ABSTRACT: In the recent years, considerable progress has been made in the understanding of the unique silicon surface passivation properties of aluminum oxide (Al$_2$O$_3$) films including its underlying mechanisms. Containing a high fixed negative charge density located close to the Si interface, Al$_2$O$_3$ provides a key merit over other available materials for the passivation of p-type surfaces and p+ emitters in silicon photovoltaics. The Al$_2$O$_3$ films also induce a high level of chemical passivation, which is vital to obtain excellent surface passivation properties. In this contribution, we highlight some recent work on the application and understanding of Al$_2$O$_3$ surface passivation films. We will discuss the material properties of Al$_2$O$_3$ including new data on the optical properties of ultrathin Al$_2$O$_3$ films (band gap is 6.4 ± 0.1 eV) for a large wavelength range. It will be shown that Al$_2$O$_3$ applied on top of SiO$_2$ resulted in a firing stable double layer passivation scheme. The application of Al$_2$O$_3$ in solar cells will also be briefly addressed. The beneficial effect of enhanced rear reflectance and increased passivation will be discussed. The industrial feasibility will be assessed on the basis of excellent surface passivation properties ($S_{eff} < 6$ cm/s) and firing stability for ~2 Ω cm p-type Si wafers with Al$_2$O$_3$ deposited in an inline thermal (H$_2$O-based) ALD tool (Levitex’s Levitrack), and in an industrial ASM batch reactor with O$_3$ as the oxidant. We furthermore demonstrate that “solar grade” Al(CH$_3$)$_3$, a precursor with reduced purity, resulted in Al$_2$O$_3$ films with similar passivation properties as semiconductor grade, high purity Al(CH$_3$)$_3$.

Keywords: Silicon Surface Passivation, Aluminum Oxide, Atomic Layer Deposition.

1 INTRODUCTION

The reports on the excellent passivation properties of crystalline silicon by Al$_2$O$_3$ synthesized with atomic layer deposition (ALD) that appeared in 2006 [1,2], sparked the interest in this surface passivation material. The first results on Al$_2$O$_3$ for surface passivation were already published by Hezel and Jaeger in 1989, when they used pyrolysis as deposition technique [3]. The renewed interest in Al$_2$O$_3$ was propelled by the intensified pursuit of the photovoltaic industry for suitable surface passivation schemes to increase solar cell efficiencies.

The key differentiator of Al$_2$O$_3$ in comparison to other passivation schemes is its high fixed negative charge density ($Q_i \sim 10^{11}-10^{12}$ cm$^{-2}$) located at the Al$_2$O$_3$/Si interface which produces effective field-effect passivation by shielding electrons from the interface [4,5]. Negative fixed charges are especially beneficial for the passivation of p-type surfaces in solar cells in which electrons are the minority charge carriers. This has also been demonstrated by enhanced solar cell efficiencies for Al$_2$O$_3$ applied on p+ emitters and on the rear of p-type solar cells [6,7]. Moreover, Al$_2$O$_3$ was found to be sufficiently stable during firing [8-11], which is essential for its compatibility with screen-printed solar cells. To date, Al$_2$O$_3$ surface passivation films have been mainly synthesized with atomic layer deposition (ALD). As an alternative for ALD, other methods have recently also been tested including physical vapor deposition (PVD, in particular sputtering) and plasma enhanced chemical vapor deposition (PECVD) [12-15]. These methods are well established in solar cell manufacturing in contrast to the ALD method, to date mainly used in the semiconductor industry. Therefore, a remaining challenge for ALD is the development of deposition tools that are compatible with the requirements of the solar cell industry, especially in terms of high throughput.

