

# Roll-to-Roll ALD Deposition of Al<sub>2</sub>O<sub>3</sub> Barrier Layers on PET

W. A. Barrow and E. R. Dickey, Lotus Applied Technology, Hillsboro, OR

## Abstract

Roll-to-roll atomic layer deposition (ALD) of TiO<sub>2</sub> barrier films on polyethylene terephthalate (PET) web has recently been reported. This paper describes the extension of ALD roll-to-roll coating to Al<sub>2</sub>O<sub>3</sub> barrier material on PET web. Water vapor transmission rate (WVTR) data for ALD Al<sub>2</sub>O<sub>3</sub> films coated in a roll coater onto PET are provided. Comparative data on ALD Al<sub>2</sub>O<sub>3</sub> barrier layers deposited on web material in a conventional ALD reactor are also presented.

## INTRODUCTION

ALD Al<sub>2</sub>O<sub>3</sub> has been reported to be an excellent barrier film on plastic web. These reports, however, have involved conventional ALD batch deposition onto stationary substrates [1-7]. In 2009 the first report of ALD barrier deposition in a roll-to-roll web coater appeared [8]. In that case the barrier material was TiO<sub>2</sub>. This paper extends the roll-to-roll web coater approach to Al<sub>2</sub>O<sub>3</sub> barrier films.

Single layer ALD Al<sub>2</sub>O<sub>3</sub> has been shown to provide barrier properties superior to single layer evaporated, sputtered and even PECVD oxide films [6]. The critical layer thickness for ALD Al<sub>2</sub>O<sub>3</sub> has been reported to be approximately 100 – 200 Å [5]. Typical deposition temperatures for ALD Al<sub>2</sub>O<sub>3</sub> barrier layers have been reported to be 100 °C or higher, although films with limited barrier properties have been reported as low as 58 °C [1].

Preliminary studies of Al<sub>2</sub>O<sub>3</sub> carried out in a conventional ALD reactor, as detailed below, verified that the barrier properties of Al<sub>2</sub>O<sub>3</sub> improve as the deposition temperature is increased. In the case of plastic web, however, it is necessary to deposit the barrier film at temperatures compatible with the web. Even at the high end of the temperature range that is compatible with PET the purge times required between precursor pulses in a conventional cross-flow ALD reactor are very large. This paper describes the results of depositing Al<sub>2</sub>O<sub>3</sub> barrier films using a new ALD deposition approach tailored to roll-to-roll web coating. In this approach the web is transported between precursor zones that are separated by a purge zone. No precursor pulsing is required and purge times are eliminated owing to the fact that the web moves in and out of the precursor zones and the precursors do not need to be evacuated from these zones between cycles. The potential does exist, however, for excess precursor to be carried from one precursor zone to the other by the motion of the web. This effect has been observed and can affect the growth of the barrier film. Using this new web coating approach, ALD Al<sub>2</sub>O<sub>3</sub> barrier layers have been grown on PET film that exhibit water vapor barrier properties comparable to ALD barriers reported from conventional cross-flow reactors.

## EQUIPMENT AND EXPERIMENTAL DETAILS

### *Conventional Cross-Flow ALD Reactor.*

A conventional cross-flow ALD reactor consists of a vacuum chamber held at a specific temperature through which a steady stream of carrier gas flows. An ALD deposition cycle consists of injecting alternating precursors into this gas flow with purge times between precursor pulses sufficient to remove essentially all of each precursor from the volume of the reaction chamber before the start of the next precursor pulse. Following the evacuation of the precursor from the volume of the reaction chamber just a monolayer of that precursor is left on all surfaces within the chamber or the monolayer of the previous precursor has been fully reacted to form molecules of the compound being deposited. For Al<sub>2</sub>O<sub>3</sub> the precursors are typically trimethylaluminum (TMA) and H<sub>2</sub>O. The total cycle time at higher temperatures (>200 °C) is on the order of 10 seconds. At room temperature, the total cycle time is on the order of 100 seconds. Film thickness and deposition temperature splits as well as dose strength tests were carried out in the conventional ALD reactor as a baseline for the web coater results.

