Status and prospects of Al$_2$O$_3$-based surface passivation schemes for silicon solar cells

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The reduction in electronic recombination losses by the passivation of silicon surfaces is a critical enabler for high-efficiency solar cells. In 2006, aluminum oxide (Al$_2$O$_3$) nanolayers synthesized by atomic layer deposition (ALD) emerged as a novel solution for the passivation of $p$- and $n$-type crystalline Si (c-Si) surfaces. Today, high efficiencies have been realized by the implementation of ultrathin Al$_2$O$_3$ films in laboratory-type and industrial solar cells. This article reviews and summarizes recent work concerning Al$_2$O$_3$ thin films in the context of Si photovoltaics. Topics range from fundamental aspects related to material, interface, and passivation properties to synthesis methods and the implementation of the films in solar cells. Al$_2$O$_3$ uniquely features a combination of field-effect passivation by negative fixed charges, a low interface defect density, an adequate stability during processing, and the ability to use ultrathin films down to a few nanometers in thickness. Although various methods can be used to synthesize Al$_2$O$_3$ films, this review focuses on ALD—a new technology in the field of c-Si photovoltaics. The authors discuss how the unique features of ALD can be exploited for interface engineering and tailoring the properties of nanolayer surface passivation schemes while also addressing its compatibility with high-throughput manufacturing. The recent progress achieved in the field of surface passivation allows for higher efficiencies of industrial solar cells, which is critical for realizing lower-cost solar electricity in the near future. © 2012 American Vacuum Society. [http://dx.doi.org/10.1116/1.4728205]

I. INTRODUCTION

Over 85% of the solar cells currently produced are based on crystalline silicon wafers. The lion’s share of these industrially manufactured cells have energy conversion efficiencies of typically $\eta = 16\%–18\%$, while the record of $\eta = 25.0\%$ for laboratory-type Si solar cells is already fairly close to the theoretical maximum of $\eta = \eta_{\text{therm}} - \eta_{\text{sh}} = 29.8\%$. The efficiency of solar cells is significantly affected by electronic recombination losses at the wafer surfaces—primarily through a suboptimal open-circuit voltage. A reduction in surface recombination is called surface passivation. At present, only a fraction of industrial solar cells has effective passivation schemes implemented, which explains a significant part of the efficiency gap between industrial cells and high-efficiency laboratory cells.

Over the years, various materials and material stacks have been investigated for surface passivation purposes of the cell’s front and rear side. The suitability of a passivation scheme depends on doping type and Si resistivity and on aspects such as the thermal-, UV-, and long-term stability, the optical properties (i.e., parasitic absorption, refractive index), and the processing requirements (e.g., surface cleaning, available synthesis methods). Silicon nitride ($a$-Si$_3$N$_4$:H) is an important material in Si photovoltaics as it is used in virtually all (laboratory and industrial) solar cells as antireflective coating. $a$-Si$_3$N$_4$:H also provides (some) surface passivation and passivation of bulk defects for multicrystalline Si. Traditionally, thermally grown SiO$_2$ has been used as effective passivation scheme in high-efficiency laboratory cells, for instance in the record passivated emitter rear locally diffused (PERL) cell. Another widely investigated material is amorphous Si ($a$-Si:H). The combination of intrinsic and doped $a$-Si:H nanolayers (<10 nm) has been successfully applied in (commercial) heterojunction solar cells.

Aluminum oxide (Al$_2$O$_3$) has recently emerged as an alternative passivation material. Although not outstanding at that time, the passivation properties of Al$_2$O$_3$ were already reported in 1989 by Hezel and Jaeger. Nonetheless, their publication was written for posterity. Al$_2$O$_3$ technology gained momentum only after its reintroduction—this time synthesized by atomic layer deposition (ALD). The level of passivation that was demonstrated by Hoex et al. in 2006 for Al$_2$O$_3$ on lowly doped Si and $p^+$ emitters was at least as good as obtained by thermally grown SiO$_2$. Compared to other investigated materials, a distinguishing property of Al$_2$O$_3$ appeared to be the field-effect passivation induced by negative fixed charges.

The popularity of Al$_2$O$_3$ can be explained by two important trends. First, the photovoltaics (PV) industry has...
recently been looking to improve the rear side of conventional screen-printed p-type Si solar cells by replacing the Al-backsurface field (Al-BSF) by a dielectrically passivated rear. The latter leads to lower surface recombination losses, better internal reflection, and reduced wafer bow for thin wafers. The adoption of a passivated rear side is inevitable concerning the demand for higher efficiencies and the use of thinner Si wafers. While the availability of (laser) processes to produce local rear contacts was not a (prominent) bottleneck anymore, the availability of suitable passivation schemes was. Due to inversion layer shunting, a-SiN_x:H was not a suitable candidate for the p-type Si rear. Due to reasons of costs, complexity, and a possible adverse impact of high temperatures on the bulk quality, thermal oxidation was also not a first choice. Although plasma deposited SiO_x/SiN_x stacks were considered as alternatives, the focus shifted to Al2O3 and Al2O3/SiN_x stacks as a solution for the p-type Si rear side. Second, for n-type Si solar cells a suitable passivation solution of the p⁺ emitter was required. The negative charges of Al2O3 are an ideal match for the passivation of such emitters. To date, the application of Al2O3-based surface passivation schemes in industrial solar cells. Finally, in Sec. VII, recent progress on the high-efficiency solar cells featuring Al2O3 films is reviewed.

II. SURFACE PASSIVATION: BASICS AND APPLICATIONS

A. Surface passivation mechanisms

It is insightful to discuss the rate of surface recombination, \( U_s \) (expressed in cm\(^{-2}\) s\(^{-1}\)), by its description in the Shockley–Read–Hall (SRH) formalism.\(^{22,23}\) \( U_s \) can be expressed as a function of the interface defect density (\( N_{it} \), expressed in cm\(^{-2}\)), the hole and electron capture cross sections (\( \sigma_{p_{it}} \), \( \sigma_{n_{it}} \)), and the hole and electron densities at the surface (\( p_s \) and \( n_s \), respectively).\(^{24–27}\)

\[
U_s = \frac{(n_p s - n^2)}{\sigma_p} + \frac{(n_i + p_i)}{\sigma_n} = \frac{n_p s - n^2}{S_p} + \frac{n_i + p_i}{S_n} \approx \frac{n_p s}{S_p} + \frac{p_i}{S_n}
\]  

(1a)

The parameter \( \nu_{it} \) represents the thermal velocity of the electrons, \( n_1 \) and \( p_1 \) statistical factors, \( n_i \) the intrinsic carrier concentration, and \( S_{n_{it}} = \sigma_{n_{it}}/\nu_{it} N_{it} \). For sake of the discussion here, the energy dependence of the parameters (\( \sigma_{p_{it}}, n_1, p_1 \), and \( N_{it} \)) is neglected by assuming a single defect at midgap. In the latter case, and for relevant illumination and doping levels, \( n_1, p_1 \) and \( n_i \ll n_s \) and \( p_s \), and can therefore be neglected in Eq. (1a). In reality, the energy levels associated with surface defects (e.g., dangling bonds) are distributed throughout the bandgap due to slight variations in structure and bond angle. Therefore, formally, \( U_s \) should be expressed by the extended SRH formalism with an integral over the bandgap energies while replacing \( N_{it} \) by \( D_{it} \) (in units of cm\(^{-2}\)).\(^{24,26}\) As follows from the simple expression in Eq. (1a), the driving force in surface recombination processes is the term \( (n_p s - n^2) \), which describes the deviation of the system from thermal equilibrium under illumination.

Equation (1a) shows that \( U_s \) can be decreased by a reduction in \( N_{it} \) (or \( D_{it} \)), which is referred to as chemical passivation. In a recombination event both electrons and holes are involved. It is notable that the highest recombination rate is achieved when \( p_s n_i \approx \sigma_{n_{it}}/\sigma_{p_{it}} \) with the ratio of the cross sections being dependent on the details of the passivation scheme. Consequently, another way to reduce the recombination is by a significant reduction in the density of one type of charge carrier at the surface by an electric field. This is called field-effect passivation.\(^{27,28}\) We note that, apart from the SRH model, also the amphoteric nature of dangling bonds can be used to describe chemical and field-effect passivation, as reported by Olibet et al.\(^{29}\)

Figure 1 shows the influence of a negative fixed interface charge, \( Q_f \), of \( 2 \times 10^{12} \) cm\(^{-2}\) (in units of the elementary charge) on the simulated electron and hole density near the surface for p-type and n-type Si. The surface charge gives rise to band bending [Fig. 1(c)]. For p-type Si, the increased majority carrier density leads to accumulation conditions, whereas the n-type Si surface is inverted. In both cases, a decrease in recombination can be expected as \( n_i \) is strongly reduced. However, for the inversion conditions, the electron and hole density become equal a distance away from the
interface. This phenomenon can be expected to enhance recombination in the subsurface when bulk defects are present.

A measure that reflects the level of surface passivation is the surface recombination velocity $S$:

$$S \equiv \frac{U_s}{\Delta n},$$

with $\Delta n$ the injection level. It is possible to deduce an effective surface recombination velocity, $S_{\text{eff}}$, from the effective lifetime of the minority carriers in the Si substrate, $\tau_{\text{eff}}$. The effective lifetime is often measured by the photoconductance decay technique and is controlled by bulk- and surface recombination processes.\textsuperscript{30–33}

$$\frac{1}{\tau_{\text{eff}}} = \left( \frac{1}{\tau_{\text{SRH}}} + \frac{1}{\tau_{\text{Auger}}} + \frac{1}{\tau_{\text{rad}}} \right)_{\text{bulk}} + \frac{1}{\tau_{\text{surf}}}. \quad (2a)$$

Equation (2a) illustrates that both intrinsic (Auger and radiative recombination) and extrinsic recombination processes determine bulk recombination. Extrinsic recombination via bulk defects is also known as SRH recombination. Impurities, such as Fe,\textsuperscript{34} lattice faults, and dangling bonds at grain boundaries (multicrystalline Si) can all represent bulk defect states. In addition, boron–oxygen complexes, formed during growth of Si, Auger recombination and, to a lesser extent, radiative recombination are generally more important processes than SRH recombination for high quality float-zone (FZ) Si, and for good quality float-zone (FZ) Si, Auger recombination and, to a lesser extent, radiative recombination are generally more important processes than SRH recombination. On the other hand, for high quality float-zone (FZ) Si, Auger recombination and, to a lesser extent, radiative recombination are generally more important processes than SRH recombination for high quality float-zone (FZ) Si, Auger recombination and, to a lesser extent, radiative recombination are generally more important processes than SRH recombination. On the other hand, for high quality float-zone (FZ) Si, Auger recombination and, to a lesser extent, radiative recombination are generally more important processes than SRH recombination. On the other hand, for high quality float-zone (FZ) Si, Auger recombination and, to a lesser extent, radiative recombination are generally more important processes than SRH recombination. On the other hand, for high quality float-zone (FZ) Si, Auger recombination and, to a lesser extent, radiative recombination are generally more important processes than SRH recombination. On the other hand, for high quality float-zone (FZ) Si, Auger recombination and, to a lesser extent, radiative recombination are generally more important processes than SRH recombination. On the other hand, for high quality float-zone (FZ) Si, Auger recombination and, to a lesser extent, radiative recombination are generally more important processes than SRH recombination.