In this contribution we will cover a number of interesting aspects, both fundamental as well as industrially relevant, concerning Al$_2$O$_3$ for surface passivation of silicon. The intention is not to give a complete, in-depth review but rather to address some new results and developments. We will briefly report on the material properties of Al$_2$O$_3$ and discuss the importance of chemical and field-effect passivation. The use of double layer passivation schemes will be addressed by demonstrating a significantly-enhanced thermal stability for SiO$_2$/Al$_2$O$_3$ stacks. In addition, solar cells will be discussed and questions will be addressed related to the potential for industrial application. Excellent surface passivation properties and good thermal stability will be shown for ultrathin Al$_2$O$_3$ films deposited in an inline ALD tool and in an ALD batch reactor. Finally, the industrial feasibility will be underlined by results demonstrating that high-purity Al(CH$_3$)$_3$ can be substituted by a lower grade Al(CH$_3$)$_3$, reducing the associated costs per solar cell significantly.

2 RESULTS AND DISCUSSION

2.1 ALD Processes

The virtue of ALD is the control of the deposition process at the atomic level by self-limiting surface reactions during the alternate exposure of the substrate surface to different gas-phase precursors (see Fig. 1). Each surface reaction occurs between a gas phase reactant (precursor) and a surface functional group creating a volatile product molecule that desorbs from the surface, and a new surface functional group that is not reactive with the precursor. After pumping away the first precursor and the volatile reaction products, a second precursor is introduced. This leads to the deposition of a second element through reaction with the new surface functional group which also restores the initial surface...
functional group. This set of reactions forms one ALD-cycle resulting in less than one atomic layer of film growth, typically 0.5 Å – 1.0 Å per cycle. The ALD-cycle can be repeated until the desired film thickness is reached.

Furthermore, unlike chemical vapor deposition (CVD), the deposition rate is not proportional to the flux on the surface. Therefore, the same amount of material is deposited everywhere on the surface, even on non-planar surfaces, when the flux is sufficiently high. Other benefits of ALD over PECVD and PVD are the good uniformity that can be achieved on large substrates, the relatively low substrate temperatures used in the process and most commonly uses trimethylaluminum (Al(CH₃)₃ or TMA) as the aluminum source and either water, ozone or oxygen radicals from a plasma as the oxidant. Processes with water (illustrated in Fig. 1) and ozone are referred to as thermal ALD while the process employing a plasma is referred to as plasma ALD. Each cycle consists of Al(CH₃)₃ dosing followed by a purge, then oxidant exposure followed by a purge. For Al₂O₃, typically 0.9 Å to 1.5 Å is deposited in each of these cycles depending on the deposition temperature and the oxidant used [16,14]. The choice of oxidant depends on the application. In general oxygen radicals generated by a plasma source are more reactive than water relying on purely thermal energy [16]. At a substrate temperature T_sub of 200°C the growth per cycle is 1.2 Å for plasma ALD and 1.0 Å for the H₂O-based thermal ALD process [14,17]. Furthermore, the increased reactivity of plasma ALD can give improved film quality with lower impurity levels, in particular also for low substrate temperatures [18]. However, the industrial scale up of plasma ALD might be somewhat more complicated as it is necessary to incorporate plasma sources into the deposition equipment.

![Figure 1: Schematic of an ALD cycle for H₂O-based thermal ALD with Al(CH₃)₃ precursor dosing and purge steps (first half cycle) and H₂O exposure and subsequent purge step (second half cycle).](image)

2.2 Material properties of ALD Al₂O₃

The material properties of Al₂O₃ vary with deposition method. For ALD processes, they vary mostly with deposition temperature, which can be attributed especially to a variation of the hydrogen content of the films. Infrared absorption measurements have indicated that hydrogen is incorporated as OH-groups, and that also some CH₃ may be present [9]. For a substrate temperature in the range of T_sub = 150–250°C, the passivation properties were optimum for both thermal and plasma ALD [14]. The resulting material properties in terms of mass density and refractive index were comparable, but the hydrogen content for thermal ALD Al₂O₃ (~3.6 at. %) was higher than for plasma ALD (~ 2.7 at. %). More details on substrate temperature dependence of the material properties can be found elsewhere [14].

