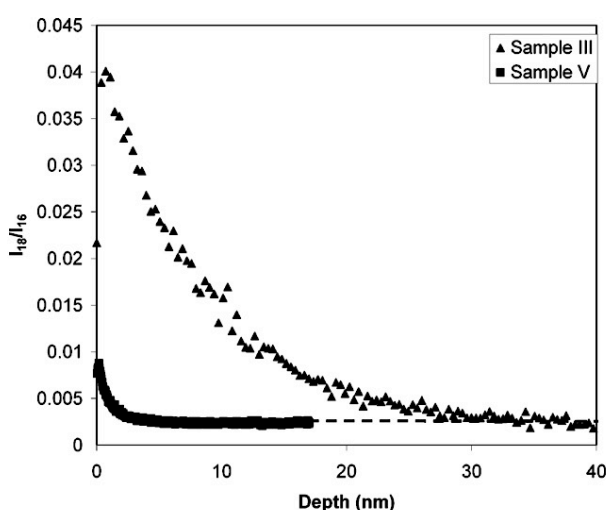


Figure 26. Reproduced from [61], sample III is the same as in Figure 25 (H₂¹⁸O passed through AlO_xN_y), with sample IV representing H₂¹⁸O that has been permeated through AlO_x.

It can be seen in Figure 26 that there is a similar adsorption of ^{18}O in AlO_x , just to a much lesser extent, indicating a similar dissociation mechanism in AlO_x [61]. Erlat describes how the magnitude of interaction and the depth to which it is observed is much greater for the AlO_xN_y layer, which he suggests supports the theory that the nitrogen sites in the oxide promote interaction with the water vapour. Nitrogen-containing sites in the nano-defect walls are suggested as the location for these reactions to take place, which is supported by the fact that 80% of the flow of water vapour is theorised to pass through these defects [61].

2.7 Barrier Architecture

2.7.1 Smoothing and Capping Layers

Post deposition handling damage [11], and rolling up of the barrier structure can lead to damage and pinholes in an oxide layer, so a capping as well as underlying smoothing layer was proposed [82]. In the study of smoothing/capping layers, it was noted that there was a difference in roughness, depending on whether the monomer was cured using UV or e-beam (see Figure 16), AFM studies suggested that the UV cured layer demonstrated the greatest smoothing [28].

Ghosh [8] advised the use of a polymer capping layer due to the corrosion of AlO_x by liquid water, through possible condensation on the barrier layer.

Struller found that an acrylate capping layer reduced WVTR by an order of magnitude for 10 nm evaporated AlO_x [30]. Further discussion of this result in particular will be outlined in Section 6.2 on page 175.

2.7.2 Carbon

Howells reported high levels of carbon (18-25%) in the PECVD deposited SiO_x films. The presence of carbon was suggested to have improved the mechanical properties of the films,

allowing very thick layers to be formed without deterioration of the barrier, an important improvement, but also reduced the interaction of water with the oxide explained by a lower than expected activation energy, a clear drawback for barrier films. Howells [77] observed that *only* thicker (400-1000 nm) barriers exhibited the increase in activation energy that was present in 100 nm barriers for Tropsha [57].

2.7.3 Multilayers

A drawback of ALD films is how slow they are to fabricate. Carcia tackled this issue in his 2009 paper. Carcia's ALD AlO_x grows at a rate of $1.1 \text{ \AA} / \text{min}$, and when deposited at a thickness of 10 nm on smoothed PEN provides a WVTR of $< 5 \times 10^{-5} \text{ g/m}^2/\text{day}$ (lower than limit of the Ca test used) [56]. However he found that if a 100 nm layer of PECVD SiN (of barrier $6.5 \times 10^{-3} \text{ g/m}^2/\text{day}$ at a rate of 1 nm/min) was deposited first, only 5 nm of ALD was needed to lower the permeation to below a measurable rate [56]. This improvement was lower than predicted by laminate theory, and it was suggested that either the AlO_x was forming in SiN defects or that the SiN provided a better (impenetrable) nucleation surface for the AlO_x allowing complete coverage at lower thicknesses [56]. It is pointed out that by sandwiching the ALD AlO_x between two SiN barriers, barrier corrosion by bulk water was avoided [56].

The use of faster (by an order of magnitude) PECVD to reduce the amount of ALD required to produce a gas "super barrier", is an example of synergy in barrier fabrication. A drawback of Carcia's study is that the mechanical implication of using thinner AlO_x is not investigated.

Another example of combining different barrier materials was provided by Choi [20]. Choi shows how RF sputtered films, which are deposited much faster than ALD (the Oxford Webcoater has a deposition rate of 10-20 nm/min), can produce barrier systems that reduce permeation to below the measurable rate. Two sputter sources are used to alternately

deposit SiO_x and AlO_x on 150 mm Polyethersulfone (PES) and the TEM cross sections are shown in Figure 27 [20].

J.-H. Choi, Y.-M. Kim, Y.-W. Park, T.-H. Park, J.-W. Jeong, H.-J. Choi, E.-H. Song, J.-W. Lee, C.-H. Kim, and B.-K. Ju, "Highly conformal $\text{SiO}_2/\text{Al}_2\text{O}_3$ nanolaminate gas-diffusion barriers for large-area flexible electronics applications.," *Nanotechnology*, vol. 21, no. 47, p. 475203, 2010. DOI 10.1088/0957-4484/21/47/475203 © IOP Publishing. Reproduced with permission. All rights reserved.

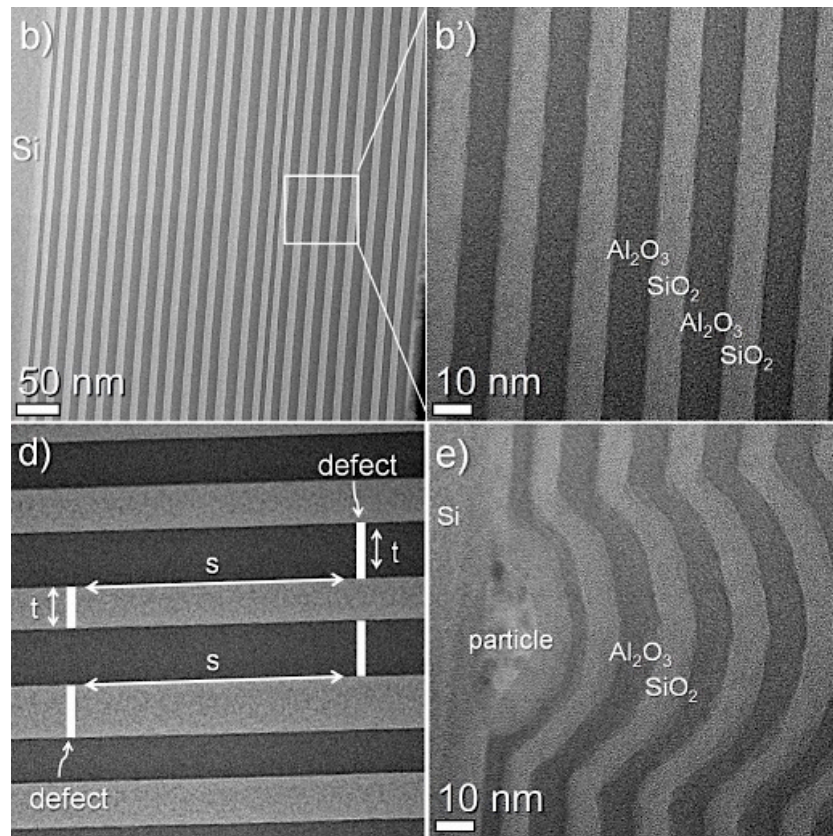


Figure 27. HRTEM of 24 bilayers of 10 nm/10 nm SiO_x (light) and AlO_x (dark). From [20].

This paper had a number of key discoveries that are of direct importance to this project. Choi found that more, thinner layers provided a better barrier than fewer, thicker ones. Single thick (480 nm) SiO_x and AlO_x layers gave only 10^{-1} g/m²/day, but that 24 bilayers of 10 nm/10 nm yield permeation values of 3.5×10^{-4} g/m²/day, Figure 28 a) shows how the lifetime of the calcium improves with more, thinner layers [20]. Figure 27 e) shows that these thin layers can even cover large particles effectively.

J.-H. Choi, Y.-M. Kim, Y.-W. Park, T.-H. Park, J.-W. Jeong, H.-J. Choi, E.-H. Song, J.-W. Lee, C.-H. Kim, and B.-K. Ju, "Highly conformal SiO₂/Al₂O₃ nanolaminate gas-diffusion barriers for large-area flexible electronics applications," *Nanotechnology*, vol. 21, no. 47, p. 475203, 2010. DOI 10.1088/0957-4484/21/47/475203 © IOP Publishing. Reproduced with permission. All rights reserved.

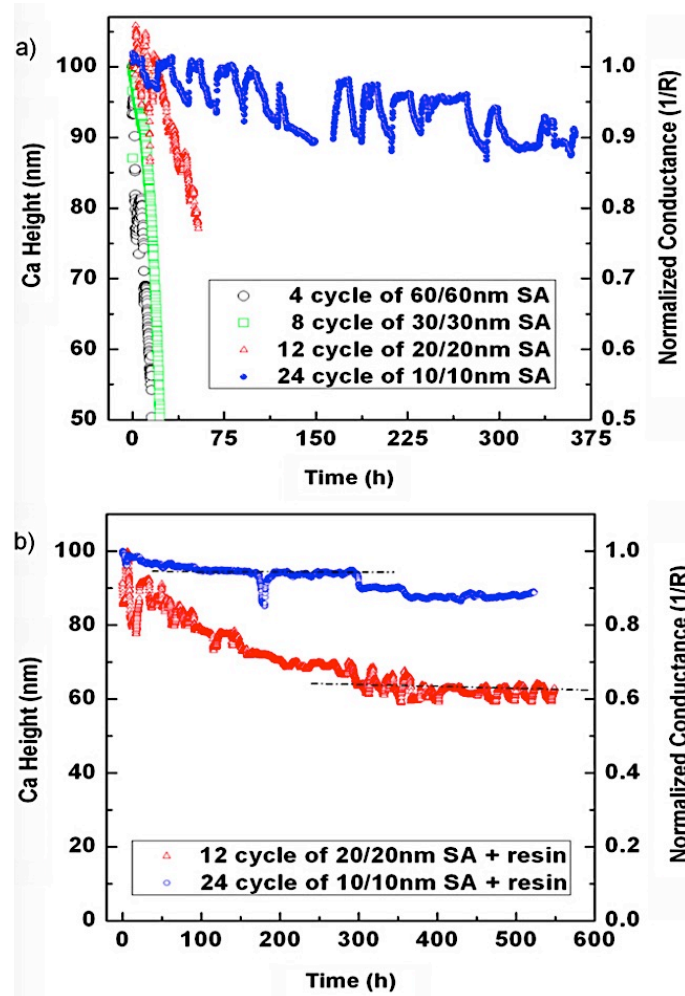


Figure 28. Conductance calcium test for various SiO_x and AlO_x multilayer architectures at 20°C at 50% RH. From [20].

Choi gives some explanation for the barrier improvement at thinner layers using Figure 27 d) showing that laterally spaced defects in the layers provide a distance s for the moisture to travel where $s \gg t$, and that as more thinner layers are added, this greatly increases the path length of the permeant [20]. Figure 28 b) shows how the addition of an organic capping layer of UV- resin improves the overall lifetime of the barrier structures by mechanically protecting the AlO_x layers and also protecting both layers from corrosion [20]. The 24 cycle 10 nm/10 nm with resin capping exhibiting a permeation rate of 3.79×10^{-5} g/m²/day [20].

Unlike the ALD paper of Garcia in 2009, Choi tested the mechanical durability of these thin films, and found (see Figure 29) that after 1000 cycles of bending, the permeation rate increased to 1.64×10^{-3} g/m²/day [20].

J.-H. Choi, Y.-M. Kim, Y.-W. Park, T.-H. Park, J.-W. Jeong, H.-J. Choi, E.-H. Song, J.-W. Lee, C.-H. Kim, and B.-K. Ju, "Highly conformal SiO₂/Al₂O₃ nanolaminate gas-diffusion barriers for large-area flexible electronics applications.," *Nanotechnology*, vol. 21, no. 47, p. 475203, 2010. DOI 10.1088/0957-4484/21/47/475203 © IOP Publishing. Reproduced with permission. All rights reserved.

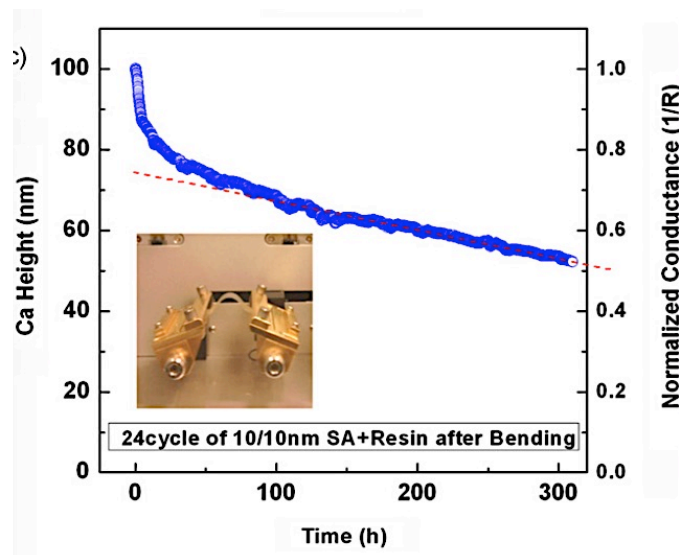


Figure 29. Lifetime of calcium conductance after 1000 cycles of bending of the barrier stack. From [20].

An even better barrier was investigated, with 30 cycles of 8 nm/8 nm, which showed no change in calcium conductance after 240 hours. The conditions were increased from 20°C at 50% RH to 60°C at 95% RH and still after a further 200 hrs, the permeation rate registered under the limit of the calcium test [20].

The remarkable permeation results and mechanical endurance underscores the concept that thinner, more numerous layers are preferable, but also that this could be due to the increase in permeant path length. This seems to correlate with Cussler's discussion in 1987 of a "tortuous path" of diffusion [94]. However, it is not clear from either paper whether this is due to increased resistance to permeation as well as path length increase. Vogt introduces the concept that multilayer superbarriers have lower-than-quoted permeation due to a long-lived transient effect whereby the barriers take over 500 days to reach equilibrium [95]. It is posited that increased path length would take longer to reach equilibrium which would fit with Vogt and Choi's observation, whereas increased resistance would increase the activation energy of permeation and reduce overall flux, but as activation energy is found from a equilibrated sample, the question raised in Vogt's paper is still of burning relevance. If one considers however, that the required lifetimes for optoelectronics, as described in Section

1.1, are between 420-1825 days, increasing this transient effect may be a route to long lived devices.

It would be interesting to know whether the UV resin used has any effect as a barrier. Choi's paper does however lend support to the concept that a capping layer is of importance to multilayer barrier architectures. Its addition will be tested in this project.

A 10 nm Cyclical-CVD (C-CVD) Al_2O_3 layer produced by Park was reported to exhibit a WVTR of $1.5 \times 10^{-5} \text{ g/m}^2/\text{day}$ (by calcium test), which was confirmed by studying the luminance of an OLED which remained above 90% of its maximum illumination for 1000 days in 85% RH 85°C [96]. After this period however, a sharp drop in luminance was observed, to 55% by 1250 days, this is explained as due to water corrosion and failure of the C-CVD films [96].

2.8 Literature Review Conclusions

Different barrier deposition processes and characterisation methods have been extensively discussed (Sections 2.1 and 2.2).

The permeation rate required by barriers for encapsulation of organic optoelectronics has been shown to be three orders of magnitude lower than the industry standard testing device, the MOCON Permatran. Notwithstanding this drawback, it remains the sole reproducible and accepted metric for barrier permeation, and it provides a useful tool for this project in determining the activation energy of the barrier layers to understand what drives permeation and how it can be reduced.

Different architectures of the **calcium test** (Section 2.2.2) were discussed, however issues of reproducibility are a concern. Instead of relying solely on this method for a value for WVTR, the defect-imaging test will be extensively used in **Chapters 4, 5 and 6** to give a qualitative overview of permeation.

Permeability (Section 2.3.1) has been shown to be a useful tool in the comparison of different thickness films and will be used throughout the experimental **Chapters (4, 5 and 6)** of this report.

It was seen that barrier microstructure and thickness had a strong connection to barrier permeation, and the study of these changes will be covered in **Chapter 4**.

It has been broadly shown that permeation through oxide barriers is a result of a combination of un-hindered transmission through **macro-defects** and hindered transmission through **nano-defects**. A clear definition of the two classes of defect has been defined for this work, and the application of activated rate theory (Section 2.3.2) will be used to probe how changes in deposition can affect the nature of permeation, as well as the number, type and ratio of these defects. The interaction of water with barrier oxides has also been covered (Sections 2.6.3 and 2.6.4) and will be significant in **Chapter 5** where barrier chemistry is varied in order to promote this phenomenon.

XPS was introduced as a sensitive surface analysis technique which can also be used to depth-profile thin films. This technique will be used in **Chapter 4** in order to ensure chemical changes *aren't* occurring whilst changing deposition conditions are investigated. However, the technique will be heavily used in **Chapter 5** to *quantify* the chemical changes in the barriers that manifest with the addition of nitrogen.

It has been show that permeation can be substantially reduced by decreasing or eliminating the prescence of macro-defects e.g by the addition of a planarizing acrylate layer. A novel alternative to this was reported: an initial ALD SiO_x layer performing a similar function, albeit allowing conformal coating of subsequently co-sputtered layers, rather than planarization. The use of acrylate layers as a top-coat or “capping layer” were shown to protect the layer from mechanical damage and bulk water-induced degradation. Both smoothing layers, and capping layers are investigated in **Chapter 6**.

Multilayers, discussed in Section 2.7.3, were shown to exhibit barrier levels and lifetimes approaching those required by OLEDs and OPVs. The concept of lag-time was also introduced. The production and characterization of multilayers and the investigation of lag time will also be covered in **Chapter 6**.

3 Methodology

This section describes the experimental methods used in this report. These can be grouped into **fabrication** (Sections 3.1 and 3.2) and **characterisation** (Sections 3.3, 3.4, 3.5 and 3.6).

3.1 Sputtering

The transparent AlO_x and AlO_xN_y coatings in this report were produced using RF magnetron reactive sputtering. The Oxford Webcoater is a roll-to-roll vacuum coating system (Arcotronics Industries SpA & Aerre Machines s.r.l.). Figure 30 shows the location and arrangement of the different coating devices.

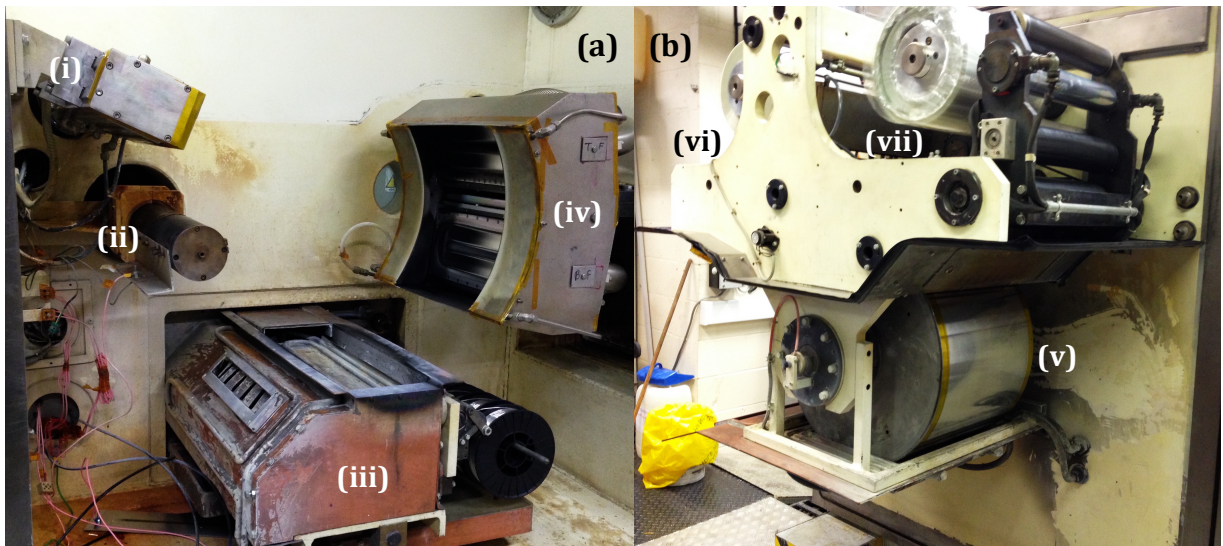


Figure 30. Deposition capabilities of the Oxford Webcoater: (i) e-beam cure, (ii) monomer ejection nozzle, (iii) metallisation unit, (iv) sputter cathodes. The drum (v), the unwind (vi) and rewind (vii) rollers occupy the empty space between and above the deposition elements (i-iv) when the vacuum chamber is closed. Two running modes are possible (1) single pass deposition: roll-to-roll with a single continuous web and (2) multiple-pass deposition: where the substrates are mounted on the drum.

For this project, all barriers are produced in the multiple-pass arrangement. The metallisation unit is not used.

The drum is initially wrapped with leftover PEN web, to protect the surface from buildup, and A4 substrates are attached to this with kapton tape. Small silicon chips (1 x 1 cm) are attached above the substrates in order to allow investigation of the coatings with techniques that require a hard or reflective substrate (see Sections 3.4.3 and 3.4.4).

The sputter cathodes are monolithic aluminium (Angstrom Sciences, PA 15110 USA). Figure 31 (a) shows the partially-worn cathodes.



Figure 31. Sputter cathodes of the Oxford Webcoater: (a) the aluminium cathodes exhibiting the sputter wear "racetrack", (b) the aluminium cathode removed, revealing the array of permanent magnets characteristic of a magnetron system.

The “racetrack” of sputter wear can be seen. With the sputter housing/sheath and the aluminium cathodes removed, Figure 31 (b) shows the array of permanent magnets behind. O-rings, which form the seal for the cooling water that circulates behind the aluminium, can be seen as black rubber lines around the magnet chamber.

Between the cathodes (seen with a rainbow-like pattern in Figure 31 (a)) is the reactive gas delivery zone.

With the substrates having been prepared, the chamber is evacuated and left to “pump-down” for 3 hours or until the Penning gauge reads $\sim 5 \times 10^{-5}$ mBar. The substrates are

positioned on the opposite side of the drum from the cathodes and the drum is kept stationary.

Once the required base pressure has been reached, sputtering can commence. The process gas (200 sccm of argon in all cases unless explicitly stated) is introduced into the chamber. Using the RF power supply (Hüttinger), the power is slowly increased from 1 kW to the operating power. This is done in 3 steps, waiting 5 minutes between each increase.

Once the operating power has been reached, sputtering continues for another 4 minutes in order to fully clean any oxide or surface build up from the cathodes. As stated above, the substrates are shielded on the other side of the drum.

In order to investigate the hysteresis of the system, reactive gas is slowly introduced to the sputter zone (with the flow rate being increased every seven minutes) until the point of poisoning is identified. This is expressed as a drop in sputter voltage. The reactive gas flow is then reduced until the system recovers and the insulating layer is removed. The recovery is heralded by the return of the sputter voltage to the pre-poisoning level.

Once the poisoning point is identified, all reactive gas is shut off, and the system is sputtered for 6 minutes in order to fully clean the cathodes and allow excess reactive gas to be pumped away.

As the poisoning point has been identified, the reactive gas is reintroduced and set at a point 3 sccm lower than the poisoning point. A further 6 minutes is allocated to allow the system to equilibrate and stabilise (see Section 4.1.1).

After this period, deposition begins. The drum is set to spin as a timer is started. During the deposition there are three things that are constantly checked:

1. **The sputter voltage** - if the reactive gas flow is set too close to the poisoning point, the spinning of the drum can disturb the equilibrium gas distribution in the sputter zone and cause target poisoning.

2. **Arcing** –excess arcing can damage the film and has been linked to issues with cleanliness or cathode damage.
3. **Optical transparency**– a window allows optical inspection of the films throughout the length of the deposition. Low reactive gas flows have been seen to produce brown films.

The plasma itself is also inspected at least once. Figure 32 shows the sputter plasma.

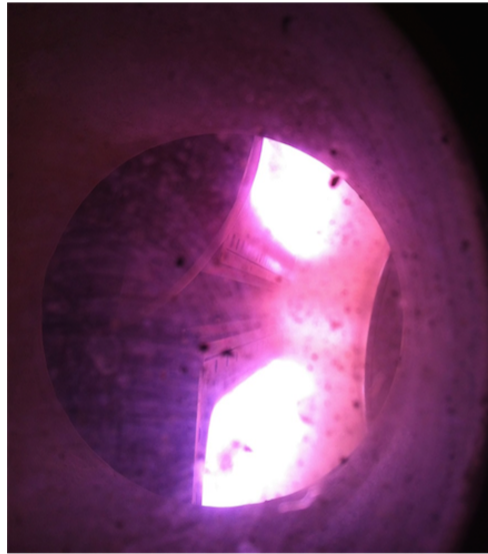


Figure 32. Sputter plasma. The chimney has been removed, only air is being used to sputter, and the characteristic pink glow of nitrogen is evident.

When the reactive gas used is oxygen, the plasma glow appears purple. When nitrogen is used as the reactive gas, the plasma takes on a pink hue.

Once the deposition time has been reached, the power and the gases are turned off. The chamber is vented, and the samples removed for testing or storage.

3.1.1 Oxynitrides

To produce AlO_x , oxygen is used as the reactive gas. However using nitrogen as the reactive gas initially only registered small increases in the nitrogen content of the coatings. Large amounts of oxygen (45%) still dominated the films. It was assumed that the large oxygen

content of the films did not originate from post-deposition oxidation, i.e. after exposure of the films to the air, as given the large proportion of oxygen observed in the films, they would have to start as highly sub-stoichiometric while under vacuum. Sub-stoichiometric films would be aluminium-rich and exhibit reduced transparency. Suttle found that if a low rate of reactive gas was supplied, RF sputtered AlO_x films appeared brown [38]. Films produced in the current report were observed to remain fully transparent during, and after deposition and thus it follows that residual chamber oxygen was reacting with the aluminium during deposition.

The amount of nitrogen that can be supplied to the cathode is limited by target poisoning. Many different approaches to increasing nitrogen content were attempted (see Chapter 5.1). Only two were successful.

In order to increase chamber nitrogen, but without poisoning the cathodes, nitrogen was piped into the vacuum chamber, but outside of the sputter chimney. The addition of a flow of 100 sccm of nitrogen into the bottom of the vacuum chamber only reduced the poisoning position of cathodes under nitrogen by 2 sccm. A film produced in this manner was scanned by XPS and was found to have an elemental composition of 12.3% nitrogen.

In order to boost the nitrogen content further, liquid nitrogen was used to scavenge excess gases in the chamber. The webcoater vacuum chamber has a coil of metal tubing beneath the sputter cathodes. The tube enters and exits the chamber but is isolated from the vacuum and is instead exposed to the ambient. Liquid nitrogen can be poured into this tube, inducing gases inside the chamber to condense on it. This is expressed by a fall in chamber pressure. After a period of time, the liquid nitrogen boils off and the pressure would return to the “normal” level as the condensed species vaporise and expand, were more LN_2 not added. In order to maintain this beneficial effect it was necessary to ascertain the time taken (11-12 minutes) for the LN_2 to boil off.

In order to produce maximum nitrogen content (15.3%) films, the procedure of Section 3.1 was followed with the addition of 100 sccm of nitrogen (pumped into the bottom of the chamber) with LN₂ scavenging topped up every 9 minutes.

3.2 Acrylate

Acrylate smoothing layers were deposited using the vacuum-integrated evaporation chamber (Sigma Technologies LLC, Tucson AZ, USA) on the Oxford Webcoater (see Figure 33).

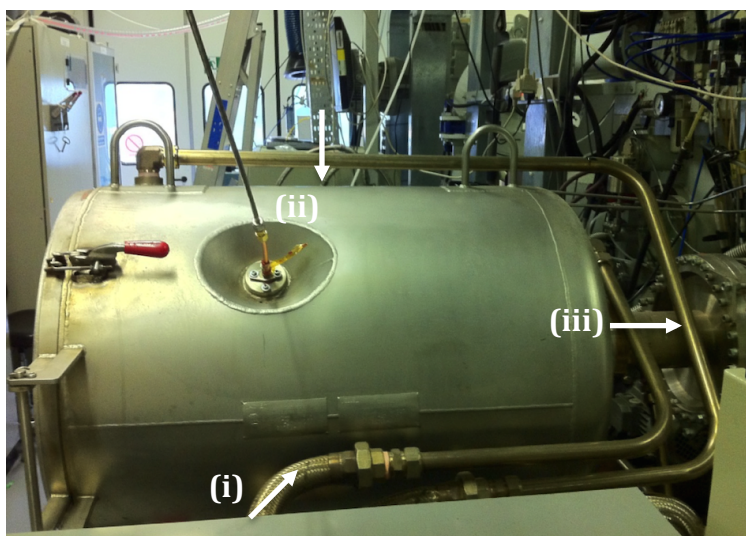


Figure 33. Evaporation chamber of the Oxford Webcoater, (i) the heating unit brings the chamber up to temperature, (ii) the monomer is injected through the septum (hidden from view) and (iii) the monomer enters the main vacuum chamber and is deposited on the drum.

Substrates and silicon chips were mounted on a wrapped drum in the manner described in Section 3.1.

The monomer, tri(propylene glycol) diacrylate (Sigma Aldrich –246832-500G), was degassed in a small vacuum chamber at 0.5 Torr and with the aid of magnetic stirrers.

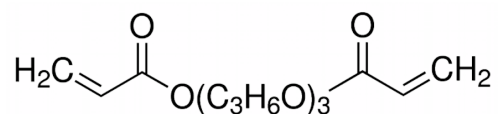


Figure 34. Chemical structure of TRPGDA, from the Sigma Aldrich website.

Without degassing, absorbed gases would expand under rapid heating and disrupt the spray of the monomer, causing it to spit [97].

The monomer was then drawn into a Terumo syringe (2.5 ml) and attached to a 25 gauge needle (Inner Diameter 0.26 mm) with tubing. The needle was injected into the septum and isolated from the vacuum by a manual valve. The syringe was loaded into a syringe pump, and programmed to dispense at a rate of 0.5-0.6 ml/minute. Before the monomer was ready to be injected, the evaporation chamber needed to be pre-heated, and the e-beam raised to the operating current.

The drum was set to spin, in order to avoid heat or e-beam damage to the substrates, both having been observed previously.

The evaporation chamber, door and nozzle, were heated to 270°C.

The e-beam was initialised, with the argon gas flow and voltage slowly increased in order to maintain a stable plasma.

Once the evaporation chamber was at the required temperature, and the e-beam was at the maximum operating current and voltage, the monomer was exposed to the vacuum and injected. If larger gauge needles, or slow injection rates were used, bubbles formed in the syringe as ambient gas was pulled into the syringe around the plunger.

3-5 minutes after the monomer finished injecting, the evaporation chamber was set to cool down. Once the evaporation chamber reached 150°C, at which temperature it is considered that no more residual monomer would be present, the e-beam was turned off.

In order to predict monomer volumes required, a rough estimation of the maximum possible thickness was considered, ignoring volume changes due to polymerisation.

Monomer volume was divided over the area of the drum (drum length – 1.88 m, drum width – 0.35 m).

This calculated value was an upper limit; in the process itself there were sources of monomer loss. Affinito highlights loss due to re-emission of the monomer from the substrate in the time between deposition and irradiation by the e-beam [98]. This was confirmed by inspection, with small droplets of partially cured monomer observed around the deposition area.

Acrylate layers can also be UV-cured, with some configurations showing improvements over e-beam cures [28]. UV-curing was not attempted as the Oxford webcoater does not currently have an integrated UV-cure system. Acrylate can also be plasma cured. Whilst it is possible to plasma cure acrylate layers using the Oxford Webcoater, it would rule out any subsequent in-line sputter deposition in roll-to-roll mode, as both processes use the same set of cathodes. In recognition of a future attempt to upscale the methods trialled in this report, plasma curing was placed outside of the scope of the practical work.

3.3 Permeation Testing

Two distinct forms of water permeation testing are done in order to understand the nature of the films.

3.3.1 Steady-State Permeation and Activation Energy: The Mocon Permatran

The WVTR of the barriers was recorded using the MOCON Permatran W 3/31 (ASTM F-1249).

Samples were carefully cut into the requisite diamond-shapes using scissors, with care taken not to bend or touch the centre of the films. The films are held by O-rings and it is these that define the 50 cm² to be tested.

The sponges in the wet sides of the testing cells were saturated with HPL water. The rims of the O-rings were cleaned and the re-greased with vacuum grease in order to maintain a good seal. The films were inserted into the two testing cells of the device. BOC 270091-L-C Zero-

Grade nitrogen, passed first through a desiccant, was used as the carrier gas for the dry side of the cell. The nitrogen flow rate was set at 20 sccm and was recalibrated before the start of each test.

Most of the films were tested at 4 temperatures (35, 38, 44 and 50°C). Some tests had to be truncated, with the lowest temperature (35°C) test left unperformed as 38°C is the temperature at which WVTR is most commonly reported.

At the start of the test, the cells are conditioned for 9-11 hours in order to achieve a constant WVTR. After the conditioning period, the films are tested 20 times over 21-hours. Inspection of the WVTR values across this period found that they were constant and confirmed that the films were in dynamic equilibrium.

After every major refit, a WVTR calibration was performed using a calibration film (RDM Test Equipment, CM22 6JX) with known transmission rates for different temperatures. These calibrations were carried out and saved for the 4 test temperatures. The calibrations were loaded each time a test was performed.

Heat Damage

For all films (unless specifically labelled), WVTR and activation energy measurements were performed on two different samples of the film. This was in order to safeguard against any local damage to one sample skewing the results overall. These samples were tested simultaneously, with a sample in each cell of the Permatran. The WVTR was measured at different temperatures, starting with the lowest, and then increasing the temperature to the next highest and so on. Samples used in the Permatran were not used again and were discarded.

The reason for these procedures was to safeguard against potential effects of heating, as evidenced by Figure 35. In this case the samples were measured at the 4 different temperatures in ascending order. Then the temperature was lowered back to the start point

and the test was repeated. The PP tests were run concurrently (cell (a) and (b)) and not consecutively.

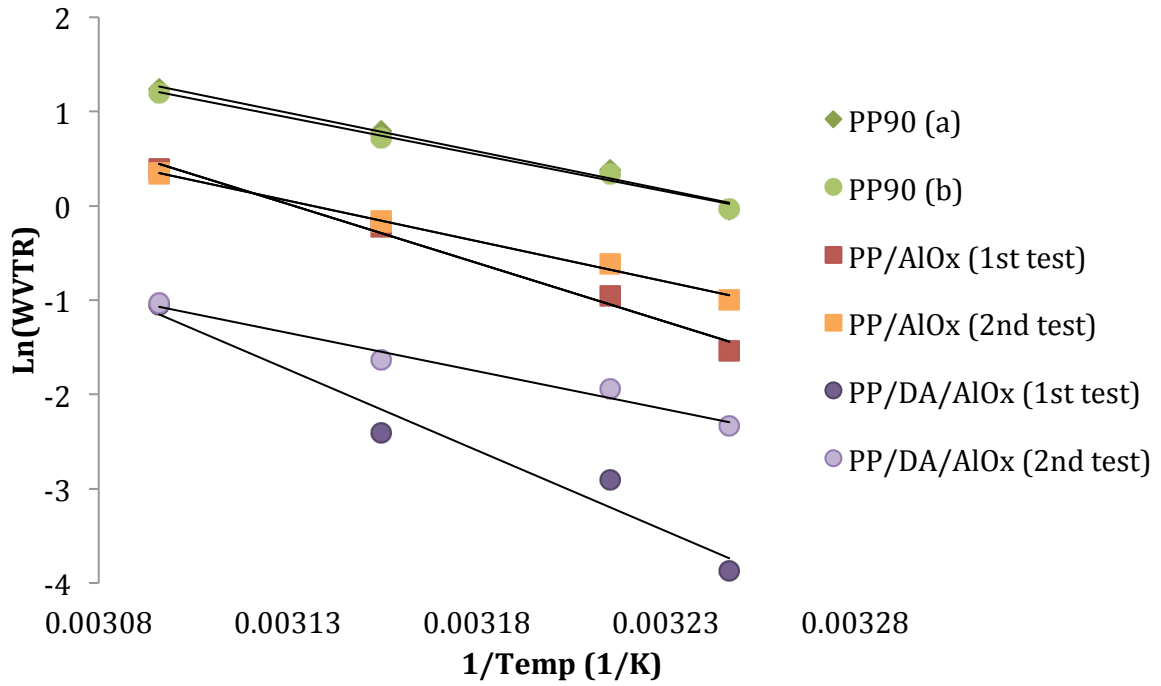


Figure 35. Arrhenius plot for films after being damaged by the high heat of the permatran.

The activation energy for the films are shown in Table 5.

Table 5. The recorded activation energy of the films for the 1st and 2nd test.

Film	Activation Energy – 1 st	Activation Energy – 2 nd
	Test (kJ/mol)	Test (kJ/mol)
PP	65-68	-
PP/AlO _x	104	71
PP/DA/AlO _x	143	67

The first test for both films shows an activation energy significantly higher than the polymer, showing that the rate-limiting process for the permeation was provided by the coatings, specifically the oxide layers. However, after the films have been tested at 50°C, and then returned to 35°C to be tested again, the WVTR increases dramatically at the lower temperatures. The activation energy of the PP/DA/AlO_x shows that the activation energy of

permeation has returned to that of the polymer. This shows that the film is now only acting to reduce the flux of permeation, but that the rate-limiting process is permeation through the polymer. The PP/AlO_x film exhibits a similar transformation in the second test, with the activation energy falling to 71 kJ/mol, just above that for the polymer. It is important to note, that although the two, heat-damaged films have activation energies equivalent to the polymer, the smoothed film (PP/DA/AlO_x, see Chapter 6) **still** has a low WVTR. Without investigation of the activation energy, it would be unclear as to the reason for this difference. The post-heat-damaged film reduced permeant flux to a greater extent than the AlO_x alone, but that the energetic cost associated with permeation is, in fact, the same for all three films in question.