### *ALD Web Coater.*

The ALD web coater described here overcomes the purge time issue by eliminating all pulsing of precursors. A test reactor was built to evaluate and develop this concept. It was used in two different modes, one referred to as band mode and one referred to as roll-to-roll mode. A schematic representation of the band mode is shown in Figure 1. In this configuration the web can be passed repeatedly through the precursor and

purge zones in a closed loop. As the web travels between zones it passes through slit valves, which are just slots cut in the plates that separate the different zones. Much of the early data has been collected in band mode for convenience. In this mode, unused slit valves (not shown) are closed off.

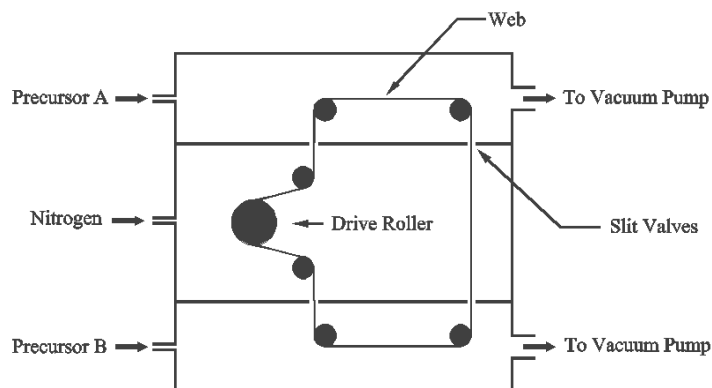


Figure 1. Schematic Diagram of the Web Coater in Band Mode.

A schematic representation of the roll-to-roll mode is shown on Figure 2. In this configuration the web is passed from an unwind roll through the sequence of slit valves from purge zone to precursor A zone to purge zone to precursor B zone to purge zone, etc., and finally to the rewind roll. The test reactor has a total of 16 pairs of slit valves, resulting in the equivalent of 8 ALD cycles per pass. Due to the nature of the ALD process, precise control of web speed is not critical. There are no deposition sources to control. As long as a saturated dose of precursor is maintained in each precursor zone the film growth is uniform.

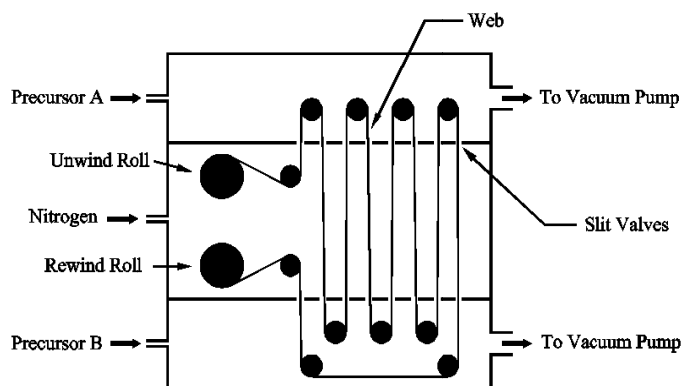


Figure 2. Schematic Diagram of the Web Coater in Roll-to-Roll Mode.

The pressure during deposition was approximately 1.5 – 2.0 Torr. Nitrogen flow was adjusted to provide a slight pressure differential between the center purge zone and the precursor zones. The deposition runs in the roll coater were carried out at 75 °C.