Having a large band gap, the Al₂O₃ films are transparent for the wavelength region which is relevant for silicon solar cells. In Figure 2 data is shown for the refractive index, n, and extinction coefficient, k, as determined for plasma ALD Al₂O₃ films from spectroscopic ellipsometry. Annealing at 400°C did not change the optical properties of the film significantly and thermal ALD with H₂O gave similar results. From the dielectric function ε, an optical band gap of E_g = 6.4 ± 0.1 eV was determined for both the as-deposited and annealed films. Note that this experimentally determined value for (amorphous) Al₂O₃ films, is lower than the typically assumed literature value of ~8.8 eV representative for crystalline Al₂O₃. Nevertheless, parasitic absorption in the Al₂O₃ films (as is the case for e.g. a-SiNₓ:H films, with E_g = 3.3-3.5 eV, for example) will not occur in the relevant range for photovoltaics as only light with λ < ~200 nm is absorbed by the Al₂O₃ films. Furthermore, it is noted that the refractive index of the Al₂O₃ is ~1.65, i.e., slightly higher than for SiO₂.

![Figure 2: Refractive index, n, and extinction coefficient, k, for plasma ALD Al₂O₃, for as-deposited films and for films annealed at 400°C in N₂ for 10 min. The optical properties were measured by spectroscopic ellipsometry using J.A. Woollam ellipsometers with an optical range extending from the vacuum ultraviolet to the near-infrared.](image)
2.3 Chemical and field-effect passivation

The excellent level of surface passivation by the Al$_2$O$_3$ films is reflected by surface recombination velocities ($S_{eff}$) < 5 cm/s for low resistivity $p$-type c-Si, after annealing at ~400°C in N$_2$ [5,10,14,17]. Also for $n$-type c-Si (3.5 Ω cm), exceptionally low $S_{th}$ values < 1 cm/s were measured [14,17]. These values represent the upper limit of $S_{th}$ as it is assumed that all recombination takes place at the surface (i.e. the bulk lifetime is infinite). On $n$-type c-Si, the negative $Q_s$ at the Si/Al$_2$O$_3$ interface inverts the surface region and repels the electrons, that become minority carriers, from the interface. The high level of passivation could be maintained for film thicknesses down to ~5 and ~10 nm for plasma and thermal ALD, respectively [17].

This is illustrated by Eq. 1, which follows from the Shockley-Read-Hall (SRH) formalism [21,22]. It be addressed, comparing plasma and thermal ALD. It can be decreased by a reduction of $D_o$ for as-deposited plasma ALD Al$_2$O$_3$ is consistent with the moderate surface passivation obtained prior to annealing ($S_{eff}$ < 30 cm/s). This is in sharp contrast with plasma ALD which did not provide passivation in the as-deposited state despite a high value of $Q_s$. It indicates that the improvement of the chemical passivation during annealing is vital to obtain excellent surface passivation properties for Al$_2$O$_3$ films.

The influence of the oxidant on $Q_s$ and $D_o$ is displayed, comparing plasma ALD with an O$_2$ plasma and thermal ALD with H$_2$O. The data were extracted from capacitance-voltage (C-V) measurements. We observe that the key effect of annealing is the increase of $Q_s$ for thermal ALD Al$_2$O$_3$, whereas for plasma ALD the chemical passivation is improved dramatically. The relatively low $D_o$ value of ~3×10$^{13}$ eV$^{-1}$ cm$^{-2}$ for as-deposited thermal ALD Al$_2$O$_3$ is consistent with the moderate surface passivation obtained prior to annealing ($S_{eff}$ < 30 cm/s). Also on screen printed Al+-emitters plasma ALD Al$_2$O$_3$ resulted in exceptionally low emitter saturation current densities of $J_{sat}$ ~10 fA/cm$^2$ and 30 fA/cm$^2$ for >100 and 54 Ω / sq sheet resistances, respectively [19].

