Ultrafast atomic layer deposition of alumina layers for solar cell passivation

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Atomic Layer Deposition (ALD) is a deposition technique capable of producing ultrathin conformal films with superior control of the thickness and composition of the films at the atomic level. In conventional ALD, the deposition reaction is divided in two time-sequenced self-limiting half-reactions, each one being separated by purge steps. In the case of $\text{Al}_2\text{O}_3$, one deposition cycle includes a dose of an aluminum precursor (mostly trimethyl aluminum, TMA), followed by a purge step to remove excess precursor and reactants, a subsequent oxidation step by dosing $\text{H}_2\text{O}$, $\text{O}_2$ or $\text{O}_3$ and, finally, another purge step. Conventional thermal ALD usually takes place at elevated temperatures and at low reactor pressure. One or more cycle steps may also be facilitated by e.g. a plasma (Plasma Enhanced ALD). The layer growth during such a cycle, or Growth Per Cycle (GPC), is typically $\sim 0.1\,\text{nm/cycle}$. Thus to obtain thicker films, the cycles have to be repeated many times. As each cycle step can take up to several seconds, the overall deposition rates are of the order of a few nanometers per minute. One way to speed up the process is by batch processing, but this is not always compatible with industrial needs.

Recently, we presented an ALD concept based on the spatial separation of the half-reactions, by which alumina layers can be deposited with deposition rates of more than 1 nm/s. The deposition rate is limited by the water half-reaction, for which a kinetic model has been developed. The alumina layers showed excellent passivation of silicon wafers for solar cell applications. Based on this concept, a high-throughput ALD deposition tool is being developed targeting throughput numbers of up to 3000 wafers/h.

Spatial ALD as an enabling technology for cost-effective passivation of crystalline silicon solar cells has been reported earlier by us and others. In this paper, we further examine the possibilities of spatial ALD regarding industrialization.

### Experimental
A proof-of-principle reactor was constructed, where the separate reaction zones' inlets are incorporated in a round reactor head, surrounded and separated by gas bearing planes (Fig. 1b). The reactor head is mounted on top of a rotating substrate table holding the substrate as illustrated in Fig. 1c. The experimental parameters are listed in Table I and described in more detail in Ref. 6. Trimethyl aluminum (TMA) and water are used as reactants. All depositions were performed at 200°C at atmospheric pressure.

### Results
With the experimental set-up, a 3 cm wide ring-shaped track of $\text{Al}_2\text{O}_3$ was deposited, corresponding to the width and position of the deposition inlets (Fig. 2). The color of the layer is caused by interference effects, where the blue color corresponds to a thickness of $\sim 100\,\text{nm}$. Layers with thicknesses of up to 500 nm were deposited, showing an excellent linear relation between the layer thickness and the total number of rotations. The concept was tested successfully up to a rotational frequency of 600 rpm. Higher frequencies could not be tested due to mechanical limits of the set-up. With a growth per cycle around 0.1 nm/cycle, this results in deposition rates in the order of 60 nm/min. The layer thickness is homogeneous along the width of the deposition track for all rotational frequencies ($\sim 5\%$ inhomogeneity can be achieved). This is proof of having a true ALD deposition regime with little or no CVD component. Prolonged experimental runs showed no accumulated parasitic deposition, thus indicating sufficient separation of the precursor by the gas bearing.

Next, the GPC as a function of rotation frequency was measured, while keeping the deposition temperature, gas- and precursor flows constant (Fig. 3). The GPC decreases slightly with increasing rotation frequency, from $\sim 0.13\,\text{nm/cycle}$ at 60 rpm to $\sim 0.10\,\text{nm/cycle}$ at 600 rpm. The shorter precursor exposure times at higher frequencies lead to an incomplete saturation of the substrate. By increasing the precursor partial pressure it should be possible to increase the level of saturation. The standard TMA partial pressure being $\sim 1\,\text{mbar}$, neither a 2.5 times higher TMA partial pressure ($\sim 2.5\,\text{mbar}$), nor half the TMA partial pressure ($\sim 0.5\,\text{mbar}$) showed any effect on the GPC at frequencies of 600 rpm. In contrast, the water partial pressure (standard value $\sim 124\,\text{mbar}$) has a significant effect on the saturation behavior, and thus the GPC. (Fig. 3), with a GPC of $0.095\,\text{nm/cycle}$ at half the standard water partial pressure ($\sim 62\,\text{mbar}$) and $0.11\,\text{nm/cycle}$ at $\sim 3$ times higher water partial pressure.
adsorbed at the Al2O3 interface. Such a reaction can be described by Eley-Rideal kinetics. The rate equation is then given by