For a symmetrically passivated wafer with sufficiently low $S_{\text{eff}}$ values, Eq. (2a) can be expressed as

$$\frac{1}{\tau_{\text{eff}}} = \frac{1}{\tau_{\text{bulk}}} + \frac{2S_{\text{eff}}}{W}, \quad (2b)$$

with $W$ the wafer thickness. The relative error in $S_{\text{eff}}$ is typically below 4% for $S$ values $<$250 cm/s.\textsuperscript{24,30} For poorly passivated surfaces, a term accounting for the diffusion of minority carriers toward the surface is required to improve the accuracy as described by

$$\frac{1}{\tau_{\text{eff}}} = \frac{1}{\tau_{\text{bulk}}} + \frac{1}{\tau_{\text{surf}}} + \frac{1}{\tau_{\text{diff}}}. \quad (2c)$$

S_{\text{eff,max}} is a good approximation for the actual value of $S_{\text{eff}}$ (for injection levels for which Auger recombination is not dominant) when the passivation properties are evaluated on Si wafers with high bulk lifetimes ($>1$ ms). On the other hand, for an excellent surface passivation quality, with the surface recombination approaching 0 cm/s, the effective lifetime becomes dominated by intrinsic recombination processes which will limit the minimal value of $S_{\text{eff}}$ that can be experimentally determined.

The influence of the chemical and field-effect passivation on the surface recombination velocity is illustrated by the simulations in Fig. 2. The trend of $S_{\text{eff}}$ was derived by using Eq. (1a) in conjunction with a Poisson solver (PC1D) to obtain values for $n_s$ and $p_s$ under illumination. $S_{\text{eff}}$ is observed to decrease linearly with a reduction in $N_d$, which directly follows from Eq. (1a) and (1b). In addition, it is observed that the reduction in $S_{\text{eff}}$ by field-effect passivation is especially prominent for $Q_f$ values $>10^{15}$ cm$^{-2}$. The simulations show that for moderately doped Si a twofold increase in $Q_f$ produces a fourfold decrease in $S_{\text{eff}}$ (i.e., $S_{\text{eff}} \sim 1/Q_f^2$, for sufficiently high $Q_f$ values).\textsuperscript{17} For significantly higher doping concentrations at the surface (e.g., emitters), a given fixed
charge density has a relatively smaller influence on band bending and the charge carrier densities (not shown). Consequently, the influence of the (additional) field-effect passivation induced by the passivation scheme becomes smaller for higher doping densities.

Figure 2 also shows that the trend between $S_{\text{eff}}$ and $Q_f$ changes significantly when the value of $\sigma_p / \sigma_n$ is increased from 1 to 10. In the latter case, a maximum appears in $S_{\text{eff}}$ at $Q_f = 2 \times 10^{11}$ cm$^{-2}$, which coincides with the condition for maximum recombination $(p_i/n_s = \sigma_n / \sigma_p = 10^5)$. In addition, higher $Q_f$ values $>4 \times 10^{11}$ cm$^{-2}$ appear to be required to activate the field-effect passivation. It is notable that, for the case of Al$_2$O$_3$, a value of $\sigma_n / \sigma_p >> 1$ is probably more realistic than $\sigma_n / \sigma_p = 1$. As will be discussed later, the Si/Al$_2$O$_3$ interface is essentially "Si/SiO$_2"$-like. The value of $\sigma_n / \sigma_p = 10^5$ reported for thermally grown SiO$_2$ interfaces may therefore be a better assumption for the Si/Al$_2$O$_3$ interface.

The experimentally accessible parameter, $S_{\text{eff,max}}$, is also given in Fig. 2. $S_{\text{eff,max}}$ was derived by combining Eqs. (2b) and (2d) and substituting a bulk lifetime of 10 ms. Figure 2 shows that for a very high level of surface passivation, $S_{\text{eff,max}}$ becomes limited by the bulk lifetime. In that case, $S_{\text{eff,max}}$ does not reflect the actual (extremely low) $S_{\text{eff}}$ values anymore. This implies, for instance, that significant variations of $Q_f > 1 \times 10^{12}$ cm$^{-2}$ are not expected to lead to drastic changes in the measured $S_{\text{eff,max}}$ values.

B. Surface passivation materials

The most important surface passivation materials used in photovoltaics include SiO$_2$, a-SiN$_x$:H, and a-Si:H. Considering the recent progress, Al$_2$O$_3$ can now be added to this list.

1. SiO$_2$

The high quality interface between thermally grown SiO$_2$ and Si contributed significantly to the dominance of Si in the microelectronics industry and is also responsible for high solar cell efficiencies. Thermal SiO$_2$ leads to very low surface recombination velocities ($S_{\text{eff}} < 10$ cm/s) after forming gas annealing or annealing (using a sacrificial Al layer). The hydrogen that is introduced during the annealing process passivates the electronically active defects such as the prominent $P_{\text{SB}}$-type defect which constitutes an Si dangling bond ($\equiv \text{Si}^-$). This leads to typical defect densities of the order of $10^{10}$ cm$^{-2}$ eV$^{-1}$. Field-effect passivation is not prominent with comparatively low values of $Q_f$ in the range of $10^{10}$–$10^{11}$ cm$^{-2}$. Hence, an important benefit of thermal SiO$_2$ is the high level of chemical passivation that can be achieved for both n- and p-type Si surfaces over a wide range of relevant doping levels. Moreover, it can be used to engineer diffusion profiles. Thermal oxidation can be carried out in H$_2$O-vapor ($T \sim 850$–900°C) or O$_2$ atmosphere ($T \sim 950$–1000°C). The growth rate for the former “wet” thermal process is significantly higher than for the “dry” process. Various other methods have been explored for developing SiO$_2$ surface passivation films at low temperatures. Low-temperature processing can be technologically interesting as it opens up the possibility for using materials that are less thermally stable and avoids the risk of bulk lifetime degradation. The most widely investigated low-temperature method is plasma-enhanced chemical vapor deposition (PECVD), which allows for high-throughput processing. Another option for the synthesis of SiO$_2$ is a chemical oxidation of the Si surface, for example using HNO$_3$. A drawback of this method is that it can only produce SiO$_2$ with a thickness of a few nanometers. In general, the level of passivation induced by single layer SiO$_2$ synthesized at low temperatures is seriously lower than obtained by thermal oxidation processes. However, these properties can be improved drastically by the application of a-SiN$_x$:H or Al$_2$O$_3$ capping layers (see Sec. VI B).

2. a-SiN$_x$:H

The working horse thin film dielectric in c-Si photovoltaics is a-SiN$_x$:H (for brevity, SiN$_x$) synthesized by PECVD. Owing to the fact that the optical properties of the material can be varied in a wide range, SiN$_x$ is the standard for antireflection coatings in solar cells. Figure 3 shows the material composition in terms of the atomic H, Si, and N density as a function of the refractive index. Films with comparatively high nitrogen content exhibit refractive indices of approximately 2, which results in optimal antireflection properties when applied on the front side of a solar cell. The films also contain a relatively large amount of hydrogen of ~10–15 at. %. The hydrogen released during firing plays an important role in the bulk passivation of multicrystalline Si. Depending on film composition, the films provide a reasonably high level of passivation. Optimal surface passivation is generally achieved for relatively Si-rich films. However, the nitrogen-rich films exhibit a superior thermal
and chemical stability and can be useful as a capping layer on Al₂O₃. The passivation mechanisms of the a-SiNx:H films strongly depend on the nitrogen content. When the nitrogen content is relatively low, the films exhibit amorphous Si-like properties. In this case, the high level of passivation is mainly governed by chemical passivation. On the other hand, for high [N], the films induce a significant amount of field-effect passivation with fixed charge densities of the order of 10¹² cm⁻², as shown in the following. This is related to the so-called K-center (an Si atom backbonded with three N atoms) that can be charged positively [see Fig. 3 (inset)]. A significant positive charge density leads to inversion conditions for p-type Si surfaces. Strong inversion can give rise to transport properties parallel to the interface. a-SiNₓ applied on the rear side of a p-type Si solar cell can therefore compromise solar cell performance by the so-called parasitic or inversion layer shunting effect. SiO₂/SiNₓ stacks are expected to reduce or nullify this detrimental effect.

C. Surface passivation in high-efficiency solar cells

From the previous discussion, the question arises how the solar cell efficiency is affected by the implementation of a surface passivation scheme. Here, we consider a conventional p-type Si solar cell as an example to illustrate the effect of rear surface passivation. By using an Al₂O₃ film as dielectric in combination with local contacts [PERC-type cell (passivated emitter and rear cell)], the solar cell efficiency can be significantly higher than obtained with a full Al-BSF. This is related to (1) lower S_eff values and (2) the enhanced absorption in photon energy range of 1–1.2 μm by an enhanced reflection from the solar cell’s rear side. For the latter, a thickness of the passivation scheme of approximately 100–150 nm is beneficial.