#### Sample Preparation.

Rolls of four inch wide, 125  $\mu\text{m}$  thick PET were used for the band mode and roll-to-roll mode web coater tests. Coupons for tests in a standard cross-flow ALD reactor were also cut from the 125  $\mu\text{m}$  PET rolls. This PET is industrial grade and was slit and rewound on four inch rolls by a converter. There were no smoothing layers added and it was not heat stabilized. Incoming PET rolls were blown off with a hand-held  $\text{N}_2$  blow-off gun without unrolling them. The first few feet of each roll was discarded and test samples were cut from the remaining roll material. Test coupons for the conventional ALD reactor and lengths of web for roll coating were then treated in an  $\text{O}_2$  plasma prior to loading into the web coater or conventional ALD reactor. No other cleaning processes were used on any of the test samples. The conventional ALD reactor as well as the roll-to-

roll ALD reactor was located in a class 10,000 lab area. No special precautions were taken to reduce particle contamination on the web material during loading of the reactors beyond standard class 10,000 procedures.

#### Film Characterization.

Thickness values for thin  $\text{Al}_2\text{O}_3$  barrier films on PET were not directly measureable due to the closeness of the refractive indices of  $\text{Al}_2\text{O}_3$  and PET. It was possible, however, to measure the thickness of much thicker films deposited under the same conditions as the thinner films in the roll coater. Films that were an optical quarter wave thick in the visible range were produced by running approximately 1000 cycles in the roll coater in band mode. The thicknesses of these films were then measured by collecting a reflectance spectrum and calculating the thickness and index from the interference minima. The reflectance spectra were measured on a HunterLab UltraScan spectrophotometer. The thickness of thin  $\text{Al}_2\text{O}_3$  barrier films on PET that were run in the roll coater were calculated based on the deposition rate in  $\text{\AA}/\text{cycle}$  measured on the quarter wave test films. The thicknesses of thin  $\text{Al}_2\text{O}_3$  barrier films from the conventional cross-flow reactor were assumed to be equal to the thicknesses measured on Si wits that were run together with the PET samples. The film thickness on Si was measured using a Rudolph Research AutoEL III ellipsometer.

Water vapor transmission was measured using an Illinois Instruments Water Vapor Transmission Analyzer Model 7001. Test discs were cut by hand using a template and scalpel. WVTR data were collected at  $38^\circ\text{C}$  and 90% RH.

## RESULTS AND DISCUSSION

### $\text{Al}_2\text{O}_3$ Films on PET Web Coupons Deposited in a Conventional ALD Reactor.

$\text{Al}_2\text{O}_3$  films were coated on PET coupons in a conventional cross-flow ALD reactor. Depositions were carried out at  $50^\circ\text{C}$  and  $80^\circ\text{C}$ . Test samples were coated on both sides by suspending the PET coupons in the

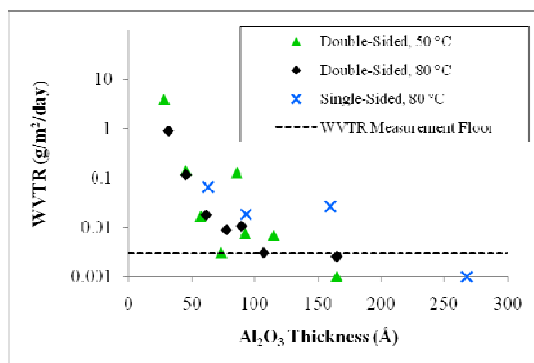


Figure 3. WVTR data for various thicknesses of single sided and double sided  $\text{Al}_2\text{O}_3$  films on PET deposited in a conventional ALD reactor at  $50^\circ\text{C}$  and  $80^\circ\text{C}$ .

