

Vacuum Deposition of High Performance Gas Barrier Materials

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ABSTRACT

High performance flexible barrier films produced by roll-to-roll processing are required for applications such as OLEDs, PVs and transistors. This paper presents the development of barrier layer technology for electronics applications on our vacuum web coating research facility. There is a capability of organic and inorganic layer deposition, with this paper focusing particularly on DC and RF sputtering onto acrylate smoothed substrates.

INTRODUCTION

The use of polymers in electronics has many advantages over materials currently being used. They are lightweight, flexible and low cost materials and may function as substrates, or encapsulation for devices such as organic light emitting diodes (OLEDs), photovoltaics (PVs) and flexible displays. Their poor performance as barriers to gases such as water, oxygen and carbon dioxide mean that they must be coated with an impermeable barrier layer to reduce the level of gas transmission across the polymer barrier layer composite. A target level for long-term OLED and polymer PV applications has been suggested of the order of $10^{-6}\text{gm}^{-2}\text{day}^{-1}$. This has not yet been achieved as the thin barrier layers contain defects and can be easily damaged and cracked. Our work aims to look in more detail at factors which tend to affect performance of barrier layer composites.

Barrier performance of a composite film is affected at first by the “lag time” to equilibrium permeation. This is the time taken for the permeant to reach saturation in each layer of the barrier composite. If this lag time can be extended beyond the lifetime of a product, equilibrium permeation will never be achieved, leading to lower permeation rates than the theoretical. Once equilibrium permeation has been reached, for low to moderate barrier materials, barrier performance is dominated by large scale or macro defects which tend to dominate the permeation across a barrier film composite [1, 2].

By introducing multiple layers of barrier material and/or smoothing the polymer substrate, the effect of macro defects such as pinholes can be reduced significantly [3]. The object is to ensure that macro defects are not continuous through the multiple layers, and so there is no direct path through which the permeant can travel easily. Once the macro defect density has been reduced sufficiently, the nano-scale defects dominate the water permeation.

Permeation through barrier composites may be reduced by addressing each element of the permeation model [1], firstly by smoothing the substrate and avoiding processing and handling defects in films the density of macro defects may be reduced; by introducing thick and multiple layers and decreasing the diffusion, the lag time to equilibrium permeation may be increased; by decreasing the diffusivity and solubility

by having a denser coating, controlling the nanostructure or by altering the barrier layer stoichiometry or chemistry the permeation at equilibrium may be reduced.

In this work we have focused on comparison of different substrate pre-treatments such as smoothing acrylate layers, RF and DC power supplies for sputtering, and reactive gas supply locations. This project aims to produce gas barrier materials close to the level required for electronics applications by optimising processing conditions as well as examining and understanding the mechanism of gas transport across the barrier.

EXPERIMENTAL

Materials

Aluminium oxide (AlO_x) coatings were deposited by reactive sputtering on $125\ \mu\text{m}$ polyethylene naphthalate (PEN) films (Dupont Teijin Films Q65FWA). Coating was carried out in a large scale single drum vacuum web coater (Arcotronics/Sigma Tech) which is capable of carrying a 350mm wide web up to a speed of 300m/min . In some cases smoothing of films with a flash evaporated acrylate layer was carried out in a roll to roll process. Smoothing layers deposited prior to the barrier layer coating have been shown to reduce the density of defects such as pinholes [4]. For sputtering of the barrier layer oxide, films were wrapped around the drum to achieve multiple passes for the reactive sputtering process, with very thin layers ($<1\text{nm}$) deposited at each rotation past the sputter cathodes. As the reactive gas, oxygen is introduced into the system there is a large hysteresis in the voltage as the target becomes poisoned. The process is also relatively unstable when using an RF power supply. The stability and hysteresis in the oxygen supply in the system can be improved by using a DC supply, however the barrier performance of coatings produced using RF and DC power supplies may be different.

The nature of the reactive sputtering process is affected by the location of the reactive gas, which in our case is oxygen. Both DC and RF power supplies were compared. Oxygen levels were kept low enough to prevent target poisoning while at the same time kept high enough that sufficient oxidation of the aluminium occurs to give a transparent coating.

Properties of films were tested as follows:

Film Transparency: A Varian UV-vis-NIR spectrometer was used to measure the transparency of the samples. An acceptable level of transmission is 80%.

Coating Thickness and Refractive Index: Coatings on silicon substrates were measured using a Rudolph EL single wavelength ellipsometer. These measurements gave information on coating thickness and refractive index. The refractive index was an indicator of film density. The thicknesses were confirmed by a Dektak surface profiler.