The optical properties for a PERC cell with Al₂O₃ on the rear surface were simulated and used as an input for the PC1D program to simulate solar cell performance. The enhanced photon absorption for the PERC solar cell relative...
to the Al-BSF cell is demonstrated by an increase in the energy conversion efficiency in Fig. 5 (i.e., a vertical shift from the dashed to the solid line), which can be attributed to improved short-circuit current \( J_{sc} \). The relative increase in \( J_{sc} \) is approximately 0.6–1.1 mA/cm\(^2\), depending on the level of reflection \( R = 80\%–65\% \) of the Al-BSF reference. On the other hand, the open-circuit voltage \( V_{oc} \) is mainly sensitive to (surface) recombination processes. A decrease of \( S_{\text{rear}} \) from 500 to 50 cm/s, for instance, gives rise to an increase in both \( V_{oc} \) (by \( \sim 12.5 \text{ mV} \)) and \( J_{sc} \) and results in an estimated efficiency improvement of approximately 1% absolute (Fig. 5). Due to synergistic effects, the influence of \( S_{\text{rear}} \) can be even more pronounced for cells with an improved front side. For increasingly low \( S_{\text{eff}} \) < 100 cm/s, the solar cell efficiency levels off. Note here that the minimum effective \( S_{\text{eff}} \) values associated with a typical Al-BSF are considerably higher than those corresponding to Al\(_2\)O\(_3\) films. (Although also values as low as \( S_{\text{eff}} \sim 300 \text{ cm/s} \) have been reached for an optimized Al-BSF.) For PERC cells with Al\(_2\)O\(_3\), the effective \( S_{\text{eff}} \) is not only determined by the Al\(_2\)O\(_3\) covered surface, which is typically \( \sim 95\% \) of the area of the rear. It is also determined by recombination under the metal point or line contacts, i.e., local Al-BSF. In other words, the quality of the rear side also depends on the quality of the local Al-BSF. The \( S_{\text{eff}} \) values in actual solar cells will therefore be intrinsically somewhat higher compared to the \( S_{\text{eff}} \) values obtained for lifetime samples. For increasingly good surface passivation, recombination losses associated with the local contacts will become of increasing importance. Therefore, innovative ways to mitigate such losses, e.g., by developing “passivated contacts” (as employed in heterojunction solar cells) will become an increasingly relevant research topic. It is also illustrated in Fig. 5 that, apart from surface recombination, the bulk lifetime of the minority carriers in the Si plays an important role in the overall efficiency. A discussion of recent experimental results for solar cells with Al\(_2\)O\(_3\) passivation schemes implemented is provided in Sec. VII.

III. Al\(_2\)O\(_3\) PROPERTIES AND SYNTHESIS TECHNIQUES

A. Synthesis methods

1. Atomic layer deposition

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 gas-phase precursors. Each surface chemical reaction occurs between a gas-phase reactant and a surface functional group. These reactions automatically stop when all available surface groups have reacted, which makes the reactions self-limiting. A standard ALD process uses two precursors (A and B), and growth proceeds by alternating the precursors in an ABAB... fashion. After reaction of precursor A with the surface groups, the remaining precursor and the volatile reaction products are pumped away, and precursor B is introduced. This leads to the deposition of a second element through reaction with the new surface functional group. Also, the initial surface groups are restored. This reaction sequence forms one ALD cycle and results in one or less than one atomic layer of film growth, typically 0.5–1.5 Å/cycle. The ALD cycle can be repeated until the desired film thickness is reached. Unlike chemical vapor deposition, the deposition rate of ALD is not proportional to the “precursor” flux on the surface. Therefore, the same amount of material is deposited everywhere on the surface, even on nonplanar surfaces, provided that the precursor exposure times are sufficient.

Al\(_2\)O\(_3\) deposited by ALD most commonly uses trimethylaluminum (Al(CH\(_3\))\(_3\) or TMA) as the aluminum source. Water, ozone, or oxygen radicals from a plasma can serve as the oxidants. Processes with water (illustrated in Fig. 6) and ozone are referred to as thermal ALD, while the process employing a plasma is referred to as plasma (-assisted) ALD. Each ALD cycle consists of Al(CH\(_3\))\(_3\) dosing followed by a purge, then oxidant exposure followed by a purge. The choice of oxidant depends on the application. In general, oxygen radicals generated by a plasma source are more reactive than H\(_2\)O. The increased reactivity of plasma ALD can give improved film quality with lower impurity levels, in particular for low substrate temperatures. However, plasma ALD equipment is more complex as a plasma source needs to be incorporated. In batch ALD processes, O\(_3\) is often used as it exhibits good reactivity and is relatively easy to purge.

ALD is suitable for depositing a whole range of different materials, including (noble) metals, oxides, and nitrides. Also mixed and doped oxides can be readily synthesized by ALD. Various ALD processes and materials have been investigated for virtually all types of solar cells. This includes CIGS, CdTe, organic-, and dye-sensitized cells. For instance, ALD ZnSe and ZnO films have been tested as buffer layers for CIGS thin film solar cells. Another example is Al-doped ZnO as a transparent conductive oxide. Moreover, ALD Al\(_2\)O\(_3\) has also
3. Other synthesis methods

In the first report on Al$_2$O$_3$ for surface passivation, atmospheric pressure chemical vapor deposition (APCVD) of aluminum-triisopropoxide was used. Very recently, good results were reported using a large-scale deposition tool based on the APCVD method. Physical vapor deposition, i.e., sputtering, has also been applied for the synthesis of Al$_2$O$_3$ passivation layers. RF magnetron sputtering of an aluminum target in an O$_2$/Ar mixture led to deposition rates of ~4 nm/min in a laboratory system. Although only preliminary data are available, sputtering appears to produce Al$_2$O$_3$ with a lower level of passivation compared to ALD or PECVD.

B. Material and interface properties of Al$_2$O$_3$ on Si

The material properties of amorphous Al$_2$O$_3$ vary with deposition method. A prominent factor influencing the Al$_2$O$_3$ composition is the incorporation of other elements than O and Al, such as carbon and most notably hydrogen. For ALD processes, the Al$_2$O$_3$ properties and the hydrogen content are primarily controlled by the substrate temperature during deposition $T_{\text{dep}}$. However, the hydrogen content in the films deposited at a temperature of $\sim$200°C was higher than for ALD (~2.7 at. %) at $T_{\text{dep}} = 200$ °C. We verified with Rutherford backscattering spectroscopy (RBS) and x-ray photoelectron spectroscopy (XPS) that the carbon content in the films deposited at a temperature of ~200°C was negligible with $|C| < 1$ at. %.

Table I lists the important material properties of ALD Al$_2$O$_3$. For the relevant range of $T_{\text{dep}} = 150$–250°C, both thermal and plasma ALD Al$_2$O$_3$ exhibited a comparable mass density and refractive index. However, the hydrogen content for thermal ALD Al$_2$O$_3$ (~3.6 at. %) was higher than for plasma ALD (~2.7 at. %) at $T_{\text{dep}} = 200$ °C. In addition, the presence of carbonates was observed for Al$_2$O$_3$ films deposited by plasma ALD. Both the hydrogen and carbon content were observed to decrease with increasing deposition temperature.

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In Fig. 7 data are shown for the refractive index, $n$, and extinction coefficient, $k$, as determined for plasma ALD Al$_2$O$_3$ films from spectroscopic ellipsometry measurements. Annealing at 400°C did not change the optical properties.

2. PECVD

Plasma-enhanced chemical vapor deposition is not a traditional synthesis method for Al$_2$O$_3$, and the amount of technologically relevant literature available on this topic is limited. Nevertheless, before Al$_2$O$_3$ became of interest for solar cell applications, some PECVD processes were reported using Al precursors such as Al(CH$_3$)$_3$ and AlCl$_3$. They used a capacitive coupled plasma in combination with Al(CH$_3$)$_3$, H$_2$, and argon as process gasses. Deposition rates of 100 nm/min could be achieved. Roth & Rau now offers a tool that enables the deposition of Al$_2$O$_3$ films from spectroscopic ellipsometry measurements. Annealing at 400°C did not change the optical
TABLE I. Properties of Al2O3.

<table>
<thead>
<tr>
<th>Physical property</th>
<th>ALD Al2O3 (Tdep = ~200°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Phase</td>
<td>Amorphous up to ~850°C (Refs. 129 and 130)</td>
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<tr>
<td>Resistivity</td>
<td>~10^16 Ω cm (Ref. 108)</td>
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<tr>
<td>Dielectric constant</td>
<td>7–9 (Refs. 94 and 97)</td>
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<tr>
<td>Mass density</td>
<td>~3.0 g/cm³</td>
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<tr>
<td>Hydrogen content</td>
<td>~2–4 at. %</td>
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<td>Optical bandgap</td>
<td>6.4 eV</td>
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<tr>
<td>Refractive index</td>
<td>1.64 (at 2 eV)</td>
</tr>
<tr>
<td>RMS roughness</td>
<td>≤2 Å on polished Si(100)³</td>
</tr>
</tbody>
</table>

³Verified with atomic force microscopy for 15 nm films, using O2 plasma, O3 or H2O as oxidants.

The properties of the film significantly and thermal ALD with H2O gave similar results. From the dielectric function ε2, an optical bandgap of Eopt = 6.4 ± 0.1 eV was determined for both the as-deposited and annealed films. This experimentally determined value for (amorphous) Al2O3 films is lower than the value of ~8.8 eV representative for crystalline Al2O3. The Al2O3 films crystallize at temperatures above ~850°C.129,130

Given the optical bandgap, parasitic absorption in the amorphous Al2O3 films will not occur in the range relevant for photovoltaics as only light with wavelengths ≥3–3.5 eV. This is in contrast to, e.g., a-SiNx:H films, with typical Eopt = 3–3.5 eV.

Apart from the bulk properties, the properties of the interface between Al2O3 and Si are obviously also of crucial importance for surface passivation. It was found that a thin (~1–2 nm) SiOx layer is present at this interface.14,131,132

This interfacial SiOx is formed even on H-terminated Si (e.g., after HF treatment). Figure 8 shows a high-resolution transmission electron microscopy (TEM) image of the interfacial region of Al2O3 on Si(100). The presence of SiOx was corroborated by FTIR by the detection of the Si-O stretching vibration around ~1000 cm⁻¹.17,128

The growth mechanism of Al2O3 is well understood,89,93,104,133 and often used to exemplify the working principle of ALD in general. A schematic representation of a thermal and plasma ALD cycle is given in Fig. 9. In the first ALD half-cycle, the Al(CH3)3 precursor reacts through ligand exchange with the surface hydroxyl under formation of methane and O–Al bonds. This reaction is very efficient due to the formation of the strong O–Al bond.89 The reaction between Al(CH3)3 and the surface can be monofunctional, but also bifunctional in which case two methyl groups react with two (neighboring) OH groups. The latter becomes more important at low substrate temperatures because of the higher density of surface OH groups.

The surface chemistry during the first half-cycle is similar for plasma and thermal ALD, and can be described by

\[ Al–OH^+ + Al(CH_3)_3(g) \rightarrow AlO–Al(CH_3)_2^++CH_4(g). \]

During the second half-cycle step, the surface changes from methyl-terminated to hydroxyl-terminated. For thermal ALD, methane is produced during the second half-cycle,

\[ AlO–AlCH_3^++H_2O(g) \rightarrow AlOAl–OH^++CH_4(g). \]

For plasma ALD, the reactions can be summarized by96,105
Note that the formation of the H$_2$O by-product during the plasma step can give rise to a secondary reaction pathway. In addition to H$_2$O and an O$_2$ plasma, O$_3$ also can be used as coreactant. The reaction chemistry during O$_3$-based ALD appeared to be more complex than the H$_2$O and O$_2$–plasma-based process (see, for example, Refs. 103–105).