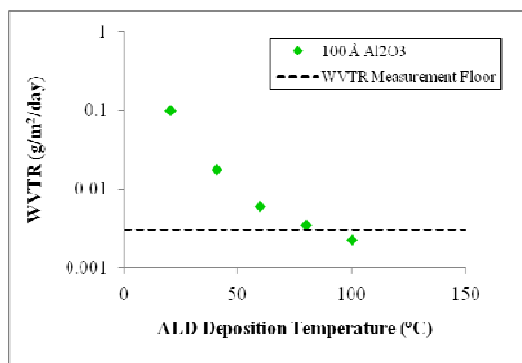


Figure 4. WVTR data for 100  $\text{\AA}$  thick, double sided  $\text{Al}_2\text{O}_3$  films on PET deposited in a conventional ALD reactor at various temperatures.

reactor chamber from clamps on two opposite edges. Single sided coatings were produced by laying the PET on the floor of the reactor chamber and placing weights around the edges. These  $\text{Al}_2\text{O}_3$  experiments were intended to establish a comparison with similarly produced films reported in the literature as well as to provide a baseline for comparison with ALD  $\text{Al}_2\text{O}_3$  barrier layers deposited in the roll-to-roll coater.

Water vapor transmission rates for various thicknesses of single sided and double sided  $\text{Al}_2\text{O}_3$  films on PET deposited in a conventional ALD reactor at  $50^\circ\text{C}$  and  $80^\circ\text{C}$  are shown in Figure 3. The detection limit of the WVTR instrument is reached at a film thickness of approximately 100-120 $\text{\AA}$  for double sided films. This agrees very well with values in the literature. [4, 5] Single sided barriers reached the detection limit of the WVTR instrument at about 150-200 $\text{\AA}$ .

Water vapor transmission rates for 100  $\text{\AA}$  thick ALD  $\text{Al}_2\text{O}_3$  barriers on PET deposited in a conventional ALD reactor at various temperatures are shown in Figure 4. The barrier properties of the ALD  $\text{Al}_2\text{O}_3$  improve with increasing temperature. The transmission rate drops below the measurement limit of the WVTR instrument at about  $100^\circ\text{C}$ .

Saturation data for the  $\text{Al}_2\text{O}_3$  process in the conventional cross-flow reactor at  $50^\circ\text{C}$  and  $80^\circ\text{C}$  are shown in Figure 5. The saturation curves were generated using 30 second purges. A few additional data points with longer purges were added to explore the purge times necessary to achieve true saturation. At these temperatures a true saturated process is difficult to achieve. It appears that a saturated process close to the known saturated deposition rate of approximately  $1.1 \text{ \AA/cy}$  for ALD  $\text{Al}_2\text{O}_3$  is approached for pulse times between about 5 seconds and 10 seconds with very long purge times of about 150 seconds. All of the previous data shown for the conventional cross-flow reactor was generated using 2 second pulses and 30 second purges. Based on the saturation data at  $50^\circ\text{C}$  and  $80^\circ\text{C}$  it is likely that there is some component of CVD in the deposition process in the conventional ALD reactor at these temperatures.

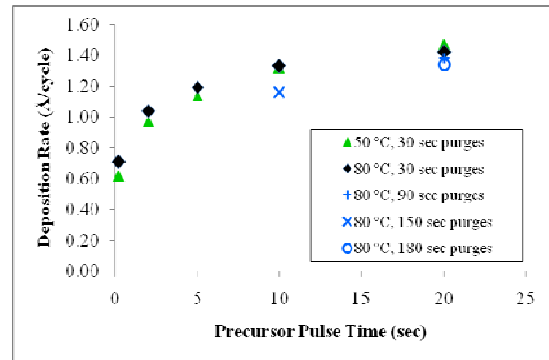


Figure 5. Deposition rate as a function of precursor pulse time at  $50^\circ\text{C}$  and  $80^\circ\text{C}$ .