In general, the surface passivation performance is controlled by the reduction of interface defect states (chemical passivation) and by shielding of minority charge carriers from the surface (field-effect passivation). This is illustrated by Eq. 1, which follows from the Shockley-Read-Hall (SRH) formalism [21,22]. The Shockley-Read-Hall (SRH) formalism [21,22] describes the interface recombination rate, $U_r$, as a function of interface defect density at midgap ($D_o$), the hole and electron capture cross sections ($\sigma_p$ and $\sigma_n$, respectively).

$$U_r = \frac{(n_e p_i - n_i^2) \nu_{th} D_o}{n_i + n_e + p_i + p_e \sigma_p \sigma_n}$$  (1)

The parameter $\nu_{th}$ represents the thermal velocity of the electrons, $n_i$ and $p_i$ statistical factors, and $n_i$ the intrinsic carrier concentration. For sake of the discussion here, the energy dependence of the parameters is neglected by assuming a single defect at mid gap. The driving force of the surface recombination process is the term ($n_e p_i - n_i^2$), which describes the deviation of the system from thermal equilibrium under illumination. Equation 1 shows that $U_r$ can be decreased by a reduction of $D_o$ (chemical passivation) and by the reduction of the density of one type of the charge carriers at the interface by an electric field (field-effect passivation). The relative importance of either mechanism depends on the passivation scheme used. For intrinsic amorphous silicon (a-Si:H), for instance, the passivation properties can be attributed to effective chemical passivation as the films do not contain a significant amount of fixed charges. Chemical passivation is also dominant for thermally-grown SiO$_2$ passivation schemes due to its relatively low fixed charge density (Fig. 3a).

The passivation by SiO$_2$ is activated by post-deposition hydrogenation for example by annealing in a gas mixture containing H$_2$ [22,23], which decreases $D_o$ significantly [24]. Films of a-SiN$_x$:H on the other hand also induce field-effect passivation due to a large positive fixed charge density ($Q_s$ ~10$^{15}$ cm$^{-2}$) in the material [3,25,26]. This positive charge reduces the hole concentration at the surface ($p_s$) and therewith $U_r$.

Figure 3b shows data with respect to the underlying surface passivation mechanisms for Al$_2$O$_3$ films [27]. The influence of the oxidant on $Q_s$ and $D_o$ is displayed. For comparison, typical values from the literature are included for thermally-grown SiO$_2$ and a-SiN$_x$:H.
The latter technique was only applied for annealed samples as it is based on the combination of lifetime measurements and corona charging. The results presented here are in agreement with a recent report that has also shown $D_{oc}$ values of $\sim 10^{11}$ eV cm$^{-3}$ after annealing for plasma ALD [29].

As both $Q_c$ and $D_{oc}$ relate to (electronic) states at the surface, the field-effect and chemical passivation will be closely related to the properties of the Si/Al$_2$O$_3$ interface. This interface is formed by a thin (1-2 nm) interfacial silicon oxide (SiO$_3$), even when Al$_2$O$_3$ is deposited on H-terminated Si. The thickness and structural properties of the SiO$_3$ change also slightly during annealing [4]. Moreover, with isotope labeling using deuterated Al$_2$O$_3$ we have recently shown that hydrogenation of the interface plays an important role in the chemical passivation of the Al$_2$O$_3$ films [30]. Differences in field-effect passivation between Al$_2$O$_3$ synthesized by plasma and thermal ALD, or by other deposition techniques, are likely related to a combination of Al$_2$O$_3$ material properties close to the interface and also to the formation of the interfacial oxide during processing.