Depending on the length of each of the steps in the ALD cycle (Fig. 9), subsaturated growth, true ALD growth, or ALD growth with a parasitic CVD component takes place. The latter refers to a growth process that is not fully self-limiting. A true, saturated ALD process is obtained when an increase in the duration of the precursor and oxidant exposure times, in conjunction with sufficiently long purge steps, does not produce a higher growth per cycle (GPC). Under such circumstances, the deposition is highly uniform and conformal. Figure 10 shows that the thickness increases linearly with the number of cycles without apparent growth delay for deposition on Si(100). The associated growth rates were 1.0 Å/cycle (thermal ALD) and 1.1 Å/cycle (plasma ALD) for $T_{\text{dep}} = \sim 250^\circ$C. Note that these values are below the approximate thickness of a monolayer (~0.3 nm), which can be attributed to incomplete surface OH coverage and steric hindrance effects of the precursor molecules.

B. ALD process parameters

The influence of the relevant ALD parameters on the GPC of Al$_2$O$_3$ is shown in Fig. 11, comparing thermal ALD and plasma ALD. The TMA dosing time had virtually no effect on the growth process in our reactor configuration (Oxford Instruments OpAL). For dosing times of 10 ms and above, saturated ALD growth was observed for both methods. However, the purge time after the Al(CH$_3$)$_3$ dosing strongly influenced the growth process. Figure 11 shows that purge times $<\sim 3$ s gave rise to higher GPC values for plasma and thermal ALD. In addition, short purge times led to a decrease in refractive index ($n = \sim 1.61$ vs 1.64 for a true ALD process) and corresponding decrease in mass density of the Al$_2$O$_3$ films. A parasitic CVD growth component also produces film nonuniformity and is expected to impair the conformality of ALD. The minimum purge times required after the Al(CH$_3$)$_3$ precursor injection are closely related to the gas residence time. For short purge times, a fraction of Al(CH$_3$)$_3$ precursor remains in the reactor and can react with the oxidant introduced in the subsequent oxidation half-cycle.

Whether parasitic CVD reactions occur can be detected by optical emission spectroscopy measurements during plasma ALD. Figure 12 shows the presence of CO*, H*, and OH* emission in the plasma. When the spectrum is recorded after a sufficiently long purge time, the emission associated with C and H fragments can only originate from a monolayer of –CH$_3$ ligands at the growth interface. However, when reducing the purge time below 3.5 s, we observe an increase in the emission of CO*, H*, and OH* as shown in Fig. 12(b). This is indicative of the dissociation of residual Al(CH$_3$)$_3$ in the plasma and corresponds well with the observed higher GPC values.

Regarding the second half-cycle, a saturated ALD process was obtained already for short H$_2$O dosing times (~10–20 ms), which also led to high refractive index values of ~1.64. A slight increase of the GPC was, however, observed for longer H$_2$O dosing times. This is typically observed for thermal ALD at relatively low substrate temperatures and is referred to as “soft saturation.” The plasma time had a more pronounced effect on the growth process. Plasma times $<2$ s clearly led to subsaturated growth. Under these circumstances the total flux of oxygen radicals during the oxidation half-cycle is insufficient to remove all the precursor ligands and restore the surface with OH groups. The plasma time can therefore be associated with the rate of the surface chemical reactions. The refractive index was also observed to drop for short plasma times, which is indicative of the incorporation of impurities into the material. Moreover, it was observed that subsaturated growth led to a significant deterioration of the thickness uniformity, especially at the edges of the substrate holder. The final purge step in the ALD cycle serves to remove the traces of the oxidant and reaction products left in the reactor. Figure 11 demonstrates that significant purging after plasma exposure was not required, while after H$_2$O purging times $\geq 1$ s were important to avoid parasitic CVD reactions. This implies that the very small amount of H$_2$O produced during the O$_2$ plasma step did not lead to significant reactions with the Al(CH$_3$)$_3$ precursor introduced in the subsequent step. This may change at lower deposition temperatures, for which generally longer plasma purge times are required.

For the optimized ALD processes in the single-wafer reactor (Oxford Instruments OpAL), nonuniformities of 1.5% and 4.3% were obtained for thermal and plasma ALD for wafers 200 mm in diameter. For smaller wafer sizes, values of $<2$% have been reported for thermal and plasma ALD before. The slight nonuniformity of plasma ALD can be attributed to a radial nonuniformity of the plasma species and can be decreased when using smaller wafers.

C. Substrate temperature

The substrate temperature is the most important parameter affecting the growth rate and, as discussed in Sec. III B,
the material properties of ALD Al₂O₃ films. Figure 13 shows that the influence of \( T_{\text{dep}} \) on film growth is markedly different for plasma and thermal ALD. For plasma ALD, the GPC and the number of Al atoms deposited per cycle decreases with increasing \( T_{\text{dep}} \). This trend can be attributed to a lower OH surface coverage at higher \( T_{\text{dep}} \), due to thermally activated dehydroxylation reactions under formation of H₂O. For thermal ALD, an increase in the growth rate was observed for increasing \( T_{\text{dep}} \) up to \( T_{\text{dep}} > 250 \) °C, whereas for \( T_{\text{dep}} > 250 \) °C the trend was similar to plasma ALD. This difference between thermal and plasma ALD at low \( T_{\text{dep}} \) can be explained by a lower reactivity of H₂O at low substrate temperatures. In contrast, the reactivity of the O₂ plasma is not controlled by the temperature. From a technological point of view, it is important to note that the purge times to remove H₂O from the reactor increase drastically with decreasing 

![Figure 11](image1.png)  
**Fig. 11.** (Color online) Growth per cycle (GPC) as a function of the length of successive ALD steps for (a) thermal ALD and (b) plasma ALD. The films were deposited in an Oxford Instruments OpAL reactor \( (T_{\text{dep}} = 250 \) °C). The nonvaried parameters (purge and dose times) were sufficiently long to be compatible with saturated ALD growth and did not affect the influence of the varied parameter on the GPC.

![Figure 12](image2.png)  
**Fig. 12.** (Color online) (a) Optical emission spectroscopy spectrum recorded during plasma ALD, (b) Emission intensity of OH, H*, and CO* as a function of the preceding Al(CH₃)₃ purge length. Every data point represents a separate measurement during the initial stages of plasma operation. Note that for the purge time of 0 s, the plasma was switched on directly after the precursor dose.

![Figure 13](image3.png)  
**Fig. 13.** (Color online) Influence of the substrate temperature on the growth per cycle in terms of (a) film thickness and (b) Al atoms deposited (Refs. 98 and 99). The latter was determined by RBS measurements.
Plasma ALD (annealed) is therefore generally preferred over thermal ALD for low-temperature applications (<150 °C).

V. SURFACE PASSIVATION BY Al2O3

A. Passivation performance

Very low surface recombination velocities $S_{\text{eff}} < 5 \text{ cm/s}$ have been reported for Al2O3 on low-resistivity $p$-type and $n$-type Si (typically, 1–4 $\Omega$ cm) after annealing at moderate temperatures.\textsuperscript{14,15,40,98,135,136} In addition, for boron-doped emitters ALD Al2O3 resulted in very low emitter saturation current densities of $J_{0,e} < 10$ and 30 fA/cm$^2$ for >100 and 54 Ω/sq sheet resistances, respectively.\textsuperscript{137} The level of passivation achieved by Al2O3 for $p^+$ surfaces was higher than obtained by thermal SiO2 and $p$-Si:H and significantly higher than by SiN.\textsuperscript{16,137} This can be explained by the differences in strength and polarity of the fixed charges present in the passivation schemes. Possibly, differences in the capture cross section ratios—a relatively lower $\sigma_p/\sigma_n$ is beneficial for $p^+$ passivation—may contribute as well (see Sec. II A). For $n^-$ emitters, it is expected that the negative $Q_e$ of Al2O3 will not contribute to optimal passivation properties when compared to SiN containing positive charges. Preliminary measurements have indeed revealed significantly higher $J_{0,e}$ values for Al2O3 ($\sim 170 \text{ fA/cm}^2$) than for SiN ($\sim 62 \text{ fA/cm}^2$) on 62 Ω/sq $n^-$ emitters.\textsuperscript{140} Another report has shown that implied $V_{oc}$ values between 640 and 680 mV can be achieved for sheet resistances between 20 and $\sim 100 \Omega/sq$ using plasma ALD Al2O3.\textsuperscript{141} It was argued that the low interface defect density induced by Al2O3 is primarily responsible for the passivation of $n^-$ emitters with low sheet resistances (<$\sim 100 \Omega/sq$).

Prior to deposition of the Al2O3 films on lifetime samples, the native oxide is generally removed from the wafers by treatment in diluted HF (e.g., 1%) followed by rinsing in de-ionized-H2O and drying (e.g., in an N2 flow). The time between this cleaning step and film deposition is not a critical parameter. In addition, even surface chemical treatments (e.g., treatment in HNO3) that result in a chemical oxide on the wafer surface can be applied prior to Al2O3 deposition.\textsuperscript{14} To activate the passivation, annealing temperatures in the range of 350–450 °C were found to be optimal.\textsuperscript{135} Annealing can be simply carried out in N2 environment, as a gas mixture containing H2 (i.e., forming gas annealing) led to similar results. Annealing times between 10 and 30 min are generally applied. However, we verified that annealing times of $\sim 1–2$ min can already be sufficient to fully activate the passivation performance of the films.

Figure 14 shows the injection-level-dependent effective lifetime for Al2O3 films deposited on $p$-type and $n$-type Si, comparing plasma and thermal ALD. The films were deposited in a saturated ALD regime at $T_{\text{dep}} = 200 °C$, which falls in the range of 150–250 °C for optimal passivation.\textsuperscript{93} In the as-deposited state, thermal ALD affords a reasonable level of surface passivation with $S_{\text{eff}} < 30 \text{ cm/s (} \Delta n = 10^{15} \text{ cm}^{-3} )$ in marked contrast with plasma ALD Al2O3 ($S_{\text{eff}} \sim 10^3 \text{ cm/s}$). After annealing at $\sim 400 °C$, very high levels of surface passivation with $S_{\text{eff}} < 5 \text{ cm/s (p-type Si)}$ and $S_{\text{eff}} < 2 \text{ cm/s (n-type Si)}$ were obtained for both ALD methods. Nevertheless, the plasma ALD process led to a slightly higher level of passivation than the thermal ALD process, which can be related to small differences in the level of chemical and field-effect passivation obtained by both methods (Sec. V B).