Surface Morphology: Non-contact mode atomic force microscopy (AFM, Park Scientific Instruments) was used to characterise the surface features and detect very small defects. A JEOL 840F Scanning electron microscope was used to see large scale surface features and to examine a wider area.

Surface Stoichiometry: X-ray photoelectron spectroscopy (XPS, Mg source, non-monochromated) was used to examine the chemical composition of the top surface layer of the coatings (it is possible to see up to 10nm but in this case the first 1nm dominates). This gives the stoichiometric ratio of aluminium to oxygen, and therefore the extent of oxidation of aluminium is known.

Permeation: Oxygen and water vapour transmission rates (OTR and WVTR) were measured using a Mocon Permatran (Mocon Co W3/31) and the Calcium Test.

RESULTS

Oxidation of Aluminium Coatings:

The position in the process where oxygen is introduced dictates the quantity of oxygen which the process can endure before poisoning of the target occurs. This is because the oxidation of the target (poisoning) can easily occur if the oxygen flow is directed towards or in the vicinity of the sputter zone [5]. A conventional system has oxygen introduced along the length of the sputter cathodes, within the sputter zone area. Oxygen may be introduced at any point in the vacuum chamber and the nature of the reactive sputtering process may be different depending on oxygen delivery location (Figure 1). For example, we would expect that at least some of the oxidation will happen prior to adsorption of sputtered species by the target, or while the arriving species are still energetic and mobile on the surface, if the oxygen gas is input into the sputter zone. However, gas arriving outside the region of the sputtering must oxidize material that has already deposited onto the substrate: the oxygen must diffuse through the already deposited layer of aluminium, in a similar manner to how the native oxide layer forms on bulk aluminium. Comparisons of permeation through coated films produced using different oxygen locations show varying results, indicating that the nature of the oxidation is different.

Ellipsometry has given us the thicknesses of deposited coatings confirmed by a Dektak surface profiler. Results have shown that between 3 and 5 Angstrom are deposited at each revolution of the drum depending on drum speed. This is approximately a tenth of the thickness of a native oxide layer of aluminium. Close to 5 Angstrom per revolution gives a coating which is not fully oxidised which shows that there is insufficient time in a single rotation for the full native oxide layer to form. Refractive indices acquired by ellipsometry give us an indication of the density of the film. These are usually constant except at low deposition times in which insufficient material has been deposited to give a full coverage of the substrate between the 'grains' forming on the surface, and hence the assumptions of ellipsometry model do not hold..

Mocons have given us WVTR results below the detectable limit of the machine (i.e. below $5 \times 10^{-3} \text{g/m}^2/\text{day}$) for films deposited with RF sputtering for 20 minutes. Calcium tests have WVTR results in the $10^{-3} \text{g/m}^2/\text{day}$ range (see Figure 2).

XPS on the surface of samples has given elemental information on the coatings. In the first few nanometres surface contamination can be seen in the form of a large proportion of carbon and the presence of other elements such as sodium, sulphur,

fluorine and chlorine. The proportion of oxygen at the surface of the sample may be different from the bulk as it may be present in the form of carbonates at the surface as well as aluminium oxide. The bulk stoichiometry may be found by ion bombardment of the surface, however sputtering of different elements occurs at different rates which will mean some distortion of results is inevitable. Samples tested to date have shown little difference in the oxygen: aluminium stoichiometric ratio in any of the top surface of sputtered coatings with an average ratio of $\text{AlO}_{2.2}\text{C}_{1.1}$. For RF sputtered samples this ratio is $\text{AlO}_{1.9}\text{C}_{1.1}$ although further work would be needed to confirm this as the test was carried out on a small sample set.

AFM shows a very flat surface, with a coating roughness of approximately 0.5 - 1nm. There are some depressions in the surface which register at about 1-2nm deep; however the AFM tip, with typical diameter of 10nm does not allow us to resolve whether these are nanoscale 'tunnels' that would allow gas permeation. The morphology of the coating was seen to be strongly a function of substrate. The granular structures are significantly smaller and appear to be more densely packed on PEN substrates than on a silicon substrate (see Figure 3). A full coverage of films was achieved after ~50nm average deposition while at lower film thicknesses substrate features were visible through the coating.

