Roll-to-roll ALD prototype for 500 mm wide webs
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Roll-to-roll (R2R) atomic layer deposition (ALD) technology is currently being developed to combine the high film quality of ALD with low-cost and high-throughput R2R manufacturing technology. While this technology can be foreseen to enable broad range of new applications, one of the most potential applications is the moisture barrier solution to the flexible PV and OLED markets. Thin single material inorganic ALD barrier layers have been shown to achieve ultra-barrier performance, and are estimated to be very cost-efficient to produce on R2R basis. The practical implementation of the characteristic ALD cycles by use of spatially separated precursor flows is the most challenging task when adopting ALD to R2R manufacturing. To address the scale-up challenges, a small R&D scale reactor for continuous mode ALD (CALD) processing was used to simulate the wider ALD coating head for process development purposes. Trials done with trimethylaluminum + water process at 120 °C show a growth rate of ~0.8 Å/cycle with 12.5 m/min web speed. The barrier performance of ~18 nm of such film is in 10⁻³ g/(m²day) level at 38 °C and in 90% relative humidity. A scaled-up R2R ALD system with an oscillating coating head is currently being ramped up and the initial results look promising. The system can be used to with up to 500 mm wide flexible substrates.

Introduction
Due to the sequential and saturating properties of ALD processes, the batch size can be rather easily scaled up to get the costs down to some 10s of $/m² in many applications. However, in some larger surface area applications like in photovoltaics even that is too much for a single part of the technology stack. The bottlenecks in increasing the throughput of an ALD batch process are in fast and uniform heating of the reaction chamber and also in getting the flows fast enough to achieve shorter purging times. These are limits that are challenging to come over by just improving the reaction chamber designs.

The concept of spatially separated ALD process was introduced already in the first patents by Suntola et al. in 1970s [1], but it got forgotten for quite some time. Figure 1 shows a figure from the patent [1] with illustrations to show the precursor zones and the ALD cycle. There are some older implementations of ALD batch tools for the semiconductor industry, where the wafers are rotated through different precursor zones. More recently as the benefits of ALD films in larger surface area applications, such as moisture barriers and back-side passivation layers in silicon solar cells, become understood, the need for larger throughput and more economical ALD production became more apparent. Since then, the search for feasible ways to commercialize the roll-to-roll ALD process has accelerated rapidly.
Spatial ALD provides a new kind of paradigm, as it will often turn the process back to single substrate (or continuous web) processing instead of large batches, which makes the uniform heating of the substrates much faster. Also, the purge step is not really the only limiting factor for the process speed, but the limit is shifted towards the speed of the chemical reactions. In many of applications, the film is wanted only on one side of the substrate, which is very difficult to achieve accurately with batch ALD process. Spatial ALD can also solve that problem as the film growth is limited to the substrate surface exposed to the precursor injection areas. This also provides huge benefits to the efficiency of the process as the walls of the reaction chambers are not coated anymore and the process is in principle clean (as long as the separation of the precursors is good enough). These properties help to reduce the cost of roll-to-roll ALD coating even to below $1/m^2$ for thin enough films.

R2R ALD has a wide range of potential applications, but our main focus has been in depositing moisture barriers on polymer webs. Good and economical moisture barrier coatings have been limiting the commercial feasibility of many flexible electronic devices such as flexible copper indium gallium selenide (CIGS) solar cells, flexible organic photovoltaic (OPV) devices, large area organic light emitting diodes (OLEDs) etc. The barrier solutions passing the rigorous tests of the devices have been based on multilayer inorganic-organic film stacks and have been way too expensive to enable wider adoption.

If a high-quality starting surface is used, ALD can be used to make single inorganic layer ultra-barrier films with water vapor transmission rate (WVTR) below $10^{-4}$ g/(m²·day) at 38°C and 85% relative humidity [2,3]. If similar performance is reached with roll-to-roll (R2R) ALD process, it could offer much improved productivity compared to physical vapor deposited (PVD) or chemical vapor deposited (CVD) barrier films by keeping the total thickness of the stack substantially smaller compared to other techniques. Evidence of this has been already been shown by Lotus Applied technology using their 100 mm wide R&D reactor [4].

Results with continuous ALD process

The R&D system TFS 200R was used to study continuous ALD processes with a set of smaller nozzles (4 ALD cycles). Figure 2 shows the conceptual thinking of the approach and a photo of the modified TFS 200R system.
The smaller R&D system TFS 200R has a removable coating cylinder with 100 mm diameter and approximately 120 mm wide coating area, giving a total usable substrate area of roughly 120 mm x 300 mm. That is enough to get the two 100 mm diameter samples for the WVTR measurements from each run. Dupont Teijin Films ST504 PET films were used as samples and they were taped to the coating cylinder with a polyimide tape. For thickness measurements, PET films metallized with titanium were used to provide a quick visual check on the uniformity and to enable thickness measurements with an ellipsometer.

Figure 3 gives an overview of the TFS 200R results gotten with trimethylaluminum (TMA) + water process at 120 °C temperature. The stripes visible in the coated sheet are coming from the imperfections in the titanium metallization and were visible also before the ALD coating. The saturated growth rate of Al₂O₃ is

< 3% non-uniformity (over 120 mm)

Sharp edge profile

WVTR: $\sim 10^{-3}$ g/(m² day) @ 18 nm

Al₂O₃ at 12.5 m/min
-GPC: $\sim 0.8$ nm/cycle
-RI: 1.62-1.63
typically ~1.1 Å/cycle at 120 °C depending on the process parameters. When the coatings were done with our test tool at 40 RPM rotational speed (12.5 m/min linear speed), the saturated growth rate dropped to ~0.8 Å/cycle. A typical run at 12.5 m/min speed with slight overdosing gives a growth rate of 0.79 Å/cycle with 2.5% thickness uniformity.

Scaling up
The WCS 500 system is based on the same gas distribution structure as the smaller system, but it is scaled in width and in number of cycles. The thickness is controlled by oscillating the head around the coating drum. The system is based on a vacuum web coater into which the ALD coating head is installed. The first WCS 500 system is currently being tested and will be later commissioned to the Advanced Surface Technology Research Laboratory (ASTRaL) research unit of Lappeenranta University of Technology based in Mikkeli. Figure 5 shows an overview photo of the system.

![Figure 5. The roll-to-roll ALD system WCS 500.](image)

The scaled up width is much more challenging when trying to get uniform precursor and diffusion barrier distributions over the whole coating head. Even a small leak through the diffusion barrier or between the precursor lines generates a large amount of particles and uncontrolled film growth over the long processing runs.

Initial results are promising and show a good separation between the precursor nozzles. Figure 6 shows a result from a trial done by oscillating the coating head over a stationary Ti-metallized web. The oscillation length was less than the distance between the precursor zones, so that the effects coming from different nozzles can be analyzed separately.
Conclusions

ALD is seen to provide value for an increasing number of large area, high-throughput applications in addition to semiconductor applications. Spatial ALD is a paradigm change and provides throughputs on a completely new level. The spatial process is conceptually scalable to rigid and flexible substrates of larger sizes as well.

One of the most promising applications for roll-to-roll ALD is in moisture barrier coatings. ALD has been shown to produce ultra-barrier level performance with coating thicknesses much smaller than any other method. The initial results with TFS 200R system show promising barrier results in the $10^3$ g/(m²day) level with 12.5 m/min linear speed. Even better results are expected as the process parameters and substrate handling procedures are optimized.

The first commercial roll-to-roll ALD system is being ramped up and the initial results are promising. The system is able to process 500 mm wide polymer webs.