#### $\text{Al}_2\text{O}_3$ Films on PET Web Deposited in the ALD Web Coater Operating in Band Mode.

The dwell times of the web in the precursor zones and the purge zone in the web coater are analogous with the pulse and purge times in the conventional ALD reactor, the key difference being that the web moves from zone to zone and the precursors are flowing continuously in the precursor zones. In the band mode the length of web resident in each precursor and purge zone at a given instant is approximately 0.6 m. Thus, even at a relatively slow web speed of 0.15 m/s the precursor dwell times are about 4 seconds and the purge dwell times are about 4 seconds in the band mode in this test reactor configuration. These times are proportionately shorter for higher web speeds. WVTR data for  $\text{Al}_2\text{O}_3$  films on PET deposited in band mode at various web speeds are shown in Figure 6. The performance of barriers deposited at 0.15 m/s and even 0.3 m/s are comparable to barriers deposited in a conventional ALD reactor using 2 second pulses and 30 second purges. The barriers deposited at 0.5 m/s require about  $40 \text{ \AA}$  of additional film thickness to achieve the same barrier performance as films deposited in the conventional ALD reactor.

One of the factors that will cause reduced barrier performance at higher web speeds is the fact that for a given precursor partial pressure in the precursor zone there is some speed at which the exposure dose of that precursor is insufficient. This insufficient dose will impact barrier performance before it impacts the deposition rate measured on the surface of the web. At very high precursor doses the precursor is able to diffuse into cracks and around particles, sealing the web from moisture penetration. As the dose is reduced, the ability of the precursors to fill in these features is reduced, resulting in reduced barrier performance. As the dose is reduced further, the deposition rate as measured on the surface of the web will eventually be reduced, but only after the dose is reduced well below the level where barrier performance starts to be affected.

Another factor that will cause reduced barrier performance at higher web speeds is the transport of excess precursor from one precursor zone to the other precursor zone. Following exposure to the  $\text{H}_2\text{O}$  precursor zone the surface of the growing  $\text{Al}_2\text{O}_3$  film should be saturated with  $-\text{OH}$  groups. If there is excess  $\text{H}_2\text{O}$  adsorbed to the surface as it enters the TMA zone, CVD deposition and gas phase particle formation can occur, resulting in degradation of barrier performance. Similar deleterious reactions could take place if water vapor is swept into the TMA zone by viscous drag caused by the moving web. In the experimental web coater no film growth on the chamber walls has been observed anywhere except in the TMA precursor zone when the web speed is significantly over 1 m/s. When there has been film growth on the walls of the TMA precursor

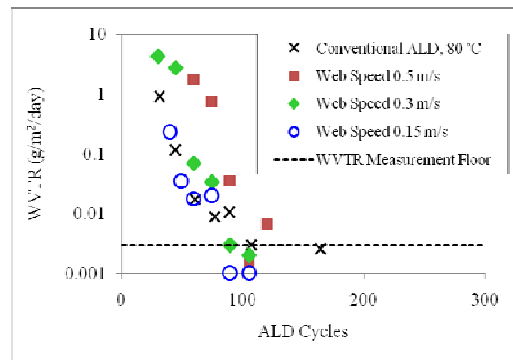


Figure 6. WVTR data for  $\text{Al}_2\text{O}_3$  deposited in band mode at  $75^\circ\text{C}$ . Data for  $\text{Al}_2\text{O}_3$  deposited in a conventional static reactor at  $80^\circ\text{C}$  are also plotted for comparison.

zone it has always occurred only where the moving web first encounters TMA. There has never been any downstream coating from H<sub>2</sub>O diffusing laterally in the purge zone and entering the TMA zone through other open slit valves. These observations suggest that excess H<sub>2</sub>O is being transported by the web into the TMA zone when the web is moving at high speed.

A similar effect occurs for TiO<sub>2</sub> barriers (from TiCl<sub>4</sub> + H<sub>2</sub>O) deposited in the web coater, although the effect is not nearly as strong. There are several possible explanations for why the effect is much smaller for TiO<sub>2</sub>. One factor is that the reactivity of TiCl<sub>4</sub> with H<sub>2</sub>O is much lower than that of TMA with H<sub>2</sub>O. It may also be possible that TiO<sub>2</sub> film deposited by CVD is a better barrier than Al<sub>2</sub>O<sub>3</sub> film deposited by CVD. Another possibility is that HCl (a byproduct of TiO<sub>2</sub> formation) will form an azeotrope with H<sub>2</sub>O in the TiO<sub>2</sub> process that may inhibit the reaction of TiCl<sub>4</sub> and H<sub>2</sub>O. In any case, it has been found to be much easier to deposit a good TiO<sub>2</sub> barrier film in the web coater at high speed than it is to coat a good Al<sub>2</sub>O<sub>3</sub> film at high speed.