It is not believed that there was evidence of heating effects in the 1st test of the films, as the data is linear in the Arrhenius plot. Damage has been shown to increase the WVTR, so if this damage had occurred during the 1st upward heating cycle, it would be observed as an upward deviation from the trend.

3.3.2 An Activation Energy Model

In order to better conceptualise the activated rate theory outlined in Section 2.3.2 and Section 2.6 the results from a simple model are presented. This was based on the Arrhenius relation (Equation 4), and is a simplified version of a model presented by Roberts [27].

The flow through a barrier is modelled using the relation described in Equation 7.

$$WVTR_b = WVTR_{md} + WVTR_{nd}$$

$$WVTR_b = N_{md} WVTR_{md}^{\infty K} e^{-\left(\frac{\Delta E_p}{RT}\right)} + N_{nd} WVTR_{nd}^{\infty K} e^{-\left(\frac{\Delta E_{nd}}{RT}\right)}$$

Equation 7

where $WVTR_b$ is the WVTR of the barrier, $WVTR_{md}$ is the sum of the WVTR through all the macro-defects, $WVTR_{nd}$ is the sum of the WVTR through all the nano-defects, N_{md} is the

number of macro-defects per unit area, $WVTR_{md}^{\infty K}$ is the WVTR of a macro-defect at ∞K , ΔE_p is the activation energy of the polymer, R is the gas constant, T is the temperature in kelvin, N_{nd} is the number of nano-defects per unit area, $WVTR_{nd}^{\infty K}$ is the WVTR of a nano-defect at ∞K and ΔE_{nd} is the activation energy of a nano-defect.

Unlike the model of Roberts [27], there is no description of the shape or dimensions of the defects (as only one permeant is considered here), with only WVTR-per-defect described.

Certain assumptions are made:

- There is only one type of macro-defect, with one mean size for all films and polymeric activation (unhindered transport).
- There is only one type of nano-defect, with one mean size and a defined activation energy.
- There is no permeation through the continuous oxide matrix (or else the effect of this is captured within the nano-defect permeation parameters).
- Activation energy of the nano-defect is arbitrary, but higher than any observed barrier activation.
- There is no effect of the distribution of defects within the plane of the films (which could otherwise lead to local concentration gradients of the permeant in the plane of the film).

In order to input an informed value for N_{md} , reference was made to the literature. Erlat [61] used AFM and SEM to evaluate sputtered AlO_xN_y and found defects >500 nm in size with a defect density of 600 mm^{-2} . The final value of N_{md} used was larger than this, in recognition of the numerous macro-defects that were smaller than 500 nm (> 1 nm). The number for N_{nd} used was chosen in order that the model output matched that of a typical experimental result. N.B. although there is a physical basis for N_{md} and ΔE_{nd} it must be considered that the values for N_{nd} , $WVTR_{nd}^{\infty K}$ and $WVTR_{md}^{\infty K}$ are realistic but arbitrary. The aim of this Section is *not* to

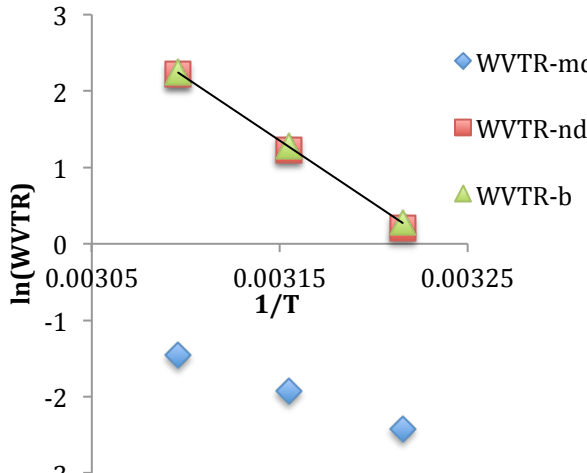
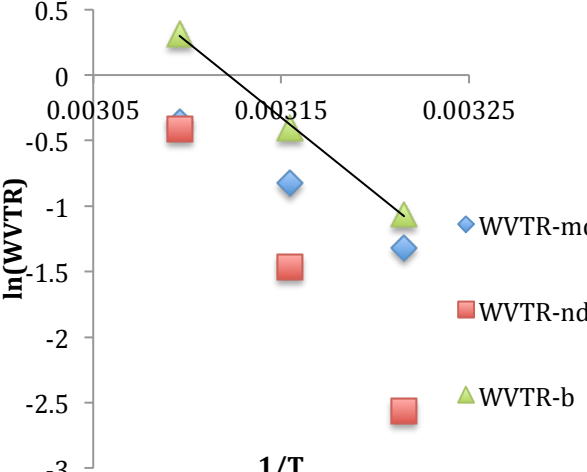
find values for these parameters, but to understand how and why different ratios of these numbers can produce varying activation energies.

The initial model test Figure 36 (1) is the **control**. The parameters used are described in the Figure, and all subsequent model tests see simple variations on these parameters to describe possible experimental outputs for $WVTR_b$.

A graph showing the $WVTR_{md}$, $WVTR_{nd}$, and their sum; $WVTR_b$ is included in order to aid visualisation of the contributions.

Test	Arrhenius Plot	Summary
1		Control Sample • $WVTR_{md}^{\infty K} = 0.1$ g/day • $N_{md} = 1.6 \times 10^{11}$ m⁻² • $\Delta E_p = 67$ kJ/mol • $WVTR_{nd}^{\infty K} = 0.001$ g/day • $N_{nd} = 4 \times 10^{26}$ m⁻² • $\Delta E_{nd} = 150$ kJ/mol Calculated Results $\Delta E_b = 96$ kJ/mol $WVTR_b(38^\circ\text{C}) = 0.12$ g/m²/day
2		Double No. of Nano-Defects • $WVTR_{md}^{\infty K} = 0.1$ g/day • $N_{md} = 1.6 \times 10^{11}$ m⁻² • $\Delta E_p = 67$ kJ/mol • $WVTR_{nd}^{\infty K} = 0.001$ g/day • $N_{nd} = 8 \times 10^{26}$ m⁻² • $\Delta E_{nd} = 150$ kJ/mol

		Calculated Results $\Delta E_b = 109 \text{ kJ/mol}$ $WVTR_b(38^\circ\text{C}) = 0.14 \text{ g/m}^2/\text{day}$
3	Graph 3: $\ln(WVTR)$ vs $1/T$. The y-axis ranges from -4 to 0, and the x-axis ranges from 0.00305 to 0.00325. Data points are shown for WVTR-md (blue diamonds), WVTR-nd (red squares), and WVTR-b (green triangles). A linear fit is shown for the WVTR-md and WVTR-b data points.	Double No. of Macro-defects $WVTR_{md}^{\infty K} = 0.1 \text{ g/day}$ $N_{md} = 3.2 \times 10^{11} \text{ m}^{-2}$ $\Delta E_p = 67 \text{ kJ/mol}$ $WVTR_{nd}^{\infty K} = 0.001 \text{ g/day}$ $N_{nd} = 4 \times 10^{26} \text{ m}^{-2}$ $\Delta E_{nd} = 150 \text{ kJ/mol}$ Calculated Results $\Delta E_b = 85 \text{ kJ/mol}$ $WVTR_b(38^\circ\text{C}) = 0.20 \text{ g/m}^2/\text{day}$
4	Graph 4: $\ln(WVTR)$ vs $1/T$. The y-axis ranges from -25 to 0, and the x-axis ranges from 0.00305 to 0.00325. Data points are shown for WVTR-md (blue diamonds), WVTR-nd (red squares), and WVTR-b (green triangles). A linear fit is shown for the WVTR-md and WVTR-b data points.	+33% ΔE of Nano-defects $WVTR_{md}^{\infty K} = 0.1 \text{ g/day}$ $N_{md} = 1.6 \times 10^{11} \text{ m}^{-2}$ $\Delta E_p = 67 \text{ kJ/mol}$ $WVTR_{nd}^{\infty K} = 0.001 \text{ g/day}$ $N_{nd} = 4 \times 10^{26} \text{ m}^{-2}$ $\Delta E_{nd} = 200 \text{ kJ/mol}$ Calculated Results $\Delta E_b = 67 \text{ kJ/mol}$ $WVTR_b(38^\circ\text{C}) = 0.09 \text{ g/m}^2/\text{day}$

5		-7% ΔE of Nano-defects • $WVTR_{md}^{\infty K} = 0.1$ g/day • $N_{md} = 1.6 \times 10^{11} \text{ m}^{-2}$ • $\Delta E_p = 67$ kJ/mol • $WVTR_{nd}^{\infty K} = 0.001$ g/day • $N_{nd} = 4 \times 10^{26} \text{ m}^{-2}$ • $\Delta E_{nd} = 140$ kJ/mol Calculated Results $\Delta E_b = 137$ kJ/mol $WVTR_b(38^\circ\text{C}) = 1.32$ g/m²/day
6		Triple No. of Nano & Macro-defects • $WVTR_{md}^{\infty K} = 0.1$ g/day • $N_{md} = 4.8 \times 10^{11} \text{ m}^{-2}$ • $\Delta E_p = 67$ kJ/mol • $WVTR_{nd}^{\infty K} = 0.001$ g/day • $N_{nd} = 1.2 \times 10^{27} \text{ m}^{-2}$ • $\Delta E_{nd} = 150$ kJ/mol Calculated Results $\Delta E_b = 96$ kJ/mol $WVTR_b(38^\circ\text{C}) = 0.35$ g/m²/day

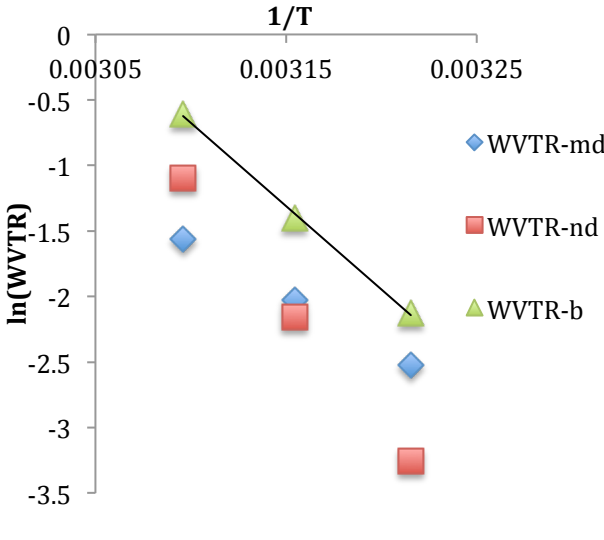
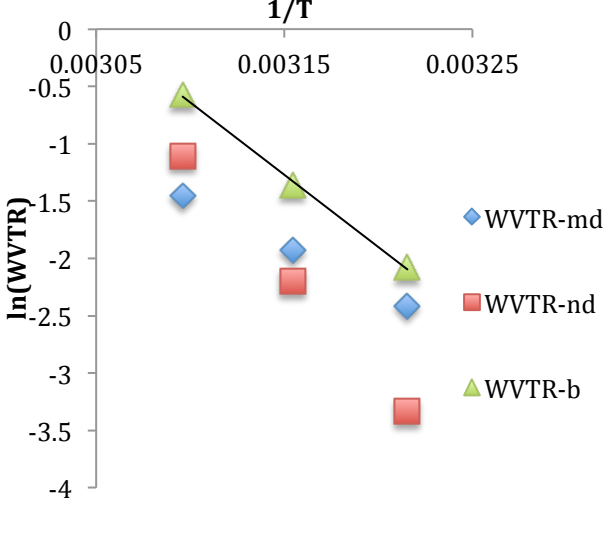
7		-10% No of Macro, +51% No. of Nano • $WVTR_{md}^{\infty K} = 0.1 \text{ g/day}$ • $N_{md} = 1.44 \times 10^{11} \text{ m}^{-2}$ • $\Delta E_p = 67 \text{ kJ/mol}$ • $WVTR_{nd}^{\infty K} = 0.001 \text{ g/day}$ • $N_{nd} = 6.03 \times 10^{26} \text{ m}^{-2}$ • $\Delta E_{nd} = 150 \text{ kJ/mol}$ Calculated Results $\Delta E_b = 106 \text{ kJ/mol}$ $WVTR_b(38^\circ\text{C}) = 0.12 \text{ g/m}^2/\text{day}$
8		+3% ΔE of Nano, +960% No. of Nano • $WVTR_{md}^{\infty K} = 0.1 \text{ g/day}$ • $N_{md} = 1.6 \times 10^{11} \text{ m}^{-2}$ • $\Delta E_p = 67 \text{ kJ/mol}$ • $WVTR_{nd}^{\infty K} = 0.001 \text{ g/day}$ • $N_{nd} = 3.84 \times 10^{27} \text{ m}^{-2}$ • $\Delta E_{nd} = 155 \text{ kJ/mol}$ Calculated Results $\Delta E_b = 105 \text{ kJ/mol}$ $WVTR_b(38^\circ\text{C}) = 0.12 \text{ g/m}^2/\text{day}$

Figure 36. Calculated Arrhenius plots for different input parameters. Test 1 is the control, to which all other tests are compared. The difference from the control sample is the headline in the summary.

Discussion

- **Test 1 and 2:** Test 2 shows the effect of doubling the number of nano-defects. The WVTR increases 13% (as there are more defects to pass through) but interestingly, the activation energy increases by 13 kJ/mol. The model barrier of Test 2 has more defects, but higher activation, as a greater amount of the total water permeation is passing through nano-defects. Comparing the graphs in Test 1 and 2, it can be seen that all of the change to the overall permeation is due to the nano-defect contribution.
- **Test 1 and 3:** Test 3 shows the effect of doubling the number of macro-defects. The WVTR increases by 67% and the activation decreases by 11 kJ/mol. This is the more intuitive result, as more unhindered transport occurs, WVTR goes up the activation decreases, approaching the value for the polymer. If the number of macro-defects is increased by a factor of 32 from the control, the overall activation is characteristic of the polymer.
- **Test 1 and 4:** Test 4 increases the activation energy of the nano-defects by a third, in order to simulate greater chemical interaction between the permeant and the defect walls. Although WVTR falls (by 25%) which would be expected, the activation energy also falls, indeed in this case to the polymer value. The reason for this is explained when comparing the Arrhenius plots. The permeation through nano-defects has decreased so much that it is barely contributing to overall permeation and $WVTR_b$ is seen to be the same as $WVTR_{md}$.
- **Test 1 and 5:** Test 5 slightly decreases the activation of the nano-defects (-7%). The $WVTR_b$ jumps significantly (due to the large number, 10^{26} , of nano-defects) to 1100% of the control value. The activation, perhaps counter-intuitively, increases by 41 kJ/mol. Again, when the Arrhenius plots are considered, it can be seen that the contribution from the nano-defects is much greater than that from the macro-defects and $WVTR_b$ is essentially $WVTR_{nd}$.

- **Test 1 and 6:** Test 6 was informed by experiment, where two films had the same activation, but differing WVTR. The activation energy of the barrier, using this model, depends directly on the ratio $WVTR_{md} : WVTR_{nd}$. Thus, if the number of nano and macro-defects were tripled, the $WVTR_b$ increases by a factor of three, but the activation remains the same. In this case, the barrier is much worse at resisting water, but still has a high activation energy (polymer + 29 kJ/mol).
- **Test 1 and 7:** Test 7, also informed by practical results, was to predict how a barrier could have the same $WVTR_b$ as the control, but a higher overall activation energy. In this case, the number of macro-defects was reduced by 10%, but the number of nano-defects was increased by 51%. As the ratio of $WVTR_{md}$ to $WVTR_{nd}$ now favours the latter, the activation energy increases by 10 kJ/mol, while $WVTR_b$ remains the same as the control.
- **Test 1 and 8:** Test 8 was to investigate how else two barriers could share the same $WVTR_b$ but have different activation energies. In this case, the activation energy of the nano-defects was increased by 3% and their number was increased by 960%. In this way, the amount of water permeating through each nano-defect decreased, but their number increased, leaving $WVTR_b$ constant, but increasing the activation by 9 kJ/mol.

These models and discussions will be referred to when considering the experimental evidence in Chapters 4, 5 and 6.

3.3.3 Qualitative Permeation: The Calcium Test

The calcium test used is based on that described by Erilat's defect imaging test [55].

The qualitative calcium test process used in this thesis consists of three stages, **calcium deposition, encapsulation and testing**.

The **calcium deposition** took place in a modified Edwards 306 evaporator, sealed in a nitrogen atmosphere glovebox. This configuration was used to minimise the sample's

exposure to moisture between the deposition step and the encapsulation step. The barrier film was cut with scissors into a 9 cm square. A mask, with four 2 cm diameter holes (made by N. Klein) was placed on the sample rig (above the evaporation boats), with the film placed, coating side down, on top of the mask. The evaporator was evacuated for 3+ hours until it reached a pressure in the range of $2\text{--}5 \times 10^{-5}$ mBar. Umicore tungsten W boats were used to evaporate 170 nm of calcium (Acros organics, granular) at a rate of 0.3-0.6 nm/sec as measured by the in-built quartz crystal rate monitor. Slight curling of the barrier sometimes produced non-circular calcium spots due to shadowing.

The glass used for **encapsulation** (3 mm float glass) was cut into 10 cm squares. The glass was cleaned with isopropanol, followed by water, and then placed into a vacuum oven (60°C) for at least 3 hours. Before evaporation and encapsulation, the glovebox was purged with nitrogen for 20 minutes and maintained at a positive pressure. After the calcium was deposited, the evaporator was vented and the barrier was removed. With the barrier and calcium face up, ~20 ml of uv-curable epoxy (Electro-lite Corporation, ELC-2500) was poured into the middle of the sample, and the glass was placed on top. The weight of the glass spread the epoxy to the edge of the barrier. The epoxy was then illuminated with a hand-held UV lamp (Intertronics IUV250 hand lamp) for 5 minutes. The time between the initial venting of the evaporation bell-jar and the curing of the epoxy was around 8 minutes.

Testing consisted of photographs of the calcium spots taken at regular intervals. The initial 0 hour photo was taken immediately after encapsulation. The sample was placed, glass side-down, on a Hancocks A4 lightbox, and the transmission photograph was taken, from above, with a Olympus SP-320 camera on a fixed height mount. The sample was placed glass side down in order to minimise contact with, and thus damage to, the barrier, but also to have a clear view of the calcium un-distorted by the bubbles present in the epoxy. The ambient lights were turned off so as to reduce glare from the polymer surface.

Once the 0 hour photograph was taken, the sample was placed inside a Genlab (MINO/6/SS/DIG, 0.35 kW, 2 A) temperature controlled oven (set to 38°C). The sample was

placed on top of a Pyrex bowl containing a solution of water and potassium chloride (Fischer Laboratory reagent P/4240/53). To stop the sample falling into the bowl, it was wrapped in a galvanized wire mesh. The solution produced a fixed humidity of 85 % RH (typical standard deviation of ~ 1.3 over 47 hours) within the oven (See Figure 37).

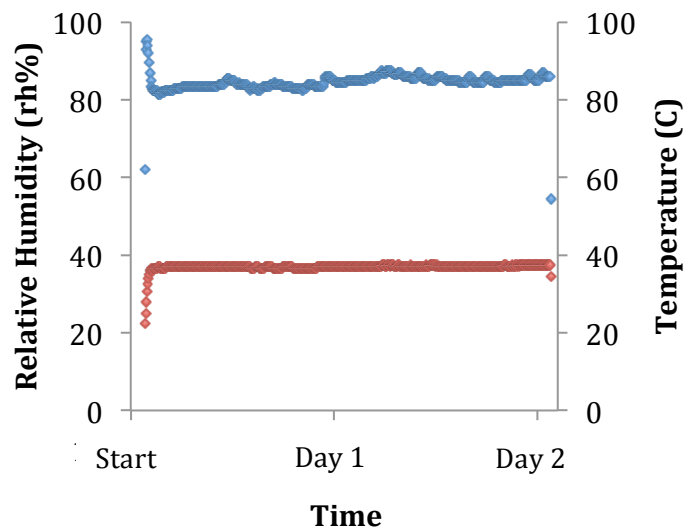


Figure 37. Example of RH and temperature measurement for the calcium test chamber.

The oven had been modified with sealant by R. Turner so as to be water proof. The humidity was recorded by a humidity sensor (Lascar Engineering EL-USB-2-LCD) placed next to, and at the same height as, the sample.

As the testing was undertaken manually (i.e. was not automated) and the camera rig was outside of the oven, the photographs were taken at different time intervals, depending on time of day. Each time the sample was removed, a photograph was taken, the humidity checked, and the salt solution was added to, before replacing the sample. This procedure could sometimes take 30 minutes, adding to the uncertainty in the method.

Multiple attempts were made to remove the source of the epoxy bubbles, but the subsequent lack of an observable contribution of these bubbles to the calcium decay (see Figure 67) lead to the epoxy being used as-received.

A note about the graphical representation of the calcium tests: the mid-point of the calcium spot corresponds to the time at which the photo was taken. This allows side-by-side comparison with samples measured at different times.

A potential source of water and oxygen is the epoxy [6]. In order to probe the sensitivity of our calcium test, a glass-glass control [6] was undertaken. This consisted of calcium deposited directly on to a glass slide with a second glass slide attached with epoxy. If it is assumed that glass is impermeable, the only sources of water would be “edge leakage” through the glass/epoxy interface or outgassing from the epoxy itself. Figure 38 shows the outcome of this test. Due to space constraints, the calcium was deposited as an irregular polygon.

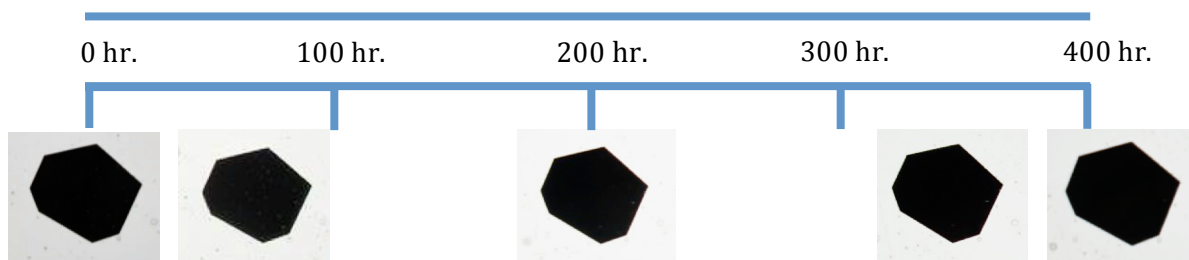


Figure 38. Qualitative calcium test of the glass-glass control slide. After 405 hours (16+ days) in 38°C and 84% RH, the calcium has not lost its opacity or shape.

Within the perceptible limits of the qualitative calcium test, the calcium in the glass-glass control slide has not become transparent anywhere.

Figure 38 also shows that the calcium has retained its shape so there has been no edge leakage. In the particular case of a Ca test of a barrier shown in Figure 39, the calcium is less than 1 mm from the edge of the epoxy. As the calcium is deposited as circles, edge leakage has occurred in the bottom right-hand corner.

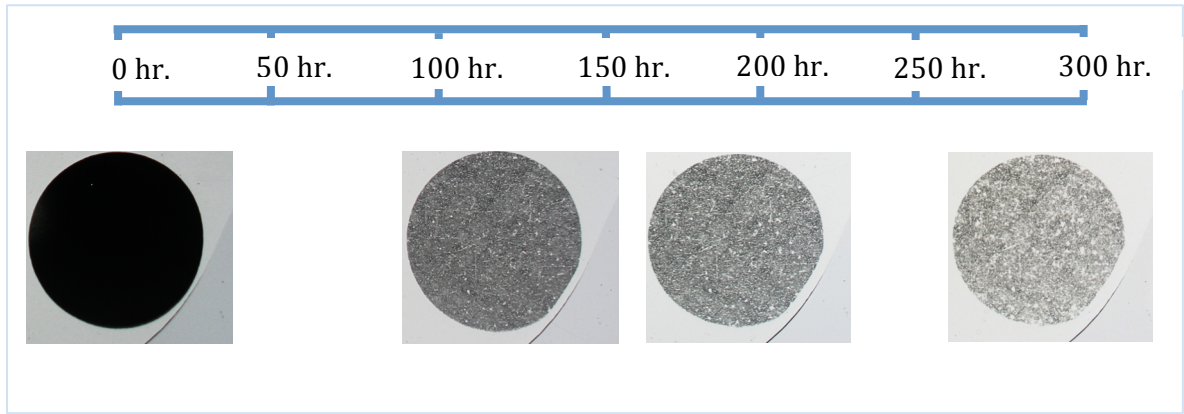


Figure 39. A calcium test that showed epoxy edge leakage. In the bottom right-hand corner, the calcium retreats from water entering through the edge.

As water permeates through the film, the calcium spot slowly becomes transparent, however, edge-leakage can still be identified, as without it, the calcium will maintain a crisp circular outline (as it does around most of the circumference), even at the later stages of the test.

For all of the calcium tests considered in this thesis, it was ensured that the distance from the edge of the epoxy to the calcium was $>1\text{cm}$. It is clear that the effect noted in Figure 39 is not present in the tests.

The uncoated substrates act as poor barriers, and this is shown clearly in Figure 40.

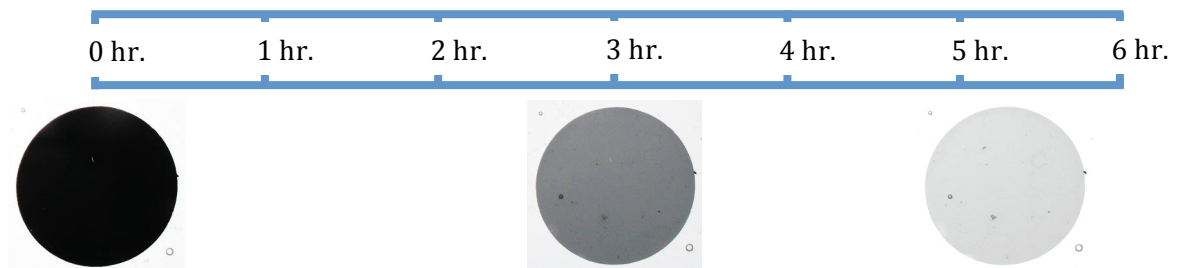


Figure 40. Calcium test of the polypropylene substrate, Rayoart CG 90. The calcium is all turned to hydroxide in only a few hours.

It is important to note that the resolution of the defect imaging calcium test is low. It is not possible to connect the concept of individual defects to spots of hydroxide in the calcium test.

Consider Figure 41.

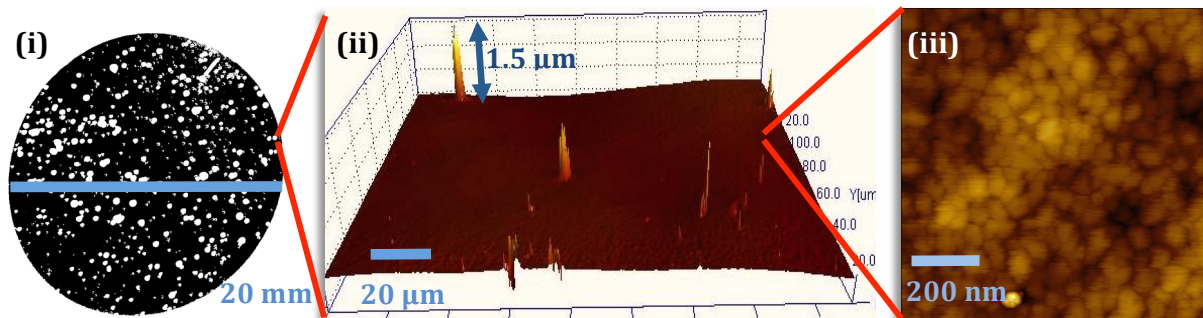


Figure 41. Schematic to explain resolution of the calcium test. A single calcium spot (i) is 20 mm in diameter, with a single small calcium hydroxide spot (pointed to) around 200 μm in size. This is the same size as the whole field of view of a MicroXAM (ii) micrograph (of the substrate). A small area of the MicroXAM image would be an entire AFM (iii) micrograph (of an AlO_x barrier).

This is a schematic to highlight that one small spot on the calcium test, is as large as the field of view of a MicroXAM image of the substrate. As was discussed in Section 1.3.2 on page 3, features on substrates can be a major source of macro-defects. Considering this, the substrate in Figure 41 (ii) has multiple micron-sized features that could be candidates for macro-defects. It would then be difficult to separate whether a spot on the calcium test was from 1, 2 or more macro-defects. This issue of resolution is compounded when looking at Figure 41 (iii). A possible candidate for nano-defects, as discussed in Section 2.3.3 on page 29, would be the intrinsic morphology of the AlO_x coatings. If the boundaries of agglomerates in Figure 41 (iii) are possible nano-defect sites, it is impossible to individually resolve these in the calcium test, and the overall gradual “greying” of the calcium could be the result of many unresolved defects acting to remove the Ca in an apparently uniform manner.

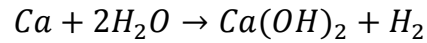
It will be shown in the following sections that cracks, pinholes and dust can be directly seen.

Lifetime Calculations

Using the measured rate of water permeation, and the known amount of calcium deposited for the calcium test, the theoretical lifetime of the calcium spots was calculated. This is the time taken for enough water to permeate through the barrier (at the rate measured by the MOCON test) to convert all of the calcium to hydroxide. Using Equation 8, and the relative

masses of the elements in question (Ca_{40} , H_1 , O_{16}) and Avogadro's constant $= 6.023 \times 10^{23}$ [99], the lifetime of the calcium was calculated.

Equation 8. Reaction between calcium (Ca) and water (H_2O) to form calcium hydroxide and hydrogen. From [6].



- Radius of calcium spot = 0.01 m
- Thickness of calcium spot = 170×10^{-9} m
- Volume of calcium in spot = 5.34×10^{-11} m³

Using the following steps, the minimum lifetime was calculated:

- Density of calcium = 1.55×10^6 g/m³
- Mass of calcium in spot = density $\times$ volume = $(5.34 \times 10^{-11}) \times (1.55 \times 10^6) = 8.28 \times 10^{-5}$ g
- Molar mass of Ca = 40 g/mol
- Mols of Ca in a spot = mass of Ca in a spot / 40
 $= 8.28 \times 10^{-5} / 40 = 2.07 \times 10^{-6}$
- Molecular mass of water = 18 g/mol
- Mass of water required to hydrolyse all the Ca in a spot = $2 \times 18 \times$ Mols of Ca in a spot
 $= \underline{7.45 \times 10^{-5} \text{ g of water}}$
- Amount of water permeating = WVTR g/m²/day
- Amount of water permeating through spot = WVTR $\times$ area of a spot = WVTR $\times \pi \times$
 $(0.01^2) = \text{WVTR} \times 3.14 \times 10^{-4}$ g/day
- Lifetime of a spot = mass of water required / (amount of water permeating through a spot)
 $= 7.45 \times 10^{-5} / (3.14 \times 10^{-4} \times \text{WVTR}) = (0.24 / \text{WVTR})$ days = $(5.76 / \text{WVTR})$ hours.

This is expected to be an underestimate of the lifetime of the spot because of the lag time of the measurement (see Section 2.2.1), which would be included in the Ca test method. If we use the permeation of substrate at room temperature (WVTR = 1.43 g/m²/day), we

predict a lifetime of 4.0 hours. This compares favourably with the Ca test result in Figure 40 (lifetime ~ 5 hours) where the difference could be accounted for by the lag time of the polymer.

3.4 Surface Characterisation

3.4.1 White Light Profilometry

In order to produce medium-range (~150 µm) micrographs, the surfaces of coatings and smoothing layers were imaged using the Omniscan MicroXAM 5000B 3d ADE Phase shift interference contrast optical profiler.

It was possible to produce clear, undistorted and representative images of the coatings on polymer substrates. Samples were cut to 2 cm x 2 cm.

Due to the multiple reflecting surfaces present, especially in the multi-layered films, the edge of the sample was located, and fringes found and enlarged, before moving in to the middle of the sample. Multiple images were produced, with the most representative presented in this report.

In the case of images taken early in the research (Figure 44, Figure 45, Figure 46 (b), Figure 86 and Figure 87) post-processing was done with the instrument's native software, MapVue.

All other images were post-processed using Origin (OriginLab, Northampton, MA).

Images presented were chosen as being representative of the general appearance of the surface or to illustrate a specific feature. All MicroXAM images were levelled but otherwise presented as-received. All images were produced using the same device at the same resolution unless specifically stated otherwise.

The MicroXAM manual reports that the device has a resolution of $z = 5 \text{ nm}$ and $x/y = 0.5 \text{ µm}$ [100].

RMS roughness values were calculated using Gwyddion [101], which calculates this value as the RMS of all of the height (Z) values in the sample [102].

3.4.2 Atomic Force Microscopy

All AFM images in this report were produced by Dr. Sverre Myhra. Small area scans of coating surfaces were carried out using the Veeco Autoprobe AFM and the Agilent 5400 AFM/SPM, in tapping and contact modes. The device, and mode used is indicated in the captions of the micrographs.

The tip used throughout, and for all devices was the MicroMasch NSC35. There was no evidence of damage to any of the samples from the AFM.

As the coatings produced in this report are insulators, surface charging made AFM imaging difficult. This effect was reduced by initially exposing the samples to a humid atmosphere at room temperature for 24 hours. The samples were then placed in a sealed container with desiccant (silica beads) for a further 24 hours to minimise any adsorbed water.

Where surface charging precluded the use of tapping mode, contact mode was used.

Post-processing of images, surface roughness and line-profiles were carried out using Gwyddion [101].

In one instance (Figure 56) additional post-processing was done using WSxM [103].

In order to ascertain the trend for agglomerate size in the coatings, these were measured manually using multiple line profiles. An example of one is reproduced in Figure 42.

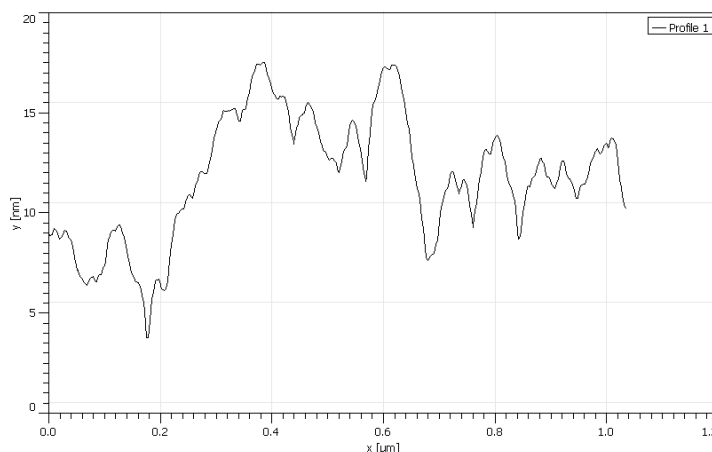


Figure 42. Line profile of an AFM micrograph.

Agglomerate heights were designated as the z-difference between minima and their adjacent maximum, with agglomerate width defined as the distance between subsequent minima.

3.4.3 Ellipsometry

Thickness measurements were carried out with the Rudolph Auto EL Ellipsometer. It uses a 0.2mW He-Ne laser with a wavelength of 632.8 nm.

A calibration film of SiO_x deposited on Si was scanned to confirm the alignment of the laser and the correct functioning of the device.

The films were measured as-deposited on silicon chips placed alongside the polymer substrates during deposition. The coatings were scanned 5 times and average values for thicknesses and refractive index were reported.

3.4.4 Contact Profilometry

Coating thicknesses were confirmed using the Veeco DekTak 6M stylus profiler. Silicon chips (1 x 1 cm) are included on the webcoater drum with the polymer substrates for every deposition. These are attached with kapton tape, which can be removed, leaving a “step” of deposited material and uncoated silicon. The profiler tip is scanned across this step. 5 scans

are performed and the mean step height is reported. Before use, the tip optically inspected scanned across bare silicon to ensure it was not contaminated or damaged.

3.4.5 Optical Microscopy

Scratches produced through the nano-scratch test (see Section 3.6.1) were imaged using the Reichert Polyvar Met Optical Microscope. Images were produced in reflection mode.

3.5 Barrier Quality

3.5.1 XPS

X-Ray Photoelectron Spectroscopy of the samples were carried out on the Thermo Scientific K-Alpha by Dr Phil Holdway and Dr Hugh Bishop.

XPS of the samples were performed, both as-received, and after 420 seconds of a 500 eV argon ion-beam etch.

Survey scans recorded the elemental ratios of the films. More detailed scans of the key elements under investigation (Al, N, O, C) were also performed in order to investigate chemical bonding.

A depth-profile of one sample was performed. This was an iterative processes that consisted of 5 seconds of IB etch, followed by an XPS scan. This was repeated 35 times in order to map the change in elemental composition with sample depth.

3.5.2 UV-VIS

The Varian Cary 5000 UV-VIS-NIR spectrometer was used in order to measure the optical transmission of the barriers.

2 cm x 2 cm sections of the barriers were cut out, with each barrier tested in two different locations to confirm uniformity.

For each batch of samples, the spectrum of the PP substrate was also measured.

A linear relation between film thickness and absorption was assumed. In order to compensate for slight variations in film thickness, the following normalization of the data was performed, before plotting:

$$Abs_{Total} - Abs_P = Abs_C$$

$$\frac{Abs_{Cn}}{(Abs_{Cn}/Abs_{C0})} = N Abs_{Cn}$$

$$N Abs_{Cn} + Abs_P = N Abs_{Total}$$

Equation 9. Normalisation of UV-VIS-NIR data for thickness.

where Abs_{Total} is the absorption measured at each wavelength by the spectrometer, Abs_P is the absorption measured for the polymer at that point, Abs_{Cn} is the calculated absorption due to the coating alone, Abs_{C0} is the absorption of the thinnest film to which all other films are being normalised, $N Abs_{Cn}$ is the normalised absorption of the coating, $N Abs_{Total}$ is the normalised absorption for the barrier.

This normalisation aids comparison within the sample batches, but care is taken with comparison between samples within different normalisation regimes.

The average transmission in the visible (390 nm- 780 nm [104]) was calculated as the mean of the transmission at each measured wavelength.