Regarding the injection level dependence, the effective lifetime is observed to decrease at high injection levels $>10^{15} \text{ cm}^{-3}$, which mainly reflects the Auger recombination. At low injection levels, the effective lifetime remains approximately constant for $p$-type Si. This is important for solar cells, as they often operate under relatively low illumination levels (e.g., $\Delta n = 10^{12–10^{14} \text{ cm}^{-3}$). In contrast, for $n$-type $c$-Si, the effective lifetime is observed to decrease significantly below injection levels of $5 \times 10^{14} \text{ cm}^{-3}$. The decrease in lifetime has been explained by enhanced (bulk)

\begin{itemize}
  \item \[ T_{\text{dep}} \]
  \item Plasma ALD (annealed)
  \item Thermal ALD (annealed)
  \item Thermal ALD (as-deposited)
  \item Plasma ALD (as-deposited)
\end{itemize}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{fig14.png}
\caption{(Color online) Injection-level-dependent effective lifetime for plasma and thermal ALD Al2O3 before and after annealing (N2, 400 °C, 10 min) on (a) $\sim 2 \Omega$ cm $p$-type $c$-Si and (b) $\sim 3.5 \Omega$ cm $n$-type $c$-Si (Refs. 107 and 135). The wafers received a treatment in diluted HF prior to deposition. Films with a thickness of $\sim 30 \text{ nm}$ were deposited using a substrate temperature of $\sim 200 °C$.}
\end{figure}
recombination in the inversion layer induced by the negative $Q_f$. Further evidence for this hypothesis is provided by the observation that the effective lifetime under low illumination conditions could be improved by a significant reduction in $Q_f$.

The influence of the ALD process parameters (i.e., dose and purge times, see Fig. 11) on the passivation quality of as-deposited and annealed $\text{Al}_2\text{O}_3$ films was also assessed. The passivation performance appeared to be insensitive to variations in the process parameters (not shown), with the exception of the plasma time. Interestingly, a reduction in plasma time led to a significant decrease in the $S_{\text{eff}}$ values for as-deposited plasma ALD $\text{Al}_2\text{O}_3$ ($T_{\text{dep}} = 250{^\circ}\text{C}$). This can be attributed to a detrimental impact of vacuum ultraviolet (VUV) radiation from the plasma which is reduced for shorter plasma times.\textsuperscript{107} This is in sharp contrast to plasma ALD with $Q_f$ of the order of $10^{12}$ cm$^{-2}$ prior to annealing; in contrast to plasma ALD with $Q_f$ of the order of $10^{12}$ cm$^{-2}$. Also after annealing, the highest $Q_f$ values have been reported for $\text{Al}_2\text{O}_3$ synthesized by plasma ALD. Furthermore, it was verified that $Q_f$ was not critically dependent on the annealing temperature ($T = 300$–$600{^\circ}\text{C}$), see Fig. 16. While an initial increase is observed between $T = 300$ and $400{^\circ}\text{C}$, $Q_f$ appeared to be relatively independent of the annealing temperature for $T \geq 400{^\circ}\text{C}$. Similar observations were reported by Benick et al.\textsuperscript{146}

In general, the $Q_f$ values that are reported for $\text{Al}_2\text{O}_3$ in various studies fall in the range of $(2–13) \times 10^{12}$ cm$^{-2}$ after annealing at moderate temperatures.\textsuperscript{12,16,98,107,123,124,127,146,147} Note that these films all afforded low $S_{\text{eff}}$ values $<10$ cm/s.

### B. Effect of annealing on chemical and field-effect passivation

Figure 15 shows the influence of annealing on the surface passivation mechanisms of $\text{Al}_2\text{O}_3$ films synthesized by plasma ALD and thermal ALD (using $\text{H}_2\text{O}$). For thermal ALD $\text{Al}_2\text{O}_3$, the key effect of annealing is the increase of $Q_f$, whereas for plasma ALD the chemical passivation improves dramatically. The relatively low $D_n$ value of $\approx 3 \times 10^{11}$ eV$^{-1}$ cm$^{-2}$ for as-deposited thermal ALD $\text{Al}_2\text{O}_3$ is consistent with the moderate level of surface passivation obtained prior to annealing (compare Fig. 14).\textsuperscript{107} This is in sharp contrast with plasma ALD, which did not provide passivation in the as-deposited state despite the high value of $Q_f$. It has been shown that the high $D_n$ values for as-deposited plasma ALD $\text{Al}_2\text{O}_3$ are, at least partially, related to the exposure of the surface to VUV radiation that is present in the plasma.\textsuperscript{107,144} After annealing, both ALD processes resulted in low $D_n \leq 1 \times 10^{11}$ eV$^{-1}$ cm$^{-2}$.\textsuperscript{107,146,147} Also for films deposited by PECVD, similar low defect densities were reported.\textsuperscript{145}

Regarding the field-effect passivation, it is notable that the thermal ALD $\text{Al}_2\text{O}_3$ films exhibited very low $Q_f$ values of the order of $10^{11}$ cm$^{-2}$ prior to annealing; in contrast to plasma $\text{Al}_2\text{O}_3$ synthesized by plasma ALD. Furthermore, it was verified that $Q_f$ was not critically dependent on the annealing temperature ($T = 300$–$600{^\circ}\text{C}$), see Fig. 16. While an initial increase is observed between $T = 300$ and $400{^\circ}\text{C}$, $Q_f$ appeared to be relatively independent of the annealing temperature for $T \geq 400{^\circ}\text{C}$. Similar observations were reported by Benick et al.\textsuperscript{146}

In general, the $Q_f$ values that are reported for $\text{Al}_2\text{O}_3$ in various studies fall in the range of $(2–13) \times 10^{12}$ cm$^{-2}$ after annealing at moderate temperatures.\textsuperscript{12,16,98,107,123,124,127,146,147} Note that these films all afforded low $S_{\text{eff}}$ values $<10$ cm/s.

Although the relevant material or processing parameters responsible for the variations in $Q_f$ have not been fully identified, it was reported that the deposition temperature during ALD can affect the passivation mechanisms of the films. It was found that a variation in $T_{\text{dep}}$ between 150 and 300 $^\circ$C also gave rise to a variation in $Q_f$ between 6 and $3.5 \times 10^{12}$ cm$^{-2}$.\textsuperscript{148}

### C. Effect of film thickness

A key benefit of ALD is the ability to deposit ultrathin films. For thermal ALD, a correlation between film thickness and as-deposited surface passivation performance was found.\textsuperscript{135} This effect may be attributed to a small “in situ annealing effect” taking place in the ALD reactor (at a deposition temperature of 200 $^\circ$C) during prolonged processing time. More interesting is the thickness dependence after annealing. A constant high level of surface passivation could be maintained down to approximately 5 and 10 nm, for plasma and thermal ALD, respectively.\textsuperscript{135,147} It has been established that the cause of the deterioration is a decrease in

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**Fig. 15.** (Color online) Influence of annealing on the negative fixed charge density, $Q_f$, and interface defect density at midgap, $D_n$, for plasma and thermal ALD $\text{Al}_2\text{O}_3$ films. In the various studies annealing took place at temperatures of $\approx 400^\circ$C.

**Fig. 16.** (Color online) Negative fixed charge density $Q_f$ vs annealing temperature ($N_2$, 10 min) for plasma and thermal ALD $\text{Al}_2\text{O}_3$ films. $Q_f$ was determined from C–V measurements. Film thickness was $\approx 30$ nm.
the chemical passivation.\textsuperscript{145,149,150} Measurements by the noncontacting technique of secondary-harmonic spectroscopy have shown that the field-effect passivation remained constant while decreasing the film thickness to 2 nm.\textsuperscript{150} This is consistent with the fixed negative charges being located near the SiO\textsubscript{2}/Al\textsubscript{2}O\textsubscript{3} interface. Similar conclusions have been drawn from C–V measurements.\textsuperscript{151,152} Also, corona charging experiments are insightful when studying the effect of film thickness on the level of chemical passivation. Figure 17 shows results for the thickness dependence (5–30 nm) of the chemical and field-effect passivation for films deposited by thermal ALD. As discussed previously, the \( S_{\text{eff}} \) value measured at the point where \( Q_f \) is nullified by the deposited corona charges (\( Q_{\text{total}} = Q_{\text{corona}} + Q_f = 0 \)) can be used as an approximate measure for the chemical passivation (note, however, that some degradation may occur during charging). At this compensation point, the field-effect passivation is rendered inactive. While \( Q_f \) remained constant in the thickness range investigated [Fig. 17(c)], the results indicate that the level of chemical passivation strongly deteriorated for films of 5 nm [Fig. 17(b)]. This suggests that a minimum film thickness is required for effective interface hydrogenation during annealing (see Sec. V D).

Although not optimal, the level of passivation induced by Al\textsubscript{2}O\textsubscript{3} films with a thickness <5 nm may still prove adequate for solar cells (Sec. II C), especially when combined with a capping layer.

D. Fundamental mechanisms

1. Defect passivation

To detect the physical and chemical nature of the interface defects, electron spin resonance (ESR) has proven to be a powerful technique. Stranskam and Afanas'ev have reported that Si/Al\textsubscript{2}O\textsubscript{3} interface exhibits \( P_{\text{h}} \)-type defects (\( P_{\text{h}0} \) and \( P_{\text{h}1} \)).\textsuperscript{41} This is also the case for the Si interface with other “high-\( k \)” dielectrics such as HfO\textsubscript{2} and ZrO\textsubscript{2}. The \( P_{\text{h}} \)-type defect is a trivalently bonded Si atom (Si\textsuperscript{2+}), which represents the prominent electronically active defects characteristic of the Si/SiO\textsubscript{2} interface.\textsuperscript{153,154} Electronically, the Si/Al\textsubscript{2}O\textsubscript{3} interface can therefore be regarded as Si/SiO\textsubscript{2}-like with the \( P_{\text{h}} \)-center density being a criterion for the interface quality. The similarity between Si/Al\textsubscript{2}O\textsubscript{3} and Si/thermally grown SiO\textsubscript{2} was recently also corroborated by a deep-level transient spectroscopy study.\textsuperscript{155} The observations are in line with the formation of an interfacial SiO\textsubscript{2} layer (Sec. III B).

To investigate the nature of the defects in plasma ALD Al\textsubscript{2}O\textsubscript{3} in the as-deposited state and after annealing, contactless electrically detected magnetic resonance (EDMR) measurements were performed.\textsuperscript{156–158} Compared to ESR, EDMR measurements are more sensitive to small defect densities, although they lack the quantitative information. From the determined \( g \)-factors in the EDMR spectra (Fig. 18), it was possible to identify the \( P_{\text{h}0} \) center (\( g = 2.0087 \) and 2.0036) as the main trapping center for the as-deposited plasma ALD Al\textsubscript{2}O\textsubscript{3}. This was similar for thermal ALD (not shown). In addition, an isotropic center with \( g = 2.0055 \), and an \( E' \)-like defect with \( g = 1.999 \) were observed. The former relates to a dangling bond at the Si surface, which was also observed for amorphous Si.\textsuperscript{159,160} The \( E' \)-like defects are associated with the SiO\textsubscript{2} interface (O\textsuperscript{2+}Si\textsuperscript{2+}). After a standard annealing step (400 °C), EDMR did not reveal the presence of remaining defect states. This is in good agreement with the low \( D_{\text{it}} \) values \( \leq 10^{11} \text{ cm}^{-2} \text{ eV}^{-1} \) obtained after annealing (Fig. 15).

