Vacuum deposition of high performance gas barrier materials for electronics applications

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The subject of transparent gas barrier layers has been of substantial interest in recent years both for existing applications, such as food packaging, but also to develop extended capability for new high-performance products both in packaging and functional films.

For many of these more recent technologies, it is the water vapour permeation rate that is the key parameter for improvement. Predicted required values vary between reports, but some examples include $10^{0} – 10^{-2}$ $gm^{-2}day^{-1}$ for advanced food or pharmaceutical packaging and organic thin film transistors (OTFTs), 10^{-3}-10^{-4} $gm^{-2}day^{-1}$ for Dye sensitised solar cells (DSSC) and Vacuum insulation panels, and $10^{-5} – 10^{-6}$ $gm^{-2}day^{-1}$ for OLEDs and excitonic (e.g. polymer) photovoltaics. When considering the requirement for gas barrier the projected lifetime of the component and its tolerance of local failure of the barrier should be considered. Coupled to any WVTR performance of course is the cost of materials and deposition (typically web speed), transparency and mechanical properties.

Permeation of water through a typical gas barrier coating depends critically on the number density and nature of defects in the layer. These might be broadly characterised into two groups: microscale defects which allow the free flow of water vapour through a restricted area, typically arising from defects in the substrate or during the coating process, or from subsequent film handling[1],[2], and nanoscale defects that arise from the imperfections in the bulk structure of the ceramic layer, for example at grain boundaries, and that we have shown are associated with an activated process of permeation in the case of water[3]. In any permeation environment there is a 'lag time' during which the film fills (or empties) of water after which an equilibrium permeation rate will be obtained. Multiple layer films made up, for example, of oxide layers separated by polymer interlayers will have the effect of increasing this lag time, by effectively increasing the thickness of the barrier coating without the build-up of residual stresses, and also decouple defects between subsequent layers meaning that if the defect density is small a higher proportion of the water permeates through the nanoscale defects. For the very high barrier requirements however, the equilibrium permeation through the barrier layer may still be too high. Hence to design a high barrier, one needs to minimize the number density of micro-scale defects by use of a smooth substrate, good process control, and possibly by a multilayer structure, but also to deposit a high density layer of appropriate chemistry with small nanoscale/molecular imperfections to minimise the solubility and diffusivity of the ceramic.

The roll-to-roll vacuum webcoating facility is able to deposit coatings at web speeds of up to $5ms^{-1}$. It has RF dual magnetron sputtering and thermal evaporation sources for depositing metals and oxides, and also polymer flash evaporation with e-beam curing to deposits polymer smoothing layers or interlayers for multiple layer stacks[4].

We have taken a 'bottom-up' approach to our studies of ultra high transparent barrier layers, but first considering polymer smoothing layers to give an ideal substrate onto which subsequent barrier layers may be deposited, then attempting to create high density AlOx barrier layers with a minimum of micro-scale defects. These are the first steps on a roadmap that could be extended to multiple layer barriers. We have shown that we are able to deposit well-cured acrylate layers (confirmed by ATR-FTIR spectroscopy) that result in an extremely smooth surface for subsequent coating (Figure 1).

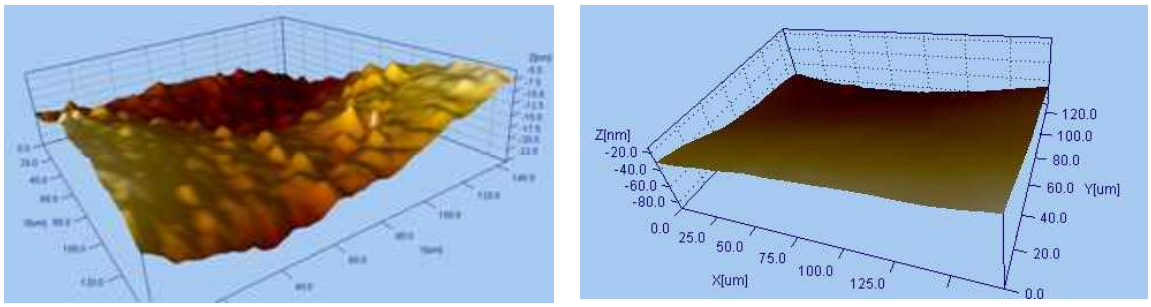

Figure 1 Optical profilometry of (left) an untreated high quality PEN substrate surface, and (right) the same substrate after an acrylate smoothing layer has been applied by flash evaporation and ebeam cure under vacuum.

Spectroscopic ellispometry, and profilometry have confirmed that we are able to deposit uniform acrylate layers of thicknesses in the range of 10s of nm to 10s of microns. Reactive magnetron sputtering of AlO_x layers has been carried out using both a poisoned Al target, and a metal target with O_2 flow rates of up to 20sccm. Films produced from a metal target deposited, as expected, more quickly, and also produced much higher barrier layers, with typical WVTR in the region of 10^{-3} $gm^{-2}day^{-1}$. Our system allows the coating of very thin layers which can be oxidized in the sputter zone or within the chamber, and part of our investigation is the relative merits of these two for the production of high quality coatings. The AlOx layers have been characterised with FTIR, ellipsometry and XPS analysis. Finally, comparison of the morphology of the AlOx with and without a smoothing layer has revealed a lower density of defects present as a result of the smoothing layer (Table 1).

Image number	10nm peaks	100nm peaks	Pinholes up to 20nm
1	Many	19	7
2	Many	14	5
3	Many	14	2

Image number	10nm peaks	100nm peaks	Pinholes up to 15nm
1	10	1	0
2	7	1	4
3	0	1	0
4	9	0	0
5	16	5	1

Table 1 Number density of defects observed by optical profilometry in an AlOx coating on (left) a PEN substrate and (right) a PEN substrate with an applied smoothing layer. Each image represents an area of 6300 μm^2

[1] *Characterization of transparent aluminium oxide and indium tin*

oxide layers on polymer substrates B.M. Henry, A.G. Erlat, A. McGuigan, C.R.M. Grovenor, G.A.D. Briggs, Y.Tsukahara, T. Miyamoto, N. Noguchi, T. Niijima, Thin Solid Films **382**, 194 (2001)
[2] *How cracks in SiOx-coated polyester films affect gas permeation* M. Yanaka, B.M. Henry, A.P. Roberts, C.R.M. Grovenor, G.A.D. Briggs, A.P. Sutton, T. Miyamoto, Y. Tsukahara, N. Takeda, R.J. Chater *Thin Solid Films* **397**, 176 (2001)
[3] *The Mechanism of Water Vapour Transport Through PET/AlOxNy Gas Barrier Films* A.G. Erlat, B.M. Henry, C.R.M. Grovenor, G.A.D. Briggs, R.J. Chater, Y. Tsukahara, *J. Phys Chem B* **108**, 883 (2004)
[4] *Microstructural and barrier properties of multilayer films* B. M. Henry, D. Howells, A.J. Topping, H.E. Assender, C. R. M. Grovenor *Proceedings of the 49th SVC Technical conference* (2006)