3.5.3 FTIR

The Varian Excalibur FTS 3500 FT-IR was used to test the cure of the TRPGDA smoothing layers.

Initially 1-2 ml of the TRPGDA monomer was placed into the sampling area and scanned. After this, the sampling area was thoroughly cleaned with IPA. Then the TRPGDA-coated substrates, cut to 2 cm x 2cm, were inserted and scanned.

The method of Affinito was used in order to contrast the peaks of the uncured monomer to the spectrum of the cured polymer [28].

3.6 Mechanical Properties

3.6.1 Nano-Indentation

The MicroMaterials NanoTest was used to for all nano-scratch tests. All measurements and analysis were done by Dr. J. Moghal. Further description of the operation of the device is described in Section 2.2.5.

The scratches were imaged (see Section 3.4.5). Dr. S. Myhra performed AFM scans on the scratches in order to characterise the nature of the barrier failure.

4 Aluminium Oxide

4.1 Making Sputtered Barriers

This chapter investigates how different deposition conditions affect the performance of barrier oxides. Section 4.1 covers the importance of understanding target poisoning and how the substrate can affect the nature of the coating that forms on it. The subsequent sections deal with how sputter power (Section 4.2), barrier thickness (Section 4.3) and drum speed (Section 4.4) affect different barrier characteristics.

4.1.1 Hysteresis

Section 2.1.6 covered the theoretical considerations of sputtering and hysteresis. It is important to investigate the hysteresis of the reactive sputtering process in order to ensure maximum delivery of reactive gas without “poisoning” the targets, i.e. producing an excess of the oxide on the cathodes. When too low an amount of reactive gas was used, the coatings appeared brown under optical inspection. This is supported by the literature, Berg states that films with low reactive gas flows are sub-stoichiometric, having too much of the metal in the films [43].

In order to produce a “hysteresis loop”, reactive gas flow is increased until a sharp drop in voltage is observed and the point of poisoning is identified. However, the time taken between these changes in gas flow affect the nature of the hysteresis loop, which can be seen in Figure 43.

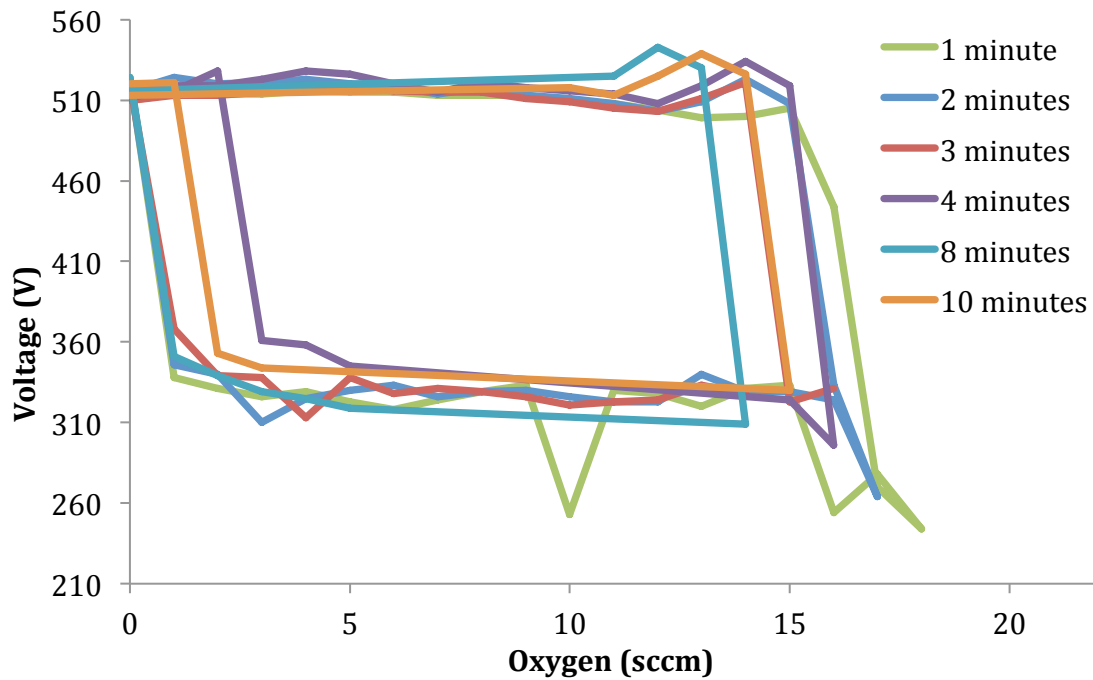


Figure 43. A comparison of the nature of the hysteresis of the RF reactive sputtering system with different time taken between reactive gas flow changes.

For example, if only 2 minutes are taken between gas flow changes, poisoning occurs when the reactive gas flow has been increased to 16 sccm. However, if the time between changes is increased, the point of poisoning can be only 14 or 15 sccm. This is because there is a delay between the alteration in the gas-flow taking place at the mass flow controller and this change making its way down the intervening pipe into the webcoater, followed by the equilibration of the partial pressure in the sputter zone.

What can be seen in Figure 43 is the expression of this delay. For the 2 minute run, at 15 sccm, enough gas had been selected to poison the cathodes, but this change had not yet registered at the cathodes. This is important because reactive-sputtering deposition takes place at a reactive gas flow below but as close to the poisoning point as possible. This balancing act is needed in order to produce clear, stoichiometric coatings with stable conditions throughout the whole deposition time.

As the time taken for gas flow changes is increased, the system comes closer to the dynamic equilibrium for that flow rate. This can be seen as the system poisoning at lower flow rates.

Hysteresis loops were recorded before each deposition.

RF sputtered aluminium oxide coatings are amorphous [87][105]. Cremer's study indicates that high temperature substrates (350-600°C) are required to produce crystalline alumina by reactive sputtering [106].

4.1.2 Substrate Considerations

Section 1.3.1 dealt with polymers and the different parameters to be considered when choosing a substrate. This section investigates the nature of the substrate used in this project, Rayoart CG 90 (bi-axially oriented polypropylene) made by Innovia Films, and compares it to an industry leader used in the fabrication of OLEDs, DuPont Teijin's Teonex Q65 (bi-axially oriented polyethylene naphthalate). Table 6 compares these two polymers' vital statistics.

Table 6. A comparison of the principal substrate for this study, Innovia's Rayoart CG 90, with an industry leader, DPT's Teonex. This information was collated from data sheets published by Innovia (*) [107] and DPT () [108], [109] with details provided through private communications with these companies (PC). MD- Machine Direction, TD –Transverse Direction. Square bracketed terms refer to the standard tests used to ascertain these values.**

Polymer	Rayoart (CG90) -PP	Teonex (Q65FA) - PEN
Thickness (μm)	90 *	125 **
Density (kg/m ³)	909.1 *	1360 **
Cost (£/kg)	3.50 ^{PC}	96.72 ^{PC}
Refractive Index	1.5 ^{PC}	1.5 **
Tensile Strength (MPa)	190 * MD [ASTM D 882]	226 MD ** [JIS C 2318]
	170 * TD [ASTM D 882]	237 TD ** [JIS C 2318]
Young's Modulus (MPa)	2000 * MD [ASTM D 882]	5060 MD ** [ASTM D 882-67]
	1900 * TD [ASTM D 882]	6240 TD ** [ASTM D 882-67]
Thermal Stability (%)	0.3 MD * (70°C/10 min)	-0.02 MD ** (150°C/30 min)
	-0.4 TD * (70°C/10 min)	-0.02 TD ** (150°C/30 min)
Melting Point (°C)	160 ^{PC}	269 **

The Rayoart CG90 is an industrial grade polymer, primarily used for packaging graphics. A clear advantage of this film over Teonex is that it is over 27 times cheaper per kilo for a multi-ton order. On the other hand, the better thermal stability of the Teonex opens up the possibility of higher temperature processing (see Section 2.1). The greater stiffness of the Teonex could help reduce the macro-defects induced by post-deposition handling, described by others [11], [12].

Another clear advantage that the Teonex has over the Rayoart is surface smoothness and uniformity. Consider Figure 44, the MicroXam micrograph shows a smooth planar surface with only asperity over the size of 50 nm.

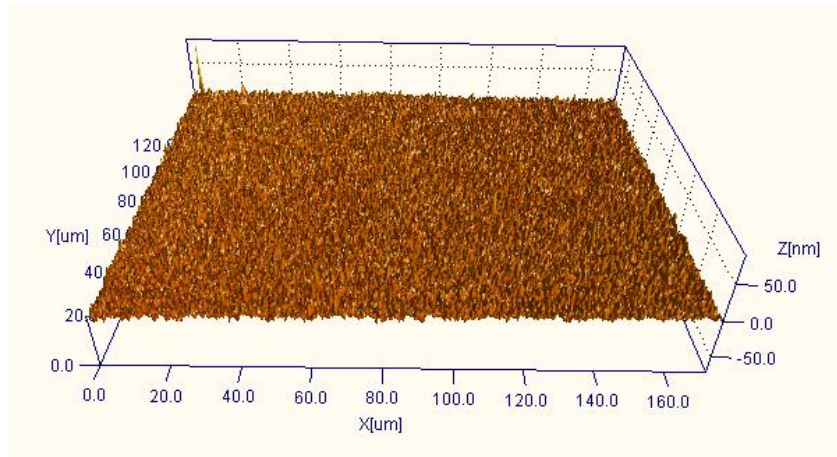


Figure 44. MicroXam image of Teonex Q65. A smooth surface with only 1 asperity larger than 50 nm.

The Rayoart CG 90, shown in Figure 45, has several large asperities with one just under 1.5 μm.

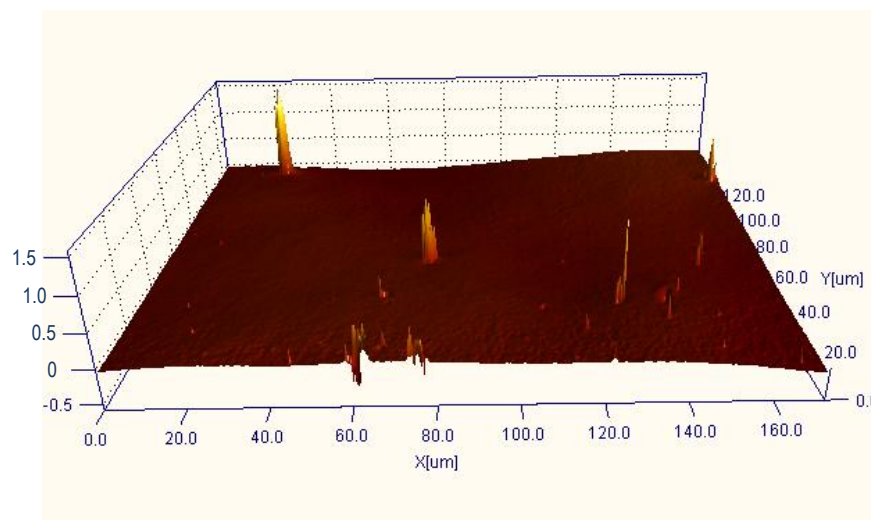


Figure 45. MicroXam image of Rayoart CG 90 (PP). The surface is characterised by 4 asperities over 500 nm in height.

Other less common features on the Rayoart include gouges (see Figure 47) and drip sites where hot polymer has pooled [Innovia, Private Communication].

Rayoart CG 90 is characterised by large asperities. Local (sub-micron) measurements of surface roughness do not give an accurate representation of the surface, and the wider views in Figure 45 are required in order to understand the permeation results. It is posited that the larger micron-sized features in the Rayoart CG90 are anti-block particles. Innovia confirmed

that anti-block particles are used in the film to avoid the adhesion of the polymer to itself when stored as a roll. These particles can be up to 5 μm in diameter and are dispersed in the polymer matrix, and by design can protrude from the surface by as much as 2 μm (by our measurement). Figure 46 shows, side-by-side, an optical and MicroXam image of different sections of the polymer.

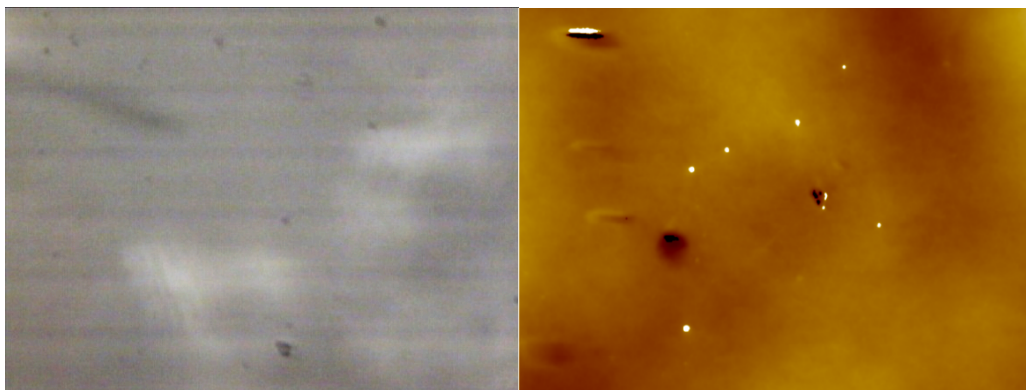


Figure 46. a) Optical reflection microscope image on a CRT (hence horizontal lines). Image width is $\sim 150\ \mu\text{m}$. Dark spots are visible. b) MicroXam Image, width of is $138\ \mu\text{m}$, height bar is from: white = $0.45\ \mu\text{m}$ to black = $-0.45\ \mu\text{m}$. Although image a) and b) are not of exactly the same area, a similar pattern of particles can be seen.

These micron-sized features were a key consideration for this project, especially as the oxides deposited are of the order of 100 nm thick. The inability of sputtered oxides to conformally cover such large features was shown in Section 2.4.2.3. Any discontinuities in the oxide could form possible permeation routes. As was mentioned in Section 1.3, these large features are a concern for OLEDs as their active elements are only of the order of 100 nm [9]. Work on covering these features is outlined in Chapter 6.

Table 7 shows the intrinsic permeation characteristics of the two polymers. It can be seen that Rayoart is the better intrinsic barrier to water permeation; the WVTR at 38°C is the same (to 2 S.F.) as the Teonex, however it achieves this with only 72% of the thickness and 66.8% of the density. It can be seen from Table 7 that the permeability (see Equation 4) of Teonex is 41.8% higher than Rayoart. The activation energy of the Rayoart is 13 kJ/mol

higher than the Teonex; the PP exacting a larger energetic cost from each mol of water passing through it.

Table 7. Permeation characteristics of substrates and films. The oxide in both cases was deposited at 1.85 kW, at 50 m/min drum speed for 10 minutes. N.B: in the WVTR measurements, Δp is a constant, representing the concentration gradient between the 100% RH (wet cell) and the 0% RH (dry cell), in the calculations it was assumed $\Delta p=1$. The lowest WVTR measured was used in the permeability calculations. Higher WVTR values could be due to induced defects or handling damage, but the lower values would tend towards the minimum value. Permeability of coatings was determined by ideal laminate theory. This table was originally published in [131].

Film	Thickness (μm)	WVTR at 38°C ($\text{g}/\text{m}^2/\text{day}$)	Activation Energy (kJ/mol)	Barrier Improvement Factor	Permeability ($\mu\text{m}.$ $\text{g}/\text{m}^2/\text{day}$)
Teonex	125	1.46	54	-	182.5
Teonex /AlO_x	125 / 0.148	0.054,0.076	84,95	19-27	0.0083 (coating)
Rayoart	90	1.43	67	-	128.7
Rayoart / AlO_x	90 / 0.145	0.38	104	4	0.075 (coating)

Table 7 also shows that adding a similar oxide film (identical deposition conditions) to each polymer gives very different results. The addition of 148 nm of AlO_x on the Teonex gives a BIF of between 19-27, whereas a film of identical composition on Rayoart CG90 only gives a BIF of 4. The permeability of the films alone has the AlO_x on Teonex as nine times less permeable than the AlO_x on PP/Rayoart. This underscores the importance of the substrate in the barrier performance of the oxide that is deposited on it.

There are a number of possible reasons for the superior performance the Teonex/AlO_x barrier. Better adhesion to the PEN, afforded by the more favourable bonding environment

(see Section 4.1.2.1), could reduce delamination and cracking. Another consideration, described in Table 6, is that the Young's modulus of the Teonex is a factor of 2.5 greater than that for the Rayoart, which could reduce post-deposition stresses from handling. This is enhanced by the fact that the Teonex is 38% thicker than Rayoart.

Bringing to bear the activated rate theory outlined in Sections 2.3.2 and 2.6, and in particular the concepts of Roberts [27] and Tropsha [57] on Table 7, it can be seen that even though the WVTR for the Teonex/ AlO_x is a factor of 7 lower than the Rayoart/ AlO_x , the latter has an activation energy 9-20 kJ/mol higher.

As water vapour transport dominated by permeation through macro-defects would exhibit the activation energy of the substrate, the higher activation energy for the oxide coated substrates points to a significant amount of permeation through nano-defects in both cases.

Considering the Model examples from Section 3.3.2, there are two clear (but perhaps not mutually exclusive) possibilities that could explain these results.

Case A: The WVTR for Teonex/ AlO_x is much lower than for PP/ AlO_x , but the activation energy of the former is also slightly lower. Thus for Teonex/ AlO_x there is a lower flux (indicating a lower area of defects) but a slightly greater proportion of this reduced flux passes through macro-defects. This does not mean that in *absolute terms* there are more macro-defects present in the Teonex/ AlO_x . The model suggests that a greater proportion of this lower flux passes through macro-defects, but there would have to be an overall lower number of these macro-defects in order to exhibit such a low WVTR. As can be seen for Test 2 in Section 3.3.2, when the number of Nano-defects are doubled, there is a 12 kJ/mol increase in activation, but only a small (0.02 g/m²/day) increase in WVTR. In order to see a reduction of 0.33 g/m²/day whilst only seeing a small reduction in activation, it would be expected that both macro and nano-defects would need to be reduced, but nano-defects more so.

Case B: The model points to another possibility; that there is a difference in the activation energy of the nano-defects. As has been discussed in Section 2.5.1, the nature of the substrate

greatly influences the formation of the oxide layer. It is possible that as with Test 5, if the nano-defects of the PP/ AlO_x are easier to pass through, there would be more flow through them, thus raising the activation energy but also greatly raising the WVTR.

It is not clear which model best describes these results, or whether it is a combination of the two. What is clear is that Teonex/ AlO_x performs better as a barrier due to the nature of the substrate.

The questions are posed:

“Why does the Rayoart produce such a large number of nano-defects in identically deposited aluminium oxide compared to that on Teonex?”

“What can be done to reduce the number of nano-defects in a film?”

4.1.2.1 Surface Morphology

A study by Deng [11] discussed the difference in the nucleation and growth of e-beam evaporated AlO_x deposited on two different substrates, PET and PP. Even though the same material was deposited, the way the oxide formed was different [11]. Deng observed that the AlO_x on the PET exhibited finer nucleation, whereas it formed larger agglomerates on the PP [11]. Cueff reports bonds formed between sputtered AlO_x and PET, recording the existence of Al-O-C bonds in the interface of the coating and substrate [87]. Deng and Cueff both suggest the carbonyl groups in the PET act as sites for bonds to form with the AlO_x [11], [87]. The following quote from Deng about AlO_x bonding on PP is instructive:

“The low surface energy and polarity and the lack of suitable chemical groups for chemisorption in PP means that growth on PP proceeds by preferential attachment to pre-existing oxide sites leaving an agglomerate morphology with increased surface roughness [11].”

PEN (Teonex) also contains carbonyl groups (see Figure 34). Preferential nucleation on these sites and the unfavourable nature of PP described above may go some way to account for the differences in permeation through the Rayoart/ AlO_x and the Teonex/ AlO_x .

Deng also noted that the AlO_x formed on PP would have greater intrinsic surface roughness due to preferential-attachment to earlier-arriving AlO_x and greater pore size [11]. This appears to agree both with the permeation data in Table 7 and the following results.

A side-by-side comparison of the substrates and the oxides deposited on them adds to this discussion. The following micrographs, produced with the MicroXam: Figure 47, Figure 48 and Figure 49 all have identical scales and z-palette colour bars, aiding this comparison.

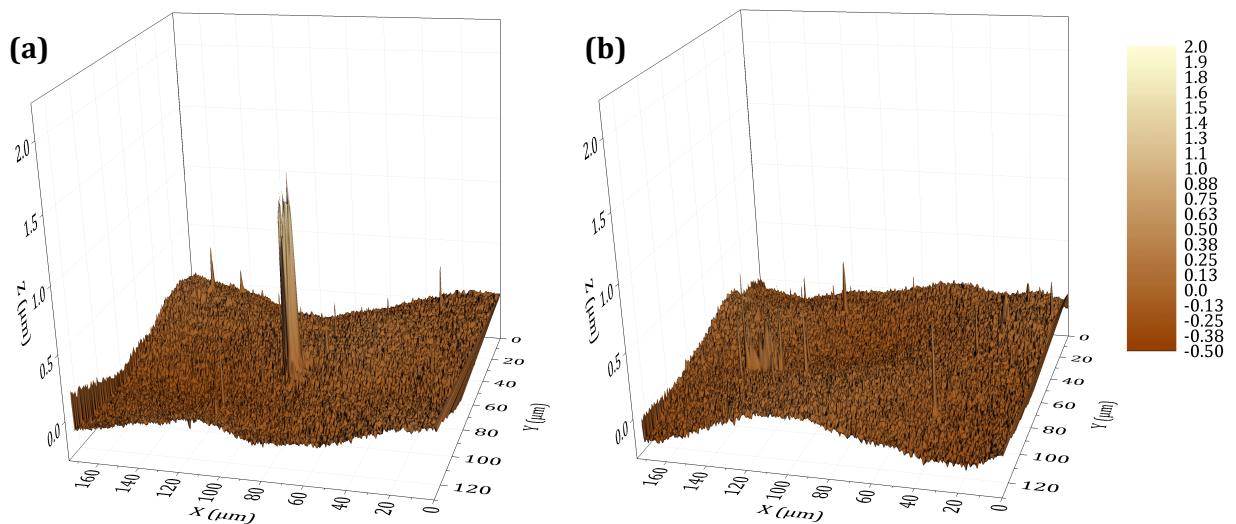


Figure 47. MicroXam (a and b) of the Rayoart CG90 polypropylene substrate. The (a) image centres on a large asperity. The (b) image shows a chain/gouge from substrate processing [PC, Innovia].

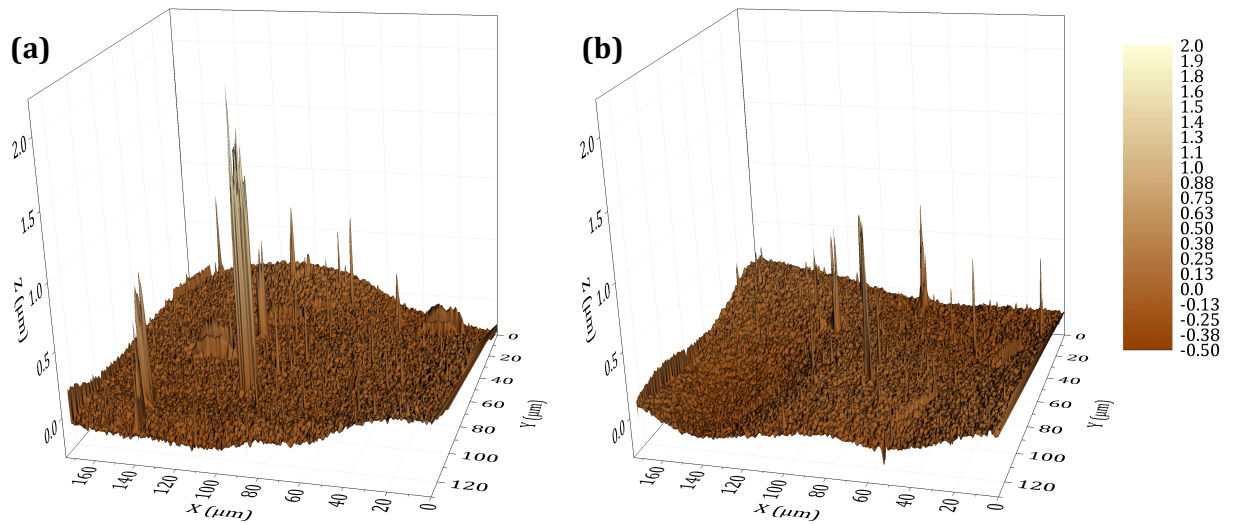


Figure 48. MicroXam (a and b) of aluminium oxide coated Rayoart CG 90 polypropylene. (a) shows multiple asperities of over 1 micron in size. (b) also shows micron-order asperities as well as gouges. N.B this is a coating of 117 nm, which is thinner than that studied in Table 7.

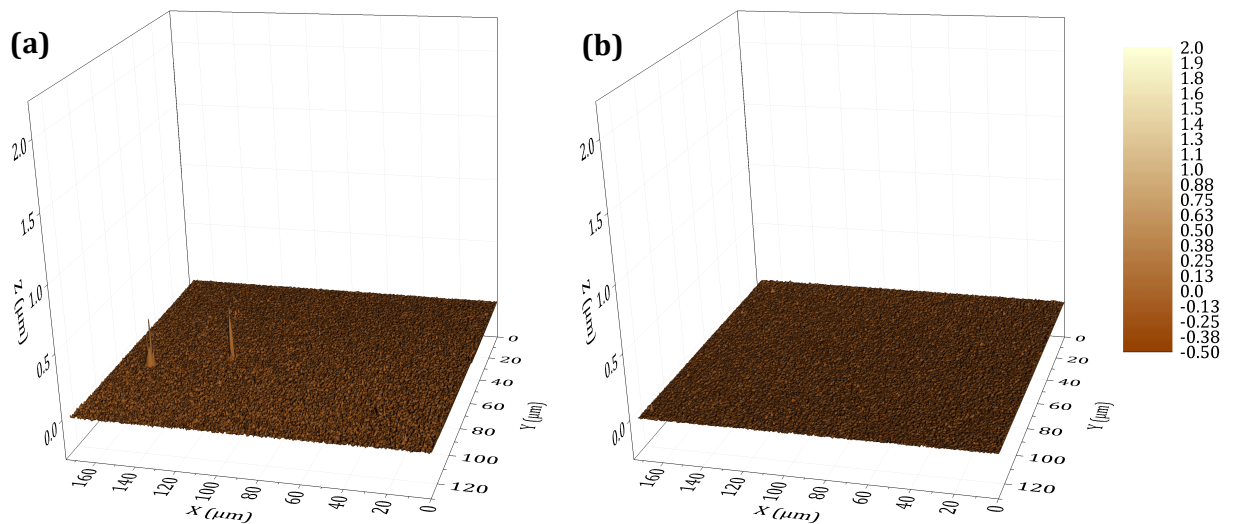


Figure 49. MicroXam (a and b) of oxide coated DPT Teonex. Two 400-500 nm asperities are visible in (a). No features over 100 nm are visible in (b).

Figure 47 displays the Rayoart CG 90 PP substrate. Figure 47 (a) shows a large asperity, probably an anti-block particle. The bottom right hand section of Figure 47 (b), shows a gouge mark, suggested [Innovia, PC] to be damage from the mass production process. Upon optical inspection the intervening polymer appears to have a fairly consistent level of surface roughness. These types of features are repeated in Figure 48, the scan of AlO_x on PP, even though this is a different sample. Figure 48 (a) shows two large asperities, one at around 1.5

μm in height, with a series of smaller, sub micron peaks. Figure 48 (b) also has a number of micron-sized peaks. Comparing Figure 47 and Figure 48 it could be argued that, qualitatively, the oxide has a greater number of features. This is borne out by the RMS data in Table 8, below.

Initial roughness data exhibited high RMS values for the PP substrate in Figure 47 ((a) = 85 nm, (b) = 73 nm), but this was partly due to the overall undulatory nature of the sample, in contrast to the “flat” Teonex in Figure 44. As RMS is calculated as the root of the average of the squared deviations from a “global” mean [110], the long wavelength waviness of the surface gives large deviations from the mean, hence a large roughness which does not necessarily correspond to “local” roughness.

The MicroXam micrographs presented are “as-received”, but all of the RMS values reported have undergone a 10th order polynomial background subtraction to remove the contribution to RMS from this long wavelength waviness.

Table 8. Root mean square roughness of the MicroXam images calculated using Gwyddion [101]. All samples underwent a 10th order polynomial background subtraction, except for *, which was levelled. This table was originally published in [131].

Sample	RMS Roughness (nm)	
PP [Rayoart] (Figure 47)	(a)	48
	(b)	22
PP/AlO _x (Figure 48)	(a)	73
	(b)	25
Teonex (Figure 44)	-	3.5*
Teonex/AlO _x (Figure 49)	(a)	5.8
	(b)	2.9

There is a stark difference between Figure 48 (PP/ AlO_x) and Figure 49 (Teonex/ AlO_x).

Although Figure 49 (a) has two clear features around 500 nm, the rest of the area has no resolvable features. This is even more striking for the Figure 49 (b), which contains no features over 60 nm.

It should be noted that the Z-scales of Figure 47, Figure 48, and Figure 49 are exaggerated. The X (175 μm) and Y (130 μm) are much larger than the Z (2.25 μm), giving all features a stretched appearance. In order to further investigate the nature of the surface roughness, images of one quadrant of each of these figures has been reproduced (See Figure 50, Figure 51 and Figure 52). In each case, a section away from the larger asperities was chosen and the Z scale was exaggerated to an even greater extent, with the maximum set to 1 μm . The colour bar is the same as in the previous figures.

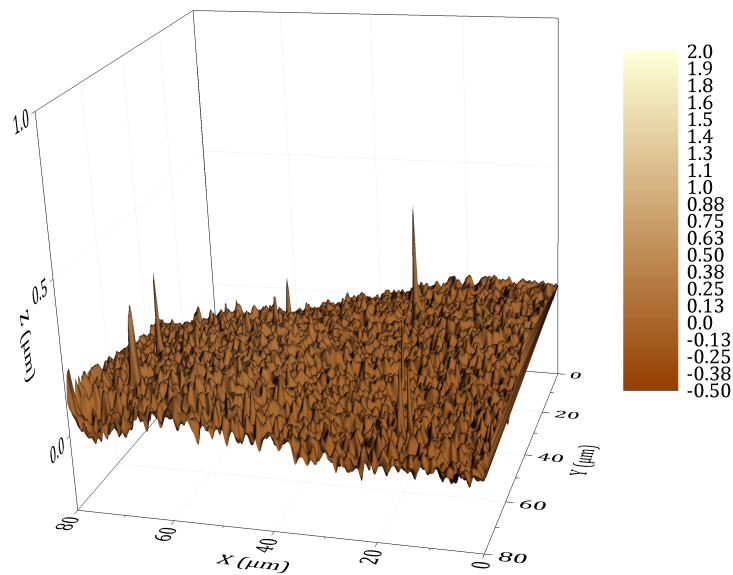


Figure 50. An expanded view of Figure 47, (a) of the top-right quadrant. Image of the Rayoart CG 90 PP substrate. Shows the nature of the surface roughness away from the major asperities.

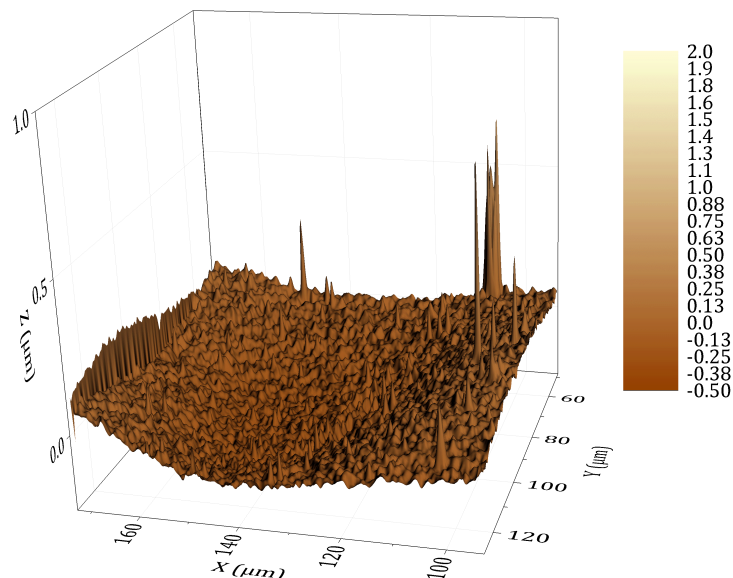


Figure 51. An expanded MicroXam image of Figure 48, (b) of the bottom-right quadrant. Image of AlO_x on PP.

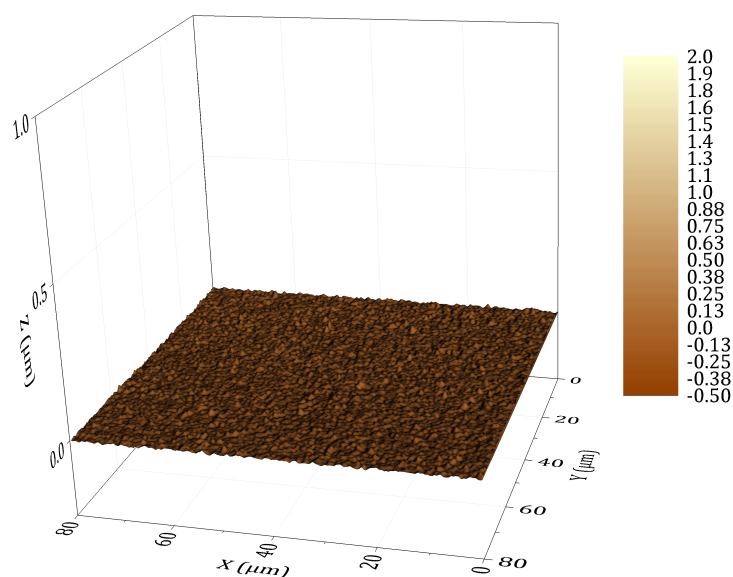


Figure 52. An expanded MicroXam image of Figure 49 (b) of the top-right quadrant. An Image of AlO_x on DPT Teonex.

These zoomed-in figures show how strongly the substrate affects the nature of the oxide formed on it. The roughness and shape of the features in Figure 50 (the PP substrate) and Figure 51 (AlO_x on PP) are indistinguishable. When Figure 51 (AlO_x on PP) is compared with Figure 52 (AlO_x on Teonex), it can be seen that although the layers of AlO_x are deposited in identical conditions, the substrate is the decisive element in the oxides' morphologies.

Table 9. RMS roughness of the expanded MicroXam scans calculated using Gwyddion [101]. All samples underwent a 10th order polynomial background subtraction except for *, which was levelled.

Sample	RMS Roughness (nm)
PP [Rayoart] (Figure 50)	23.5
PP/AlO_x (Figure 51)	16.8
Teonex (Figure 44)	3.5*
Teonex/AlO_x (Figure 52)	2.9

If these micrographs are considered in conjunction with the permeation results outlined in Section 4.1.2, Table 7, it is argued that the increased general roughness, not to mention the large asperities of the Rayoart PP, could contribute to the numerous permeation routes.

4.1.2.2 Qualitative Permeation: The Calcium Test

Calcium tests were performed for the Teonex/AlO_x and the Rayoart/AlO_x. As was the case with the micrographs in Section 4.1.2.1, the Rayoart/AlO_x is a different sample, with a thinner oxide coating of 117 nm. For ease of comparison, Table 10 shows the permeation values of the same samples used in the calcium test.

Table 10. Comparison of the permeation characteristics of oxides deposited on two substrates, DPT Teonex and Innovia Rayoart. Deposition conditions were 1.85 kW sputter power and 50 m/min drum speed.

Film	Thickness (μm)	WVTR at 38°C ($\text{g}/\text{m}^2/\text{day}$)	Activation Energy (kJ/mol)	Permeability ($\mu\text{m. g}/\text{m}^2/\text{day}$)
Rayoart / AlO_x	90 / 0.117	0.21, 0.23	100, 100	0.037 (coating)
Teonex / AlO_x	125 / 0.148	0.054, 0.076	84, 95	0.0083 (coating)

As was the case in Table 7, Table 10 shows that Teonex/ AlO_x exhibits a low WVTR, with nearly 4 times more water vapour passing through the Rayoart/ AlO_x . However the activation energy of the Rayoart/ AlO_x is 5-16 kJ/mol higher.

The results of the calcium test can be seen in Figure 53.

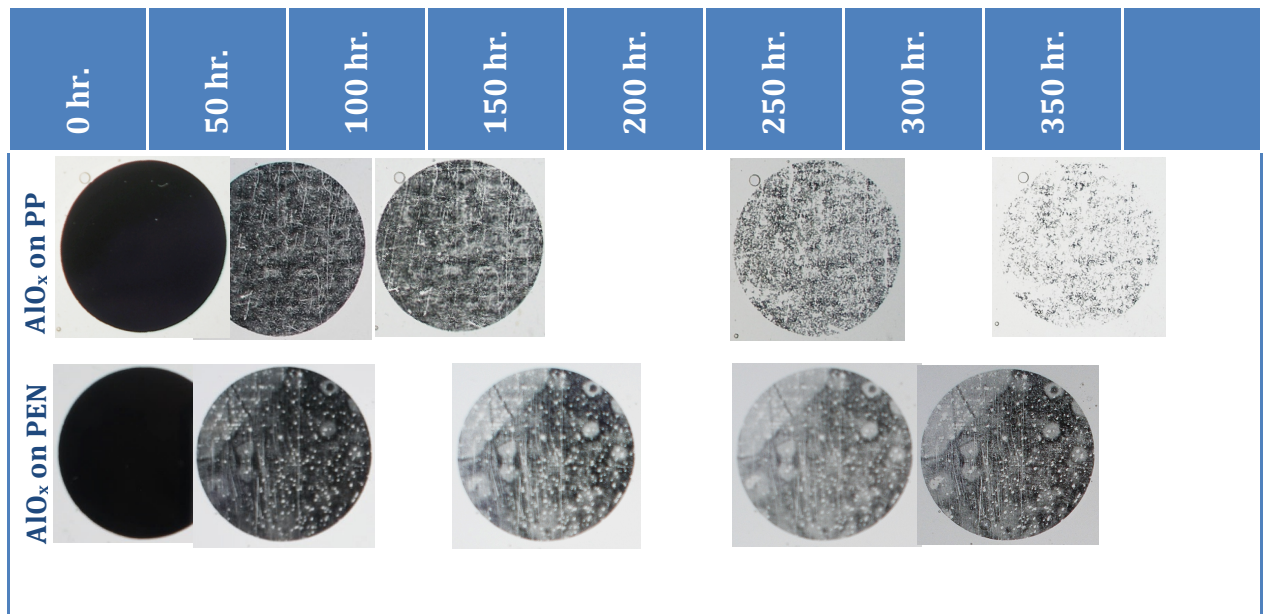


Figure 53. Calcium test of AlO_x on two different substrates, PP (Rayoart, Innovia) and PEN (Teonex, DPTJ). Note, the AlO_x thickness on the PP is 117 nm, and the AlO_x on the PEN is 149 nm. This figure was originally published in [131].