It is well known that the trivalent Si interface trap is chemically active and can be passivated by hydrogen. For SiO\textsubscript{2}, the \( P_{\text{h}} \)-type defect density is typically \( \sim 1 \times 10^{12} \text{ cm}^{-2} \) after oxidation and can be reduced \( < 10^{10} \text{ cm}^{-2} \) after annealing in H\textsubscript{2} ambient.\textsuperscript{46,50,153} The passivation of \( P_{\text{h}} \)-type defects in H\textsubscript{2} exhibits an activation energy of \( \sim 1.5 \text{ eV} \), which is significantly lower than the energy for dissociation of Si–H (~2.8 eV) in the range of optimal annealing temperatures.\textsuperscript{153} With isotope labeling using deuterated Al\textsubscript{2}O\textsubscript{3}, it has been shown experimentally that hydrogenation of the interface plays an important role in the chemical passivation of the Al\textsubscript{2}O\textsubscript{3} films.\textsuperscript{161} Moreover, the diffusion of hydrogen in Al\textsubscript{2}O\textsubscript{3} was found to critically depend on the annealing temperature and the Al\textsubscript{2}O\textsubscript{3} structural
properties.\textsuperscript{162} For films that exhibited either a low mass density (and high hydrogen content) or a very low initial hydrogen content (and a high mass density), the passivation was less thermally stable at temperatures of \(\sim 600^\circ\text{C}\) compared to films with intermediate properties. Finally it is speculated that, apart from the interface hydrogenation, the chemical passivation may also be influenced by film relaxation, Si–O bond rearrangements, and some additional interfacial oxide growth during annealing.

2. Negative charge formation

The microscopic origin of the defect states in the Si–Al\(_2\)O\(_3\) system that lead to negative \(Q_f\) has not been clearly established (see the discussion in Ref. \textsuperscript{17}). Moreover, dedicated theoretical or experimental work on this topic has not yet been carried out in the context of field-effect passivation. However, in a broader context, defects in Al\(_2\)O\(_3\), and especially in other (high-\(k\)) metal oxides, have been studied for their important role in metal–oxide–semiconductor applications. It is well known that the origin of the charge traps are (ionized) point defects,\textsuperscript{163–166} with candidates such as (oxygen or metal atom) vacancies and interstitials. The latter may also include extrinsic defects, such as interstitial hydrogen.\textsuperscript{167} The defects in these ionic metal-oxides are different from those in thermally-grown SiO\(_2\).

Various simulation studies have identified the point defects in Al\(_2\)O\(_3\), i.e., the O vacancy, the O interstitial, the Al vacancy, and the Al interstitial, and their energetic positions in the bandgap.\textsuperscript{164,168–170} Liu \textit{et al.} have provided evidence that the O vacancy is responsible for transport and trapping properties.\textsuperscript{164} However, it is not likely responsible for negative charge. In a simulation study, Matsunaga \textit{et al.} have reported that the Al vacancy (\(V_{Al}\)) and the O interstitial (\(O_i\)) can be charged negatively.\textsuperscript{168} \(V_{Al}\) was found to be stable in the \(-3\) state, and \(O_i\) in the \(-2\) state.\textsuperscript{168,169} Using more advanced simulations, Weber \textit{et al.} have recently analyzed the defects in Al\(_2\)O\(_3\) in the context of III–V electronics.\textsuperscript{169} They found that \(V_{Al}\) and \(O_i\) produce levels in the Al\(_2\)O\(_3\) bandgap below midgap. Both defects are therefore likely candidates to trap negative fixed charge in, e.g., the InGaAs/Al\(_2\)O\(_3\) system which has a valence band offset of \(E_v \sim 3\) eV compared to the Al\(_2\)O\(_3\) valence band maximum. As \(E_v \geq 3\) eV for Si,\textsuperscript{164,171,172} we may expect that the negative fixed charge in the Si/Al\(_2\)O\(_3\) system has a similar origin.

Experimentally, however, it is difficult to determine unambiguously the presence and type of point defects in the bulk of ultrathin films. Moreover, the concentration and type of defects that form near the Si/Al\(_2\)O\(_3\) interface may differ from the bulk. When the negative charge is related to the presence of \(V_{Al}\) and \(O_i\) defects, a slightly oxygen-rich structure in proximity of the Si interface would be expected. In agreement with this, Shin \textit{et al.} have demonstrated that negative fixed charges were indeed correlated with the presence of an O-rich region near the interface for InGaAs/Al\(_2\)O\(_3\) MOS structures.\textsuperscript{170} Also for the Si/Al\(_2\)O\(_3\) system, depth-dependent structural properties have been reported by Kimoto \textit{et al.}\textsuperscript{173} Both tetrahedrally and octahedrally coordinated Al atoms exist in Al\(_2\)O\(_3\), but the former appeared to be more dominant near the surface.

Regarding the stoichiometry of the ALD films, an O/Al ratio very close to \(\sim 1.5\) was determined by RBS for a film deposited using 250 ALD cycles (\(T_{dep} \geq 200^\circ\text{C}\)).\textsuperscript{98} However, due to the presence of a small amount of OH groups (~1–3 at. \%) it is expected that the films are slightly O-rich. To investigate whether the stoichiometry of Al\(_2\)O\(_3\) is thickness dependent, XPS spectra were recorded for films grown using 10 cycles (~1.2 nm) and 100 cycles (~12 nm). The Al 2p peak is sensitive to structural variations in the Al\(_2\)O\(_3\) films, and it was found to consist of multiple contributions for the ultrathin 1.2 nm film. The most prominent contributions can be assigned to an Al\(_2\)O\(_3\) structure (~74.4 eV) and the presence of Al–OH bonds (~75.6 eV),\textsuperscript{174} see Fig. 19(b). At the surface, carbon was detected [Fig. 19(c)], which also appears in the Al 2p spectrum. To obtain a semiquantitative analysis of the atomic Al and O density for ultrathin Al\(_2\)O\(_3\) films, the O contribution originating from the carbonates on the surface and from the interfacial oxide is significant and has to be corrected for. Moreover, an adsorbed H\(_2\)O layer on the surface can also contribute.\textsuperscript{175} This leads to an inherent uncertainty in the O/Al ratio for very thin films. Also for thicker films, a sensitivity factor is required to calibrate the O/Al ratio as determined by XPS to the more precise value determined by RBS. Figure 19(d) shows that small variations in the stoichiometry near the interface, most likely a higher oxygen concentration, may exist. In contrast, a more dramatic change in stoichiometry near the interface was recently suggested by Werner \textit{et al.}, with the O/Al ratio reaching a value as high as \(\sim 8\), as was inferred from XPS measurements.\textsuperscript{147}

However, in this context, it is relevant to consider that the number of defect states near the interface that is required to account for \(Q_f\) is relatively small. Using atomic densities obtained by RBS, we can estimate the number density of “Al\(_2\)O\(_3\) units” to be approximately \(7 \times 10^{14} \text{units/cm}^2\) at the SiO\(_2)/\text{Al}_2\text{O}_3\) interface. Therefore, for a fixed charge density of...
\[ 7 \times 10^{12} \text{ charges/cm}^2 \text{, we find that only one “surface charge” is present for every } 10^2 \text{ Al}_2\text{O}_3 \text{ units. Thus, a very large deviation from stoichiometry appears not to be a prerequisite to account for the typical negative fixed charge densities of Al}_2\text{O}_3. \]

Another important issue is the role of charging of defect states. The charge state of an (ionized) defect can be changed by electron (or hole) injection into the conduction (or valence) band of the dielectric and by tunneling from the dielectric into the substrate or from the dielectric surface into the metal (gate). For the Si/Al2O3 system, there are some indications that charge injection from Si into Al2O3 may play a role in the formation of the negative \( Q_f \). Second-harmonic generation experiments have demonstrated that \( Q_f \) can increase under influence of laser irradiation. This is consistent with (multi-) photon-induced charge injection from Si into preexistent defect states at the SiO2/Al2O3 interface. In addition, we have observed a hysteresis during corona charging experiments that is consistent with a charge injection phenomenon. For annealed Al2O3 samples, the fixed charge density was observed to increase by \((1–2) \times 10^{12} \text{ cm}^{-2}\) after deposition of positive corona charges \((\sim 10^{13} \text{ cm}^{-2})\) on the Al2O3 surface (not shown). The net positive charge may attract electrons from the Si wafer into defect states at the SiO2/Al2O3 interface. In addition, it has been demonstrated that an increase in the SiO2 interlayer thickness over the range of 1–30 nm gave rise to a decrease in negative \( Q_f \). For instance, flatband conditions were observed for an ALD SiO2 interlayer thickness of \( \sim 5 \text{ nm} \). The simplest explanation is that the SiO2 acts as a barrier, reducing charge injection from the Si substrate into defect states at the SiO2/Al2O3 interface.

In conclusion, simulations and experiments have provided evidence that the negative charge at the SiO2/Al2O3 interface may be related to \( V_{AI} \) and \( O_2 \) defects. Charge injection phenomenon across the interface may play a role in the formation of the negative charge associated with these defects. It is important to point out that also other mechanisms can contribute to negative charges, and that more research is required to draw final conclusions.

VI. IMPLEMENTATION IN SOLAR CELLS
A. Stability
1. UV stability

The ultraviolet (UV) stability of a passivation layer is important when applied at the front side of a solar cell. With an optical bandgap of \( \sim 6.4 \text{ eV} \), amorphous Al2O3 is transparent for the UV radiation in the solar spectrum. The surface passivation induced by Al2O3 was not found to degrade during the UV exposure of an Hg lamp \((\sim 254 \text{ nm})\). In fact, in some cases the effective lifetime of an Al2O3-passivated wafer exposed to UV light was even observed to increase by \( \sim 40\% \). This was tentatively explained by an increase in \( Q_f \) by photon-induced charge injection from the Si substrate. Other reports have shown that during light soaking the passivation performance remained stable.

2. Firing stability

When Al2O3 surface passivation films are implemented in screen-printed solar cells, the thermal stability of the films during high-temperature firing processes \((> 800 \text{ °C})\) is crucial. The impact of direct firing and firing after a preceding low-temperature annealing step on the passivation properties of Al2O3 has been evaluated. The reports show that the level of passivation by Al2O3 decreases, but that its thermal stability is generally sufficient for application in screen-printed solar cells. On the other hand, the exact level of passivation that can be expected after firing is strongly dependent on the peak temperature and the duration of the firing step.