\[
\frac{\partial [\text{CH}_3]}{\partial t} = -k[\text{CH}_3][\text{H}_2\text{O}] \quad \text{or} \quad \frac{\partial N_{\text{Me}}(t)}{\partial t} = -kN_{\text{Me}}(t)p_w \tag{2}
\]

where \(N_{\text{Me}}(t)\) is the time-varying methyl group concentration, \(k\) is the rate constant and \(p_w\) is the water partial pressure. It is assumed that there is a high water refresh rate and the water partial pressure can be considered constant, i.e. \(\frac{\partial p_w}{\partial t} = 0\). Solving Eq. 2 gives

\[
N_{\text{Me}}(t) = N_{\text{Me}}^0 \exp[-kp_w t] \tag{3}
\]

with \(N_{\text{Me}}^0\) the initial methyl group concentration. The number of newly formed hydroxyl groups \(N_{\text{OH}}(t)\) formed in reaction 1 is given by

\[
\frac{\partial N_{\text{OH}}(t)}{\partial t} = -\frac{\partial N_{\text{Me}}(t)}{\partial t} \tag{4}
\]

Combining 3 and 4 gives

\[
N_{\text{OH}}(t) = N_{\text{OH}}^0 + N_{\text{Me}}^0 \left(1 - \exp[-kp_w t]\right) \tag{5}
\]

assuming that \(\lim_{t \to 0} N_{\text{OH}}(t) = N_{\text{OH}}^0\) and \(\lim_{t \to \infty} N_{\text{OH}}(t) = N_{\text{OH}}^0 + N_{\text{Me}}^0\).

The GPC is related to the total number of hydroxyl groups formed after the water dose plus the remaining unreacted hydroxyl groups from before the water dose

\[
\text{GPC} \propto N_{\text{OH}}(t) = N_{\text{OH}}^0 + N_{\text{Me}}^0 \left(1 - \exp[-kp_w t]\right) \tag{6}
\]

or, in a more general form

\[
\text{GPC} = A - B \exp[-kp_w t] \tag{7}
\]

with \(A, B,\) and \(k\) as fit parameters.

Figure 4 shows the GPC versus \(p_w\) (or \(p_w\) (in mbar)) divided by the rotation frequency (rpm)), with a fit of Eq. 7. Fit parameters are: \(k = 1.27 \text{ mbar}^{-1} \text{min}^{-1}, A = 0.13 \text{ nm/cycle} \text{ and } B = 0.038 \text{ nm/cycle}\). Because a relatively inaccurate bubbler system is used to evaporate the water, there is a rather large uncertainty in the water partial pressure.

### Table I. Experimental parameters proof-of-principle reactor

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>(T_{\text{deposition}})</td>
<td>50–350°C</td>
</tr>
<tr>
<td>Total flow TMA injector</td>
<td>1 slm</td>
</tr>
<tr>
<td>Total flow H2O injector</td>
<td>1 slm</td>
</tr>
<tr>
<td>Gas bearing pressure</td>
<td>5 bar</td>
</tr>
<tr>
<td>Gap substrate–gas bearing gap</td>
<td>20 μm</td>
</tr>
<tr>
<td>Gap substrate–TMA/H2O injector</td>
<td>100 μm</td>
</tr>
<tr>
<td>Rotation frequency</td>
<td>Max. 600 rpm</td>
</tr>
<tr>
<td>TMA partial pressure</td>
<td>1–5 mbar</td>
</tr>
<tr>
<td>H2O partial pressure</td>
<td>50–350 mbar</td>
</tr>
<tr>
<td>Total pressure</td>
<td>Atmospheric</td>
</tr>
<tr>
<td>Reactor diameter</td>
<td>15 cm</td>
</tr>
<tr>
<td>Deposition track width</td>
<td>3 cm</td>
</tr>
</tbody>
</table>
pressure. Nevertheless, the model gives an adequate description of the experimental data. From the fit to the data, a maximum obtainable rotation frequency can be estimated. Note, that from the fit a maximum GPC of 0.13 nm/cycle can be obtained at high $p_{w,t}$ values, so at very low rotation frequencies and very high water vapor pressures.

A typical value of $p_{w,t}$ is 1, corresponding to a GPC of 0.12 nm/cycle. In principle the maximum possible water vapor pressure is 1000 mbar (steam). As such, the maximum rotation frequency that can be used is 1000 rpm. This would result in a theoretical maximum deposition rate of 2 nm/s. Higher deposition rates are possible when understaturated half-reactions are allowed. However, this might also influence the quality of the deposited films.

Using high partial pressures and high rotation frequencies might be challenging from a practical point of view. A more straightforward approach to achieve high deposition rates is to use more precursors injectors in-line, to obtain more than one cycle per rotation.