Saturation of the ALD process in the roll coater is indicated by a leveling off of the deposition rate as a function of dwell times. As the web speed is reduced a point should be reached at which the dwell time of the web in each precursor zone is sufficient to saturate the surface of the web with adsorbed precursor or react fully with the previous precursor layer and the dwell time in the purge zone is sufficient to allow any excess precursor to be removed. The particular speed at which these criteria are met depends on the specific precursors, the temperature and pressure, and other parameters such as tool geometry and purge gas flow, etc. Saturation data for the configuration in the experimental ALD web coater used here are shown in Figure 7. The process appears to be saturated for dwell times over about 2 seconds (web speeds below about 0.3 m/s). Comparing this with the data shown in Figure 5 for the conventional cross-flow reactor clearly demonstrates the efficiency of eliminating the pulses and purges of the conventional process. True saturation was never achieved with the conventional process at these temperatures even with purge times of several minutes per cycle. The web coater process follows a normal saturation curve down to about 0.6 second dwell times (1.0 m/s web speed). For shorter dwell times (faster web speeds) the rate starts rising again due to transport of excess H<sub>2</sub>O by the fast moving web, which results in CVD deposition. These higher deposition rates at very fast web speeds are not useful since the barrier properties of the film are poor, the growth is non-uniform, and the chamber walls start to get coatings of film and powder.

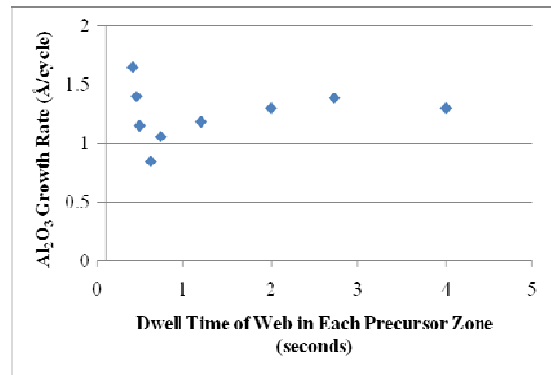


Figure 7. Deposition rate as a function of dwell time of the web in each precursor zone (saturation curve) for ALD Al<sub>2</sub>O<sub>3</sub> deposited in band mode.

#### Al<sub>2</sub>O<sub>3</sub> Films on PET Web Deposited in the ALD Web Coater Operating in Roll-to-Roll Mode.

In the full roll-to-roll mode in the web coater the precursor dwell times are shorter than in the band mode but the purge dwell times are approximately the same due to the geometry of the system. In roll-to-roll mode the web does not traverse across the entire machine length in each precursor zone but instead just turns around one roller and back into the purge zone. At a web speed of 0.15 m/s the precursor dwell times are about 1 second and the purge dwell times are about 1-2 seconds. As in the band mode, these times are proportionately shorter for higher web speeds. WVTR data for Al<sub>2</sub>O<sub>3</sub> films on PET deposited in roll-to-roll mode at two different web speeds are shown in Figure 8. The barriers deposited at 0.15 m/s require about 30-40Å of additional film thickness to achieve the same barrier performance as films deposited in the conventional ALD reactor. Barriers deposited at 0.3 m/s require about 100Å of additional film thickness to achieve the same barrier performance as films deposited in the conventional ALD reactor. These