The decay of the calcium is markedly different between the two samples. The Teonex has a larger proportion of calcium remaining at 300-350 hours (i.e. it is less permeable, consistent with the WVTR measured with the MOCON). Whereas the calcium deposited on the Rayoart/ AlO_x undergoes a fairly uniform thinning, with some cracks and substrate scratches

visible, the calcium on the Teonex/ AlO_x barrier displays an asymmetric “moonscape” of decay. Small spots where all of the calcium has been converted into calcium hydroxide appear after only 50 hours, and large features that turn clear more quickly than other regions. However there are regions between these features, which after 300 hours still maintain a significant level of opacity over that of the Rayoart/ AlO_x . These features are unique in this project to the calcium test of Teonex/ AlO_x .

As with Section 4.1.2, Table 10 shows that the lower activation of the Teonex/ AlO_x coupled with the low permeation indicates fewer permeation routes than the Rayoart/ AlO_x . The differences in Figure 53 could be an expression of a higher amount of flux in Rayoart/ AlO_x through macro and nano-defects, but as was described in Figure 41, the low resolution of this technique in comparison to the small size of the nano-defects ($\sim 0.3\text{-}1\text{ nm}$ [27]) precludes the results in Figure 53 being used as a direct measure.

The minimum theoretical lifetime of the calcium is considered, using the method described in Section 3.3.2, which consists of calculating the time taken for the lowest recorded WVTR to convert all the calcium in the test spots:

- PP/ AlO_x = 27 hours
- PEN/ AlO_x = 105 hours

This application of the WVTR results, calculated by a steady-state test like the MOCON Permatran, illustrates a clear difference between the tests. All calcium tests in this report vastly out-perform the theoretical lifetimes for the samples but the Ca test does not include the lag time; unlike the MOCON, where a conditioning period established a steady flow before measurement, the calcium test starts the moment the sample is encapsulated and removed from the glove box. Also, Graff points out that the calcium test is not a steady-state test, and that water vapour collects inside the encapsulation [3].

4.2 Power Comparison

This section looks at how the power of the sputtering process can affect the nature of the barriers deposited. As was discussed in Sections 2.1.6 and 3.1, RF reactive sputtering is sensitive to many different deposition conditions. Increased power increases the deposition rate, which is consistent with theory (Section 2.1.6). The maximum power used throughout this project was 2.05 kW, since at 2.2 kW, the PP underwent observable thermal shrinkage. As can be seen from the intercept of the trend-line with the x-axis, a rough estimate can be made of the minimum power required to sputter from the Oxford system (~ 1 kW, at the recorded pressures of $\sim 3 \times 10^{-4}$ mBar).

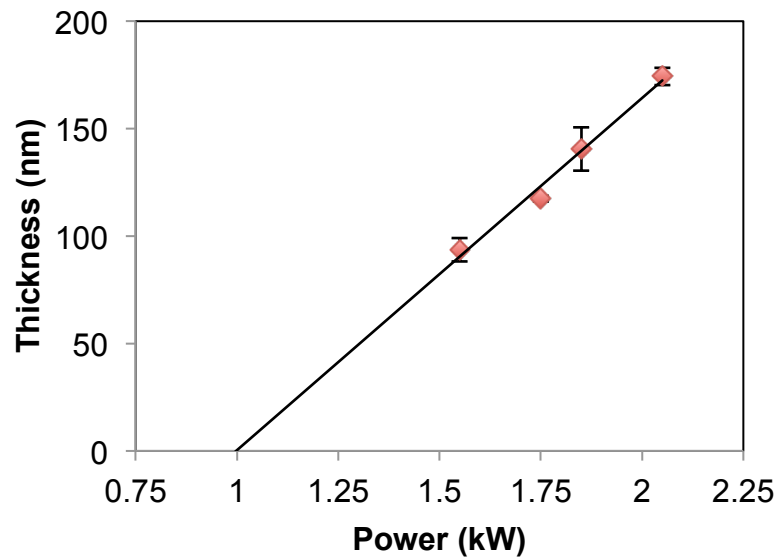


Figure 54. Thickness of coatings produced at different powers with fixed deposition time of 10 minutes.

In this section, three barrier layers produced at different powers were made with the same thickness by changing the duration of deposition (see Figure 55).



Figure 55. Schematic to illustrate deposition power is inversely proportional to deposition rate.

Three barriers produced at different powers are qualitatively different from each other.

This figure was originally published in [131].

High power sputtering produces barriers of desired thickness in fewer rotations, thus with fewer “sub-layers”. It should be noted that the term “sub-layer” is a conceptual tool, and we have no evidence of distinct, sub-layers; the oxide appears as a monolithic layer. Suttle’s detailed depth profiling (ToF SIMS) of AlO_x saw no repeated stoichiometric changes and the oxide appeared as a homogenous material [38]. As will be seen in the following sub-sections, the structural and optical nature of these barriers is different.

4.2.1 Surface Morphology

The surface morphology of the coatings was studied by AFM. All AFM images were recorded by Dr Sverre Myhra. Initial attempts to produce images were frustrated by surface charge (perhaps remaining from the sputter deposition), which did not allow tapping mode to be used (PC, S. Myhra). The charge was reduced using the technique outlined in Section 3.4.2. The 2.05 kW sample, with relatively large features, was imaged using the Veeco Park AutoProbe AFM in tapping mode. The Veeco AutoProbe, however, struggled to produce resolvable images of the 1.85 kW and 1.55 kW samples. Therefore the Agilent 5400 AFM/SPM was used for these samples, but residual charging made it impossible to use tapping mode. Contact mode was used for these images, albeit with a tapping mode tip.

Considering Figure 56, Figure 57, and Figure 58, it can be seen that the surface is made up of regular aggregates of material. Upon comparison, it can be seen that higher deposition power produces coatings characterised by larger aggregate sizes.

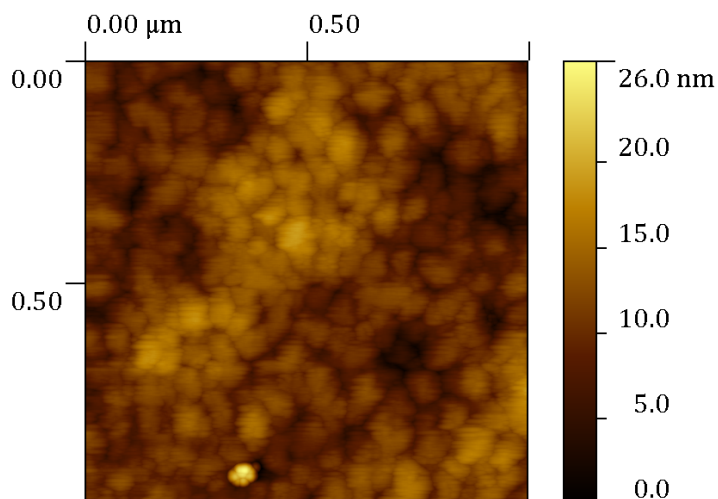


Figure 56. AFM image of the 2.05 kW AlO_x coating on PP. Produced using the Veeco Autoprobe AFM, in tapping mode using the MicroMasch NSC35 tip. Area is 1×1 μm, 512×512 pixels. Post-processing was done using Gwyddion [101] and WSXM [103]. Image taken by Dr Sverre Myhra. The material coating measured here was a different sample to that used for XPS the calcium test, MOCON but produced in identical deposition conditions. This figure was originally published in [131].

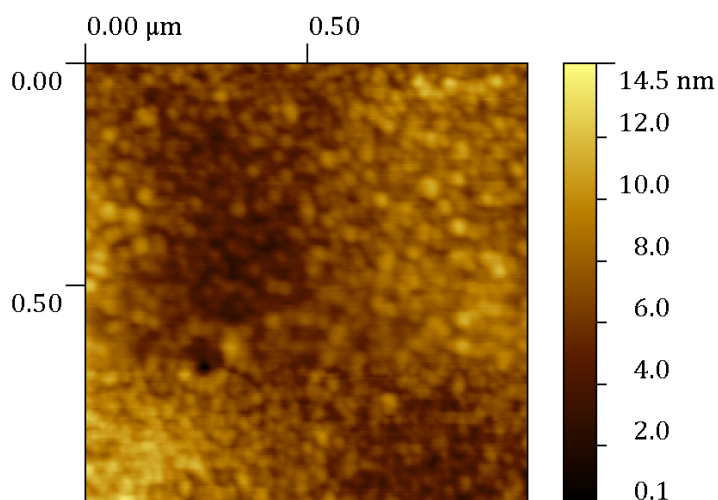


Figure 57. AFM image of the 1.85 kW AlO_x coating on PP. Produced using the Agilent 5400 in contact mode, using MicroMasch NSC35 tip. Area is 1×1 μm, 256 × 256 pixels. Post-processing done with Gwyddion [101]. Image taken by Dr Sverre Myhra. This figure was originally published in [131].

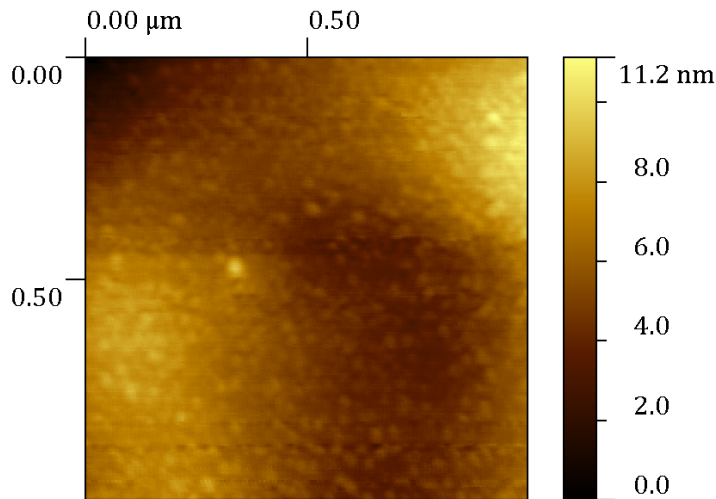


Figure 58. AFM image of the 1.55 kW AlO_x coating on PP. Produced using the Agilent 5400 in contact mode, using MicroMasch NSC35 tip. Area is 1×1 μm, 256 × 256 pixels. Post-processing done with Gwyddion [101]. Image taken by Dr Sverre Myhra. The material coating measured here was a different sample to that used for XPS, the calcium test, MOCON but produced in identical deposition conditions. This figure was originally published in [131].

By studying profile scans of Figure 56, Figure 57, and Figure 58, and using the method discussed in Section 3.4.2, an idea of the average dimensions of the aggregates can be formed. These are outlined in Table 11. The following assumptions were made in order to arrive at these figures:

- A small sample of 27-28 aggregates was investigated. Although less than 10% of the total, it was felt these were representative.
- An aggregate was defined as the middle of the topographical minimum to the next minimum, with the height being from the lowest minimum to the maximum.
- If unclear, it was discounted.

Table 11. Comparison of aggregate sizes for the coatings (1.55 kW, 1.85 kW, 2.05 kW). These values were arrived at by measuring the dimensions of 27-28 of the features in each of the AFM images.

Coating Deposition Power (kW)	1.55	1.85	2.05
Average Aggregate Width (nm)	40 ± 10	50 ± 10	70 ± 20
Average Aggregate Height (nm)	0.6 ± 0.3	2 ± 1	4 ± 2
Aspect Ratio	67:1	25:1	18:1

Taking the dimensions in Table 11 into account, it can be seen that these aggregates are not spherical but “pancake-like”, with high aspect ratios (inversely proportional to power).

Table 12. RMS Roughness of AFM micrographs.

Oxide Power (kW)	RMS (nm)
2.05	3.3
1.85	1.8
1.55	1.7

It can be seen from Table 11 that as sputter power increases so does agglomerate height and width. This is also reflected in the RMS data for these coatings, recorded in Table 12.

Erlat suggests that higher deposition power results in denser oxide and nitride coatings [61]. His study of sputtered AlO_xN_y on PET also appears to show increased agglomerate size with increased power [61].

4.2.2 XPS

XPS analysis of the three coatings was done using the Thermo Scientific K-Alpha by Dr Phil Holdway or Dr Hugh Bishop (as indicated). As-received analysis of the samples were characterised by a large carbon signal of 23-26 atm%. This is adventitious carbon, a thin

coating of which exists on all air-exposed material [64], and a few minutes of *in situ* sputtering reduced this carbon to below 0.1% in many samples, as has been previously observed [65].

All samples, as described in Section 3.5.1, were subjected to 420 seconds of a 500 eV argon ion-beam to clean away these adsorbed species. Table 13 shows the results of this analysis.

Table 13. XPS data of the different power barriers. An argon ion beam (500 eV) etch was performed for 420 seconds in order to remove surface build up. N.B – the XPS for the 2.05 kW sample is different, but identically produced sample to that used throughout section 4.2. *Dr P Holdway, all others by Dr. H. Bishop. This table was originally published in [131].

Power (kW)	Al (%)	O (%)	N (%)	C (%)	Ar (%)
1.55*	37.7	56.5	1.0	4.8	<0.1
1.85	40.3	56.9	1.8	<0.1	1.0
2.05*	39.0	55.7	1.3	4.0	<0.1

The lower limit of detection of the technique is reported as being 0.1 % but as can be seen in Table 13, there are other elements present that reduce the accuracy with which the ratio of the elements in the oxide are known [PC, OUMCS]. Argon ion implantation is discussed in Section 2.2.4.

With these caveats, the values for the aluminium and oxygen are the same for all samples within the measured uncertainty.

The Al2p XPS peak for the three samples can be seen in Figure 59. The results have been normalised and overlaid.

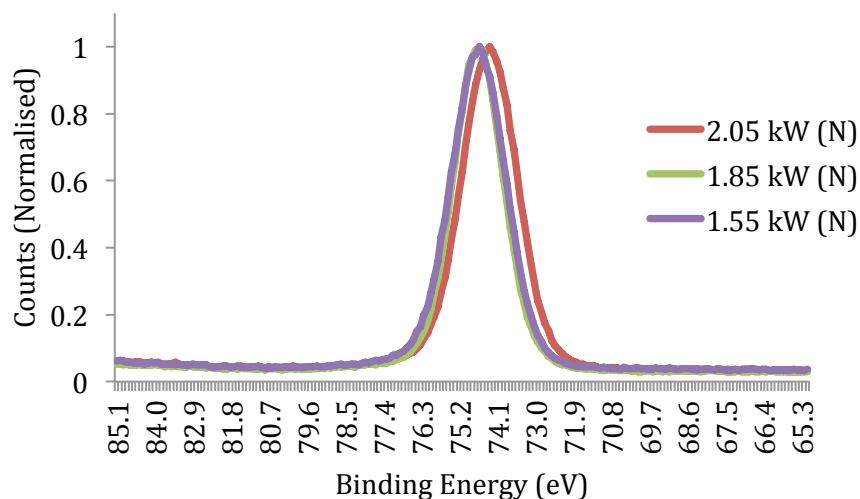


Figure 59. XPS scan of the Al 2p peak for the three coatings.

Considering Figure 59 and the reference binding energies from Table 14, the peaks in all traces are consistent with AlO_x bonding. The slight shift in the peak location for the 2.05 kW sample is thought to be due to surface charging. Any increase in elemental aluminium (in oxidation state zero) would be seen as a peak at 72.9 eV.

Table 14. Binding energies of Al, Al_2O_3 and AlN .

Peak	Binding Energy (eV)
Al (2p)	72.9 [111]
Al_2O_3 (2p)	73.85 – 74.10 [112]
AlN_y (2p)	74.0 [112]

4.2.3 UV-VIS

The UV-VIS spectra of the three coatings on PP were recorded, along with a sample of bare substrate as a reference. The results can be seen in Figure 60. A grey line signifying a 90 % transmission rate has been included—Ghosh cites this figure as the benchmark required by optoelectronics in the visible region [8].

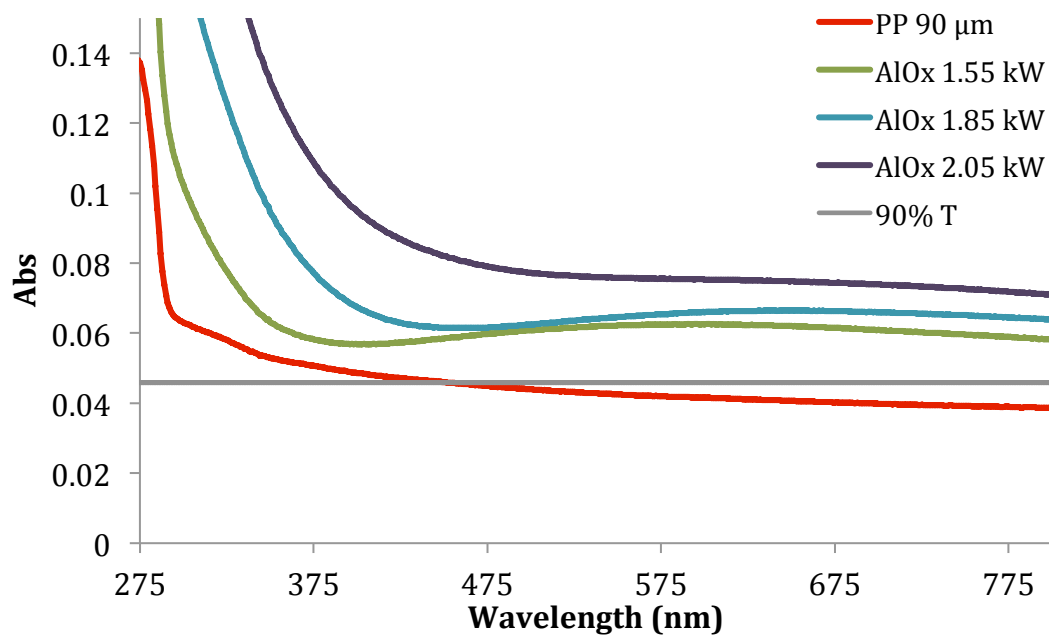


Figure 60. UV-VIS scan of films of different power. The intensities are normalised for thickness. The 90% transmission as required by industry is indicated as the grey, straight line. The average transmissions in the visible (390-780 nm) for the films are 2.05 kW = 83.7 %, 1.85 kW = 86.2%, 1.55 kW = 87.0 % and for the substrate alone it is 90.7%.

It can be seen from Figure 60 that absorbance increases with deposition power. Table 15 summarises the average transmission in the visible region for the films.

Table 15. Transmission in the visible of the coatings on the PP substrate.

Deposition Power (kW)	Average transmission 390-780 nm range (%)
2.05	83.7
1.85	86.2
1.55	87.0
Substrate	90.7

4.2.4 Steady-State Permeation and Activation Energy

Steady-state water permeation measurements of the three barriers were carried out as described in Section 3.3.1. Figure 61 shows the Arrhenius plot of the WVTR measurements, with the gradient signifying the activation energy.

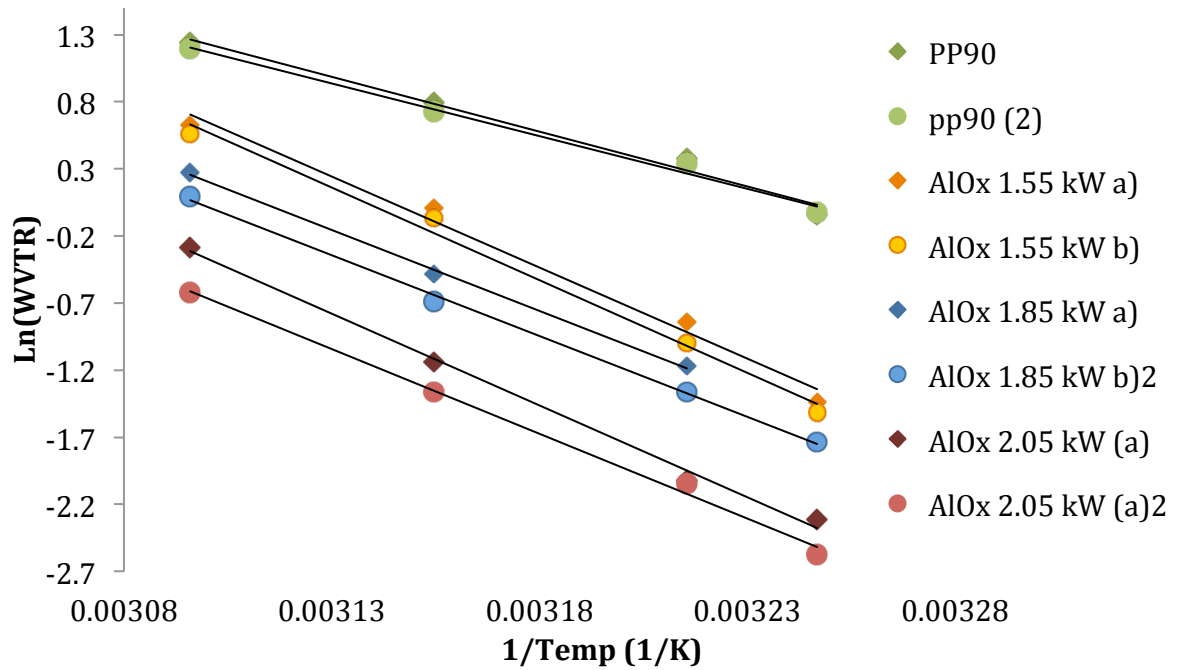


Figure 61. Comparison of AlO_x barriers deposited at different sputter powers on PP. Activation energies for 2.05 kw (E= 105-114 kJ/mol), 1.85 kW (E= 100 kJ/mol), 1.55 kW (E=114 kJ/mol). (a) and (b) refers to the Mocon cell used to measure the sample, and the 2 indicates if it was a second test. This figure was originally published in [131].

It can be seen that overall WVTR decreases with increasing sputter power. The activation energies of all three barriers are similar but larger than the polymer film. Table 16 compares activation energy, permeability, WVTR and thickness.

Table 16. Permeation characteristics of AlO_x films with different deposition powers. The drum speed for all samples is 50 m/min. This table was originally published in [131].

Film Power (kW)	Film Thickness (nm)	WVTR at 38°C (g/m²/day)	Activation Energy (kJ/mol)	Permeability (μm. g/m²/day)
0 (polymer)	-	1.43	67	182.5
1.55	113	0.37, 0.43	113, 115	0.056 (coating)
1.85	117	0.21, 0.23	100, 100	0.037 (coating)
2.05	109	0.13	105, 114	0.016 (coating)

The 2.05 kW coating exhibited a permeability of 0.016 μm. g/m²/day; over three times lower than the 1.55 kW coating. All three barriers have activation energies at least 33 kJ/mol greater than the polymer, meaning a significant proportion of the water vapour passes through nano-defects.

The 2.05 kW sample and the 1.55 kW sample have similar activation energies (for the best performing test) but the former exhibits a WVTR 3.3 times lower. Considering the Model in Section 3.3.2, this would mean that both films have a similar ratio of water vapour flow through macro and nano-defects, but that the 2.05 kW sample has far fewer defects overall. Considering the nature of sputter deposition (Section 2.1.6), this could be understood as due to incident material being able to better cover large substrate defects (reducing macro-defects), but also forming larger agglomerates (fewer nano-defects).

Considered with regard to the AFM micrographs in Section 4.2.1, there seems to be agreement between the surface morphology and the permeation characteristics. It can be seen from the AFM micrographs that the 2.05 kW coating is made up of larger agglomerates, thus having a smaller number of boundaries, (i.e., discontinuous regions) [57]. This is also supported by the refractive index measurements (Figure 63), which as a metric for density,

show that refractive index increases with power, increasing the amount of continuous material in the films and reducing the gaps.

This concept agrees with literature reports for barriers on PET. Henry's study showed an inverse relation between refractive index and OTR of sputtered AlO_x on PET [113]. Henry ascribes this improvement to increased film density.

Erlat also noticed a decrease in WVTR (37.5%) with an increase sputter power (54.5%) for sputtered AlO_xN_y films on PET, with only a marginal increase (1-3 kJ/mol) in activation energy [61].

4.2.5 Qualitative Permeation: Calcium Test

Figure 62 compares the calcium tests of the three barriers.

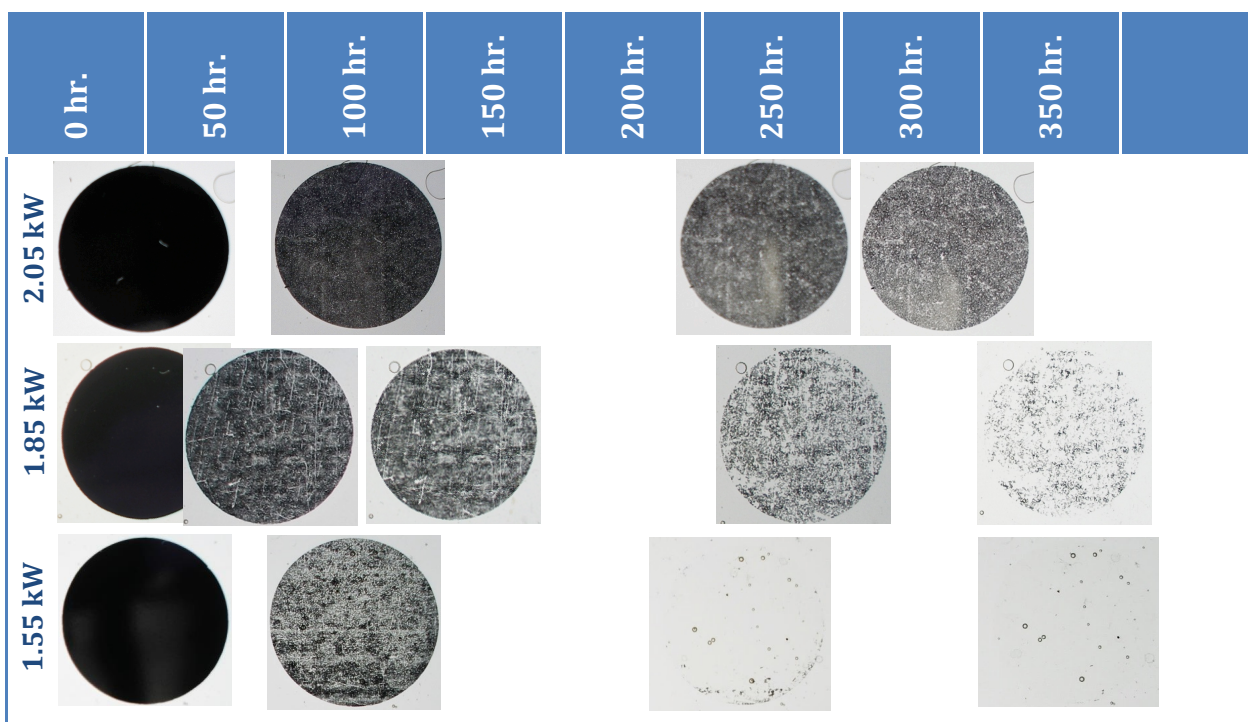


Figure 62. Calcium test of barriers with coatings produced at three different sputter powers, 2.05 kW, 1.85 kW and 1.55 kW. This figure was originally published in [131].

There is a clear correlation with sputter power and calcium test lifetime. At 300 hours, the 2.05 kW sample still shows a crisp dark grey circle, but the 1.55 kW sample has been

completely converted to calcium hydroxide. The nature of the permeation appears to be identical, albeit at different rates.

Theoretical lifetime calculated from Mocon measurements:

- 2.05 kW = 43.8 hours
- 1.85 kW = 27.1 hours
- 1.55 kW = 15.4 hours.

As was the case in Figure 53, the theoretical lifetimes of the calcium on the barriers are much shorter than those observed in Figure 62, but the trend with power is the same.

4.2.6 Refractive Index

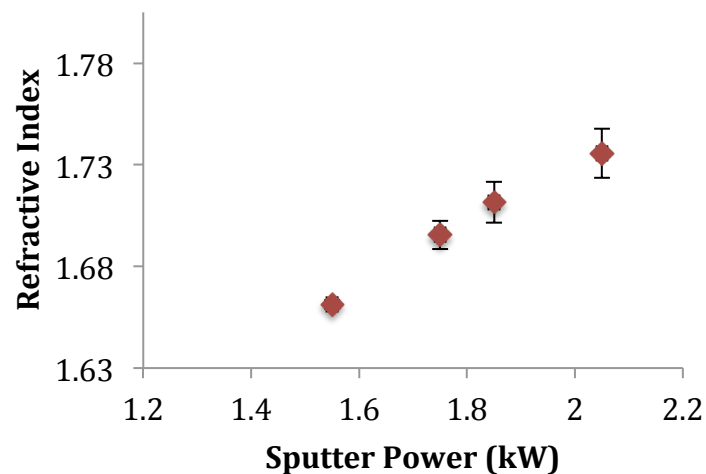


Figure 63. Refractive index measurement of oxides deposited on silicon chips. Note the scale of the y-axis has been exaggerated. This figure was originally published in [131].

It can be seen from Figure 63 that refractive index of the oxides increases with sputter power. It is important to note that the oxides measured are on silicon chips that were attached to the substrate. As we have seen in section 4.1.2, the nature of the substrate is significant in the formation of the oxide, so it is expected that the coatings deposited on the polymer will be different. However, this data is still useful in showing the general trend with power.

Refractive index tends to increase with density. When the results of Figure 63 are considered in the context of the atomic-force micrographs of Section 4.2.1, it seems that the higher power sputtering produces denser films. This density appears to be the result of larger agglomerate sizes and reduction of discontinuous regions. This agrees with the characterisation of Erlat as, mentioned in Section 4.2.1.

4.2.7 Summary and Discussion

To summarise Section 4.2, higher power sputter deposition produces coatings that:

- Have been shown to have significantly lower permeability.
- Are made up of larger agglomerates of AlO_x .
- Have similar activation energy in comparison to lower power films, but it is believed, a lower number of both macro and nano-defects.
- Exhibit increased refractive index.
- Are more absorbing across the UV-VIS spectrum.
- Have increased calcium-test lifetimes, but allow permeation with qualitatively similar characteristics to lower-power films.
- Are stoichiometrically identical to lower-power films.

The 2.05 kW barrier has an average visible-light transmission of 83.7%, 3.3% lower than the 1.55 kW barrier, and 6.3% lower than the industrially-set benchmark of 90%. However the 2.05 kW barrier is characterised by permeability nearly 3 times lower than the 1.55 kW barrier, which is highly desirable. The fact that all three barriers have high activation energies even when deposited directly onto untreated polymer is also encouraging, suggesting that these layers have been deposited without a sufficient density of macroscopic defects to dominate permeation.

The barriers were chemically identical, but exhibited different optical and permeation characteristics. It is concluded that this was due to the reduction of free space (i.e. defects),

which follows from the deposition of denser, better packed films (higher sputter power), consistent with the measured barrier performance.

4.3 Thickness

This section investigates how coating thickness affects overall barrier properties. Three coatings were produced using identical deposition conditions with the thickness being controlled by deposition time. The nature and quantity of the oxide deposited per drum-rotation was the same, thus thicker barriers consisted of building up a greater number of these “sub-layers”, as illustrated by Figure 64.

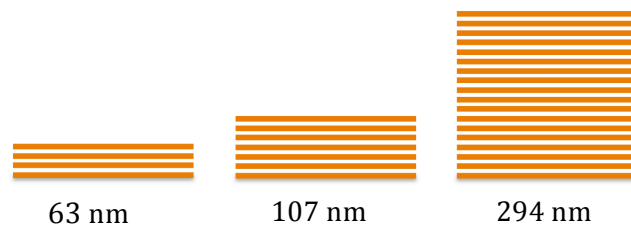


Figure 64. Schematic to show how different thicknesses are built up. The same sputtering power (i.e. deposition rate) is used, and the time for deposition is increased. The drum speed remains constant (in this case, 50 m/min). This figure was originally published in [131].

Table 17 shows the refractive index and average calculated “sub-layer” thickness for the different oxide thicknesses.

Table 17. Refractive index of barriers of varying thickness. Sub-layer thickness, i.e. the thickness of each layer of material deposited per pass of the cathodes is included.

Coating Thickness	Refractive Index	Sub-layer Thickness (nm)	Number of sub- layers
63	1.718 ± 0.007	0.28	221
107	1.660 ± 0.002	0.37	289
123	1.642 ± 0.001	0.38	324
294	1.60 ± 0.01	0.39	754

It can be seen that refractive index decreases as coating thickness increases. It is believed that this is due to the films reducing in density with increasing thickness. The average sub-layer thickness for the thinnest coating (63 nm) is only 71.8% of the average for the other three coatings. The reason for this is not known.

4.3.1 UV-VIS

UV-VIS spectra of the three barriers were taken with a substrate for comparison (see Figure 65).

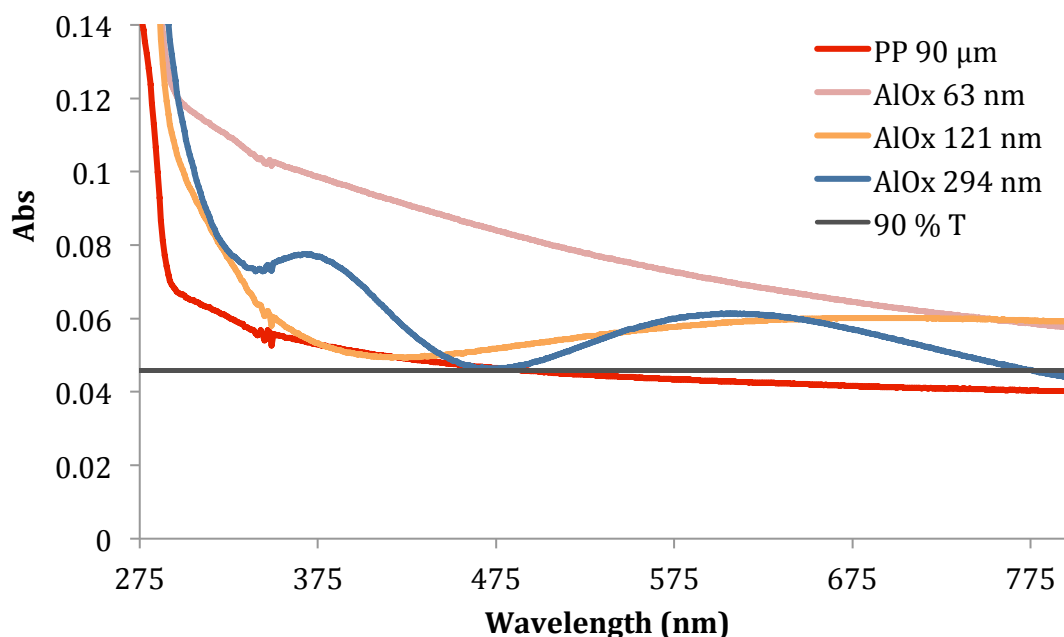


Figure 65. UV-VIS scan of the substrate, and three coatings of increasing thickness. All other deposition conditions are the same, power at 1.85 kW, drum speed 70 m/min. The straight grey line represents the 90% transmission required by industry. The average transmission for each barrier is 63 nm =84.4%, 121 nm= 87.8%, 294 nm=88.1%, with the substrate in this run having average transmission of 90.4%.

Because this is an examination of the effect of oxide thickness, Figure 65 has not been normalised for thickness, in contrast to all other UV-VIS spectra in this report. Also, the middle thickness film is 121 nm, not 107 nm, and is a different film to the one used in the rest of this section.

Table 18. Average transmission in the visible region of the EM spectrum (390-780 nm).

Coating Thickness (nm)	Average transmission (%)
Substrate	90.4
63 nm	84.4
121 nm	87.8
294 nm	88.1

It can be seen that, counter-intuitively, the thickest layer has the highest transmission. Also, qualitatively, the 63 nm and 121 nm samples conform to the absorbance behaviour observed in the UV-VIS spectra in Sections 4.2.3 and 4.4.2, but the 294 nm barrier exhibits two absorbance maxima.

If the refractive index information of Table 17 is considered in light of the UV-VIS data, it can be seen that the refractive index decreases for increasing film thickness. This could perhaps explain the increased transmission for the thicker barriers.

The double absorbance minima appear to be interference fringes, which are visible in parallel, homogenous films [114][115], and the relative “size” of the observed undulations are a metric for barrier quality, as larger fringes represent lower scattering and greater reflection [116]. Significant examples of this are shown in Chapter 6.

4.3.2 Steady-state Permeation and Activation Energy

Figure 66 shows the Arrhenius plot for films of different thickness.