DISCUSSION AND CONCLUSIONS

What makes a good barrier layer is not yet fully understood, although it is very much dependent on process conditions. Any imperfections in the coating will lead to reduction of the barrier. This means that substrate cleanliness and process conditions are of paramount importance in producing a good barrier. We have been able to make very high barrier AlO_x coatings that only allow permeation of water vapour below the detection limit of the Mocon Permatran™, and which survive in excess of 500 hours in the Ca test (corresponding to a WVTR of the order of $10^{-3}\text{g/m}^2/\text{day}$). The Ca test results shown in Figure 2 for an AlO_x sample of 300nm thickness deposited by RF sputtering (oxygen delivery at sputter cathodes), show the rich morphology in the degrading Ca layer as a result of the permeation through the barrier. The two areas of sample shown on the right of the diagram give examples of linear features, such as a scratch or crack, which develops only slowly with time, indicating perhaps that it is very much finer than a conventional scratch or crack in the glass that might form, as a result of handling for example. There are spots of permeation that show a large variety of sizes and timescale for development suggesting that some 'pores' in the oxide layer are likely to be very small. Of course if there are large defects in the sample within the test area, the whole area would lighten due to water permeation very much more quickly, and the effect of these smaller defects would be hidden.

The balance of introducing sufficient oxygen to produce fully oxidised samples while avoiding process instability in both DC and RF sputtering is difficult to control. The introduction of oxygen away from the sputter zone in the web coater appears to improve the process stability; however it is still not yet clear what the consequence is for ultimate barrier performance of the composite barrier films.

The morphology of coatings on samples is dependent on the substrate material. The difference between coatings on different substrates is evident with much larger granular structures on silicon (6-8nm) as opposed to PEN (3-4nm) (Figure 3). While the morphology of coatings on both smoothed and unsmoothed PEN samples appears

to be similar it is the large scale defects which are eliminated which makes the introduction of a smoothing layer significant for barrier performance.

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Figure 1

Oxygen delivery locations were varied between direct delivery in the sputter zone, oxygen delivery adjacent to the drum outside the sputter zone, and indirect delivery into the main chamber

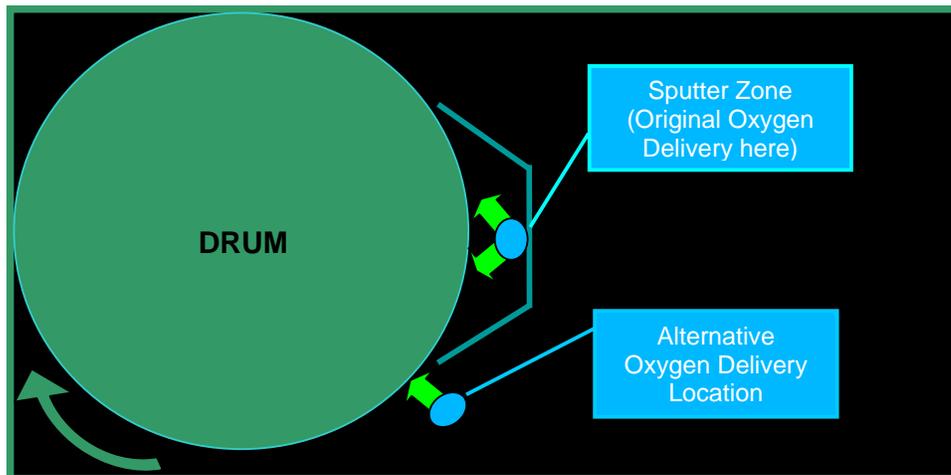


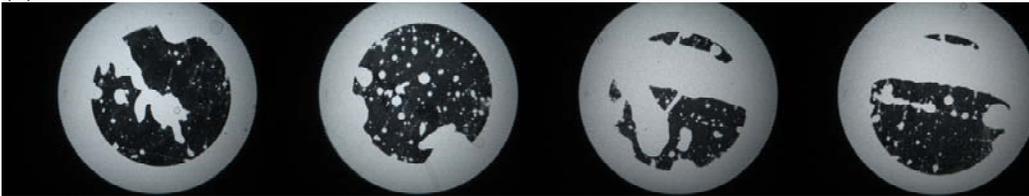
Figure 2

Calcium Test samples at (a)48 hours, (b)240 hours, and (c) 508 hours showing unreacted calcium metal (black) and reacted calcium (white). The samples were kept in an environmental chamber at 60°C and 95% Relative Humidity.