For low resistivity \( n \)- and \( p \)-type c-Si, \( S_{eff} < 14 \) and \( 25 \text{ cm/s} \) have been reported after annealing \((400 \text{ °C})\) and subsequent firing \((800 \text{ °C})\). After direct firing at \( 750 \text{ °C} \), an \( S_{eff} \) value of \( \sim 20 \text{ cm/s} \) could be achieved for \( p \)-type Si. Moreover, a good thermal stability was obtained for the passivation of \( p^+ \) emitters. The latter also appeared to be less sensitive to the peak temperature than the passivation of low resistivity Si wafers. For instance, the level of passivation of a 90 \( \Omega/\text{sq.} \) \( p^+ \) emitter was compatible with
open-circuit voltages > ~695 mV after firing at 825 °C.40 Also, for Al2O3 synthesized by PECVD and spatial ALD good thermal stabilities have been reported.180,182,183 Furthermore, when ultrathin films <20 nm were considered, the firing stability for Al2O3/SiN stacks was found to be better than for single layer Al2O3. For uncapped 3.6 nm thick Al2O3, very high $S_{\text{eff}}$ values of ~300 cm/s were obtained after firing (830 °C), while a corresponding stack comprising a 75 nm thick SiN capping film resulted in a significantly lower value of $S_{\text{eff}} < 44$ cm/s.136

The results on lifetime samples have recently been corroborated by a good thermal stability for Al2O3 films implemented in screen-printed solar cells. For example, Gatz et al. have extracted an $S_{\text{eff}}$ value of 70 ± 30 cm/s (contact pitch 1 mm) for an Al2O3/SiN stack at the rear side of a screen-printed p-type PERC solar cell leading to an efficiency of 19%.184

The relative deterioration in passivation quality during firing can be attributed mainly to an increase in $D_n$ at high annealing temperatures, while the value of $Q_f$ was found to be less affected.138 The increase in $D_n$ can be ascribed to the dissociation of interfacial Si–H bonds at elevated temperatures. Thermal effusion measurements revealed that hydrogen is released from the film at such high annealing temperatures.178 Furthermore, it was found that the firing induced degradation could not be improved significantly by subsequent annealing in forming gas.178 This contrasts the behavior of fired thermally grown SiO2, and can likely be explained by the fact that Al2O3 film acts as a barrier for the diffusion of H2 from the annealing atmosphere at moderate temperatures (~400 °C).

Apart from the stability of the passivation, the physical and optical properties of the Al2O3 (bulk) material should, preferably, not deteriorate at high temperatures. While cracking of the Al2O3 films did not occur, small blisters have in several cases been observed after high-temperature processing.185,186 The key parameters (e.g., synthesis method, film thickness, structural properties, firing recipe, capping layer) that affect blister formation have not yet been conclusively identified, and it should be noted that in some cases (e.g., when using ultrathin films) no blistering was observed after firing. Figure 20 shows an SEM image of thin Al2O3 film that exhibited round blisters with a typical diameter of ~50 μm. Figure 20 clearly illustrates that blistering is associated with local film delamination. The formation of blisters can likely be attributed to the local accumulation and subsequent release of gaseous hydrogen and/or H2O from the films. It should be noted that the passivation performance was not (strongly) affected by film blistering, which may be expected on the basis of the typically low surface coverage of blisters (5%–10%). More research is required for a better understanding of the conditions that lead to film blistering.

B. Surface passivation stacks

1. Al2O3/a-SiNx stacks

a-SiNx:H capping layers, synthesized by PECVD, have been applied on top of thin Al2O3 films at the rear and front side of solar cells.184,187,188 The thermal budget during a-SiNx:H deposition (~350–450 °C) can activate the surface passivation induced by Al2O3.178 As discussed before, the application of an SiN capping layer can extend the process window for screen-printed solar cells in terms of Al2O3 film thickness and firing temperature.136,138 Richter et al. have recently reported that five ALD cycles of Al2O3 in combination with an SiN capping layer already produces good passivation properties for a-type emitters.157

An important reason for the use of Al2O3/SiNx stacks at the rear side of screen-printed solar cells is the improved chemical stability. It has been observed that the application of metal pastes directly on Al2O3 can disintegrate the material during firing. N-rich SiNx layers appear to be robust and to remain chemically stable. These capping films can therefore protect the Al2O3 films from damage caused by metal paste. Moreover, when ultrathin Al2O3 films are considered at the rear side, an SiN capping layer can be useful to increase the physical thickness to improve the rear reflection properties of the solar cell.

The stacks exhibit a negative fixed charge density.60,138 This is consistent with the expectation that the positive fixed charge density in SiNx films applied on Si is related to the...
Si/SiN<sub>x</sub> interface. When the SiN<sub>x</sub> is used as capping layer on Al<sub>2</sub>O<sub>3</sub>, the positive charges in SiN<sub>x</sub> may be absent or much lower in density when compared to SiN<sub>x</sub> applied directly on Si.

2. SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> stacks

A different approach is to use Al<sub>2</sub>O<sub>3</sub> as a capping layer on SiO<sub>2</sub>. These SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> stacks have significant technological potential for the passivation of both n- and p-type Si. They lead to a considerable improvement in the passivation properties and stability of SiO<sub>2</sub> regardless of the synthesis method. Results on stacks comprising thermally grown SiO<sub>2</sub> and SiO<sub>2</sub> synthesized at low temperatures by PECVD and ALD have been reported.

Stacks comprising thermally grown SiO<sub>2</sub> exhibited S<sub>eff</sub> values &lt;5 cm/s after annealing in N<sub>2</sub>, which was slightly better than obtained by single layer SiO<sub>2</sub> after forming gas annealing. An Al<sub>2</sub>O<sub>3</sub> thickness of 10 nm and above was found to be sufficient to fully activate the passivation performance of the stacks (Fig. 21). Moreover, the poor passivation properties of SiO<sub>2</sub> synthesized at low temperatures could be improved dramatically by application of an ultrathin Al<sub>2</sub>O<sub>3</sub> capping layer. S<sub>eff</sub> values &lt;5 cm/s (n-type Si) were obtained for SiO<sub>2</sub> films (10–85 nm) synthesized by PECVD and ALD. Moreover, the stacks exhibited an excellent firing stability, and did not suffer from a poor long-term stability as is sometimes observed for single layer SiO<sub>2</sub>.

The low S<sub>eff</sub> values obtained for the SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> stacks can be attributed to (very) low interface defect densities D<sub>it</sub> &lt; 10<sup>11</sup> cm<sup>-2</sup>eV<sup>-1</sup>. This is illustrated for PECVD SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> stacks by the capacitance–voltage measurement in Fig. 22. The C–V characteristics reveal an almost negligible frequency dispersion (i.e., insignificant time-dependent response of interface defects) indicative of an excellent interface quality. In turn, the low defect densities can be attributed to the effective hydrogenation of the Si/SiO<sub>2</sub> interface during annealing under influence of the Al<sub>2</sub>O<sub>3</sub> capping layer. Evidence has been provided that atomic hydrogen could play a role for Al<sub>2</sub>O<sub>3</sub> films. These observations are reminiscent of the “annealing” process for which a sacrificial aluminum capping layer is used during annealing of the SiO<sub>2</sub> layer. It has been hypothesized that the annealing effect is related to an oxidation reaction of Al (e.g., reaction with H<sub>2</sub>O) under formation of (atomic) hydrogen and AlO<sub>x</sub>. Also the Al<sub>2</sub>O<sub>3</sub> layer could be removed after annealing (by etching in diluted HF) without compromising the passivation properties.

The field-effect passivation induced by the stacks was found to decrease strongly for increasing SiO<sub>2</sub> thickness. This is illustrated by the reduced flatband voltage shift in Fig. 22 for the PECVD SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> stacks. For stacks comprising ALD SiO<sub>2</sub>, a strong decrease in field-effect passivation was observed for a thickness range of 1–5 nm. For increasing SiO<sub>2</sub> thickness, the negative Q<sub>f</sub> at the SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> decreases and, consequently, the positive charges associated with SiO<sub>2</sub> start to play a more prominent role. The latter also depends on the synthesis method of the SiO<sub>2</sub> as thermally grown SiO<sub>2</sub> generally contains less positive charges than SiO<sub>2</sub> deposited at low temperatures. Therefore, depending on the SiO<sub>2</sub> film thickness and synthesis method, the net fixed charge density of the stacks can vary from negative to positive. The results for SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> stacks appear to be more general as a decrease in field-effect passivation was also observed for SiO<sub>2</sub>/SiN<sub>x</sub> stacks. Therefore, material stacks are not only useful to optimize the optical and physical properties but also to tailor the underlying surface passivation mechanisms.

C. Industrial-scale ALD

The traditionally low deposition rate of ALD has been regarded as the main obstacle for the use of ALD in photovoltaics where the throughput requirements are significantly higher than in the microelectronics industry. For single-wafer reactors, the deposition rate is typically ~1–2 nm/min for cycle times of a few seconds in length. However, while the growth per cycle for Al<sub>2</sub>O<sub>3</sub> is fixed at roughly ~1 Å for
all ALD equipment, the duration of the cycle and the number of wafers that can be deposited simultaneously, and therefore the deposition rate (i.e., thickness per unit of time per wafer), can vary substantially. With the incentive to overcome the throughput limitations of existing ALD Al₂O₃ methods, equipment manufacturers such as Beneq and ASM have redesigned or adapted their ALD batch tools, which were originally designed for the semiconductor industry, to meet the throughput requirements of typically >3000 solar cells/h. Moreover, spatial ALD equipment has recently been developed specifically for the deposition of Al₂O₃ for PV applications.²¹

The concept of spatial ALD was already described in the original ALD patent of Suntola.¹⁹⁰ More recently, technology to enable atmospheric spatial ALD has been explored by Levy et al.¹⁹¹ The difference between spatial and temporal ALD pertains to the separation of the precursor and oxidant steps (Fig. 23). In conventional temporal ALD processes, such as used in batch reactors, the precursor and oxidants are injected sequentially into the same reactor volume. In spatial ALD, the precursor and oxidants are separated spatially in different zones of the reactor. Two spatial ALD concepts have been commercialized—by SoLayTec and by Levitech.¹⁹²,¹⁹³ Both concepts are quite similar with the main difference being the transport of the wafers (Fig. 23). The Levitech approach is based on an inline reactor (the Levitrack) where transport is controlled by an atmospheric gas bearing on which the wafer floats. While the wafer moves through the reactor, it is sequentially exposed to Al(CH₃)₃, N₂, H₂O, and again N₂. The precursor zones are repeated over the length of the track, which also has a heating and cooling zone in the initial and final part of the reactor. The system yields ~1 nm Al₂O₃ per 1 m system length in its current configuration. In the SoLayTec reactor, the wafer moves back and forth underneath TMA and H₂O injection zones. Therefore, film thickness is independent of system length. As is the case in the Levitrack, wafer movement is fully controlled by gas flows. In the SoLayTec concept, the deposition rate depends on the number of injection slots integrated in the injector head and the number of passages of the wafer per second.