2.4 Film stacks comprising Al$_2$O$_3$

ALD is most suitable for the deposition of ultrathin films. When thicker films are required, the application of a capping layer of a different material could be a solution. $a$-SiN$_3$H capping layers, synthesized with PECVD, have for instance been applied on top of thin Al$_2$O$_3$ films in solar cells [6]. This double layer is essential for the application on front side $p^+$ emitters in $n$-type solar cells to benefit from optimal passivation and antireflection properties. It was reported that the application of $a$-SiN$_3$H films deposited at temperatures of 400$^\circ$C did not compromise the surface passivation performance of Al$_2$O$_3$ [8,9]. The thermal budget during $a$-SiN$_3$H deposition was sufficient to activate the surface passivation induced by the Al$_2$O$_3$ film. Furthermore, it was found that the $a$-SiN$_3$H capping layer did not significantly influence the firing stability of Al$_2$O$_3$ films with a thickness of 30 nm [9]. Another study has suggested that for very thin Al$_2$O$_3$ films this can be different [11]. However, from the results discussed below (Fig. 7) we observe that also very thin Al$_2$O$_3$ films (~5 nm) without capping layer can exhibit good thermal stability. We would further like to point out that the firing recipes and peak temperatures may change from process to process which can complicate direct quantitative comparisons between various reports. In a solar cell the firing will obviously be carried out with an Al layer on top of the Al$_2$O$_3$. In this case, a protective capping layer may be beneficial to increase the chemical and mechanical stability. Apart from stability issues, another reason for using capping layers is to optimize the rear reflection in a solar cell device, as will be discussed later.

A different approach is to use Al$_2$O$_3$ itself as a capping layer. It is well known that thermally grown SiO$_3$ exhibits a poor firing stability, and requires subsequent hydrogenation to reactivate the surface passivation performance (to some extent). To test the stability of SiO$_3$ with an Al$_2$O$_3$ capping layer, an industrial firing process was carried out. Thermal ALD Al$_2$O$_3$ films with a thickness of 30 nm were applied on top of thermally grown SiO$_3$ layers. Figure 4 shows that annealing in N$_2$ atmosphere (i.e. no forming gas) was sufficient to reach

![Figure 4: Comparison between thermally-grown SiO$_3$ (thickness ~ 200 nm) and SiO$_3$/Al$_2$O$_3$ stacks. The stacks exhibited significantly-enhanced stability against firing compared to single layer SiO$_3$. As substrates, ~12 cm $n$-type $c$-Si FZ wafers were used. Annealing for the stacks was done at 400°C (N$_2$, 10 min), whereas SiO$_3$ was annealed in forming gas at 400°C for 10 min. SiO$_3$ was grown using a wet-thermal process at 900°C.](image-url)

$S_{eff}$ values $< 4$ cm/s for the stacks. A dramatically enhanced firing stability of the double layer passivation scheme is observed compared to single layer SiO$_3$, with $S_{eff,max}$ values remaining as low as 9 cm/s. This experiment was done for relatively thick layers, but the film thickness can be decreased significantly for both SiO$_3$ and Al$_2$O$_3$ without compromising the performance. Improved stability has also been observed for SiO$_3$/SiN$_x$ stacks [30]. More details on the passivation mechanisms of SiO$_3$/Al$_2$O$_3$ stacks can be found elsewhere [31].

2.5 Application of Al$_2$O$_3$ in silicon solar cells

Apart from the reduction of surface recombination, the application of Al$_2$O$_3$ films at the rear of $p$-type solar cells leads to enhanced absorption of near-band gap light in the Si bulk by improved rear reflection properties. The relatively low refractive index of Al$_2$O$_3$ (~1.65 at 600 nm) is beneficial in this respect.