(a)



(b)



(c)

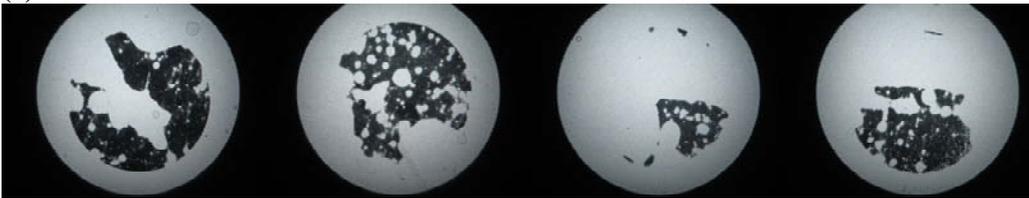
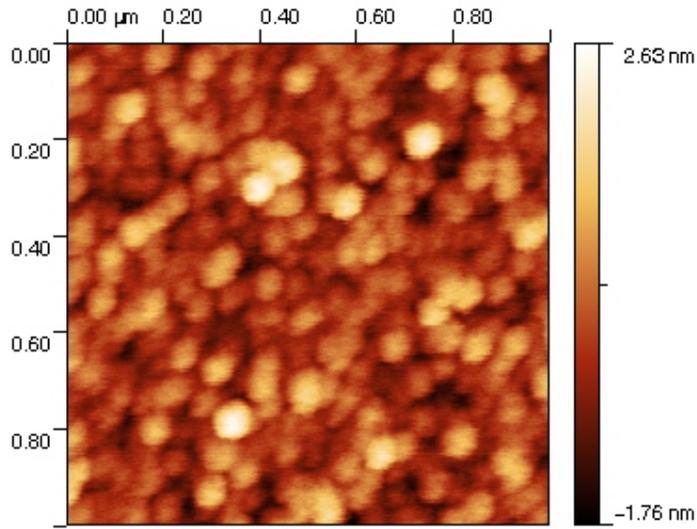


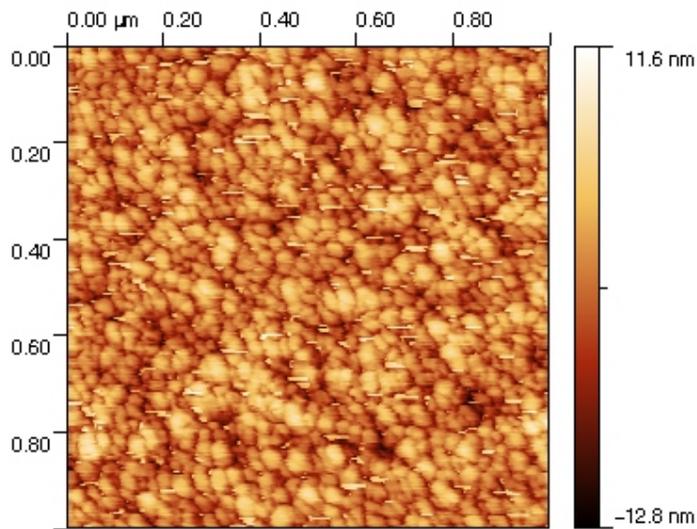
Figure 3

AFM images (1x1 micron) 20 minute RF sputtered coatings (a)Si substrate (b) smoothed PEN substrate (c) unsmoothed PEN substrate ((i)2d (ii)3d representation).

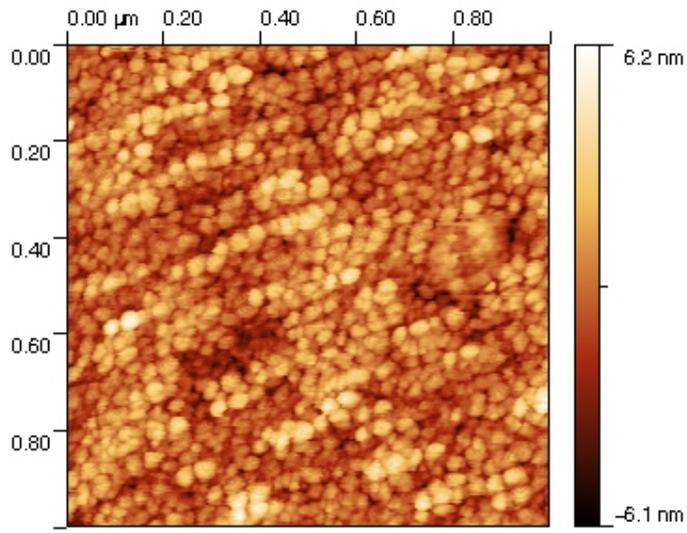
(a)



(b)



(c) (i)



(c)(ii)