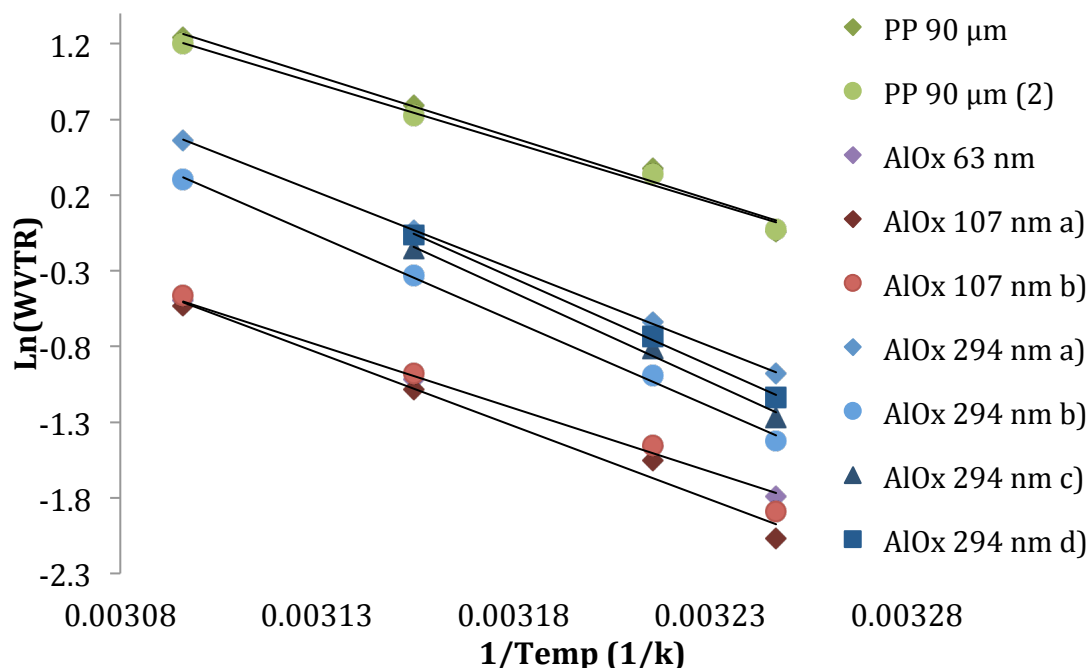


Figure 66. Comparison of the permeation characteristics of barriers all produced at 1.85 kW sputter power, 70 m/min drum speed, but with varying thicknesses. The activation energies of barriers are 294 nm (84-95 kJ/mol), 107 nm (76-81 kJ/mol), and 63 nm (70 kJ/mol).

This figure was originally published in [131].

Although the 294 nm film has a higher activation than the thinner oxides (albeit with a greater range of values for the thickest layer), the film is more permeable. Table 19 compares the characteristics of the films, and importantly, the calculated permeabilities.

Table 19. Permeation characteristics for barriers of varying AlO_x thickness.

This figure was originally published in [131].

Oxide Film	WVTR at 38°C	Activation Energy	Permeability
Thickness (nm)	(g/m ² /day)	(kJ/mol)	(μm. g/m ² /day)
0 (substrate)	1.43	67	128.7 (substrate)
63	0.23	70	0.017 (coating)
107	0.21, 0.23	76, 81	0.026 (coating)
294	0.52, 0.37, 0.32, 0.28	85, 94, 96, 99	0.102 (coating)

It can be seen that the 294 nm barrier has a permeability six times greater than the 63 nm barrier. This is despite the fact that the 63 nm sample has an activation barely 3 kJ/mol

greater than the polymer. The activation of the 294 nm sample is between 18-32 kJ/mol greater than the polymer, thus sees the greatest proportion of the permeation through nano-defects, but the high permeability suggests a large number of these defects. The best-performing barrier (63 nm) has an activation energy comparable with the substrate, which points to the majority of permeation occurring through macro-defects.

Even though the thickness of the 294 nm film is nearly 5 times thicker than the 63 nm film, it lets through more water. Considering the best test for each, the 294 nm film lets through 0.05 g/m²/day more water, while exhibiting an activation energy 29 kJ/mol greater.

The small increase in WVTR with a large increase in activation is similar to Test 1 and 2 of the Model in Section 3.3.2. This seems to point to the fact that there is a large increase in nano-defects for the 294 nm sample.

More macro-defects would have the effect of reducing activation energy whilst increasing WVTR. Reduction in the number of macro-defects would increase activation energy but also reduce permeation. As neither is observed, any changes in macro-defect number would be believed to be small.

Another explanation for the results in Table 19 would be a reduction in the activation energy exhibited by the nano-defects in the 294 nm film. However, there is not the large increase in WVTR that was seen in the model for Test 5, so this is not considered to be the main difference between the films.

The 294 nm barrier has the lowest refractive index (Table 17), and greatest optical transmissivity (Table 18). As was seen in Section 4.2, there was a trend seen between refractive index (and transmissivity) and permeability. The inference being that the refractive index was a metric for density, the denser films in that study were the better performing barriers.

It would appear that in this case, with very thick multiple pass layers, the thicker oxide is less dense, with a greater number of nano-defects. Although there has been no critical thickness

(see Section 2.3.1) shown here, due to the small number of thicknesses measured, there is an increase in permeability with thickness and this is due to an increase in nano-defects.

4.3.3 Qualitative Permeation: Calcium Test

The calcium test of the three barriers is shown in Figure 67.

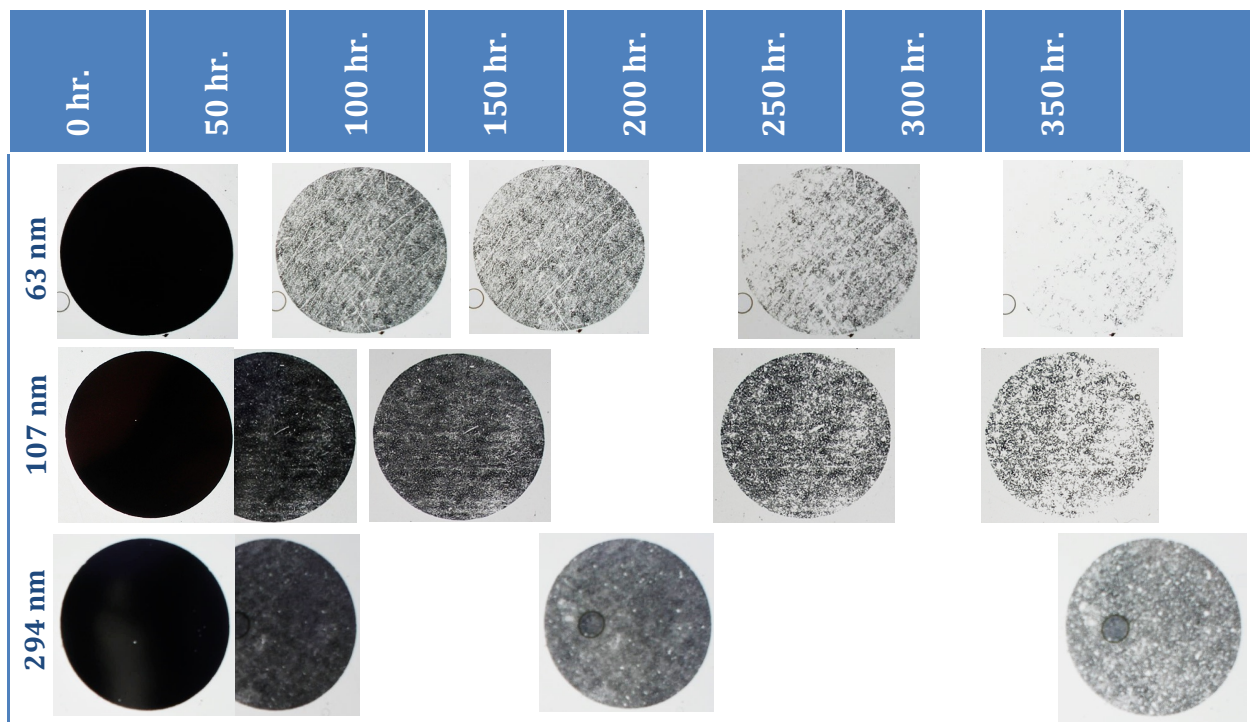


Figure 67. Calcium test comparing three films of increasing thickness AlOx.

This figure was originally published in [131].

The calculated lifetimes of calcium spots using the data in Table 19 for these barriers are:

- 63 nm – 24.7 hours
- 107 nm – 27.1 hours
- 294 nm – 20.3 hours

and as before, the best WVTR value available is used in the calculation. Qualitatively, the calcium test suggests the 63 nm barrier exhibits the poorest barrier performance, with most of the calcium converted to its hydroxide by 350 hours. Comparing the 63 nm to the 107 nm the latter has a much longer lifetime but a similar (depending on the value chosen) WVTR from MOCON measurements. It could be argued that perhaps the 107 nm film has a larger

transient or “lag time”— a delay before the water has fully permeated all the channels—with the 63 nm sample not noticeably exhibiting this effect.

The 294 nm barrier displays slightly different calcium-decay characteristics. There are white spots by 50 hrs that expand over the course of the test. This stands in contradistinction to the other films’ gradual uniform decay, although this background uniform decay is also present. Also the calcium lifetime is remarkably long: a significant amount remains at 360 hours, despite the MOCON measurement suggesting this thickness is the most permeable. Once again this, even thicker film perhaps shows the effect of an even longer lag time contributing to the longer lifetime of the Ca spots.

4.3.3.1 Dust and Bubbles

For the 294 nm AlO_x barrier in Figure 67, in the middle of the 0 hr image, a white dot is visible. At this point the calcium/barrier has not yet been put into the humid oven. It can be seen that over time, this dot does not increase in area, as would be expected if this was evidence of a hole in the barrier. This points to evidence of dust, or surface contamination. The dust, having the calcium deposited on top of it, degasses and turns the calcium immediately surrounding it into calcium hydroxide, but then it stops. If this is compared to the crack in the middle of the calcium spot for the 107 nm barrier, also in Figure 67, it can be seen that the transparent area increases with time. The crack is not present in the initial 0 hr image, and only appears after time in the oven, and thus can be attributed to a defect in the barrier layer. Scratches, in contradistinction to cracks, appear to be features of pre-calcium-deposition substrate damage, which also manifest in the calcium test. These are different in that the features do not rapidly expand in the manner of an oxide crack/hole. Examples of these can be seen in Figure 67 for the 63 nm sample.

Another feature of the 294 nm AlO_x barrier in Figure 67, is the circular feature, left of centre. This is attributed to a bubble in the epoxy behind the calcium, as there is no observable contribution to the conversion of calcium into calcium hydroxide.

4.3.4 Summary and Discussion

The results from this section suggest that for the thick 294 nm film:

- A great proportion of the permeation occurs through nano-defects.
- Refractive index, ergo film density, is lower than the thinner films even when sub-layer thickness is comparable.
- There is a longer calcium-test lifetime than the 63 nm film, despite higher measured WVTR.

The results from this section show that for the thin film 63 nm:

- The majority of permeation occurs through macro-defects.
- It exhibits a large refractive index despite having a lower average sub-layer thickness.
- It has the lowest permeability of any of the films, despite the fact that the majority of permeation is through macro-defects.

N.B. there are no XPS data for the 63 nm and the 294 nm barriers, with the 107 nm barrier XPS results reported in Table 22 labelled as “70 m/min” which precluded ruling out of any excess aluminium contributing to refractive index results.

There appears to be a direct relation between permeability and barrier thickness. That the thinnest layer (63 nm) has the best permeability and highest refractive index but is negatively affected by macro-defects points to the possibility for improvement by planarising layers. If the macro-defects can be removed, the films activation should increase and WVTR decrease.

The question remains. “Why do thicker barriers have greater permeability?”

The refractive index for the thickest film is also lower. This paints a picture of a lower quality film, consistent with the permeation results suggesting a greater population of nano-defects. Felts suggested that worsening barrier characteristics at greater thicknesses could be due to thermal degradation of the coating or the substrate [74]. The deposition time of the 294 nm coating is 20 minutes and 20 seconds, meaning the initial sub-layers were deposited over 20 minutes before the final sub-layers. The thermal gradient across the coating and the substrate could increase the amount of defects and inhibit dense packing.

4.4 Drum Speed

This section investigates how “sub-layer” thickness affects barrier characteristics. Three coatings were produced with identical deposition conditions, with only the drum speed varied. These coatings had approximately the same overall thickness (see Table 20).

Considering Figure 68, it can be understood that the same amount of film is deposited in the same time, but that these sub-layers are thinner and more numerous as the drum speed increases.

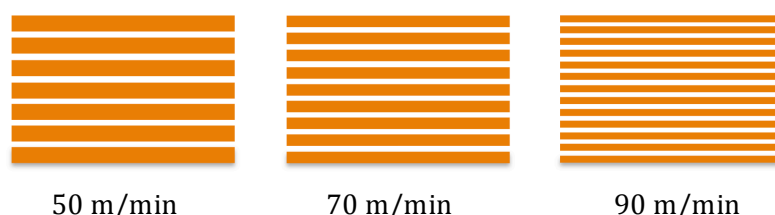


Figure 68. Schematic to understand how coatings produced at different drum speeds are formed. All other deposition conditions, specifically deposition rate/sputter-power were identical.

4.4.1 Deposition Conditions

Table 20 summarises the measured thicknesses and refractive indices of these films, with the calculated sub-layer characteristics.

Table 20. Investigation of sub-layer characteristics and refractive indices for three films of similar thickness.

Drum Speed (m/min)	Thickness (nm)	Average Layer Thickness (nm)	Number of sub-layers	Refractive Index
50	117	0.57	205	1.707 (± 0.001)
70	107	0.37	289	1.660 (± 0.002)
90	113	0.31	365	1.661 (± 0.001)

The thicknesses of the films are not exactly identical, with the 70 m/min sample being 10 nm thinner than the 50 m/min. The 50 m/min film has the highest refractive index at 1.707. The 70 m/min and 90 m/min films have the same refractive index (to 2 d.p), but as was seen in Section 4.3, for the 107 nm and 123 nm films, a small increase in thickness (16 nm) produced a decrease in refractive index of 0.018. With these thickness effects considered, there is not a clear trend observable.

The barriers produced in this report are manufactured with substrates fixed to a rotating drum. Table 20 shows that the 90 m/min sample requires 365 passes of the sputter cathodes. In a roll-to-roll application this would be nearly impossible to implement and not playing to the strengths of the technique. For industrial up-scaling, this needs to be kept in mind, and the number of cathode passes minimised. However, prior to industrial implementation, it is important to better understand what controls permeation behaviour.

4.4.2 UV-VIS

UV-VIS spectra of the three barriers, with a substrate as reference, are presented in Figure 69.

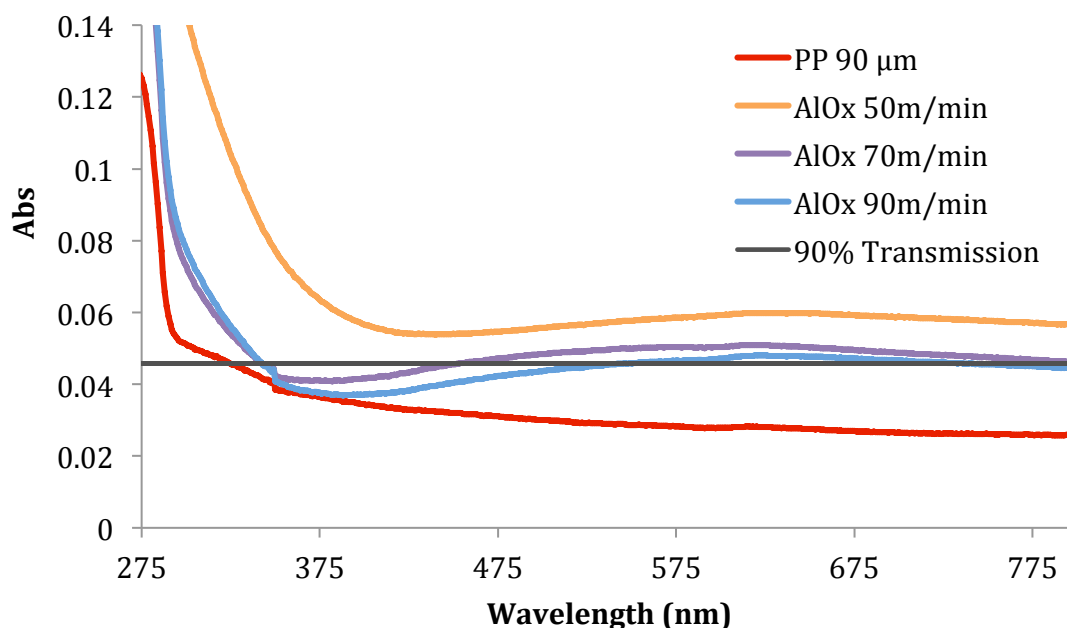


Figure 69. UV-VIS scan of AlOx produced at different drum speeds. All other deposition conditions remain the same. Normalised for film thickness. NB the discontinuity at 350 nm is from the automated changing of the diffraction grating. The straight grey line shows the 90% transmission required by industry. The average transmission in the visible region (390 nm – 780 nm) for the films is 90 m/min = 90.3%, 70 m/min = 89.5%, 50 m/min = 87.6%, and for the substrate 93.6%.

The UV-VIS spectra are normalised for barrier thickness. Table 21 summarises the average transmission in the visible for the barriers.

Table 21. Average transmission of barriers produced at different drum speeds.

Sample	Average Transmission (%)
Substrate	93.6
50 m/min	87.6
70 m/min	89.5
90 m/min	90.3

It can be seen that average transmission increases with drum speed. This somewhat follows the trend seen in the refractive index data in Table 20, however there is some differentiation between the 70 and 90 m/min samples for the UV-VIS data.

4.4.3 XPS

XPS analysis of the films is collated in Table 22.

Table 22. XPS analysis of three oxide coatings produced at different drum speeds. A section of the samples was initially etched for 420 seconds with an argon ion beam (500 eV). All XPS measurements in this project have been performed by Dr Phil Holdway (*) or Dr Hugh Bishop.

Drum Speed (m/min)	Al (%)	O (%)	N (%)	C (%)	Ar (%)
50	40.3	56.9	1.8	<0.1	1.0
70	40.3	57.1	1.5	<0.1	1.2
90*	38.5	57.3	1.0	3.1	<0.1

It was initially thought that the improved UV-VIS data at higher drum speeds resulted from more stoichiometric films because of the possibility of more oxidation of each thin sub-layer as the sample drum rotates around, away from the cathodes. However there is not sufficient evidence of this in Table 22. If the 50 m/min sample is considered, the ratio of Al:O+N is 40.3:58.7, below the 40:60 or 2:3 of Al_2O_3 . There is minimal difference in these ratios for the 70 m/min with Al:O+N at 40.3:58.6. When considering the peak data (Figure 70) there is no evidence of an Al peak and the normalised peaks agree that the aluminium is bonded with oxygen.

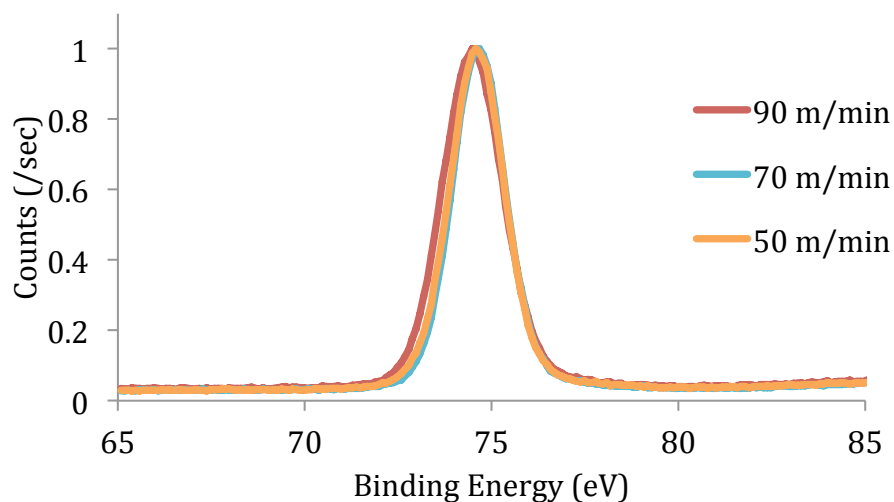


Figure 70. Peak scans of the Al₂p binding energy. Each peak is normalised to allow for comparison regardless of strength of signal.

4.4.4 Steady-state Permeation and Activation Energy

The Arrhenius plot of the different drum speed barriers is presented in Figure 71.

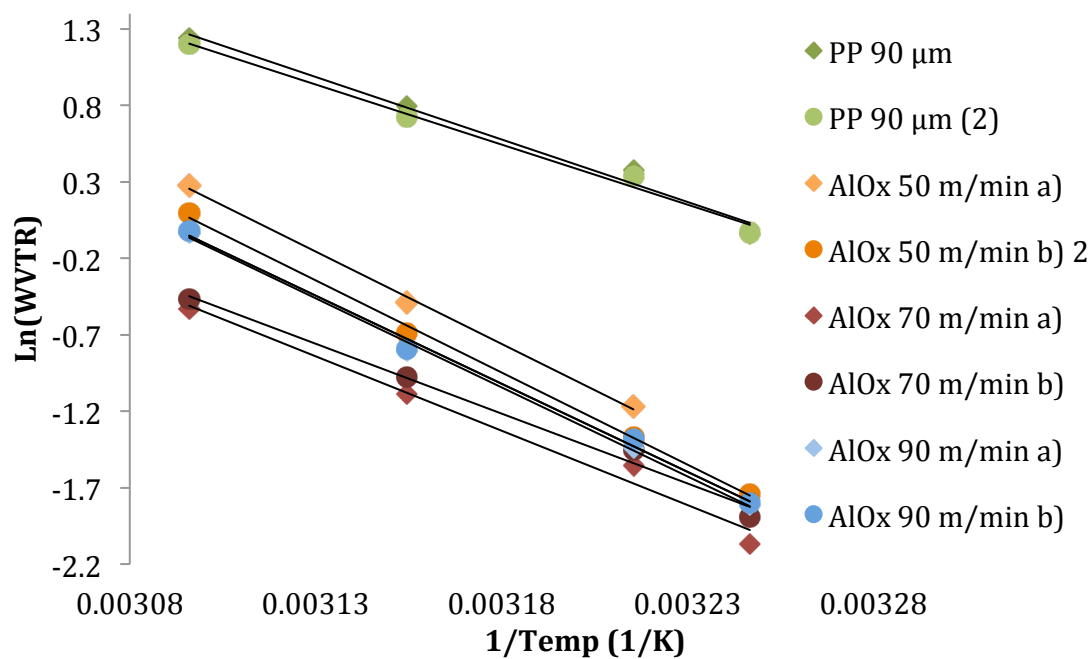


Figure 71. Comparison of the permeation of barriers with oxide coatings produced at 1.85 kW, with different drum speeds.

Table 23 compares the WVTR, activation energy and permeability of the barriers.

Table 23. Summary of the permeation characteristics and calculated permeabilities of the three barriers.

Deposition Drum Speed (m/min)	WVTR at 38°C (g/m²/day)	Activation Energy (kJ/mol)	Permeability (μm. g/m²/day)
0 (substrate)	1.43	67	128.7 (substrate)
50	0.26, 0.31	100, 100	0.037 (coating)
70	0.21, 0.23	81, 76	0.026 (coating)
90	0.24, 0.25	97, 96	0.033 (coating)

It can be seen that for all 3 coatings, the activation energy is greater than that of the polymer, indicating a significant amount of permeation through nano-defects. However there is not a linear relationship between drum speed and permeation. The poorest performing barrier is the 50 m/min sample, which has the highest WVTR and permeability, and also exhibits the highest activation energy consistently recording a 33 kJ/mol increase over the polymer.

Applying the Model from Section 3.3.2, it would seem that this film has a greater ratio of nano to macro-defects. The 70 m/min sample has the lowest WVTR and permeability, and also the lowest activation registering only 9-14 kJ/mol increase over the polymer.

Bringing previous discussions to bear on this data, it would have been expected that the film with the higher refractive index would exhibit the best performance, but the reverse is the case here. However across the three samples there are relatively small differences in WVTR, with the lowest recorded value for each sample only differing in a range from 0.21 to 0.26.

4.4.5 Qualitative Permeation: Calcium Test

The calcium test for these barriers is shown in Figure 72.

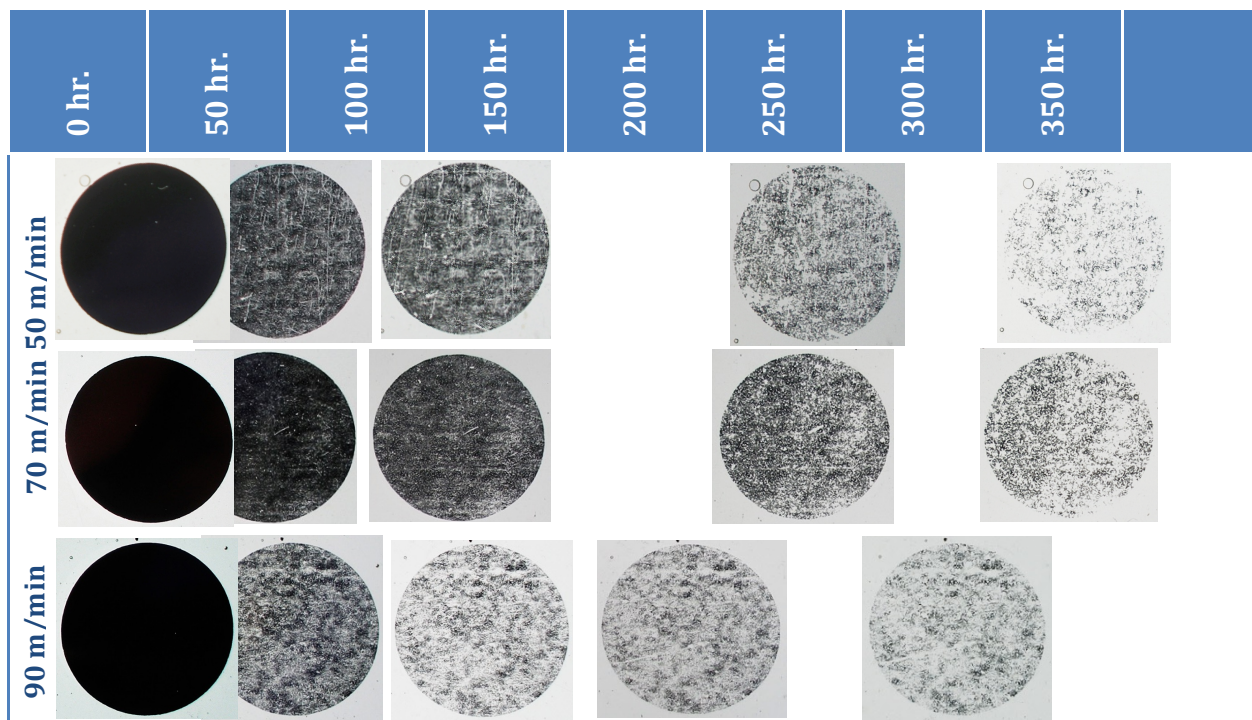


Figure 72. Calcium test of barriers consisting of oxide coatings made at differing drum speeds.

As with the permeation data, there is not a clear pattern observable. In fact, the calcium test sees the 90 m/min sample displaying the poorest barrier performance over the life of the test. The barrier with the best permeation statistics, the 70 m/min sample, has significantly more calcium remaining at the 50 hour mark, and marginally more at 300-350 hours. The 50 m/min performs better than the 90 m/min up to around 125 hours, but by 300-350 hours they appear with a similar level of calcium conversion.

4.4.6 Summary and Discussion

The results from this section show that:

- Lower drum speeds produce films with higher refractive indexes.
- UV-VIS spectra of the films follow refractive index data. The 50 m/min film having the lowest observed transmission.
- There is no evidence for differing stoichiometry caused by drum speed. The films are fully oxidised even at high speeds.

- The lowest drum speed exhibits the highest activation energy indicating more of the permeation is through nano-defects.
- There is not a clear relation between drum speed and permeation, or calcium test lifetime or features, with relatively small differences in behaviour.

There is no clear overall trend in behaviour as a function of drum speed, with only small differences observed between the samples, suggesting that the sub-layer thickness does not have a great effect on barrier properties.

5 Aluminium Oxynitrides

This chapter covers changes to the chemistry of the RF sputtered coatings and the implications for barrier quality. This includes discussion of the deposition characteristics (Section 5.1), XPS characterisation of coating chemistry (Section 5.2), refractive index and UV-VIS absorption studies (Section 5.3), permeation and calcium tests to rate barrier performance (Section 5.4), a nano-scratch study to investigate the films' mechanical properties (Section 5.5), and finally a discussion of the implications of these results with regard to producing barriers (Section 5.6).

The coatings in Chapter 4 consist of AlO_x with small background levels of nitrogen (1-1.8%). The work of Erlat suggested that the addition of nitrogen to AlO_x greatly reduced barrier permeation and increased activation energy of films [61]. Erlat's results proved that there was a strong chemical interaction between water and AlO_xN_y films and suggested that this was the reason for the reduced permeation [61].

This chapter investigates increasing the nitrogen content of AlO_xN_y films in order to improve on the performance of the AlO_x barriers produced in Chapter 4.

5.1 Making Aluminium Oxynitride

The introduction of nitrogen into the RF sputtered films proved difficult. Initial attempts only saw low levels of nitrogen. With no oxygen added into the plasma during sputtering and with the maximum nitrogen flow rate that was possible without poisoning the target, the AlO_xN_y films produced still contained less than 10% nitrogen content. High oxygen content persisted in the coating, consistently over 45%, even with no oxygen added, and at base vacuum levels of $\sim 3 \times 10^{-4}$ mBar. The difficulty in producing oxygen-free sputtered films has been noted by others [12][61]. Higher reactivity of oxygen compared to nitrogen [117] [92][118] and the continued presence of the former, even at low pressure ($\sim 1 \times 10^{-4}$ Pa), has been suggested as an explanation [46].

Many attempts were made to increase the proportion of nitrogen in the films.

- Poisoning in reactive sputtering, discussed in Section 3.1, is a balancing act between process gas and reactive gas. As the maximum un-poisoned nitrogen flow rate ($N_2=14$ sccm) saw only <10% film nitrogen, the deposition was run in a poisoned state with a large amount of reactive gas ($N_2=100$ sccm) and a reduced amount of process gas ($Ar=100$ sccm). As was expected, the deposition rate fell precipitously to 0.03 nm/sec from 0.23 nm/sec for a regular AlO_x film. Unfortunately XPS analysis revealed that this film had only 3% nitrogen.
- Adsorbed species onto the chamber are a source of excess water/oxygen. A full clean of the chamber and chimney however yielded no visible improvement.
- The web drive has unwind and rewind chucks which contain air tubes to aid polymer roll grip. These were removed as possible sources of excess oxygen. Running without these saw no improvement in film nitrogen.
- Liquid nitrogen scavenging, as described in Section 3.1, was the only method that registered a significant improvement. It lowered the chamber pressure, and produced the maximum nitrogen content films.

The highest nitrogen content achieved in this project was 15.6%, far short of 37% nitrogen content reported for sputtered AlO_xN_y on polymer substrates reported elsewhere [12].

5.1.1 Hysteresis

As has been described in Section 3.1 and Section 4.1.1, it is important to understand the hysteresis of the reactive sputtering process. Figure 73 shows the hysteresis of reactive sputtering comparing nitrogen or oxygen as the reactive gas.

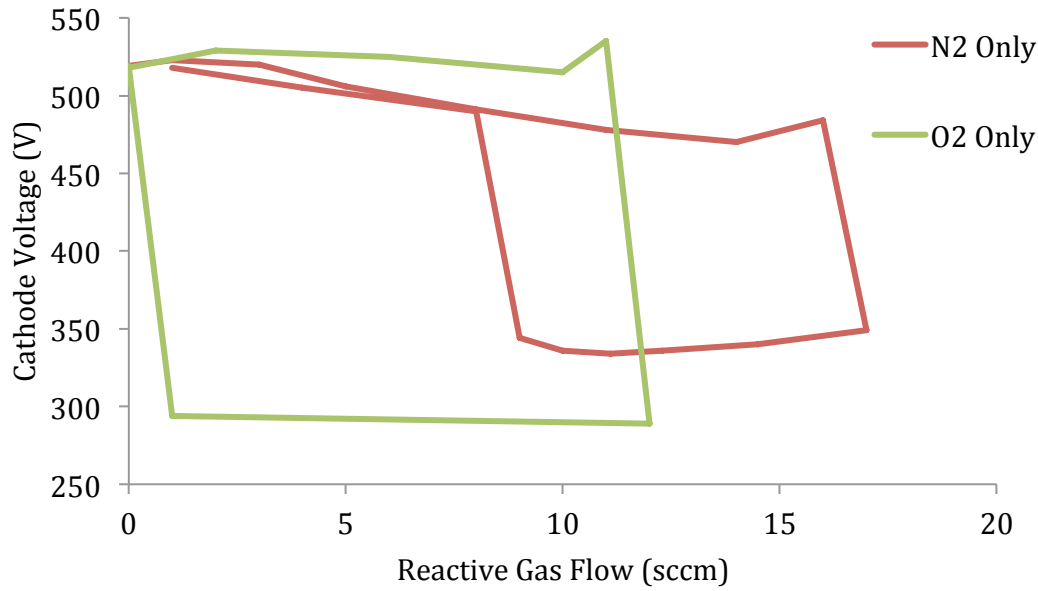


Figure 73. Hysteresis of reactive sputtering. The hysteresis due to oxygen and that due to nitrogen are compared. Argon flow was 200 sccm for both.

There are two key observations of the difference in hysteresis for the gases. The nitrogen hysteresis poisons at a higher reactive gas flow and recovers at a higher gas flow. In order to discuss this, Equation 1 in Section 2.1.6 is reproduced below:

$$\frac{J}{q} Y_c \theta_t = \alpha 2F(1 - \theta_t)$$

Equation 10 from [43].

where J is the ion current density, q is the elemental charge, Y_c is the sputter yield of the compound, θ is the area fraction of the target covered in compound, α is the sticking coefficient and F is the amount of molecules of reactive gas impinging on the target per unit area per unit time. Equation 10 describes the dynamic-equilibrium reaction taking place during reactive sputtering and is from the model described by Berg & Nyberg [43].

The energy needed to remove an atom from the top-most layer of a sputter target is defined as the Surface Binding Energy (SBE) and it is inversely related to the sputter yield (Y_c) [119]. Kim (using the work of Malherbe [120]) reported that Al has a lower SBE (3.4 eV) than AlN (9.1 eV) [121]. Kubart reports that the SBE for AlO_x is 12.0 eV [122].

Using this information and Equation 10, the behaviour of Figure 73 can be explained. The left side of the equation corresponds to the rate at which compound is sputtered, and the right hand side of the equation is the rate at which the compound forms [43]. Consider this dynamic equilibrium at a N_2 flow rate just before poisoning occurs. The sputter yield of AlN is greater than AlO_x , therefore the fixed ion density, J , can balance a greater rate of reactive-gas (proportional to F). This is why the point of poisoning is at a rate of 17 sccm for nitrogen, 5 sccms greater than for oxygen. The sticking coefficient α is a measure of the reactivity of the reactive gas [43], and as aluminium bonds with oxygen more readily than nitrogen [65] the sticking coefficient is lower for the latter [43]. This would also contribute to the shift of the poisoning position (as well as the recovery position) to higher reactive gas flows (i.e. a narrowing of the hysteresis region) [42], [43].

5.2 XPS

Table 24 summarises the elemental composition of 5 samples with increasing nitrogen content following the method described in Section 3.1.1. All XPS measurements were performed by Dr Phil Holdway or Dr Hugh Bishop.

Table 24. XPS of coatings containing different amounts of nitrogen. All samples were etched with an argon ion beam of 500 eV for 420 seconds. The minimum measurable result is 0.1% atomic percentage. A squared-bracketed gas flow indicates that it was piped into the bottom of the chamber, outside the sputter zone. LN₂ indicates that liquid nitrogen scavenging was used.

Input N ₂ (sccm)	Al (%)	O (%)	N (%)	C (%)	Ar (%)
0 (oxide)	40.3	57.1	1.5	<0.1	1.2
4	40.9	52.8	4.7	0.7	1.0
8	41.0	48.6	8.6	0.8	1.1
17 + [80]	40.5	44.6	12.3	1.6	1.0
15 + [100] (LN ₂)	40.5	40.1	15.6	2.8	1.0

As with Section 4.2.2, the accuracy of the measurements is limited by the carbon and argon present. Figure 74 highlights the changing relationship between the elements in the films.

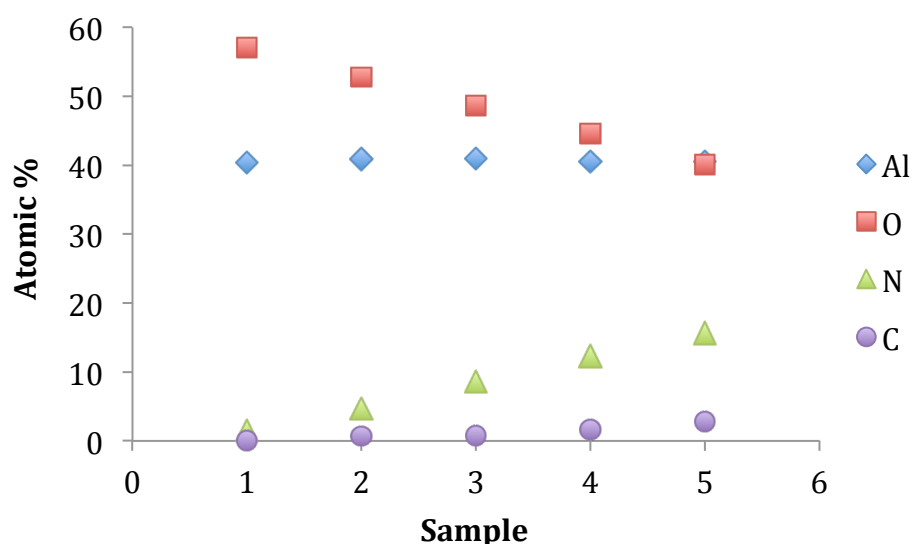


Figure 74. Changing elemental composition as a function of increasing N₂ input.

As the nitrogen content of the films increases, the oxygen content decreases, with the aluminium content remaining the same (within uncertainty).

In order to probe the bonding environment of the films, focussed scans of the Al2p emission peak and the N1s emission peak (Figure 75) were performed.

Table 14 showed that the Al2p binding energies for Al₂O₃ and AlN overlap. This overlap was observed for the Al2p scans of the films and it was not possible to identify separate contributions from AlN and AlO_x. This overlap requires peak fitting software to resolve, as has been observed by others [123][124].

Table 25 shows the reference binding energy for N1s.

Table 25. Binding energy of chemical species for the N1s emission peak.

Peak	Binding Energy (eV)
AlN 1s	397.3 [125]

Figure 75 shows the N1s scan for the films.