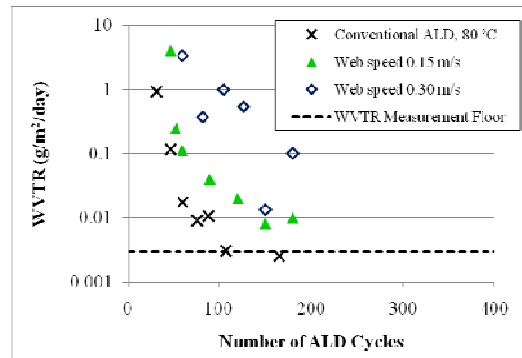


Figure 8. Water Vapor Transmission Rates for ALD Al<sub>2</sub>O<sub>3</sub> barrier layers deposited on PET at 75 °C in roll-to-roll mode. Data for Al<sub>2</sub>O<sub>3</sub> deposited in a conventional static reactor at 80 °C are also plotted for comparison.

differences are mainly attributed to mechanical damage done to the barrier layer and web during the roll-to-roll process.

Web handling in this experimental web coater is rudimentary. The drive roller is powered by a simple electric motor with a manual speed control knob. Power is transferred from the motor shaft to the drive roller via a large O-ring wrapped around pulleys. The end of the web is taped to the drive roller and manually threaded through the system and over the various guide rollers. The guide rollers are all free-wheeling, solid steel rods of one inch diameter. The guide rollers are supported from one end by roller bearings. There is no control of acceleration or tension in the web. Furthermore, since the experimental web coater only has eight cycles (approximately eight Angstroms) per pass, the web must be wound and unwound multiple times to deposit thicker films. For example, the web must be wound from the source roller to the wind-up roller and back onto the source roller six times to deposit a film of approximately 100Å. The web is undoubtedly being dragged across itself each time it is wound and unwound from the spools. Due to these handling limitations of the experimental reactor, a great deal of mechanical damage to the web and barrier layer is believed to occur during the roll-to-roll runs, limiting the barrier performance of the film. These deleterious effects should be significantly reduced by a properly engineered web handling system. These effects might also be mitigated somewhat by using smoother starting web material or applying a smoothing layer to the rough web surface being used here.

## CONCLUSIONS

ALD Al<sub>2</sub>O<sub>3</sub> barrier layers deposited on PET web material utilizing a novel roll-to-roll deposition process have been demonstrated. At moderate web speeds, barrier performance comparable to the best so far reported has been achieved for films deposited in a conventional ALD reactor. In initial roll coater experiments the barrier film deposited in the band mode at 0.3 m/s or less achieved barrier performance similar to films deposited in a conventional reactor. At 0.5 m/s an offset of about 40Å was required to achieve the same performance. Barrier films deposited in true roll-to-roll mode at 0.15 m/s required an additional 40Å thickness to achieve the same barrier properties achieved with similar films deposited in the band mode.

Depositing good barrier films of Al<sub>2</sub>O<sub>3</sub> at high web speeds has proved more challenging than depositing good barrier films of TiO<sub>2</sub> at high speeds. Achieving improved Al<sub>2</sub>O<sub>3</sub> barrier performance at higher web speeds will require improvements in the web handling mechanism, optimized precursor introduction and a reduction of excess H<sub>2</sub>O entering the TMA zone due to the moving web. Improvement of the web handling system should be a straightforward engineering exercise. Precursor introduction can be improved by applying standard techniques such as heating the precursor or injecting a carrier gas, using bubbler sources, etc. There are also several possible avenues to addressing the excess H<sub>2</sub>O issue. These include:

1. Utilize azeotropes (alcohols, etc.) to help remove excess H<sub>2</sub>O or inhibit the reaction between the H<sub>2</sub>O vapor and the TMA
2. Replace H<sub>2</sub>O with a precursor that does not tend to form excess adsorbed layers (O<sub>3</sub>, O<sub>2</sub> plasma, etc.)
3. Use a plasma in the purge zone to remove excess H<sub>2</sub>O from the web.
4. Use microwaves to remove excess H<sub>2</sub>O from the web

These methods are currently being explored.

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