**Spatial ALD for surface passivation of Si solar cells**

The level of surface passivation is quantified by the effective surface recombination velocity. Assuming an infinite bulk lifetime, the upper limit of the effective surface recombination velocity $S_{eff}$ can be calculated by

$$S_{eff} \leq \frac{d}{2\tau_{eff}}$$  \[8\]

with $d$ the substrate thickness and $\tau_{eff}$ the effective lifetime. Figure 5 shows the effective lifetimes $\tau_{eff}$ measured as a function of the injection density $\Delta n$ for 1.3 \Omega cm p-type float-zone silicon (FZ-Si) wafers passivated using Al$_2$O$_3$ deposited by plasma-assisted, thermal and spatial ALD (deposition temperature 200°C, rotation frequency 120 rpm). Lifetimes were measured by the photoconductance decay (PCD) method using a Sinton lifetime tester. All Al$_2$O$_3$ films received a post-deposition anneal at (400 ± 50)°C for ~15 min to activate the surface passivation. As can be seen from Fig. 5, all three ALD techniques result in Al$_2$O$_3$ films of outstanding surface passivation quality, which shows an extremely weak injection dependence over the complete relevant injection range between $10^{13}$ and $10^{15}$ cm$^{-3}$. Most importantly, it can be deduced from Fig. 5 that both traditional thermal ALD as well as spatial ALD provide Al$_2$O$_3$ films with an extremely high level of surface passivation, as indicated by lifetimes of >2 ms, corresponding to an upper surface recombination velocity (SRV) limit of $S_{eff} < 7$ cm/s, for both techniques and a practically negligible injection dependence over the relevant injection range. Furthermore, excellent firing stabilities of the alumina films have been observed.$^{11,12}$ It is quite remarkable that spatial ALD with its high deposition rates produces exactly the same excellent level of surface passivation as the slow (< 2 nm/min) thermal ALD. Although further optimization is required, our preliminary results show already that Al$_2$O$_3$ deposited by spatial ALD combines excellent surface passivation with high deposition rates.

It goes without saying that surface passivation of square silicon solar cell wafers requires uniform deposition of Al$_2$O$_3$ over the entire wafer area, rather than a circular track. Thus a rotary spatial ALD reactor cannot be used. For this reason, a reciprocating spatial ALD tool has been developed capable of processing full wafers at high throughput numbers (Fig. 6). Inside this tool, substrates are moved back and forth all the way underneath a spatial ALD injector with the same width as the substrate.$^{16}$ By using a double gas bearing (below and above the substrate, Fig. 6a), the substrate will float virtually frictionless underneath the injector zones. By pulsing flows of inert gas in the substrate drives next to the injector (Fig. 6b), the wafer can be moved back and forth without utilizing carriers. The wafers are centered by flows of gas perpendicular to the movement direction, on both sides of the wafer (Fig. 6b). When a deposition is finished, the substrate will be transported away from the injector head and a new substrate comes in immediately. A significant benefit of using a single injector with a reciprocating wafer is that the
The total deposition rate depends on the number of TMA and water slots that are integrated in the injector head, in combination with the number of passages of the substrate per second. Currently, each substrate passes 4 times per second through the injector head containing a single TMA slot, resulting in an effective deposition rate of ~0.4 nm/s. This allows for throughput numbers of the order of 100 wafers/h, based on a passivation layer thickness of 10 nm. However, it is possible to integrate two or three TMA and water half-reaction zones, thus increasing the throughput accordingly. With this tool, homogeneous deposits (2–4% thickness variation) with low effective recombination velocities are obtained over the entire area of the wafer, with minimal backside deposition (~30 cm/s for 180 μm p-type CZ wafers, 1–5 Ω cm, but highly dependant on type, quality, pre- and post-treatment of the Si wafer).

Further upscaling to industrial scale can be achieved by incorporating 10 or up to 15 injectors in parallel use, as a modular system (Fig. 6c). In this way throughputs of more then 3000 wafers/h can be obtained while keeping a relatively small footprint.

Conclusions

We have demonstrated that by spatially separated ALD in combination with gas bearing technology, high-quality Al₂O₃ layers can be deposited at deposition rates of at least 1.2 nm/s. With these films, very low effective surface recombination velocities were obtained, showing excellent surface passivation. This disruptive and high-throughput method has great potential in many other large-scale applications. Other materials than Al₂O₃ will further expand this potential. Currently, an in-line industrial spatial ALD tool for passivating square silicon solar cells is being developed, aiming at throughput numbers of 3000 wafers/h as a lead to cost-effective, next generation production tools.

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