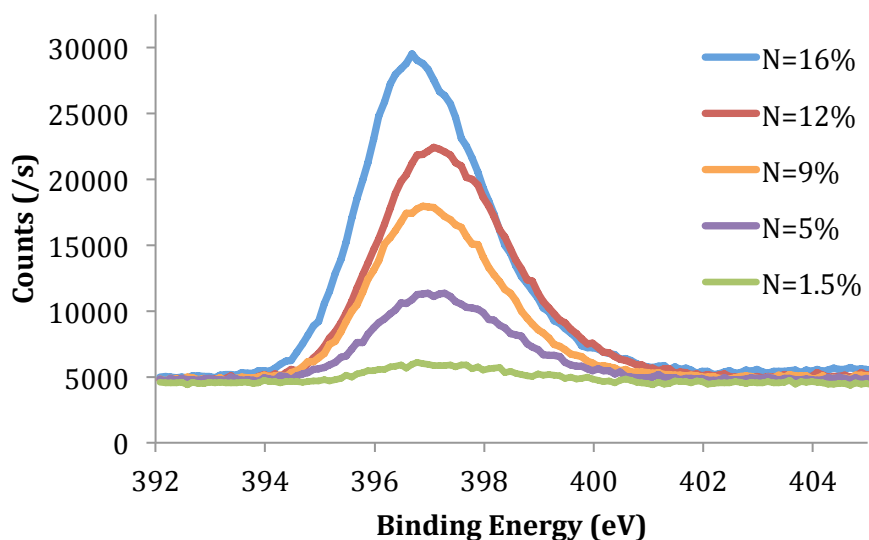


Figure 75. XPS N1s scan of differing nitrogen content. Results are absolute counts and not normalised. The shift of the N1s peak to lower BE with increasing N content is thought to be due to changes in surface charging and is also observed in the XPS scans of Al2p and O1s.

Figure 75 shows that each of the films has an AlN peak, which increases in intensity with increasing nitrogen content.

It can be seen in Figure 75 that the higher nitrogen content films see a shift of the N1s peak to lower BEs. A similar shift was observed in the scans of the Al2p and O1s peaks. It is known that as photo-electrons leave the surface after X-ray irradiation, the surface becomes charged, and this charge causes a shift in BE for all of the emission peaks [62]. This is counteracted through the use of an electron flood-gun to neutralise the charge imbalance [65]. However it has been observed by others that conductivity of sputtered AlO_xN_y varies with the ratio of oxygen to nitrogen [118], so it is concluded that this change is the source of the observed shift in BE in Figure 75.

XPS Depth Profile

A depth-profile scan was performed for the N=16% sample. This scan consisted of performing XPS on the as-received sample (carbon=23.9%), then IB etching the sample for 5 seconds before recording the spectra again. This was repeated until there had been 180 s of etch time (35 etch stages). The results are shown in Figure 76.

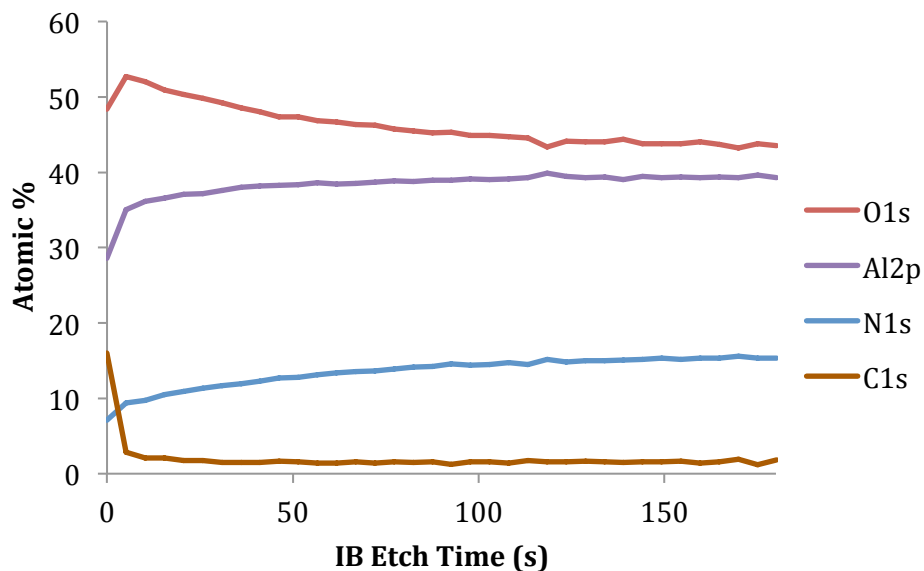


Figure 76. XPS depth profile 16% nitrogen coating. Atomic make up of the film was measured after every 5 seconds of IB etch.

There are three regions to be considered: 0-10 seconds, 10-160 seconds, and 160+ seconds.

1. **0-10 seconds:** The initial high carbon peak (16%) drops to 2.1%. The short etch rate removes this carbon which is considered to be adventitious carbon as described by Barr [64] and discussed in Section 4.2.2. It can be seen how the presence of such a large carbon signal affects the recorded N, O and Al percentages.
2. **10-160 seconds:** The nitrogen slowly increases from 9.7% (10 seconds) to 15.3% (160 seconds), the oxygen decreases from 52% to 44%, and the aluminium registers a slight increase, from 36% to 39%. It is known that AlN will react with ambient moisture and oxygen and form a coating of AlO_x [126], [127]. Slack describes how 5-10 nm of AlO_x forms on AlN single crystals after one day in the ambient [126]. This could explain why the oxygen signal is greatest at the surface, but decreases as the IB-etch continues; oxygen from the ambient diffuses into the disordered AlO_xN_y material (to a greater depth than was the case for the single crystal AlN) and substitutes for some N during the period in air between deposition and XPS characterisation. Erlat et al. [61] report a similar effect by SIMS profiling, with an increase in the AlN concentration through the thickness. However, as was discussed in Section 2.2.4, it is possible that some compositional changes are influenced by differential milling of the different elements by the ion beam.
3. **160+seconds:** Small changes in elemental composition, closest to the final recorded percentages in Table 24.

5.3 Optical Properties

5.3.1 Refractive Index

Figure 77 shows the refractive index of coatings as a function of their XPS-recorded nitrogen content.

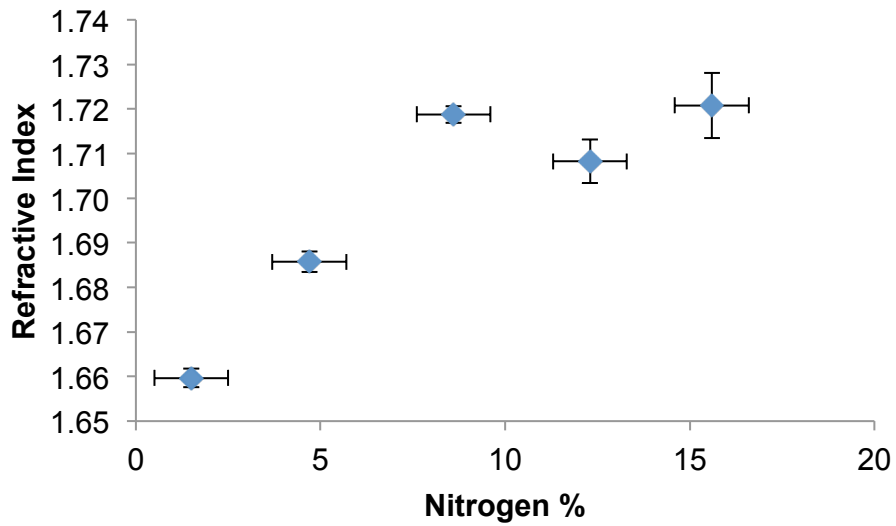


Figure 77. The refractive index of barriers with different levels of nitrogen content.

The trend indicates that increased nitrogen content in AlO_xN_y films induces a higher refractive index. A similar trend has been observed by others [92] [128]. Shimada reports the refractive index of bulk Al_2O_3 as ~ 1.64 and bulk AlN as ~ 2.06 [129].

5.3.2 UV-VIS

The UV-VIS absorption spectra of the films can be seen in Figure 78.

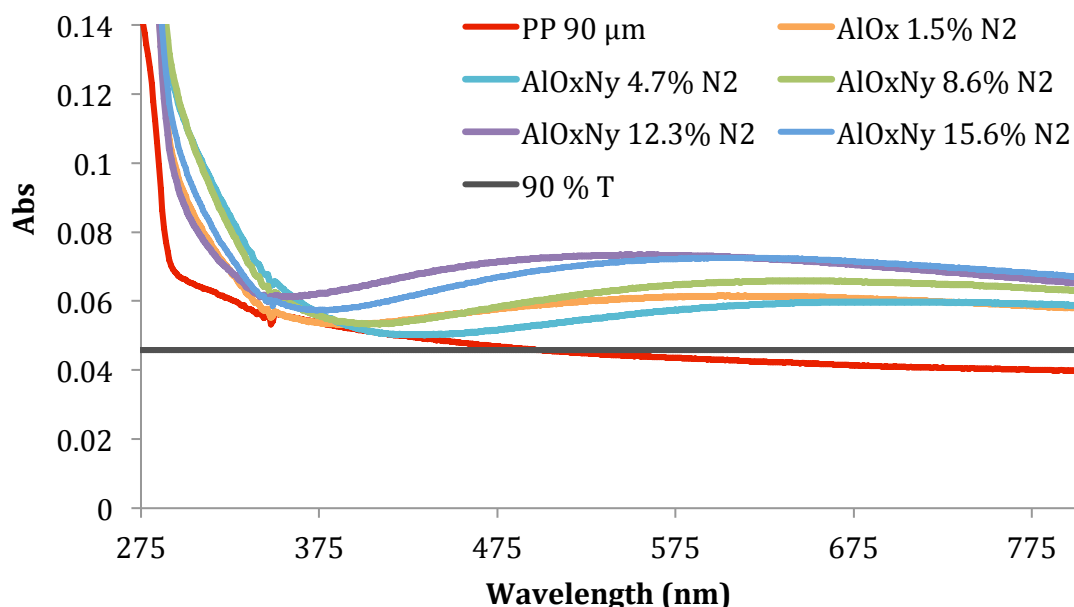


Figure 78. UV-VIS spectra, normalised for film thickness (to the N=12.3% film), of AlO_xN_y films of different amounts of nitrogen. The straight grey line shows the 90% transmission required by industry, the average transmission in the visible (390 nm -780 nm) for the films are N=15.6% (T= 85.3%), N=12.3% (T=85.0%), N=8.6% (T=86.7%), N=4.7% (87.9%), N=1.5% (T=87.3%) and for the substrate in this scan T= 90.3 %.

The absorption spectra have similar shape, but a straightforward correlation with nitrogen content is not forthcoming. For the region 750 nm – 800 nm, absorption is proportional to nitrogen content. There appears to be a general tendency that higher nitrogen content films are more absorbing (see Table 26), however this is not linear as the most absorbing barrier is the one with the 12.3% N_2 coating, not the 15.6% content one. But there is no clear correlation between absorption maxima and minima and nitrogen content.

Table 26. Comparison of average transmission in the visible (390- 780 nm) for films of different nitrogen content. Refractive index and thickness are included to aid discussion.

Sample	Coating	Refractive Index	Average Visible
	Thickness (nm)		Transmission (%)
Substrate	-	1.5	90.3
N=1.5	107	1.66	87.3
N=4.7	121	1.69	87.9
N=8.6	115	1.72	86.7
N=12.3	98	1.71	85.0
N=15.6	102	1.72	85.3

The tendency, seen in Chapter 4, that an increase in refractive index reduces sample transmission can also be observed in Table 26. Interestingly, though the refractive index of N=8.6% and N=15.6% are the same, the average transmission of the latter is 1.4% lower. Also the lowest transmission is from the N=12.3% film, which has a marginally (0.01) *lower* refractive index than the N=15.6%. It was noted that the results in Figure 78 have been normalised to the thickness of the thinnest film, and in Section 4.3 it was observed that thickness was inversely proportional to refractive index for our films. The range in thicknesses of these samples has the thickest at 121 nm and the thinnest at 98 nm. Such a large variation in thicknesses, and the fact that the average transmission is normalised whereas the refractive index is as-received, frustrates a clear appraisal of the barriers optical characteristics.

It is not possible in this set of films to separate the contribution of refractive index change due to *thickness*, from that due to *nitrogen content*.

5.4 Barrier Testing

5.4.1 Steady-state Permeation and Activation Energy

The permeation results for the AlO_xN_y films are shown in Figure 79.

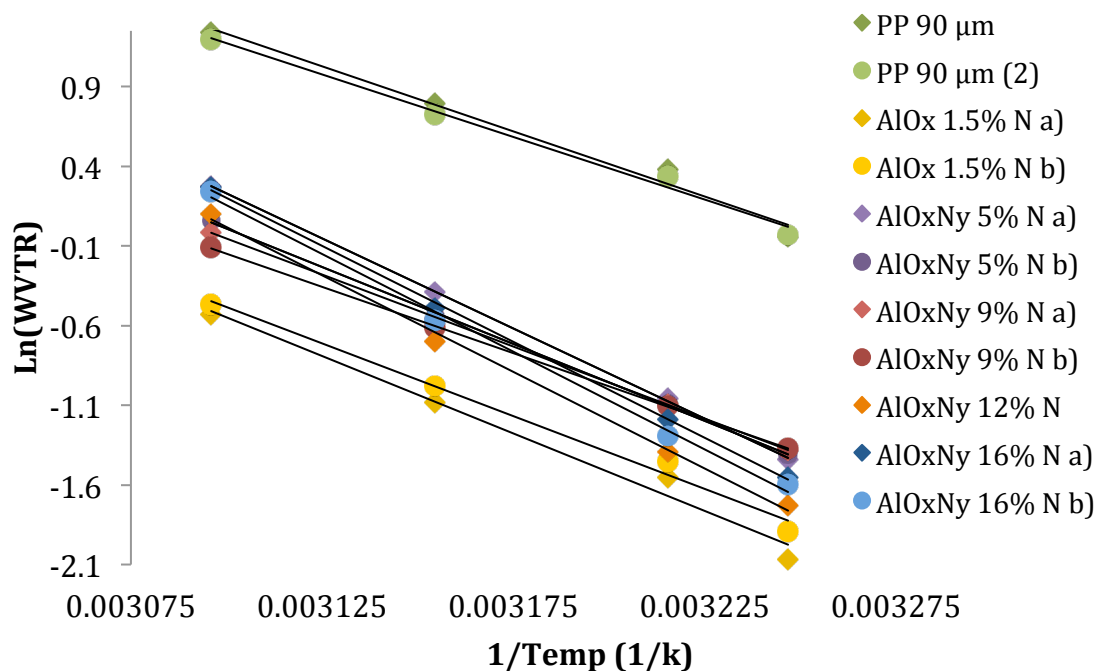


Figure 79. Arrhenius plot for barriers consisting of films with different nitrogen content.

It can be seen graphically that the lowest WVTR is exhibited by the AlO_x sample, but that as nitrogen content is increased, there is a resultant increase in activation energy.

The full permeation characteristics are summarised in Table 27.

Table 27. Permeation characteristics of barriers with coatings of different nitrogen content. All the samples are made at 1.85 kW and 70 m/min drum speed.

Film Nitrogen Content (%)	Film Thickness (nm)	WVTR at 38°C (g/m ² /day)	Activation Energy (kJ/mol)	Permeability (μm. g/m ² /day)
1.5 (oxide)	107	0.21, 0.23	81, 76	0.026
5	121	0.34, 0.35	94, 80	0.054
9	115	0.33, 0.34	75, 69	0.049
12	98	0.25	101	0.030
16	102	0.27, 0.30	100, 102	0.034

There is not an obvious trend observed with increasing nitrogen content.

As was discussed in the Section 5.3.2, the range in thicknesses (shown in Table 26) may frustrate the ability to pick apart the different contributions for these films. As was seen in Section 4.3.2, permeability decreased with thickness.

Using the model described in Section 3.3.2, there could be two possible explanations for the permeation data. Comparing the AlO_x (N=1.5%) and the N=16% AlO_xN_y:

Case A: A similar result as seen in Table 27 can be generated in the model if, compared to the control, the number of nano-defects are tripled. An increase in activation energy of 21 kJ/mol is observed along with a 0.05 g/m²/day increase in the WVTR.

As the activation energy has increased, it is understood that a greater proportion of the permeation is through nano-defects, but as the WVTR has also slightly increased, it could be that this was due to the increase in nano-defects in the oxynitride layer.

Case B: As was discussed earlier, nitrogen was added to foster a reaction between the permeant and the oxynitride. This, it is believed, would be seen as an increase in the

activation energy of the nano-defects (ΔE_{nd}). But as was observed in Section 3.3.2 (Test 4), when the activation energy of the nano-defects is increased, WVTR is reduced, and the proportion of the remaining flux passing through nano-defects is greatly reduced, resulting ultimately in polymeric activation. In order for any increase in the activation energy of the nano-defects to be present in the experimental data, it would have to be alongside an even greater increase in the number of nano-defects than was seen in Case A.

Another difference for this data-set regards refractive index. In Section 4.2 and 4.3, there was a trend observed that films of higher refractive index exhibited lower permeability. However, considering the refractive index data in light of the results in Table 27, it can be seen that the lowest refractive index film has recorded the lowest permeability. It may be that because the differences in composition also affect the refractive index, there is no strong correlation between refractive index and number of nano-defects in this case.

Erlat's key paper saw an 8-fold decrease in WVTR for AlO_xN_y over AlO_x . However, the AlO_x films had polymer-like activation (40 kJ/mol) and a WVTR of 2 g/m²/day whereas the AlO_xN_y films had an activation of 68 kJ/mol and WVTR of 0.25 g/m²/day [61]. The difference in *this project* is that Chapter 4 reported AlO_x films with up to 115 kJ/mol activation (48 kJ/mol greater than the substrate) and single oxide permeation as low as 0.13 g/m²/day. It appears that the AlO_x and AlO_xN_y layers in Erlat's paper were manufactured quite differently, so it is not clear that it was the increase in nitrogen content that produced the observed improvement in barrier. Using the model in Section 3.3.2 (Test 4), it was seen that an increase in nano-defect activation *alone* would not increase the activation energy of the film.

Although there has not been an 8-fold decrease in WVTR seen with the addition of nitrogen for *this project*, it can be seen that many of the AlO_x barriers already achieve low permeation. There has been evidence in this section that the addition of nitrogen has increased the number of nano-defects, which has limited the beneficial effect on permeation performance.

5.4.2 Qualitative Permeation: Calcium Test

The calcium test for the two highest nitrogen-level AlO_xN_y films is shown in Figure 80. The calcium test of an AlO_x film is included for comparison.

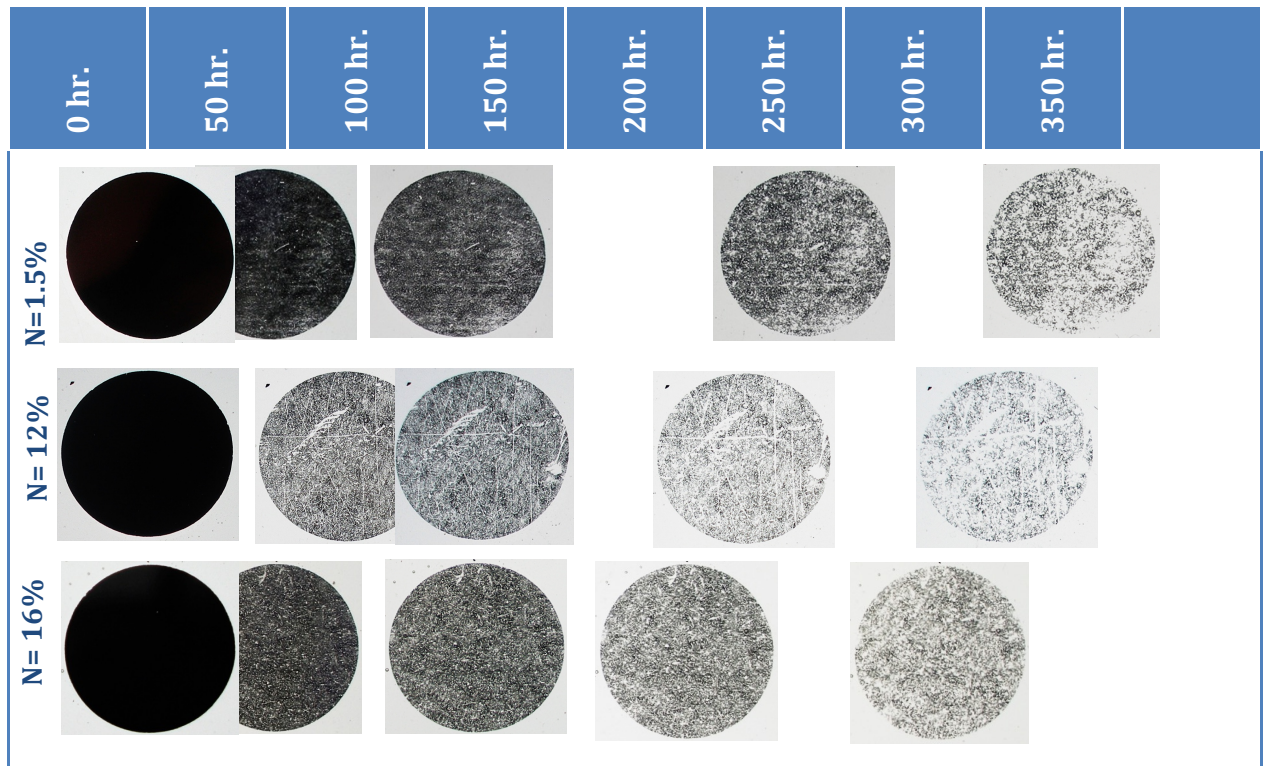


Figure 80. Calcium test for AlO_xN_y films of high nitrogen content. The N=1.5% sample is included for comparison.

The three samples (1.5%, 12%, 16%) have similar WVTR (0.21, 0.25, 0.27, respectively).

Figure 80 shows that the nature of the permeation for these films is similar: a uniform thinning is observed. Qualitatively, it seems that the oxide has more calcium remaining at the end of the test. There was no evidence in Section 5.4.1 for any change in the number of macro-defects across the three films, so the difference in performance would be due to the increased number of nano-defects for the 12% and 16% films.

The 12% appears to exhibit the worse performance, but this could be skewed by the large crack/scratch in the barrier.

5.5 Mechanical Testing – Nano-Indentation

Nano-scratch tests of the AlO_x and the N=16% AlO_xN_y coatings were carried out by Dr. J. Moghal.

5.5.1 Nano-indentation

The nano-indenter tip was scanned across and then driven into the coating surface. The load profile can be seen in Figure 81.

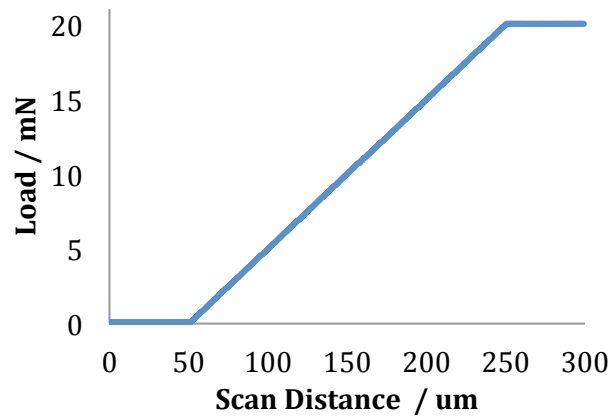


Figure 81. Load profile of the nano-scratch test. By Dr. J. Moghal.

A series of scratches were made on both films, as can be seen in Figure 82. The colour difference is due to image processing.

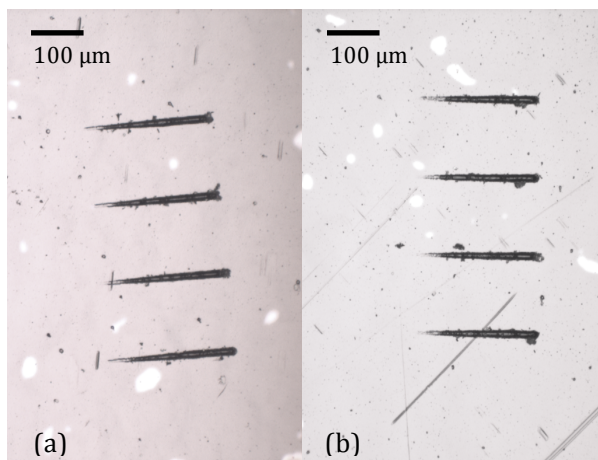


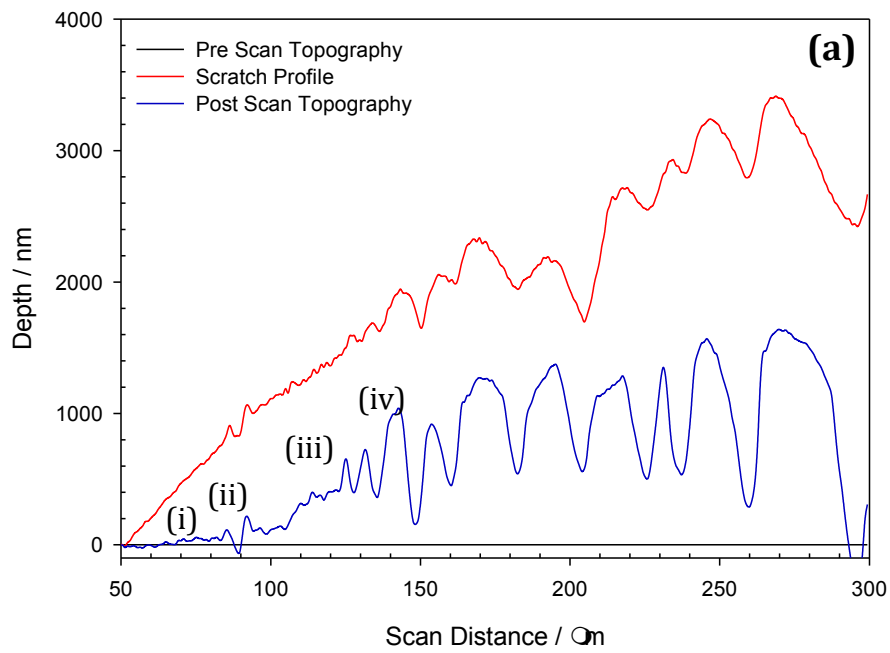
Figure 82. Polyvar optical microscopy image of nano-indentation scratches on (a) the AlO_x and (b) the AlO_xN_y (N=16%).

5.5.2 Post-Scratch Study

In order to study the nature of failure, AFM images of the scratches were compared with the scratch depth profiles.

Oxide

Figure 83 shows the scratch features on AlO_x .



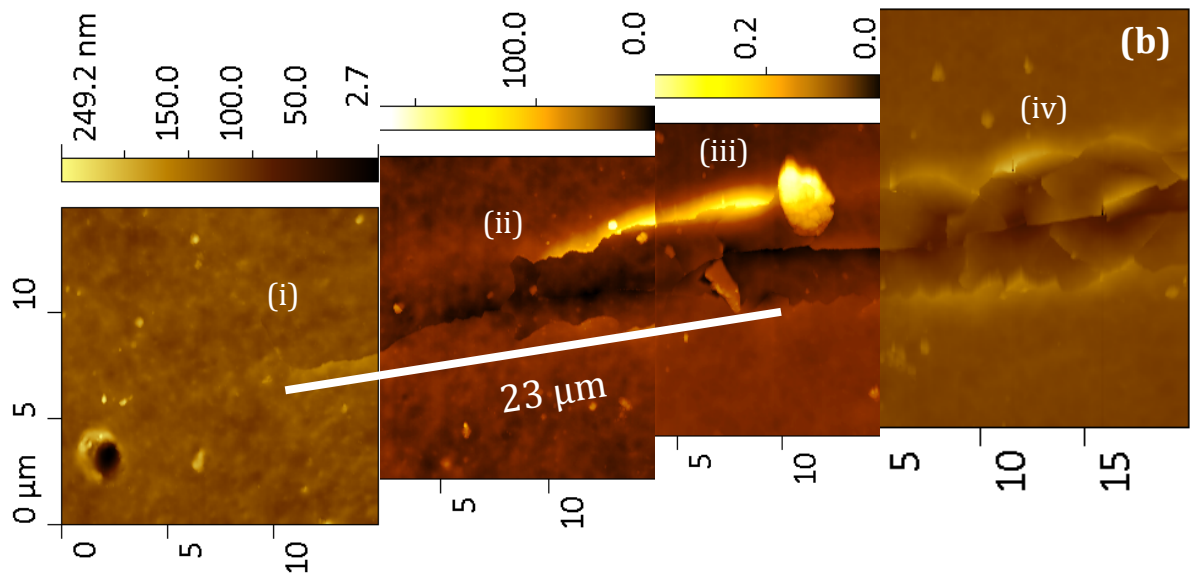


Figure 83. (a) scratch profile showing pre-scratch topography, scratch profile and post-scan topography (b) overlaid AFM micrographs of the scratch on an AlO_x coating. Hi-lighted positions correspond to (i) plastic deformation [$70\ \mu\text{m}$, $2.03\ \text{mN}$], (ii) cracking and film failure [$86\ \mu\text{m}$, $3.59\ \text{mN}$], (iii) indenter pierces film through to substrate, (iv) stick and slip substrate damage. All nano-indentation performed and initial descriptions of morphology behaviour by Dr. J Moghal, all AFM performed by Dr. S. Myhra.

It was seen that the film underwent plastic deformation at a load of $2.03\ \text{mN}$ (i) after scanning a distance of $70\ \mu\text{m}$. Once the load was increased to $3.59\ \text{mN}$, the film cracks (ii), indicating film failure. After a further $20\ \mu\text{m}$ of scanning, the indenter pierces through the film (iii). The “stick and slip” behaviour characteristic of polymer damage is seen (iv).

Oxynitride

The scratch analysis for the AlO_xN_y film is shown in Figure 84.

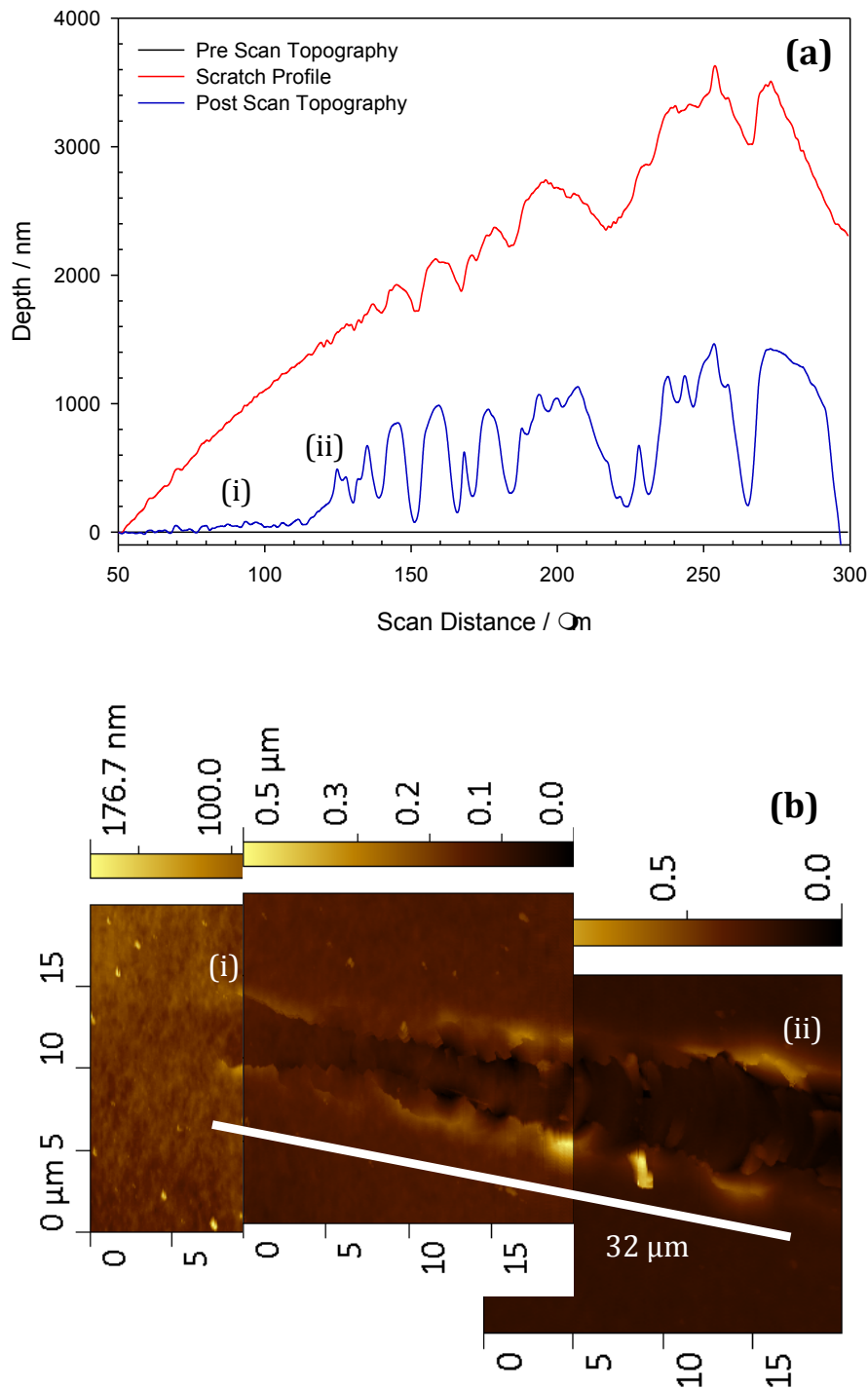


Figure 84. (a) scratch profile showing pre-scratch topography, scratch profile and post-scan topography (b) overlaid AFM micrographs of the scratch on an AlO_xN_y . Hi-lighted positions correspond to (i) plastic deformation [90 μm, 4.62 mN], (ii) total film failure [122 μm, 7.81 mN]. All nano-indentation performed and initial descriptions of morphology behaviour by Dr. J Moghal, all AFM performed by Dr. S. Myhra.

The failure of the AlO_xN_y film is different from the AlO_x . The initial plastic deformation does not occur until a higher force, 4.62 mN, is applied. Cracking behaviour is not observed. The film fails when it enters the substrate, at 7.81 mN, 122 μm into the scratch. Similar polymer-like stick and slip behaviour is observed from 122 μm onwards.

5.5.3 Film Failure Comparison and Discussion

The failure of the two films is summarised in Table 28.

Table 28. Comparison of AlO_x and AlO_xN_y film failures. The force *and* the distance at which these occurred are presented.

Sample	Plastic Deformation (mN) / (μm)	Film Cracking (mN) / (μm)	Film Failure (mN) / (μm)
AlO_x	2.03 / 70	3.59 / 86	5.6 / 106
AlO_xN_y	4.62 / 90	-	7.81/122

The AlO_xN_y plastically deforms at a factor of 2.3 higher load than the AlO_x , and film failure giving rise to slip-stick behaviour also occurs at a greater load for the AlO_xN_y .

Cracking can be observed in the scratch profile and post-scan topography of AlO_x in Figure 83 (a) as the feature at point (ii), however there is no such feature present in the data recorded for AlO_xN_y in Figure 84 (a). The AFM images in Figure 83 and Figure 84 indicate that in AlO_x , the scratch is a little narrower and characterised by “plates” of cracked oxide, in contrast to the more “crumbled” or plastically deformed morphology of the oxynitride.

The apparent greater resistance of the AlO_xN_y to initial mechanical damage is consistent with the higher refractive index of this material (as seen in Section 5.3.1), suggesting stronger bonding/greater density. However the propensity of the AlO_xN_y not to crack, but rather to plastically deform before the tip penetrates through to the substrate, might suggest that there

are a numerous points where deformation can happen, rather than deforming by formation of larger cracks as was the case for AlO_x . This perhaps suggests that the AlO_x contains larger monolithic regions through which cracks must propagate to deform the coating. This would be consistent with the analysis of Section 5.4.1, which suggests (in either case) that the AlO_xN_y has a greater number of nano-defects than the AlO_x .

5.6 Chapter Summary and Discussion

- The highest achievable nitrogen content possible was 16%. Different attempts were made to increase this, but the greater reactivity of oxygen means better control of residual oxygen containing species in the deposition environment is required for greater N content.
- XPS showed all nitrogen to be bonded to aluminium.
- Increased nitrogen content produced films with greater refractive indices, as has been seen by others.
- UV-VIS, followed the trend that higher refractive index films are more absorbing.
- Increasing the nitrogen content of the AlO_xN_y films did not show a clear improvement in permeation characteristics. Better process control of coating thicknesses and nitrogen content (under the same process characteristics) is required to separate contributions from thickness from those of barrier chemistry.
- Calcium test observations show no clear improvement for increased nitrogen, but the nature of calcium decay appears the same for all compositions observed.
- Nano-scratch shows that the AlO_xN_y film deforms and fails at a load a factor 2 greater than the AlO_x , but with less tendency to form discrete cracks, which might suggest a high density of nano-defects in the coating, consistent with the permeation characteristics.

It was not possible to reproduce the permeation improvements for AlO_xN_y observed by Erlat et al. Erlat's SIMS evidence of a dissociative reaction between permeating H_2O and the oxynitride matrix is convincing [61], however, the attribution of this reaction as the reason for the barrier improvement could be a case of *post hoc ergo propter hoc*. It was shown through the model that an increase in activation for permeation through each nano-defect would have the effect of reducing WVTR, but also reducing the proportion of permeation through nano-defects, and hence the overall activation energy. Erlat's AlO_x (in contrast to their AlO_xN_y) has a large WVTR with polymer-like activation, which points to permeation mainly through a large number of macro-defects. A change to the activation energy of the nano-defects of this type of film would not produce a significant change in permeation characteristics.

Erlat et al. suggested that too high a level of nitrogen in their AlO_xN_y films led to detrimental effects: an Al/N ratio of 1.5 recorded a WVTR of $\sim 0.1 \text{ g/m}^2/\text{day}$, but if Al/N ratio was increased to 0.75, the WVTR increased to $\sim 0.45 \text{ g/m}^2/\text{day}$ [61]. However the maximum Al/N ratio produced for this project was 2.6, so it is not believed that this is the reason for the lower-than-expected performance.