The standard for state-of-the-art industrial $p$-type $c$-Si solar cells is a screen printed Al back surface field (BSF). The BSF is created during the firing step when the Al forms an alloy with Si forming a $p^+$ region. The Al BSF serves as back contact and provides (some) rear surface passivation by shielding minority carriers of the surface. However, with the current trend towards thinner wafers, an Al BSF becomes less attractive. By using an Al$_2$O$_3$ film as dielectric in combination with an Al back contact instead of a standard BSF, the solar cell efficiency can be increased significantly. The improved rear reflection is illustrated in Figure 5. The absorption characteristics for a typical solar cell with a 100 nm Al$_2$O$_3$ film at the rear is shown, as determined with simulation software [32]. As a reference, a solar cell with typical rear reflection properties for an Al BSF is included. It is observed that a 100 nm Al$_2$O$_3$ film leads to a significantly enhanced absorption in the Si bulk for near-band gap photons with wavelengths in the range of 1 – 1.2 µm compared to the Al BSF cell. This leads to an enhancement of the short-circuit current $J_{sc}$ of the cells (approximately 0.6 - 1 mA/cm$^2$, depending on the choice for the reflection $R = 80$% - 65% of the Al BSF reference). The improved reflectivity can be attributed to interference effects in
the dielectric, similar to the working principle of an antireflection coating on the front side.

The simulated optical characteristics are used as an input for the simulation tool PC1D, to estimate the effect of the rear surface recombination velocity on the solar cell performance. The input parameters are listed in Table 1. The enhanced absorption for the solar cell with dielectric rear, as displayed in Fig. 5, is demonstrated by an increase of the solar cell efficiency in Fig. 6 (i.e. a vertical shift from the dashed to the solid line) which can be attributed to improved $J_{sc}$. Furthermore, it is observed that $S_{rear}$ has a dramatic impact on the solar cell efficiency. A decrease of $S_{rear}$ from 500 cm/s to 50 cm/s, for instance, results in an increase of the open-circuit voltage $V_{oc}$ and $J_{sc}$ and consequently in an estimated efficiency improvement of approximately 1% absolute ($\tau_{bulk} = 0.5$ ms). For increasingly low $S_{rear} < 100$ cm/s, the solar cell efficiency levels off. Note here that the minimum effective $S_{rear}$ values that can be obtained with an Al BSF are considerably higher than for Al$_2$O$_3$ films.

For the latter, however, the effective $S_{rear}$ is also determined by recombination under the metal (point) contacts. Therefore, the $S_{rear}$ values in a solar cell will be intrinsically somewhat higher compared to the $S_{eff}$ values obtained for lifetime samples. For increasingly good surface passivation, recombination losses associated with the point contacts will become of increasing importance. It is also illustrated in Figure 6 that, apart from surface recombination, the bulk lifetime of the minority carriers in the Si plays an important role in the overall efficiency.

Table 1: Input parameters corresponding to the results in Fig. 6 as used in the PC1D simulation tool.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$n^+$ emitter doping</td>
<td>60 $\Omega$ / sq</td>
</tr>
<tr>
<td>$S_{rear}$</td>
<td>10$^3$ cm/s</td>
</tr>
<tr>
<td>Wafer thickness</td>
<td>200 $\mu$m</td>
</tr>
<tr>
<td>Wafer resistivity</td>
<td>1 $\Omega$ cm $p$-type</td>
</tr>
<tr>
<td>Si bulk lifetime</td>
<td>50 or 500 $\mu$s</td>
</tr>
<tr>
<td>$S_{rear}$</td>
<td>0 – 10$^5$ cm/s</td>
</tr>
</tbody>
</table>

Figure 5: Simulated absorption in the Si bulk as a function of the wavelength for a $n^+/p$-type silicon solar cell (thickness 200 µm), with on the rear side a 100 nm Al$_2$O$_3$ film covered by Al (with $n$, $k$ and layer thickness as input parameters, i.e. no assumption for the reflection properties was required). As a reference, a solar cell with reflection properties for an Al BSF (reflection $R \sim 65\%$) is shown. The cells included a textured front surface with a-SiN$_x$:H antireflection coating.

