Roll-to-roll equipment for atmospheric atomic layer deposition for solar applications

Raymond Knaapen, VDL Enabling Technologies Group
E-mail: Raymond.Knaapen@vdletg.com

Amongst thin-film deposition techniques, Atomic Layer Deposition (ALD) has unique properties like high conformality, high layer quality and thickness control down to Å level. Deposition rate, however, is very low in conventional ALD reactors. To achieve high throughput and to reduce costs, there have been recent developments regarding spatial ALD. Whereas in conventional ALD, precursors are dosed separated in time using a purge or pump step, in spatial ALD, precursors are dosed simultaneously and continuously at different physical locations. As purging is no longer needed, the spatial ALD process can be operated at much higher speeds, limited by layer deposition chemistry rather than pumping times. Thus, deposition rates exceeding 1 nm/s have been reported for spatial atmospheric ALD of Al₂O₃ [1]. This has led to the launch of high throughput, industrial scale ALD tools for surface passivation of crystalline silicon solar cells.

Usually, substrates in existing ALD applications are flat and rigid, like silicon wafers or glass plates. Performing spatial ALD on these substrates involves e.g. substrate reciprocation or rotation under a flat ALD injector head. Precursors are not allowed to come into contact with each other, other than on the substrate surface. Separation of precursors is achieved using gas bearing technology, which also enables small precursor chamber volumes.

Because of the increased throughput and decreased cost levels, new application fields are opening up for spatial ALD, such as flexible electronics, including system-in-foil, flexible displays, OLEDs and solar cells. Examples of layers are transparent oxide (semi)conductors (e.g. ZnO), moisture permeation barriers (e.g. Al₂O₃), and buffer layers in CIGS solar cells (e.g. Zn(O,S)).

A new type of atmospheric, spatial ALD reactor has been developed for deposition on flexible substrates [2]. Instead of a flat ALD injector head, a rotating drum is used to supply the precursor gases to slots at the peripheral surface of the drum, parallel to its rotation axis (see Fig. 1). The foil substrate is transported around the drum surface, where gas bearings are used to separate the foil from the drum as well as separate the different precursors. The foil being contactless enables the drum to rotate at high speed while the foil is slowly advancing. Thus every part of the foil surface will come into contact with a predefined number of precursor cycles. Each individual precursor pair cycle will deposit one monolayer of e.g. Al₂O₃. In the current design, the drum has six precursor slot pairs at its outer surface. Thus, when the drum rotates at a frequency of 1 Hz, the number of precursor pairs per second is approximately 6, for low foil traversing speeds. When the foil effectively covers ~50% of the drum surface, a ~20 nm thick layer of alumina can be applied in a continuous roll-to-roll process. Such layers can e.g. be used as moisture barrier.

A prototype roll-to-roll ALD reactor has been realized according to the 3D representation in Fig. 2. In this prototype, contactless deposition of alumina has been shown on, amongst others, PET substrates.
As part of the EU FP7 project “R2R CIGS”, a second generation tool has been realized, aimed at deposition of zinc oxysulfide (Zn(O,S)) buffer layers in CIGS solar cells as replacement for CdS (Fig. 3). The foreseen precursors are diethylzinc (DEZn), H₂O and H₂S. The deposition of Zn(O,S) using ALD using premixing of precursors is enabled by spatial processing [3]. The oxygen to sulfur ratio can be manipulated using variation of precursor premixing ratio in the gas supply as well as variation in exposure time by changing drum rotation speed. Using only DEZn and H₂O it is possible to deposit intrinsic zinc oxide (i:ZnO), and by admixing H₂S to H₂O it is possible to obtain a Zn(O,S) compound, which is required for the CIGS buffer layer. The described R2R ALD tool has been used to apply buffer layers with various O to S ratios on CIGS stacks. Finalizing the stacks has resulted in functioning CIGS solar cells with promising efficiency values [4].
In the ALD reactor, all active chemicals are used in gas phase. The gas supply system for the active
gases has supply lines for DEZn, H₂O and H₂S. DEZn is evaporated in a bubbler system using nitrogen
and further diluted depending on required process settings. Optionally, the bubbler can be heated to
increase evaporation rate. The H₂S supply uses prediluted H₂S in nitrogen as source and is further
diluted as required for the deposition process. H₂O is evaporated using a controlled evaporator mixer
(CEM) and further diluted in nitrogen. The diluted H₂O and H₂S streams can be mixed to a
predetermined ratio for deposition of Zn(O,S).

The ALD reactor output contains reaction products and unused precursor gases, which have to be
neutralized. All output gases are fed through a caustic soda scrubber (NaOH solution in water) which neutralizes, both, DEZn and H₂S.

The ALD reactor is integrated with a web handling system that enables controlled web speed of 0.1
m/min up to at least 10 m/min, web tension of 10 N and higher, and lateral steering to ensure proper
web alignment to the ALD drum. There is no mechanical contact at the deposition side of the web to
avoid damage to the active layers. To further improve yield, the machine can be placed in a
cleanroom environment.

Fig. 4 shows a schematic of the web handling system. The ALD reactor is schematically shown in the
center, inside a double enclosure. The web unwinder, at the left side, is controlling the web speed
whereas the rewinder, at the right side, is controlling the web tension. Both winders have an option
to apply or remove a protective interleave (ILF).

Any accidental gas leak towards the environment shall be avoided, especially since H₂S is poisonous.
Therefore, there is a double enclosure around the ALD drum as shown in Fig. 5. Both enclosures have
an adjustable exhaust for controlled internal pressure. The pressure in the outer enclosure is just
below environment pressure, and the pressure in the inner enclosure is just below outer enclosure
pressure. It is not a vacuum system, i.e. pressure levels are approximately atmospheric. There is an
option to purge the enclosure volumes with a clean/inert gas, e.g. nitrogen.
The machine is controlled from a central control system, which controls the sub-systems like motion control (web handling, drum motion), heating control (gas heating, component heating), pneumatic control, safety and gas supply & abatement.

### Conclusion

Based on the spatial ALD reactor concept as published in [2], a second generation roll-to-roll spatial ALD reactor has been designed and built for deposition of zinc oxy sulfide (Zn(O,S)) buffer layers in CIGS solar cells as replacement for CdS. This development is part of the EU FP7 project “R2R CIGS”. The tool incorporates spatial atomic layer deposition using premixed precursors for deposition of mixed compounds. Web handling has been integrated with the ALD reactor to enable web transport with controlled speed, tension and lateral steering. The ALD reactor is furthermore integrated with central control, gas supply and abatement, heating, pneumatics and safety system. The described R2R ALD tool has been used to apply buffer layers with various O to S ratios on CIGS stacks. Finalizing the stacks has resulted in functioning CIGS solar cells with promising efficiency values [4].

Beside CIGS buffer layers, the tool can also be used for other applications such as barrier layers. For deposition of alumina, the zinc precursor could e.g. be exchanged for an aluminum precursor such as trimethyl aluminium (TMAI). A 3D overview drawing is shown in Fig. 7.
Fig. 7. Roll-to-roll spatial ALD reactor layout