In Chapter 4 it was shown that the AlO_x coatings produced in the current project exhibited the majority of permeation through nano-defects, and that changes in thickness, power, and, less convincingly, drum speed, could decrease this permeation further. However, in Chapter 5 addition of nitrogen has not been shown to improve the permeation characteristics.

The improved hardness figures for AlO_xN_y are encouraging. The nature of the barrier failure was different, with the AlO_x cracking and the AlO_xN_y plastically deforming through its thickness. A study of which barrier failure regime is preferred for the application of flexible barrier technology would be interesting. As the AlO_xN_y remained intact to greater loads, it might perform better as a barrier after moderate mechanical deformation of the coated films.

6 Acrylates and Multilayers

This chapter covers the integration of di-acrylate layers into barrier fabrication. The following sections look into the use of DA layers as single planarising layers (Section 6.1), as capping layers (Section 6.2) and their inclusion in multi-layered barriers (Section 6.3).

6.1 Acrylate Smoothing Layers

It was desirable to deposit the acrylate and oxide layers without breaking vacuum, but with early PP/DA/ AlO_x samples the deposition of acrylate 20 minutes before RF sputtering reduced the O_2 gas flow required to poison the cathodes by 5 sccm. These results underscore the importance of hysteresis in RF sputtering, but also the sensitivity exhibited by the system with regard to poisoning. This effect could be caused by residual organic species in the chamber atmosphere and/or by acrylate contamination on the cathodes.

For all barriers except the PP/DA/ AlO_x samples, therefore, at least 6 hours were allowed to pass following DA deposition, with excess gases being pumped away, and the cathodes were “cleaned” by sputtering without reactive gas for 5 minutes (with the deposits falling on the opposite side of the drum from the substrates) prior to sputtering. This procedure was done to ensure the poisoning position returned to the expected flow rate.

6.1.1 Curing – FTIR

The FTIR was used to ensure the DA was fully cured. The methodology is described in Section 3.5.3. These measurements were performed any time major changes to the e-beam system were made.

Three samples of PP/DA were fabricated with varying thickness but the same injection rate (0.5 ml/min). As the PP substrates were attached to the drum, the increased thickness was

due to longer deposition times, that is more passes of the substrate past the deposition source. The FTIR results for the three films are shown in Figure 85.

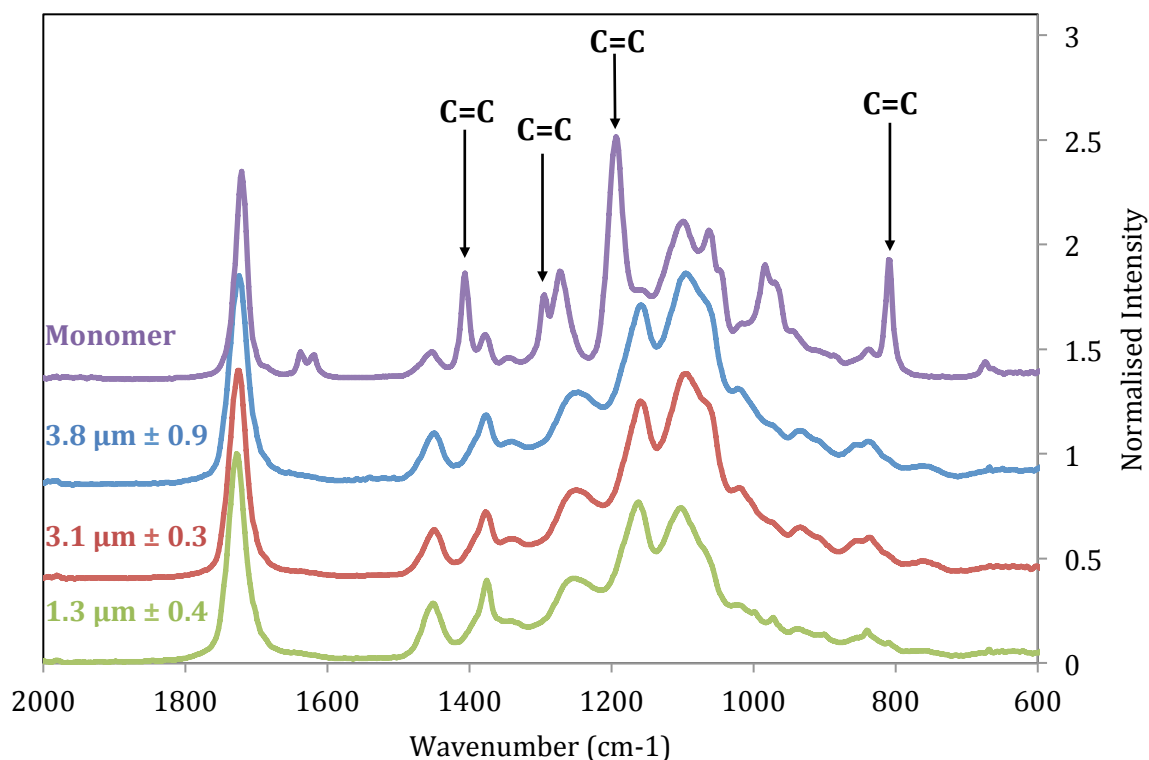


Figure 85. FTIR of TRPGDA coatings on PP compared with the pure, un-cured liquid monomer.

A number of peaks can be observed in the FTIR scan of the monomer. Using the analysis of Affinito, peaks highlighted in Figure 85:

“...disappear upon polymerization as the C=C bonds are converted to C–C bonds” [28].

These peaks were absent for all three thicknesses of DA produced. Affinito emphasises the importance of fully curing the monomer, and that even small amounts of uncured monomer can lead to poor barrier performance [28]. Affinito does not specify why this is.

Due to the in-line nature of the system, it was not possible to test the cure of each DA layer *as-deposited*, since most were subsequently coated with an RF sputtered AlO_x or AlO_xN_y layer, which could contribute to DA curing.

6.1.2 Surface Morphology

Early in the project, studies of the morphology of the planarizing layer found that—far from being smooth—the samples still exhibited large features as can be seen in Figure 86. This was even after the deposition of $\sim 2\text{-}3\ \mu\text{m}$ of acrylate.

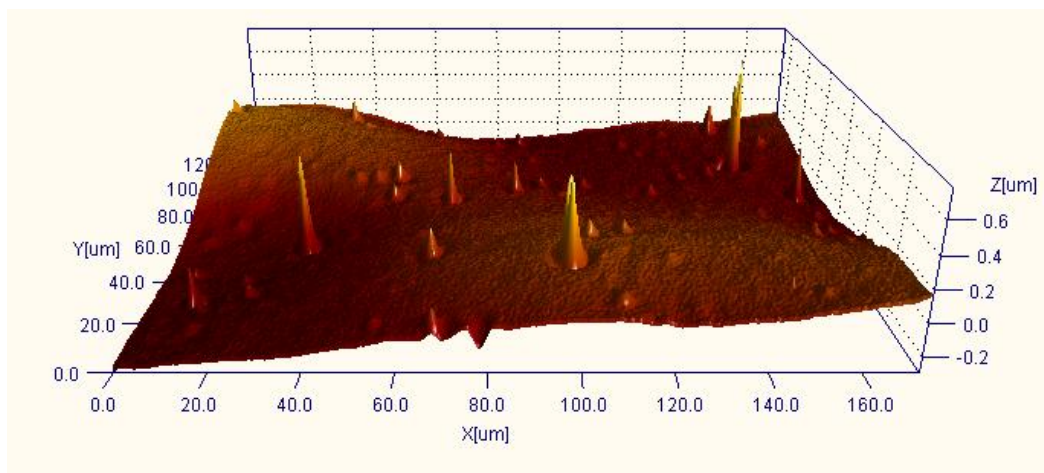


Figure 86. MicroXAM micrograph of PP/DA (2-3 μm)/AlO_x($\sim 140\ \text{nm}$). Large peaks are visible.

It was initially thought that these features may be due to substrate prominences not being completely covered. However when the same materials were deposited on the Teonex, these features were still visible (Figure 87).

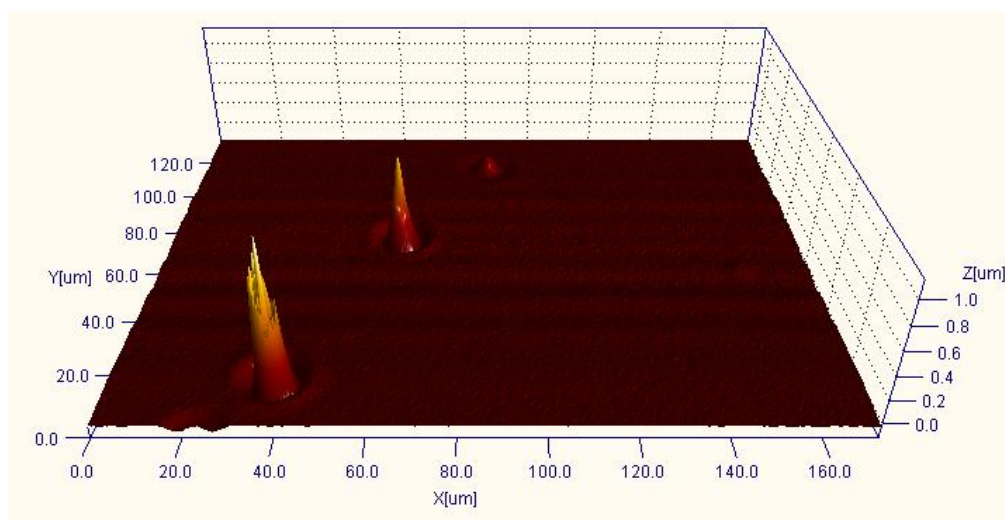


Figure 87. MicroXAM micrograph of Teonex/DA(2-3 μm)/AlO_x ($\sim 140\ \text{nm}$). Large features are visible. N.B. the long straight ripples are artefacts of the white-light profilometer. Please note the Z-scale is different from that of Figure 86.

Please note the differing Z-scales between Figure 86 and Figure 87, and the fact that they are greatly exaggerated. The largest feature in Figure 87 is $\sim 1\text{ }\mu\text{m}$ tall but $\sim 10\text{ }\mu\text{m}$ wide. These features are characteristically round, with a dip around their circumference. It is hypothesised that the presence of these features on the smooth Teonex points to their source as artefacts of acrylate deposition. Many attempts were made to remove these (the evaporation chamber and nozzle were cleaned, different monomers used, filtration applied, drum speed altered) but no solution was found. It was subsequently observed that these smoothed systems performed well under barrier tests, so the project moved forward. It is worth noting that issues such as these may be important for some technologies, especially for the integration of these layers with organic optoelectronics, as was pointed out in Section 1.3.1.

The following Figures show micrographs of a smoothing layer on PP/ AlO_x (Figure 88) and an AlO_xN_y coated smoothing layer on PP (Figure 89).

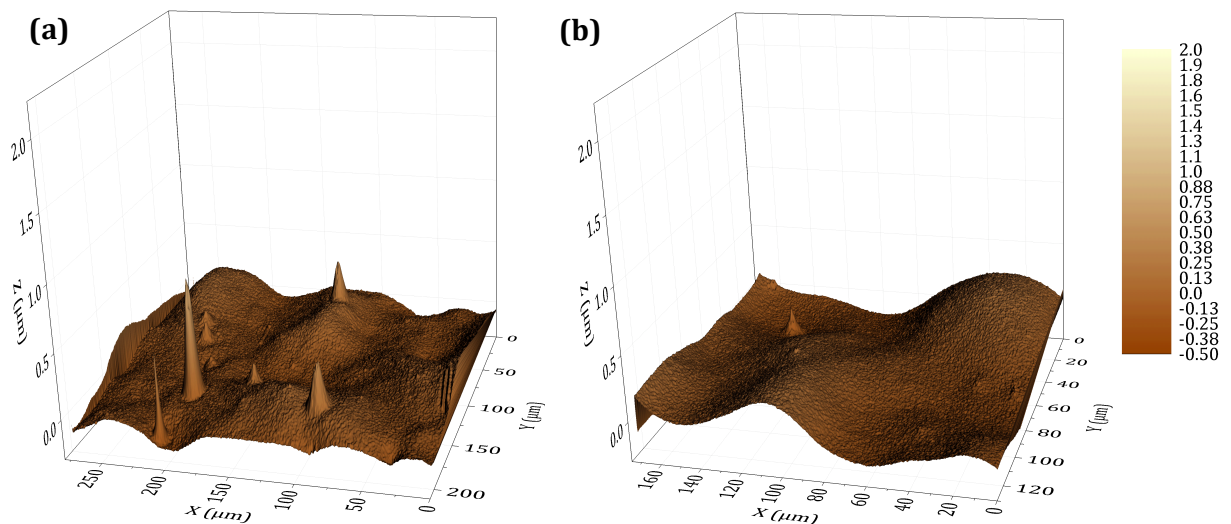


Figure 88. MicroXam (a and b) of PP/ AlO_x (~98 nm)/DA(~3 μm). This thick DA layer is believed to cover any features on the substrate or roughness introduced by the oxide. Micrograph (a) is of a wider (280 x 210 μm) area of the coating than all other micrographs.

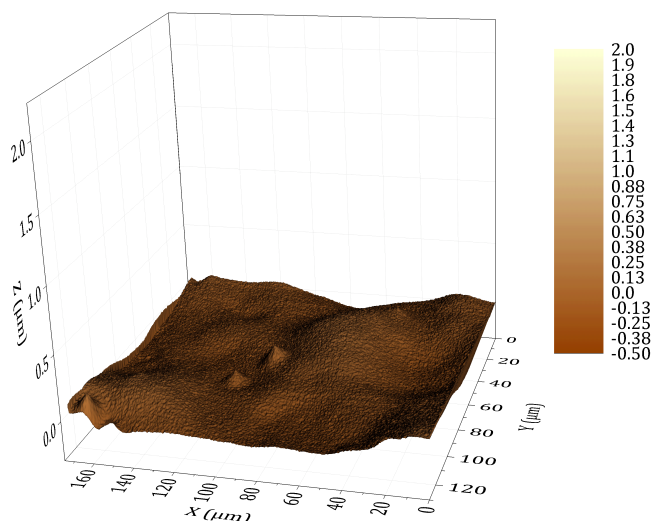


Figure 89. MicroXAM of PP/DA(~3 μm)/AlO_xN_y(~100 nm).

The RMS roughness of these micrographs are shown in Table 29. As was discussed in Section 4.1.2.1, all micrographs are presented “as-received”, however 10th order polynomial background subtraction was applied prior to measuring RMS. This was done to remove the contribution to the RMS from the long wavelength waviness of the surface.

Table 29. RMS roughness of the MicroXAM figures above, calculated using Gwyddion [101]. All samples underwent a 10th order polynomial background subtraction.

Sample	RMS Roughness (nm)	
PP/AlO _x /DA (Figure 88)	(a)	27.1
	(b)	8.0
PP/DA/AlO _x N _y (Figure 89)	-	8.3

These micrographs are investigated in order to study the nature of the roughness and features of the di-acrylate layer and the roughness and features of AlO_x and AlO_xN_y that have been deposited on a di-acrylate layer. The following assumptions have been made:

1. The DA layer studied has been deposited on top of a ~100 nm AlO_x layer, which had been initially deposited on a Rayoart PP substrate. It was for reasons of limited resources that a separate PP/DA sample could not be made. It is assumed that any

independent contributions to roughness from the AlO_x have been coated by the $\sim 3\mu\text{m}$ of DA.

2. The DA layer, being over $3\mu\text{m}$ in thickness, has fully covered any Rayoart PP asperities.
3. The $\text{PP/DA/AlO}_x\text{N}_y$ sample is not AlO_x , which, as with point 1, would have aided comparison with Figure 48, the PP/AlO_x . Therefore here it is assumed there is no contribution to roughness due to the nitrogen content of the coating, and that these different coatings appear the same under study by MicroXAM.

Comparing the $\text{PP/AlO}_x\text{/DA}$ (Figure 88) to the Rayoart PP substrate in Figure 47 on Page 98, reveals striking differences. Figure 88 (b) has one visible asperity of 190 nm in height and is characterised by long wavelength waviness. Figure 88 (a) has one large feature of 800 nm in height and 7 other peaks $\leq 500\text{ nm}$. The features of Figure 88 (a) tally with those seen in Figure 86 and Figure 87 and are considered to be artefacts of acrylate deposition. Although these features exist, they are more rounded and less prominent than the features on the Rayoart substrate. Figure 90 compares the large asperity on the Rayoart PP in Figure 47 (a) with the largest feature of the $\text{PP/AlO}_x\text{/DA}$ in Figure 88 (a).

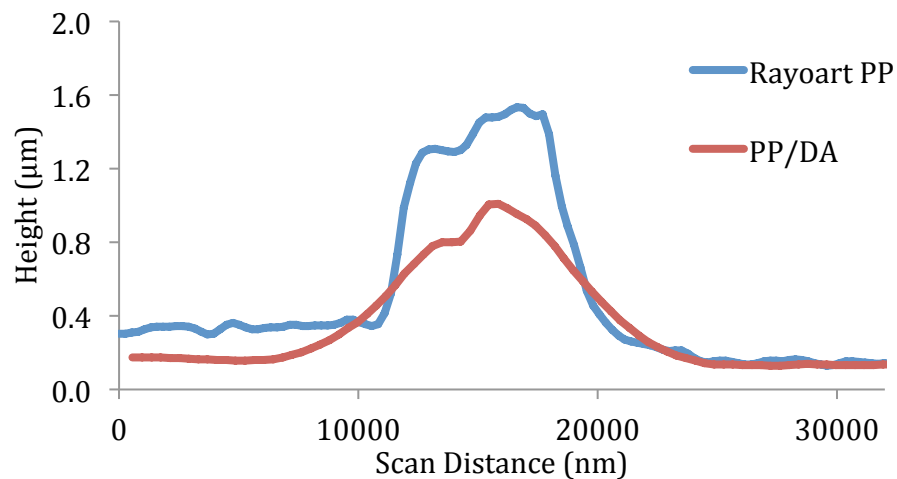


Figure 90. Profile scans of the largest feature in Figure 47 (a) (Rayoart PP) and the largest feature in Figure 88 (a) ($\text{PP/AlO}_x\text{/DA}$).

It can be seen that the Rayoart PP asperity has a larger aspect ratio, 1.2 μm in height and 11.2 μm in width (1:9), whereas the feature on the DA is 0.8 μm in height and 20 μm wide at its base (1:25). It is thought that the sharp change in gradient present in the Rayoart PP asperity would be much more detrimental to AlO_x coverage than the more gentle changes evident in even the worst section of DA.

In order to better compare the surface roughness between the large asperities, such as could influence nano-defects in the barrier layers, expanded views of one quadrant of the PP/ AlO_x /DA (Figure 91) and the PP/DA/ AlO_xN_y (Figure 92) have been produced. Please note: the Z-scale has been exaggerated to an even greater extent in order to compare roughness away from surface asperities.

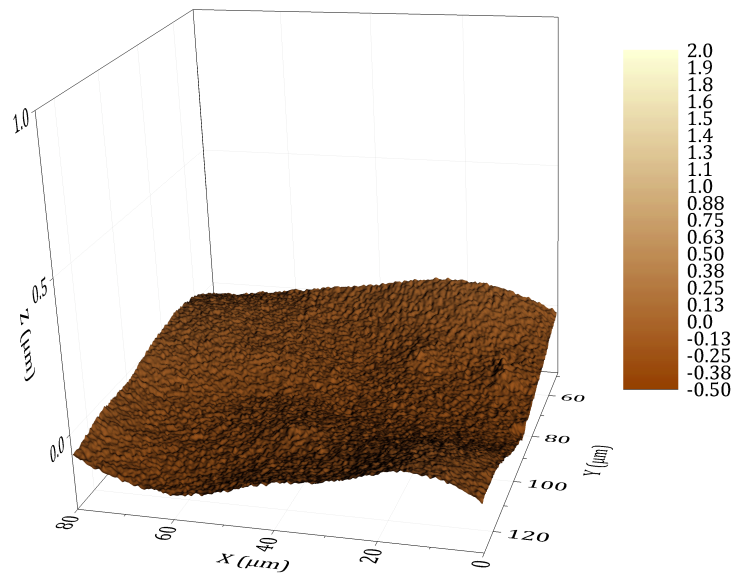


Figure 91. MicroXAM image of PP/ AlO_x /DA. This is an expanded view of Figure 88 (b), bottom-right quadrant.

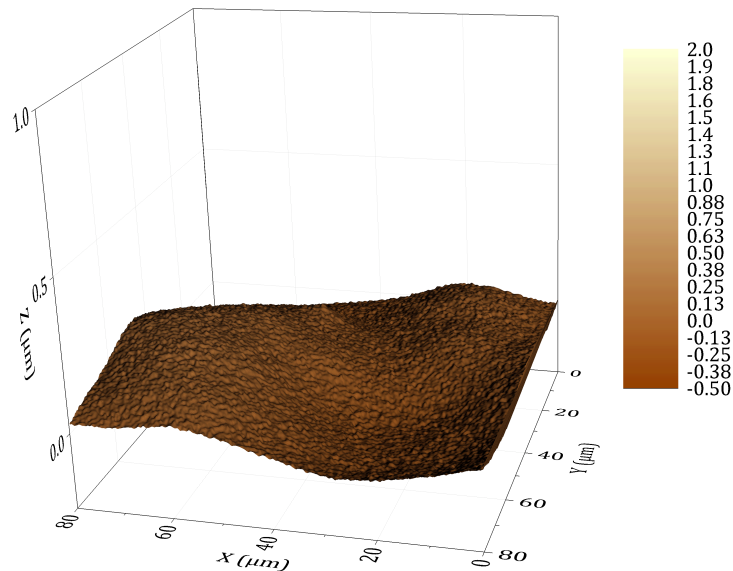


Figure 92. MicroXAM of PP/DA/AlO_xN_y. This is an expanded view of Figure 89, top-right quadrant.

Table 30. RMS roughness of expanded MicroXAM views. Each crop was additionally levelled.

Sample	RMS Roughness (nm)
PP/AlO _x /DA (Figure 91)	7.0
PP/DA/AlO _x N _y (Figure 92)	6.6

Qualitatively, it is argued that the nature of the surface roughness of the smoothing layer (Figure 91) and the AlO_xN_y coated smoothing layer (Figure 92) are similar. This is supported by the RMS data in Table 30, which shows that the PP/DA/AlO_xN_y has similar RMS roughness, 5.7% lower than the PP/AlO_x/DA.

Comparing Figure 91 of the expanded-view of DA surface roughness with that of the expanded-view PP substrate, shown in Figure 50 on Page 101, it can be seen qualitatively that the local surface roughness is greatly improved by the addition of the DA layer.

Quantitatively, the RMS for the DA is 70% lower than the RMS of the PP.

6.1.3 Steady-state Permeation and Activation Energy

Table 31 compares the permeation characteristics of barriers incorporating single smoothing layers with those of the simple Polymer/ AlO_x barriers described in Section 4.1.2.

Film	Thickness (μm)	WVTR at 38°C ($\text{g}/\text{m}^2/\text{day}$)	Activation Energy (kJ/mol)	BIF	Permeability ($\mu\text{m}.$ $\text{g}/\text{m}^2/\text{day}$)
PP	90	1.43	67	-	128.7
PP/DA	90/3.1 $\pm$ 0.3	1.55*	-	-	-
PP / AlO_x	90 / 0.145	0.38	104	4	0.075 (coating)
PP/DA/ AlO_x	90 / 1.3 $\pm$ 0.4 / 0.145	0.055	143	26	0.0083 (coat. assumed.)
Teonex / AlO_x	125 / 0.148	0.054, 0.076	84,95	19-27 (Teonex)	0.0083 (coating)

Table 31. Comparing the WVTR, activation energy, BIF, and permeability of the substrate, a DA coated substrate, an AlO_x coated substrate, and AlO_x deposited on a DA smoothed substrate. N.B. the PP/DA/ AlO_x layer thicknesses are typical and not directly measured, thus the calculation of permeability is done with these assumed values.

Certain assumptions have been made:

- All multiple layer systems (with AlO_x and DA) described here are reported with estimated thicknesses. Due to the in-line nature of deposition and lack of integrated QCM, only the sum of their thicknesses is known. The estimations are based on recent single-layer depositions under identical conditions.
- The WVTR result for PP/DA was not fully calibrated; however, the result is to establish that the DA has no independent barrier properties, which has been also been found by others [30][3].

Comparing PP/AlO_x to PP/DA/AlO_x

The DA layer is shown to have no independent barrier properties. However, when comparing PP/AlO_x to PP/DA/AlO_x it can be seen that there *are* improvements in the barrier characteristics of the oxide layer due to the effect of the DA. The PP/DA/AlO_x exhibits permeability a factor of 6.5 lower and activation energy 39 kJ/mol higher than the AlO_x coating alone. This points to an even higher proportion of the greatly reduced permeation passing through nano-defects.

Referring to the Model in Section 3.3.2, this is clearest in looking at the change between Test 3 and Test 1 (the Control). When the number of macro-defects is reduced by a factor of 2, the activation energy jumps up (reflecting the greater proportion of the measured WVTR passing through nano-defects) and the WVTR reduces.

To try and match the figures of the experimental results more closely, a model test was run with the macro-defects of the control reduced by a factor of 8. In this case the activation increased from 96 kJ/mol to 133 kJ/mol and the WVTR reduce from 0.12 to 0.04 g/m²/day. This large increase in activation and concomitant drop in WVTR is consistent with a large reduction in the number of macro-defects. This does not exclude the possibility of a small change in nano-defects (due to different oxide formation), but it does point to the reduction in macro-defects as being the decisive change between these films.

Another possibility (as was seen in Test 4), is an increase in the activation energy of the nano-defects (ΔE_{nd}), which would result in reduction in WVTR, but this would reduce the activation energy of the barrier to that of the polymer. Conversely, if the activation energy is at all decreased, there is a large jump in WVTR.

What is clear is that for PP/DA/AlO_x, the results reveal permeation mainly through nano-defects and at a greater ratio than any other barrier in this report. The addition of a smoothing layer to the substrate has been shown to significantly lower overall permeation by reducing the flux through macro-defects.

Comparing Teonex/ AlO_x to PP/DA/ AlO_x

Comparing the barrier characteristics of the Teonex/ AlO_x to the PP/DA/ AlO_x , it is clear that although coincidentally the films exhibit the same WVTR, there is a significant difference in activation energy. The Teonex/ AlO_x appears to have a comparatively greater proportion of permeation through macro-defects, whereas the PP/DA/ AlO_x has a greater proportion through nano-defects.

Referring to the model in Section 3.3.2, comparing the Control to Tests 7 and 8 elucidates two ways in which films of the same WVTR but different activation energies can be formed.

Case A: Test 7 shows one possibility, where a reduction of macro-defects but an increase in nano-defects would alter the ratio of permeation through these defects, so as to increase the measured activation energy, while leaving the WVTR the same.

Case B: Test 8 shows that another possibility would be to increase the nano-defect activation energy (making them harder to pass through) but then increasing the number of nano-defects.

Case C: This third case was not presented in the model. This would include the reduction of the nano-defect activation energy (i.e., less energetically taxing), with the expected large increase in WVTR being offset by a reduction in the number of macro-defects and nano-defects.

Discussion: The DA could provide a smoother layer for the AlO_x to form on, thus reducing macro-defects (**Case A**). Another possibility is that the Teonex induces the formation of an AlO_x layer that has fewer nano-defects, with **Case A and B** pointing to this. **Case C**, however, is predicated on the film with higher overall activation, having lower nano-defect activation (ΔE_{nd}), which also undermines the quality of the AlO_x barrier deposited on PP/DA. All examples point to a higher quality film (in terms of microstructure) on the Teonex, albeit one with a larger number of macro-defects (perhaps from the substrate).

A clear take-home message here is that the addition of the DA layer to the cheaper industrial-grade PP has induced barrier performance in the AlO_x equal to that of AlO_x on Teonex.

6.1.4 Qualitative Permeation: Calcium Test

A comparison of the calcium test of PP/ AlO_x and PP/DA/ AlO_x can be seen in Figure 93.

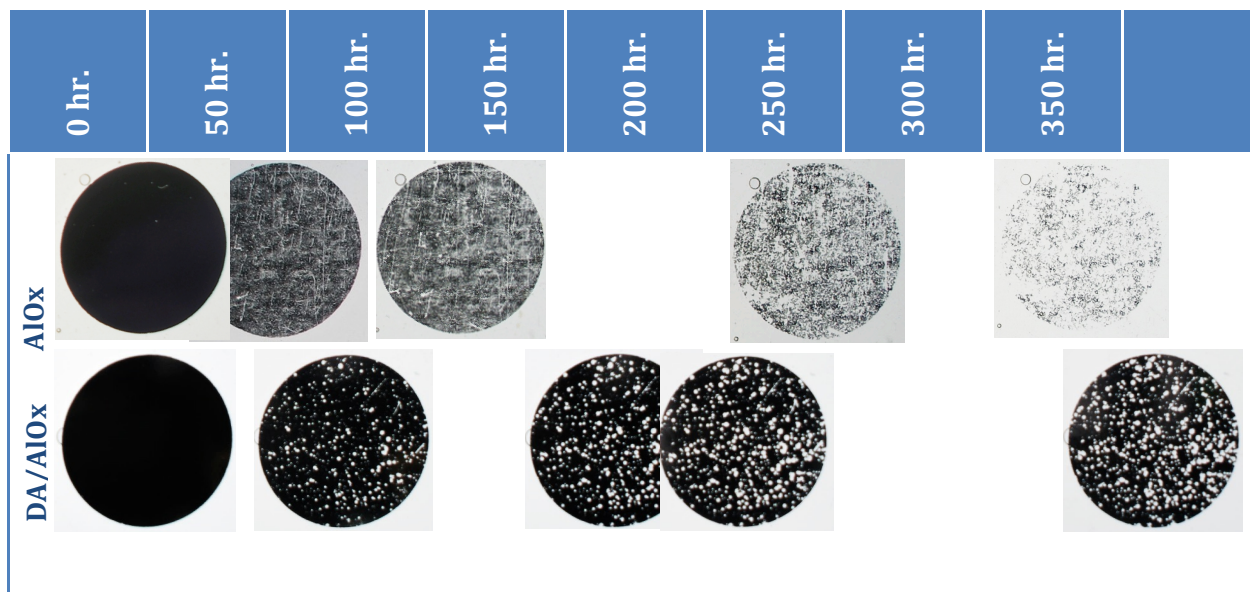


Figure 93. Calcium test comparing AlO_x (117 nm) to a di-acrylate smoothed PP coated with AlO_x (~145 nm).

It should be noted that the AlO_x coating on the PP is thinner than the one on the PP/DA. This is an important difference, since shown and discussed previously in Section 4.3, the thickness differences tend to change the WVTR and thus calcium-test lifetime. In this comparison, however, the key difference is the *nature* of the permeation.

The figure shows the improved performance of the PP/DA/ AlO_x over the PP/ AlO_x : increased lifetime (remembering the preceding caveat) and the nature of the remaining calcium.

The nature of the permeation through the PP/DA/ AlO_x barrier is remarkably different. For this barrier, the calcium decay proceeds as small white spots of hydroxide forming and expanding. There is no gradual thinning of the intervening calcium, and areas untouched by the expanding hydroxide still appear opaque at 360 hours.

The PP/AlO_x thins uniformly with few purely white spots until ~230 hours. However, the first image at ~50 hours shows 2-3 discernable cracks that also allow permeation. By contrast, the first image (70 hours) of the PP/DA/AlO_x has numerous spots of calcium hydroxide. These spots have been exposed to enough water within 70 hours to have their full thickness converted to hydroxide. Although the PP/AlO_x exhibits a global thinning, it is also quite uniform. The PP/DA/AlO_x has local permeation surrounded by regions of no (discernable) permeation.

The permeation results of Section 6.1.3 suggest that PP/DA/AlO_x has seen a reduction in the number of macro-defects, but it is not clear how this translates to the localised permeation observed in this Section.

Another interesting comparison can be made between the PP/DA/AlO_x in Figure 93 and the Teonex/AlO_x in Figure 53 on page 104. The best results for both of these barriers yield nearly the same WVTR, 0.055 and 0.054 g/m²/day respectively. When considering the calcium tests of these barriers it is striking how different they are. The PP/DA/AlO_x appears to perform much better. The calcium test of the Teonex/AlO_x appears to exhibit features of both the PP/DA/AlO_x and PP/AlO_x: uniform greying and spots that expand. This again shows the importance of substrates and substrate preparation.

Figure 94 shows the calcium test of PP/DA/AlO_xN_y with the calcium test of PP/AlO_xN_y for comparison. Please note: There is no activation energy data for the PP/DA/AlO_xN_y sample. The WVTR at 38°C, as measured by RDM (M. James, RDM Test Equipment, CM22 6JX), was 0.31 g/m²/day. This is higher than that measured for PP/AlO_xN_y, which was 0.27, 0.30 g/m²/day with activation of 100, 102 kJ/mol.

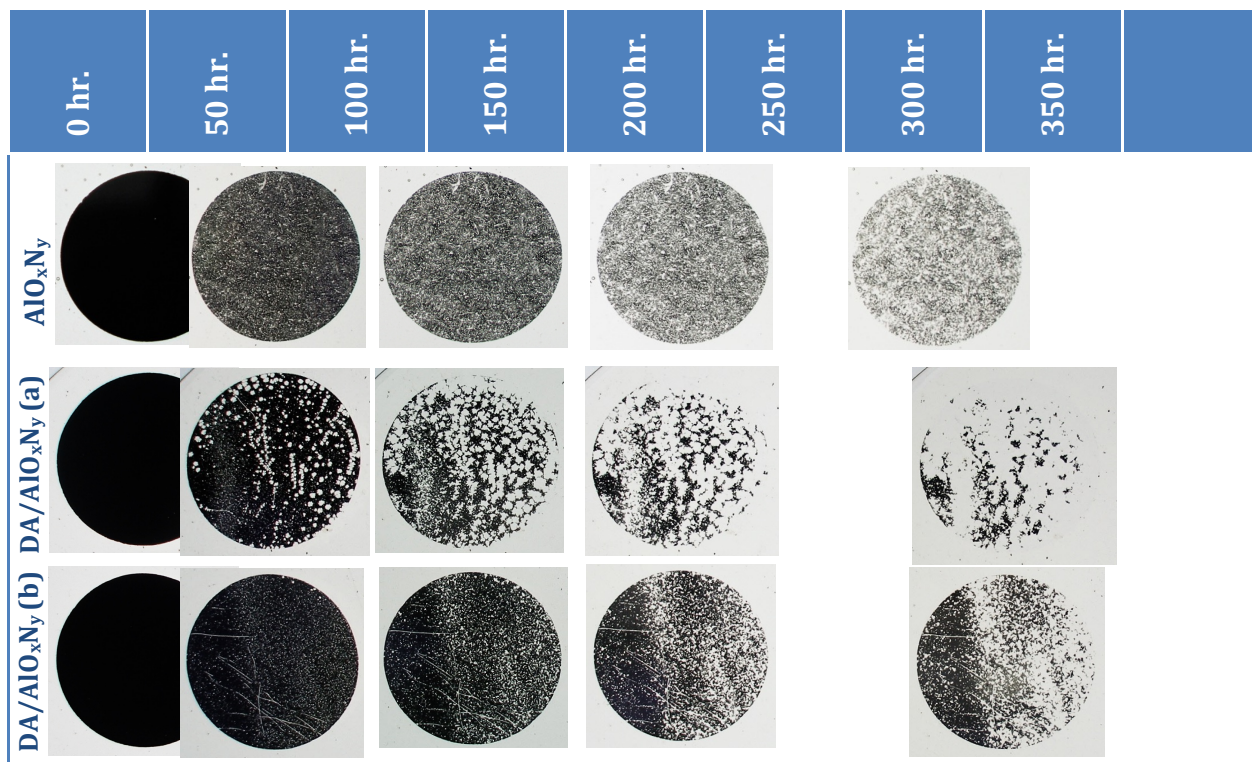


Figure 94. Comparison of AlO_xN_y with DA/ AlO_xN_y . In this calcium test comparison, there was such variation between different Ca that two were included.

The poor permeation characteristics show that there are issues with the PP/DA/ AlO_xN_y that transcend the differences between the AlO_x and the AlO_xN_y observed in Section 5.4.1.

The take-home message of Figure 94 is that even with the unexplained detriment to the WVTR, the nature of the permeation through the PP/DA/ AlO_xN_y resembles that of the PP/DA/ AlO_x , although an improvement over the unsmoothed PP/ AlO_xN_y is not evident.

Direct comparison of the PP/DA/ AlO_xN_y and PP/DA/ AlO_x directly is frustrated by differences between these films that must be kept in mind:

- The DA for the AlO_xN_y is much thicker, $\sim 3 \mu\text{m}$, compared to $1.3 \mu\text{m}$ for the AlO_x .
- The PP/DA/ AlO_xN_y was produced after a major e-beam refit. It is difficult to directly compare the e-beam performances, as there was little characterisation of the e-beam done before the refit became necessary.
- The DA/ AlO_x were deposited in quick succession, with only 20 mins between stages.

This had a detrimental effect on the poisoning position, but infers that there was a base level of poisoning species, so the resulting effect on the barrier is unclear.

However by waiting 6+ hours between the DA and AlO_xN_y , there could have been a change the nature of the DA surface.

With these caveats considered, there are clearly differences and similarities between the calcium test for the PP/DA/ AlO_x (Figure 93) and the PP/DA/ AlO_xN_y (Figure 94). Both are characterised by the formation of spots of hydroxide that expand as the test progresses. They both have dark, calcium rich, opaque regions after 300 hours. They differ in that this expansion is much more rapid for the PP/DA/ AlO_xN_y with very little calcium left after 300 hours.

Figure 94 is different from all other calcium tests in this report in that two examples for the PP/DA/ AlO_xN_y have been shown. This was because of the large difference in calcium decay for these two spots.

The calcium test for PP/DA/ AlO_xN_y (a) bears the greatest resemblance to that of the PP/DA/ AlO_x , but the spots of hydroxide do not expand in a circular fashion, i.e. converting calcium to hydroxide in at an equal rate in all directions. The calcium hydroxide in (a) instead expands in a spiky, staggered way. The calcium test for PP/DA/ AlO_xN_y (b) bears less resemblance to PP/DA/ AlO_x , and seems to form much smaller spots of hydroxide, which expand rapidly. Another curious feature is that there is not the uniformity observed in all other calcium tests in this report, as the left side has more calcium remaining after 300 hours than the right. Also (b) performs better than (a) in terms of the amount of calcium remaining at the end of the test.