Figure 6: Simulated efficiency as a function of the surface recombination velocity at the rear, $S_{rear}$, of a $p$-type silicon solar cell with 100 nm Al$_2$O$_3$ / Al rear or an Al BSF. A Si bulk lifetime of 500 and 50 $\mu$s was used. Simulations were performed with PC1D using the absorption characteristics as displayed in Fig. 5, and the parameters listed in Table 1. The simulations only serve to show general trends.

The application of Al$_2$O$_3$ as a rear surface passivation scheme in $p$-type $c$-Si solar cells has been demonstrated by enhanced efficiencies for ($p$-passivated emitter and rear cell) PERC solar cells. Schmidt et al. have demonstrated that the performance of Al$_2$O$_3$ can be on par or superior to annealed SiO$_2$. An effective surface recombination velocity of ~70 cm/s was deduced for Al$_2$O$_3$ with a PECVD SiO$_2$ capping layer [7]. More recently, excellent passivation and rear-reflection properties have been reported with efficiencies of up to 21.5% [33]. Also for solar cells using screen-printed metallization and an Al$_2$O$_3$/a-SiN$_x$:H rear, enhanced efficiencies were reported [34]. The combination of increased surface passivation performance and enhanced rear reflection led to an increase of $J_{sc}$ by 1.5 mA/cm$^2$ compared to reference cells with an Al BSF: Apart from the application on the rear of a solar cell, Al$_2$O$_3$ deposited on a boron-doped emitter on the front of a $n$-type solar cell has resulted in significantly-enhanced efficiencies as high as 23.4% [6,35]. Progress towards an industrial feasible process for Al$_2$O$_3$ passivated $p$-$n$ cells has also been reported [36]. For such cells, the stability of Al$_2$O$_3$/a-SiN$_x$:H stacks is essential.

The abovementioned solar cell results were obtained using lab-scale ALD tools for the deposition of Al$_2$O$_3$. In the next section aspects related to the industrial scale up of ALD processes will be discussed.

2.6 Industrial feasibility of ALD Al$_2$O$_3$ for solar cells

The question arises whether the scale up of ALD processes from a single-wafer lab-scale reactor to high-throughput systems compromises the Al$_2$O$_3$ material and surface passivation quality. The traditionally low deposition rate of ALD has been regarded as the main obstacle for the use of ALD in photovoltaics where high throughput manufacturing is essential. It should be stressed however that in contrast to the growth-per-cycle, the duration of the cycle and therewith the deposition rate, can depend significantly on the reactor configuration and the type of ALD process employed. For our lab scale reactors, the deposition rate was typically ~1-2 nm / min
earlier reports [8-11,38]. It was found that the loss of hydrogen from film and interface plays an important role for cycle times of 4-7 s. The current limitations in terms of growth rate and throughput for lab scale ALD reactors are not fundamental. There are essentially two ways to make ALD compatible with high-throughput processing: 1) the use of batch processes and 2) a drastic decrease of the cycle time and associated increase of deposition rate.

Here we show new results for both approaches. Al₂O₃ films were deposited in an ASM ALD batch reactor using O₃ as the oxidant and in an inline ALD reactor from Levitech, the so-called Levitrack. The Levitrack is an inline ALD reactor, where transport is controlled by an atmospheric gas bearing on which the wafer floats. Another innovative concept of this reactor is related to the separation of the Al(CH₃)₃ and H₂O precursor doses. Normally the exposure to the different precursors is separated in time, i.e. each precursor exposure is followed by a purge sequence with an inert gas, e.g. N₂, before the next precursor is dosed. Such a purge sequence significantly adds to the total cycle time. In the Levitrack the precursor and purge pulses are separated spatially. While the wafer moves through the reactor it is sequentially exposed to Al(CH₃)₃, N₂, H₂O and again N₂. In this concept, the cycle time is ultimately dictated by the speed of the precursor reactions at the growth surface. Other benefits are that the Levitrack does not require vacuum pumps as it is operated under atmospheric pressure conditions, that there are no moving equipment parts, and that only the wafer is coated (either single-side of double-side depending on the reactor design) and not the reactor walls. More details on the system can be found elsewhere [37–39].