It is not clear from the data in this report why these differences are observed.

6.1.5 Summary and Conclusions: Smoothing layer

Section 2.3.3 and 2.4 explained that substrate surface features caused a significant proportion of macro-defects. It was elaborated that these macro-defects allowed unhindered permeation through barrier coatings. Section 2.4.2.2 reviewed how acrylate smoothing layers might be

used to cover substrate surface features so as to provide a planarised layer for the deposition of oxide barrier coatings. Acrylate layers were included into barrier structures in this project in order to lower permeation through the reduction of macro-defects.

PP/AlO_x and PP/DA/AlO_x

MicroXam studies of the PP surface in Section 4.1.2.1 showed that it was characterised by (a) large micron-sized surface asperities and (b) a general high RMS surface roughness (23.5 nm – away from asperities). The studies of DA and DA/AlO_xN_y in Section 6.1.2 revealed surfaces with fewer micron-order features, with those remaining having a more gradual change in gradient. Lower RMS roughness was exhibited away from these features with the DA – 7 nm, and DA/AlO_xN_y – 6.6 nm.

The permeation results for PP/DA/AlO_x (Section 6.1.3), interpreted in conjunction with the model, exhibited a large decrease in WVTR and an increase in activation. This data was interpreted as due to a reduction in macro-defects, with a greater proportion of the remaining permeation passing through nano-defects. The permeation test results appeared to bear out the hypothesis that a reduction in macro-defects (observed by MicroXam) produces a reduction in permeation (MOCON and the model).

The calcium test exhibited a significant reduction in permeation and a change in the distribution of the remaining permeation. Localised permeation, a “starry night” of conversion of calcium into calcium hydroxide, was observed. It is possible that the reduction in macro-defects observed is expressed in the calcium test as the “starry night”, which would imply that the general greying (seen for PP/AlO_x) is due to a high density of defects that are not resolved from one another due to the limitations of calcium test imaging (see Figure 41). This comes with the caveat that the PP and DA surfaces present significantly different adhesion (discussed in Section 4.1.2.1) and nucleation (discussed in Section 2.5.1) regimes,

and without further investigation into these, it cannot be said how much of an influence these have on the results outlined in this sub-section.

PP/DA/AlO_x and Teonex/AlO_x

MicroXam studies in Section 4.1.2.1 elucidated the striking difference between AlO_x coatings on the PP and Teonex (PEN) substrates. One of the Teonex/AlO_x scans exhibited no features over 100 nm and the other, only 2. A scan, away from asperities exhibited a low RMS roughness of 2.9 nm.

The WVTR of the Teonex/AlO_x was shown to be up to 7 times lower than the PP/AlO_x but an activation energy 9-20 kJ/mol lower. The model presents two possible reasons for these different permeation characteristics for Teonex/AlO_x: (a) a reduction of macro-defects and an even greater reduction in nano-defects and/or (b) an increase in nano-defect activation energy.

The calcium test for Teonex/AlO_x exhibited unique thinning behaviour, but also some evidence of the localised permeation observed for PP/DA/AlO_x. The smooth surfaces of Teonex/AlO_x (2.9 nm RMS) and PP/DA/AlO_x (6.6 nm RMS), the low WVTR, and similarities between the calcium tests could point to evidence for a similarly low level of macro-defects for the two samples. However, the permeation results for Teonex/AlO_x and the aforementioned differences in the calcium test also suggest key differences in the nature and number of nano-defect between the samples. Studies into the nature of adhesion and microstructure are required to further investigate the differences between barrier formation on these surfaces.

PP/DA/AlO_xN_y

MicroXam studies of PP/DA/AlO_xN_y in Section 6.1.2 showed a large improvement in the number of asperities and overall roughness over that of the PP substrate and the PP/AlO_x samples of Section 4.1.2.1. Although no activation energy was recorded for the PP/DA/AlO_xN_y

sample, the WVTR was shown to be similar to the unsmoothed oxynitride ($0.31 \text{ g/m}^2/\text{day}$ compared to $0.27\text{-}0.3 \text{ g/m}^2/\text{day}$ for the $\text{PP/AlO}_x\text{N}_y$). Despite being produced on a smoother surface, there was no evidence of a reduction of permeation. The calcium test expressed some features of the localised permeation observed for the PP/DA/AlO_x , however the decay was seen to proceed at a faster rate, and exhibited unique features not observed for either PP/DA/AlO_x or $\text{PP/AlO}_x\text{N}_y$. Discussions in Chapter 5 identified that oxynitride barriers exhibited permeation characteristics that suggested a greater number of nano-defects. The calcium test for $\text{PP/AlO}_x\text{N}_y$ appeared to decay in a similar way to PP/AlO_x albeit at a faster rate. The differences identified for $\text{PP/DA/AlO}_x\text{N}_y$ have an unknown source, and further study of the smoothing layer and its effect on subsequently deposited oxides and oxynitrides is required.

6.2 Capping Layers

In Section 2.7 the concept of capping layers was introduced. These are organic layers deposited on top of the barrier oxides in order to protect them from handling damage [30][82][130] or bulk-water damage [8].

Struller's study investigated the use of DA ($0.75 \text{ }\mu\text{m}$) as a smoothing or capping layer to improve the barrier performance of evaporated AlO_x (10 nm) on thin BOPP ($20 \text{ }\mu\text{m}$) [30]. The study found that there were improvements in WVTR of the barrier with the addition of either the smoothing/undercoat (factor of 2.5 better) or the capping/topcoat (factor of 10.3 better). However there was no observed improvement in activation energy with the addition of a top coat, which remained polymer-like, as did their PP/AlO_x sample, [30]. Struller suggests the capping layer protects the film— reducing permeation—but that the dominant permeation mechanism is still through macro-defects [30].

In order to investigate whether this would be observed for the deposition process and substrates used in *this* project, a sample of PP/AlO_x/DA was produced with thicknesses 90 µm/100 nm/3 µm respectively.

6.2.1 Steady-state Permeation

Figure 95 shows the permeation characteristic of the PP/AlO_x/DA sample, with PP and PP/AlO_x included for comparison. Please note: all PP/AlO_x/DA WVTR measurements were performed by M. James of RDM Test equipment on a MOCON Permatran-W 3/33.

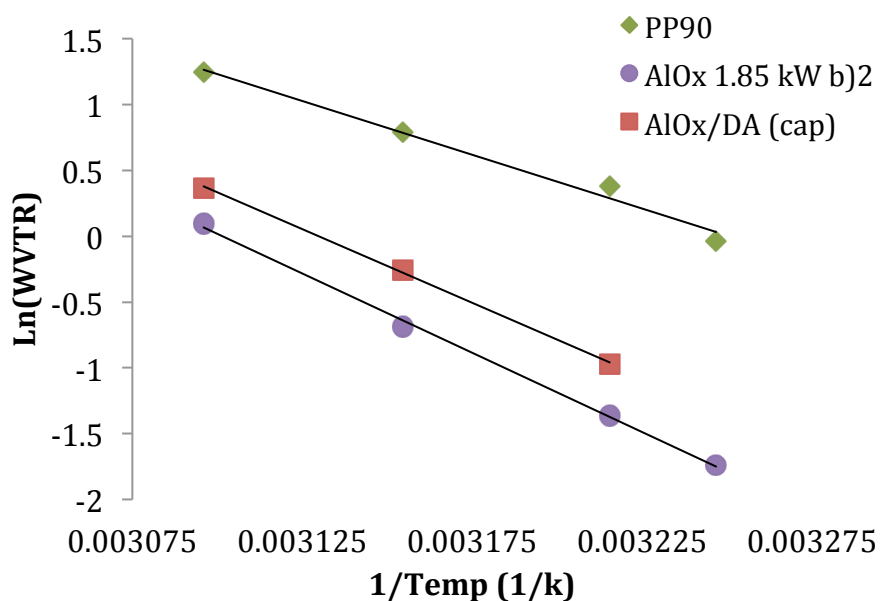


Figure 95. MOCON measurements of the substrate and two barriers, one of AlO_x (117 nm) and one of AlO_x (~98 nm) coated with di-acrylate (~3.1 µm). This dataset was measured by RDM Test Equipment, CM22 6JX). The activation energy of the AlO_x is 100 kJ/mol and the capped AlO_x is 93 kJ/mol. The activation energy of the substrate is 67 kJ/mol.

Activation energies and WVTR at 38°C are summarised in Table 32.

Table 32. Comparing the permeation characteristics of an AlO_x coated PP barrier with a DA-capped AlO_x coated PP barrier.

Sample	WVTR at 38°C (g/m²/day)	Activation Energy (kJ/mol)
Substrate	1.43	67
PP/AlO_x	0.26, 0.31	100, 100
PP/AlO_x/DA	0.38	93

It can be seen from Table 32 and Figure 95 that the top coat appears to offer no improvement in either WVTR or activation energy. In fact the WVTR of the PP/AlO_x/DA is 46% higher than the PP/AlO_x alone. This raises the issue of whether the deposition of the acrylate has damaged the rate-limiting layer (i.e. the AlO_x). However this is difficult to believe when it is considered that for the study of Struller, which only had an AlO_x layer of 10 nm, there was no evidence of damage induced by the identical process (and machine). Perhaps the variation between the PP/AlO_x and PP/AlO_x/DA was due to sample-to-sample variation and/or that these samples were tested by different groups on different (albeit similar) devices.

6.2.2 Qualitative Permeation: Calcium Test

The slightly increased permeation exhibited by PP/AlO_x/DA over PP/AlO_x does not explain the drastically different calcium test. After less than 42 hours all of the calcium was turned into calcium hydroxide. If this result is contrasted to the PP/AlO_x in Figure 93, which still has an appreciable amount of calcium remaining even after 250 hours, this seems to contradict the MOCON measurements. However, as we shall go on to see in Section 6.3, the PP/DA/AlO_x/DA degrades faster than the PP/DA/AlO_x. The difference in performance is considered to be due to the fact the PP/AlO_x/DA and the PP/DA/AlO_x/DA have the calcium deposited directly onto a di-acrylate layer. All the other calcium tests have the calcium

deposited on aluminium oxide or oxynitride. It could be that the di-acrylate, which affords no barrier improvement alone (Table 31), allows a greater amount of lateral transmission of permeant molecules, hence Ca decay over a larger area.

Another possibility is that the DA layer outgasses and directly contributes to the decay of the Ca deposited on it. Further investigation of this effect would be required to find the dominant process. Unfortunately, the effect of this rapid degradation of the Ca means the Ca test makes no contribution to the study of the capping layer.

6.2.3 Discussion

In comparing the results seen for the PP/AlO_x and those of Struller et al, it is important to emphasise the difference in fabrication. The method of Struller used reactive evaporation rather than reactive sputtering, with the latter having been previously shown to produce better barriers [28]. Whereas the barriers in this report have been produced with substrates fixed to the coating drum (i.e., with multiple rotations/depositions), the samples of Struller were produced roll-to-roll. Having 1/10th of the thickness, and undergoing the stresses involved in roll-to-roll, has produced barriers where the majority of the water vapour passes through macro-defects. The improvement observed, suggested Struller, was due to the reduction in macro-defects induced post-deposition. By contrast, the samples produced for this report recorded activation energies consistent with nano-defect permeation. It could be that as the barriers do not exhibit the macro-defect permeation associated with post-deposition handling, the capping layer produced no improvement.

In terms of absolute values, Struller's lowest WVTR (at 37.8°C) was for the PP/AlO_x/DA at 0.46 g/m²/day with polymeric activation energy [30], which is remarkable as it is lower than their PP/DA/AlO_x, which should have seen a reduction in macro-defects and thus WVTR.

6.3 Multilayers

This section covers the performance of two multilayer barriers: PP/DA/AlO_x/DA and PP/DA/AlO_x/DA/AlO_x. Due to the effect the deposition of DA had on the sputtering hysteresis (as mentioned in Section 6.1), these barriers were fabricated over 2 and 3 days respectively. All AlO_x barriers used were ~100 nm thick, sputtered at 1.85 kW and 50 m/min drum speed. All DA layers were ~3 μm thick produced at 0.6 ml/min monomer injection rate and 25 m/min drum speed.

Unfortunately (as the equipment failed), there was no WVTR or activation energy recorded for either of these multilayer systems, limiting the investigation recorded here to Morphology (Section 6.3.1), Optical – UV-VIS (Section 6.3.2), and the qualitative permeation of the Calcium Test (Section 6.3.3). However, despite these limitations, the results are encouraging and point the direction toward future work.

6.3.1 Surface Morphology

The surface morphology of the PP/DA/AlO_x/DA/AlO_x was investigated with the MicroXam (Figure 96).

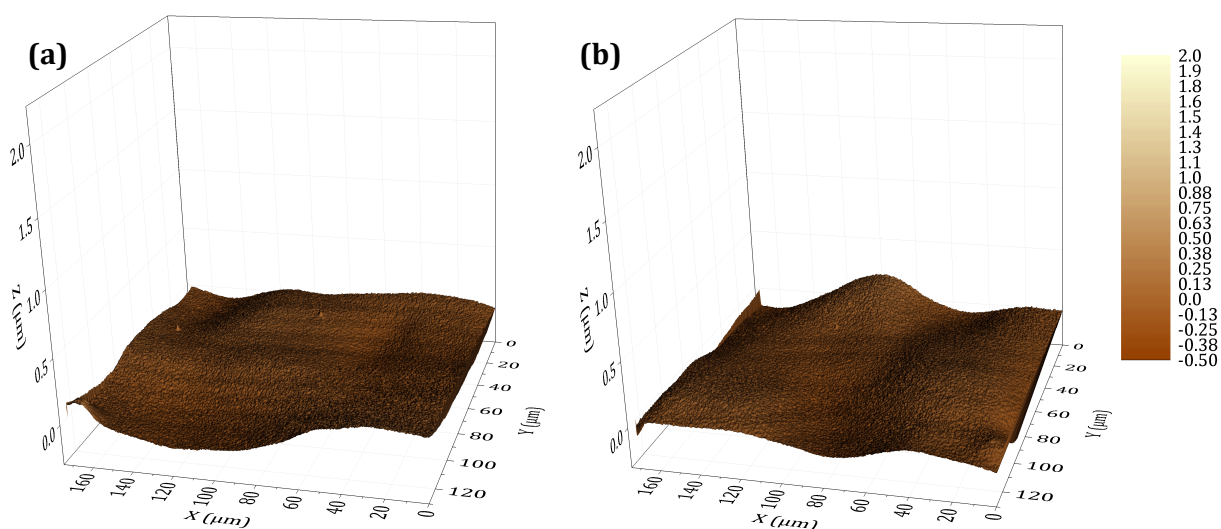
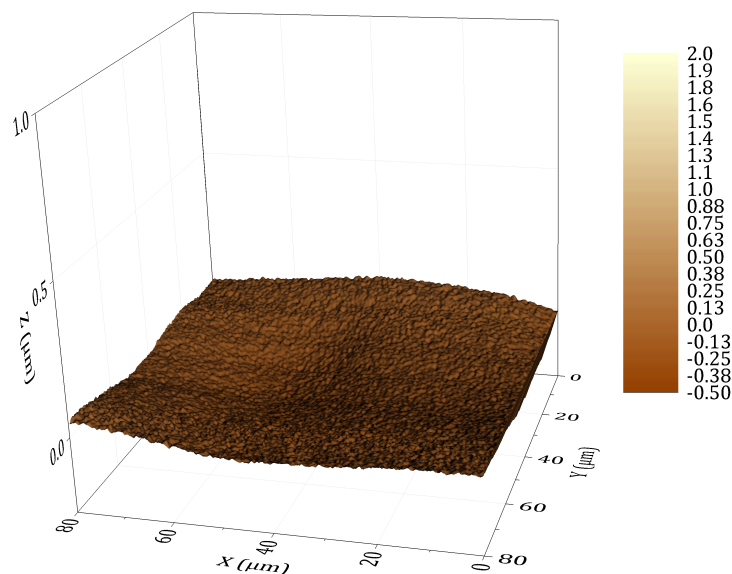


Figure 96. MicroXam, (a) and (b), of PP/DA/AlO_x/DA/AlO_x. Estimated DA thickness ~3 μm, AlO_x thickness, 100 nm.

There are no features/peaks over 50 nm in either the (a) or (b) micrographs. The surface is characterised by long wavelength waviness, meaning the samples are not “flat” in the typical sense, but there are no sharp gradient changes on the surfaces. Comparing these to the single DA samples, Figure 88, Figure 87, and Figure 86, there are no characteristic 500-800 nm conical peaks present. If the conical peaks are indeed artefacts of the DA deposition process, it is strange that there are none visible in either of the micrographs of Figure 96. If it is considered that those peaks were in fact substrate surface features, and that the 3 μm of DA had not fully covered them, it could be argued that the double layer of DA could have finally covered these. However, that does not explain the fact that these features are present in Figure 87, which has Teonex as its substrate. Teonex has no features as large as those seen in Figure 87. There were differences in the deposition of these DA layers: some older samples (Figure 86, Figure 87) were thinner (2-3 μm) and were made with the older e-beam set up, whereas the newer samples (Figure 88, Figure 89, Figure 96) were slightly thicker (3 μm) and were cured with the new e-beam configuration. Despite these differences, the conical peaks were present in all but the double dyad (DA/ AlO_x /DA/ AlO_x - Figure 96).

An expanded view of Figure 96 (a), top-right quadrant, is presented in Figure 97.



**Figure 97. Expanded view of the top-right quadrant of Figure 96 (a). PP/DA/ AlO_x /DA/ AlO_x .
Estimated DA thickness ($\sim 3 \mu\text{m}$), estimated AlO_x thickness (100 nm).**

The RMS roughness of the micrographs (Figure 96 and Figure 97) are presented in Table 33.

Table 33. RMS roughness of the micrographs of PP/DA/AlO_x/DA/AlO_x, with the expanded views of PP/AlO_x/DA and PP/DA/AlO_xN_y from Table 30 and PP/AlO_x and Teonex/AlO_x from Table 9 included for comparison. RMS calculated using Gwyddion [101]. All samples underwent a 10th order polynomial background subtraction.

Sample	RMS Roughness (nm)	
PP/DA/AlO _x /DA/AlO _x (Figure 96)	(a)	5.2
	(b)	5.3
PP/DA/AlO _x /DA/AlO _x expanded view (Figure 97)	-	5.4
PP/AlO _x /DA expanded view (Figure 91)	-	7.0
PP/DA/AlO _x N _y expanded view (Figure 92)	-	6.6
PP/AlO _x expanded view (Figure 51)	-	16.8
Teonex/AlO _x expanded view (Figure 52)	-	2.9

Qualitatively that PP/DA/AlO_x/DA/AlO_x (Figure 97) appears to exhibit similar roughness to that of the PP/AlO_x/DA (Figure 91); quantitatively the former is revealed to be smoother with 23% lower RMS. The PP/DA/AlO_x/DA/AlO_x with two smoothing layers is not as smooth as the Teonex/AlO_x (Figure 49), with the latter exhibiting an RMS 46% lower. What is remarkable from any comparison with the Teonex/AlO_x is how globally flat the surface is.

The PP/DA/AlO_x/DA/AlO_x exhibited the lowest RMS roughness of any of the barriers produced on the PP substrate. However, as was covered in Section 4.1.2.1, 10th order polynomial background subtraction has been used to remove the visible long wavelength waviness (see Figure 96) from the RMS data. The reduction of this waviness would be a focus of future work.

6.3.2 UV-VIS

The UV-VIS spectra for the multilayers were compared with the substrate, PP/AlO_x and PP/DA/AlO_x and are shown in Figure 98.

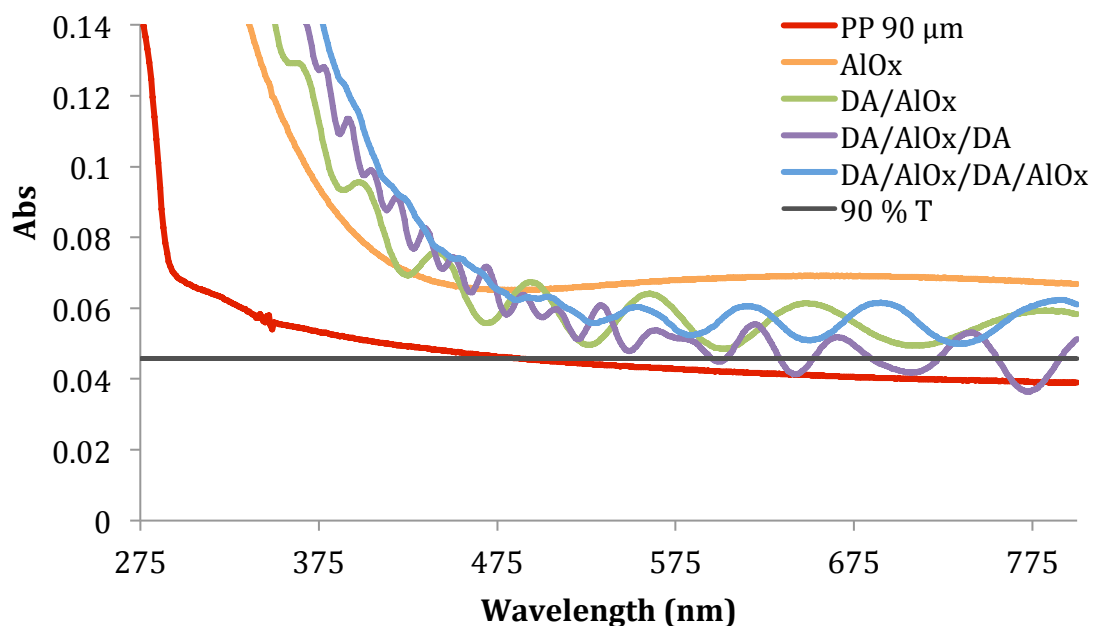


Figure 98. UV-Vis scan of different multi-layered barrier films. All deposition conditions are the same. Acrylate drum speed is 25 m/min; AlO_x drum speed is 50m/min. The straight grey line represents the 90% transmission required by industry. The average transmission for the different barriers is DA/AlO_x/DA/AlO_x (T= 86.4 %), DA/AlO_x/DA (T=87.8%), DA/AlO_x (T=87.1%), AlO_x (85.4%) and the substrate alone is 90.5%.

The average transmission (390 nm-780 nm) for each of these samples is summarised in Table 34.

Table 34. Comparison of Average Transmission in the visible region of the EM spectrum (390-780 nm) from the UV-Vis data.

Sample	Average Visible Transmission (%)
Substrate	90.5
PP/AlO_x	85.4
PP/DA/AlO_x	87.1
PP/DA/AlO_x/DA	87.8
PP/DA/AlO_x/DA/AlO_x	86.4

Barring the PP and the PP/AlO_x samples, all the spectra in Figure 98 exhibit the undulatory behaviour characteristic of interference. These were discussed in Section 4.3.1.

The wavelength at which the absorption maxima and minima occurred was seen to be location specific. Repeat measurements returned identical results, but when samples were moved, the interference effects were seen to shift. This is considered to be due to local variations in thickness, which change the overall optical path length.

Upon optical inspection, the multi-layered samples exhibit “rainbow”-like interference fringes, which backs up the results seen in Figure 98.

One striking characteristic of Figure 98 and Table 34 is that the addition of multiple layers of DA and AlO_x only reduces the average transmission by 3-4% over that of the substrate. But even more remarkable is that the PP/DA/AlO_x/DA/AlO_x, the thickest barrier architecture studied in this report (~ 6.2 μm in total), has an average visible transmission greater than the PP/AlO_x (only 117 nm). This is powerful evidence for the positive effect DA layers have on the optical performance of barriers. Even though these coatings are thicker, they are more homogenous and planar as evidenced by their interference fringes [114] [115]. This is even clearer when comparing the PP/AlO_x to the PP/DA/AlO_x, with the latter having a 1.7%

greater optical transmission even with a thick (3 μm) DA layer integrated into the barrier. It would be suggested that flatter layers would allow light to pass through barriers with less scattering.

6.3.3 Calcium Test

Figure 99 shows an extended calcium test for multilayer barriers. PP/AlO_x is included for comparison.

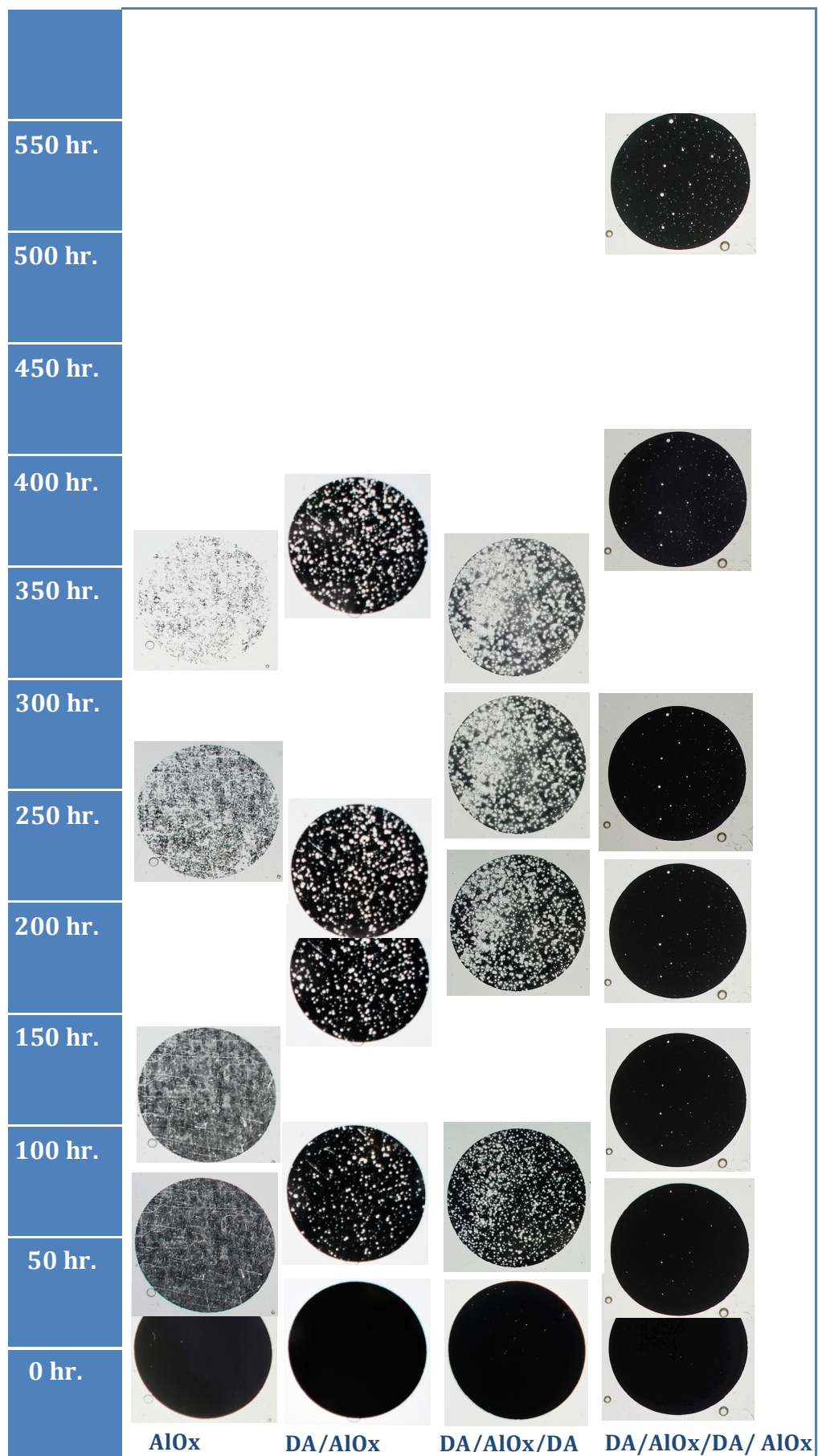


Figure 99. Calcium test for multi-layered barriers. This test was extended in order to probe the longer lifetime of the PP/DA/AlOx/DA/AlOx.

All other calcium tests in this report finish at ~350 hours, but due to the improved barrier performance of the PP/DA/AlO_x/DA/AlO_x an additional 7-8 days of testing was included.

The two multilayers performed very differently.

The Ca test lifetime of the PP/DA/AlO_x/DA is shorter than that of PP/DA/AlO_x, for the same reasons as discussed in Section 6.2.2. It was suggested that the shorter lifetime was due to the calcium having been deposited directly onto a DA layer, which was established in Section 6.1.3 to be a poor water barrier. Also, the nature of the permeation is different in these two cases. Some areas (top-right of the circle for instance) behave like the PP/DA/AlO_x, with white spots appearing, then expanding outward. The left side, however, appears to have had a higher initial density of degradation, thus leaving no intervening un-converted calcium. When the final ~350 hour photos of PP/DA/AlO_x and PP/DA/AlO_x/DA are compared side by side, the differences are even starker. The latter has larger white spots, but that appears to be the amalgamation of smaller white spots from the initial higher density. The “untouched” calcium between the white areas appears to have thinned, which was not observed for PP/DA/AlO_x.

It is suggested that this could be due to lateral transmission of water within the DA immediately below the calcium layer. Another possible explanation would be that the DA layers for the PP/DA/AlO_x/DA are different to those used for the PP/DA/AlO_x. The former are 3 μm, with the AlO_x subsequently deposited after a 6+ hour delay under pressure, whereas the latter is ~ 1.3 μm, deposited 20 minutes before the AlO_x. These differences could explain the difference in density and initial size of the hydroxide spots. Further investigation of how these conditions affect surface energy and barrier nucleation are needed.

It is also instructive to compare the PP/DA/AlO_x/DA/AlO_x to the PP/DA/AlO_x. The headline result is that the 525 hr photo of the former looks better than the 70 hr photo of the latter. The nature of the permeation through the PP/DA/AlO_x/DA/AlO_x appears to be the same as the PP/DA/AlO_x but at a lower rate and/or greater transient. The concept of a high transient will be discussed in Section 6.4. It is important to note, however, that even though there is a

significant amount of the calcium remaining for the double-dyad structure, there are numerous spots of hydroxide present. If these spots at 525 hours are considered to be individual routes through to the calcium, there appears to be a greater density of these routes than for the PP/DA/AlO_x, albeit presenting as smaller spots initially. This seems to suggest a long (22 day) transient for some of the small spots, with water having taken a long time to pass through the layer structure. The intervening calcium appears as opaque after 3 weeks as it did at the start.

6.4 Discussion

The seminal study of Graff investigates the concept of a transient effect or lag time between the initial permeation and equilibrium permeation. His study of a PET/DA/AlO_x/DA (178 µm/0.34 µm/37 nm/0.2 µm) was found to have a lag time of 22 hrs before reaching steady-state permeation [3]. Unfortunately it was not possible to record the WVTR data for the multilayer films produced in this project, however all other WVTR measurements were undertaken (as described in Section 3.3.1) with a 8-10 hour conditioning period and 24 hours of testing. Although the WVTR was constant for all samples studied in this report, it does raise the issue of lag times for multilayers.

Graff's paper looks at direct permeation measurements as well as modelling barriers of increasing numbers of dyads. The principal findings in Graff's paper, relevant to this discussion, are summarised in the following bullet points (please note - all are from [3])

- Adding dyads increases the path length the water has to permeate through. This does very little to reduce the steady-state flux and mainly increases the lag-time before reaching equilibrium permeation.
- Graff suggests much of the reported WVTR values in the literature are within this lag time, and therefore have under-estimated the equilibrium permeation rate.

- The defining parameter for lag time is defect spacing (lateral distance between defects in subsequent layers), which increases the permeation path length.
- His model observes that increasing average defect spacing from 100 μm to 1000 μm for a 4-dyad system increases lag time from ~ 1 month to 15 months, but barely affects equilibrium permeation. He observes that for defect spacing of 100 μm , adding an extra dyad only increases the lag time by a few weeks.
- He suggests lag time could be increased to several years, which would eliminate the need to produce a low steady-state WVTR.
- In order to reduce equilibrium flux, the diffusivity through either DA or AlO_x layers must be reduced, but that it is 4 orders of magnitude greater through the former than the latter, pointing to oxide improvement as the main avenue of progress.

Bringing the analysis of Graff to bear on the results of Section 6.3, an effective lag time seems to have been observed in the calcium test for the double dyad ($\text{PP/DA/AlO}_x\text{/DA/AlO}_x$). There does not seem to have been a reduction in permeation routes, but that perhaps it has taken longer for this permeation to make its way to the calcium. This would need to be confirmed by long-term WVTR testing. However, this does have implications for the perceived hydroxide spot density. If permeation spot density has increased for the $\text{PP/DA/AlO}_x\text{/DA}$ and the $\text{PP/DA/AlO}_x\text{/DA/AlO}_x$ over that for the PP/DA/AlO_x , this would be detrimental to lag time and therefore calcium test lifetime. The effect the DA layer has on the formation of sputtered AlO_x requires investigation. The Ca test data presented here supports the thesis of Graff that extra numbers of dyads could produce barrier lag time greater than the lifespan of consumer optoelectronics. Graff points out that:

“Single-layer encapsulation at the level required for an OLED demands the deposition of a near-defect-free inorganic layer in a low temperature process” [3].

The difficulty of (a) achieving this, and (b) maintaining this after bending, suggests that adapting to defect-containing oxide coatings may be a sensible route of enquiry.

7 Conclusions and Future Work

7.1 Conclusions

Three distinct investigations into the nature of permeation through transparent flexible barrier layers were carried out. Understanding of the nature of permeation was used to devise a simple model that considered the relative permeation through macro-defects (with negligible interaction of the permeant with the defect) and nano-defects (with activated permeation) to help interpret experimental results.

The effect of process conditions on the performance of barrier coatings was covered in Chapter 4. It was shown that higher power sputtering produces dense films that exhibit low WVTRs. The model explained that this was due to a lower number of both macro and nano-defects, confirmed by the surface morphology, which exhibited larger agglomerations.

It was also found that thicker barriers exhibited greater permeability, with the model pointing to the incorporation of a greater number of nano-defects into the barrier.

Barriers produced at higher drum-speed yielded no clear permeation improvement but it was shown these were less absorbing in the UV-visible range.

Chapter 4 also covered the role of the substrate in the formation and performance of barrier oxides. It was found that the quality of the barriers deposited had a strong dependence on the chemical and topographical nature of the substrates. AlO_x layers produced on two different substrates, but under identical deposition conditions, were shown to exhibit different permeation characteristics, which pointed to microstructural differences.

Chapter 5 investigated the nature of nano-defect permeation by altering the chemistry of the barriers to induce more permeant interaction. The increase of nitrogen in the AlO_xN_y matrix was found to increase the refractive index of the coatings, increase their hardness, and change the nature of failure under stress. The plastic deformation of the coating was suggested to be due to the increase in nano-defects, as supported by the permeation results.

However, there was no clear relation between permeation and nitrogen content, perhaps because there was not a well-controlled series of samples of varying nitrogen content with the same deposition conditions. The integration of nitrogen was shown to be fraught with challenges, from initial deposition integration to post-deposition exchange with ambient oxygen.

Chapter 6 was a study of the effect of integration of di-acrylate smoothing layers into a transparent barrier architecture. It was found that DA smoothing layers reduced the number of macro-defects in subsequently deposited oxides, as hoped, but that these layers may contain more nano-defects than those deposited onto the smooth PEN/Teonex. The calcium test revealed that the DA smoothing layer not only reduced permeation, but also appeared to cause permeation to be localised with a “starry night” of hydroxide spots observed, as opposed to the “grey dawn” of the unsmoothed barrier. Collectively, this suggested that the reduction in macro-defects caused the localised permeation observed in the calcium test.

Capping layers were also covered in Chapter 6, with no positive effects found for the processes used in this report, in contrast to previous results for reactively evaporated thin layers. Multi-layers were shown to introduce a significant lag-time for permeation through the barriers, but no change was observed in the density of hydroxide spots once this lag-time was overcome.

The model presented here was shown to be a useful metric to understand the different nature of permeation in different films. It has been shown here that activation energy can be used to probe barrier quality and the ratio of permeation through macro and nano- defects for these films, which are not dominated by one or other mechanism. By recreating these experimentally derived results in the model, possible sources of these changes can be readily identified.

Comparison of the results obtained by the MOCON Permatran and the calcium test yielded a deeper understanding of the nature of permeation. Whereas the Permatran recorded WVTR

and activation energy, the calcium test provided qualitative information into the distribution of water ingress and allowed extended duration testing, furnishing the study with a measure of lag-time.

7.2 Suggestions for Future Work

Process conditions were studied and optimised for barrier and optical characteristics, but further investigations of the mechanical behaviour would aid optimisation of barrier fabrication for real applications. The investigation of the water permeation properties after bending/stretching (a la Choi [20]) would show if the *nature* of failure could aid barrier life time, i.e. plastic deformation over cracking or *vice versa*.

Chapter 4 pointed to the different microstructure evident for barriers formed on different substrates. This was complicated by the vastly different topography of the substrates. If substrates of differing materials but identical roughness were used, the nature of the oxide formation of these coatings could be better understood through AFM investigation and WVTR and activation energy measurements.

Further development of the model would be useful. Physical investigation of the barriers with optical and electron microscopes could better inform the number and size of macro-defects. Development of the complexity of the mathematical expression could incorporate a range of defect sizes as well as modelling defect shapes (as informed by AFM) and defect distribution.

Developing the process control in the fabrication of oxynitrides is another key area for work. Controlling background species in the chamber and researching techniques to produce AlN in the Oxford Webcoater would need to be mastered. Incorporating the information about process controls from Chapter 4, with strict thickness control, would allow a more definitive investigation of the effect of nitrogen content on permeation.

Investigating the possibility of increasing the lag-time of multilayer systems to beyond the requirement set out in Section 1.1 is suggested, firstly, by producing a dyad informed by the process control study of Chapter 4, followed by a 3 and 4 dyad system. Better control of the calcium test would aid this study, chiefly automation of photographs and calibration with a photo-diode. The former would allow more regular sampling, while the latter would allow WVTR to be ascertained as well as doing this to a greater sensitivity than is currently achievable with the MOCON Permatran.

8 References

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