To evaluate the surface passivation properties, Al₂O₃ films were deposited in the Levitrack on ~2 Ω cm p-type c-Si wafers. Prior to deposition the wafers only received a short treatment in diluted HF to remove the native oxide. In the as-deposited state, the films afforded some surface passivation with Sₚ eff < 50 cm/s for a film thickness of ~15 nm, in agreement with results for thermal ALD in a lab scale reactor [14,17]. After annealing at 400 °C (10 min, N₂) the effective lifetime increased significantly to τ eff = 2.5 ms, resulting in very low S eff < 6 cm/s. Furthermore, it was verified that also shorter annealing times of only 1 minute were sufficient to activate the surface passivation to the full extent. Reference samples deposited with plasma ALD Al₂O₃ in a single-wafer reactor showed similar low S eff values. The impact of the Al₂O₃ film thickness on the surface passivation performance is displayed in Fig. 6. For annealed films, S eff decreases with increasing film thickness and saturates for a thickness > ~10 nm. This is in good agreement with earlier results for thermal ALD Al₂O₃ [17], and can be attributed to a decrease of the chemical passivation [28]. Interestingly, after a subsequent firing process in an industrial belt line furnace (T > 850°C), the thickness dependence disappears. Ultrathin films of ~ 5 nm yield relatively low S eff values < 25 cm/s after firing. The relative decrease in S eff during the firing of thicker films is in agreement with earlier reports [8-11,38]. It was found that the loss of hydrogen from film and interface plays an important role in the stability of the Al₂O₃ passivation [9,31]. The S eff values obtained after firing are sufficient to reach high solar cell efficiencies (as illustrated by Fig. 6) and the Al₂O₃ can therefore be considered sufficiently firing stable. Note that these results were obtained without the use of an a-SiNₓ:H capping layer. However, to benefit from optimal (anti) reflection at the front or at the rear of the solar cell thicker films or film stacks may be required. Recently, ultra-fast ALD has also been reported by Poedt et al. [40]. A high level of surface passivation was achieved in a proof-of-principle reactor with deposition rates of ~1.2 nm/s. Instead of increasing the deposition rate, a high throughput can also be achieved by using batch processes. Figure 8 shows the injection-level-dependent lifetime for an Al₂O₃ film deposited in an ASM batch ALD reactor. For this process, O₃ was used as the oxidant and the lifetime wafers were deposited at both sides simultaneously. In the as-deposited state, a low level of surface passivation is obtained very similar to results for plasma ALD. The surface passivation is activated by annealing, resulting in very low S eff values < 6 cm/s [27]. The high level of passivation can be explained by the high fixed negative charge density of 3.4x10¹³ cm⁻² and the low interface defect density Dox of ~1x10¹¹ eV⁻¹ cm⁻² after annealing [27].
3 CONCLUSIONS

We have demonstrated that a high level of surface passivation can be obtained by Al₂O₃ films independent of the oxidant used during ALD. This holds for lab-scale processes but also appears to be the case for industrial-scale reactors. The outstanding surface passivation of Al₂O₃ is governed by the low interface defect density and the high fixed negative charge density obtained after annealing. It was also shown that Al₂O₃ capping films on thermally grown SiO₂ led to a dramatic improvement of the firing stability of SiO₂. This concept has recently been exploited in a subsequent study, reporting on an industrially-feasible passivation stack. [41]

The surprisingly rapid developments which increase the compatibility of ALD of Al₂O₃, with high volume manufacturing have shifted the paradigm of ALD in the field of photovoltaics considerably. At present, ALD may already be a realistic alternative for PECVD processes for the deposition of ultrathin Al₂O₃ films in a cost-effective way. However, it can be concluded with confidence, that irrespective of the deposition method, Al₂O₃ films will significantly contribute to enhanced efficiencies of industrial-type solar cells in the foreseeable future.

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