In spatial ALD, the cycle time is ultimately dictated by the speed of the precursor reactions at the growth surface and not by the purge steps that avoid parasitic CVD reactions between precursors. Both spatial ALD reactors lead to significantly higher deposition rates (e.g., 30–70 nm/min) than generally obtained by temporal ALD (a few nm/min at most). Other benefits of these reactors are that no vacuum pumps are required as the reactors are operated under atmospheric pressure conditions, and that, in the ideal case, only the wafer is coated (either single-side or double-side depending on the reactor design) and not the reactor walls. In addition, there are no moving equipment parts apart from the wafers. More details on spatial ALD and the systems can be found in Refs. 20 and 21 and 194–198.

An important question to address is whether the scale-up of the ALD processes compromises the passivation properties of Al₂O₃ films in comparison with single-wafer laboratory systems. Here, we focus on the passivation properties of Al₂O₃ films that were deposited in an ASM ALD batch reactor and in the inline ALD reactor from Levitech.

1. Batch ALD

The surface passivation properties of Al₂O₃ deposited in the ASM ALD batch reactor were optimized for substrate temperature and precursor dosing times. O₃ was used as the oxidant and the lifetime wafers were deposited at both sides simultaneously. The wafers can also be placed back-to-back, which results in single-side deposition of twice the amount of wafers and, therefore, a higher wafer throughput. The Al₂O₃ films afforded a low level of surface passivation in the as-deposited state. This is similar to the results for plasma
ALD. The surface passivation was activated by annealing, resulting in low $S_{\text{eff}}$ values < 6 cm/s for Al$_2$O$_3$ films with a thickness of ~15 nm for 2 Ω cm $p$-type Si wafers.\cite{107} This high level of passivation after annealing can be explained by a low interface defect density of $3.4 \times 10^{12}$ cm$^{-2}$ and a low interface defect density $D_{\text{it}}$ of $7.1 \times 10^{11}$ eV$^{-1}$ cm$^{-2}$ as determined by $C–V$ measurements.\cite{107}

2. Spatial ALD

The Al$_2$O$_3$ films deposited in the Levitetch afforded some surface passivation in the as-deposited state with $S_{\text{eff}}$ < 50 cm/s for a film thickness of ~15 nm. This is in agreement with results for thermal ALD with H$_2$O in a lab scale reactor (Fig. 14). After a standard anneal, the effective lifetime increased significantly to $\tau_{\text{eff}}$ = 2.5 ms, resulting in very low $S_{\text{eff}}$ < 6 cm/s [Fig. 24(a)].\cite{107} Reference samples deposited with plasma ALD Al$_2$O$_3$ in a single-wafer reactor showed similar low $S_{\text{eff}}$ values. For annealed films, $S_{\text{eff}}$ decreased with increasing film thickness and saturated for thicknesses $>\sim$10 nm. Interestingly, after a subsequent firing process in an industrial belt line furnace ($T > 800$°C), the thickness dependence of the passivation disappeared. Ultrathin films of ~5 nm yielded relatively low $S_{\text{eff}}$ values <25 cm/s after firing. Regarding the field-effect passivation, it was verified by corona charging experiments that the spatial ALD Al$_2$O$_3$ films exhibited a high negative $Q_{\text{eff}}$ of $(4 \pm 0.5) \times 10^{12}$ cm$^{-2}$ after annealing [Fig. 24(b)].

The excellent passivation results for the spatial and batch ALD Al$_2$O$_3$ processes are comparable to those obtained for single-wafer reactors. This is also true for the Al$_2$O$_3$ films deposited in the spatial ALD tools of SoLayTec, which led to low $S_{\text{eff}}$ values of <8 cm/s on low-resistivity $p$- and $n$-type Si.\cite{197,198} Therefore, no apparent compromised performance in terms of resulting passivation quality was observed when going to scaled-up ALD processes. To date, spatial and batch ALD equipment has already been installed in pilot production lines at a number of solar cell manufacturers and research institutes.

3. ALD or PECVD?

PECVD is a serious contender for the deposition of Al$_2$O$_3$ in the PV industry. Good surface passivation properties ($S_{\text{eff}} < 10$ cm/s, 1 Ω cm $p$-type Si), on par with ALD, have already been reported for Al$_2$O$_3$ synthesized by PECVD in an industrial Roth & Rau reactor.\cite{124} A difference may be the refractive index of the PECVD deposited films, which is generally somewhat lower (~1.60) than for ALD (~1.64).\cite{124,125} This is indicative of a slightly lower film density.

The PECVD and the ALD processes both have strengths and weaknesses. Hence, it is likely that there are opportunities for both—and perhaps also other—deposition technologies depending on specific demands and applications. When ultrathin Al$_2$O$_3$ films are required (<10 nm), the thickness control and uniformity of ALD may provide key benefits over PECVD. This will also be the case for concepts in which Al$_2$O$_3$ films are required on both sides of the solar cell, and for more advanced passivation schemes comprising stacks of ALD materials, nanolaminates, or perhaps doped and mixed oxides. However, when thick Al$_2$O$_3$ films are required, PECVD may be the preferred option. In the end, cost-of-ownership considerations (such as operational costs, footprint, equipment down-time, precursor consumption, etc.) may be at least as important as the purely technological specifications of the system.

D. Alternative precursors

1. Solar grade TMA

Cost-of-ownership for Al$_2$O$_3$ deposition technology could be reduced when, instead of highly purified “semiconductor grade” Al(CH$_3$)$_3$, a lower cost precursor can be used. The precursor costs are directly related to the number of purification steps required during precursor synthesis. Possible impurities that can be present in lower grade TMA include Ga, Zn, Cl atoms. To assess the possible influence of the purity level on the passivation properties of the Al$_2$O$_3$ films, Al(CH$_3$)$_3$ with two different purities, i.e., semiconductor grade and solar grade, were compared.\cite{180} For both thermal and plasma ALD, no significant difference was observed between the two precursors in terms of resulting passivation performance. This holds for both $p$- and $n$-type silicon. It can therefore be concluded that the surface passivation is not compromised by the higher impurity level of solar grade Al(CH$_3$)$_3$. This compatibility is crucial for large-scale production.

2. DMAI

As an alternative to Al(CH$_3$)$_3$, dimethylaluminium isopropoxide [AlMe2(0Pr)] can be used as Al precursor during ALD. This novel precursor (in brief DMAI), commercialized by Air Liquide, is not pyrophoric. DMAI is therefore safer to handle and store than TMA. In the DMAI molecule, the Al atom is bonded to an isopropoxide group and to two methyl groups [Fig. 25(inset)]. DMAI can be used in combination with O$_3$, H$_2$O, or an O$_2$ plasma as coreactants. A saturated process was developed for plasma and thermal ALD in our OpAL reactor.\cite{199} Slightly longer dosing times (~100 ms) were required for DMAI than for TMA, which can be
attributed to a lower vapor pressure for DMAI (9 Torr at 66.5 °C) than for TMA (9 Torr at 16.8 °C). The plasma ALD process yielded a growth rate of 0.9 Å/cycle for T_{dep} = 200 °C, which is lower than the 1.2 Å obtained when using TMA in plasma ALD. In addition, the DMAI-Al₂O₃ films exhibited a higher hydrogen content of ~7 at. % and, consequently, a lower mass density of ~2.6 g/cm³ (T_{dep} = 200 °C) compared to Al₂O₃ deposited from TMA. These differences illustrate that a relatively small change to the precursor molecule can give rise to different growth and material properties.

The surface passivation performance of the DMAI-Al₂O₃ films is displayed in Fig. 25, comparing results for n- and p-type c-Si. Before annealing, the passivation performance was very poor with S_{eff} values of the order of 10³ cm/s, as expected for plasma ALD. After annealing, the effective lifetime is observed to improve significantly. S_{eff} values <6 and <3 cm/s were obtained for p- and n-type Si, respectively. These values are quite comparable to those reported for plasma ALD Al₂O₃ using Al(CH₃)₃.

VII. SOLAR CELLS FEATURING Al₂O₃

One key aspect of all high-efficiency solar cells is the incorporation of effective surface passivation schemes on the front and/or rear side. Figure 26 illustrates a selection of solar cell structures based on p-type and n-type Si base material. It is evident that the number of process steps required for the fabrication of the different cells varies widely. The industrial standard screen-printed p-type Si solar cell, which can be manufactured in only eight process steps, exemplifies the simplest device structure [Fig. 26(i)]. The energy conversion efficiency of this type of solar cell can be increased by improving the front side, e.g., by using a selective emitter and higher aspect ratio front contacts. However, to achieve a significant increase in efficiency, it is necessary to also improve the rear side by the implementation of a passivated rear with local backsurface field (PERC-type solar cell). The PERC-type design is compatible with high cell efficiencies, and is currently being introduced in mass production. The adaptation from the standard Al-BSF cell to a PERC cell requires the deposition of a rear passivation film, local contact formation by, for example, laser processing, but it also changes, for example, the requirements for the optimal Si bulk resistivity and the composition of the metal pastes. Another route to realize high efficiencies is the use of n-type Si base material. The effective passivation of p⁺ emitters by Al₂O₃ has been an important step forward for various types of n-type Si solar cells. An advantage of using n-type Si is the high bulk lifetime, which does not suffer from light-induced degradation by the formation of boron-oxygen complexes as is the case for Czochralski (Cz) p-type Si. This is one of the reasons why cells based on n-type Cz Si have a higher efficiency potential than those using Cz p-type Si. However, for n-type cells, an n⁺ BSF [or front surface field (n⁺ FSF)] cannot be simply formed.

FIG. 25. (Color online) Injection-level-dependent effective lifetime for Al₂O₃ films synthesized by plasma ALD using DMAI as precursor for Al. Annealing was performed at 400 °C (10 min, N₂). Data for n- (3.5 Ω cm) and p-type (2 Ω cm) Si is shown (Ref. 199). Inset shows precursor drawings, comparing TMA and DMAI.

FIG. 26. (Color online) Various solar cell concepts based on p- and n-type Si wafers. (i) Full Al-BSF; (ii) passivated emitter and rear (PERC) cell; (iii) backcontacted emitter wrap through (BC EWT) cell; (iv) passivated emitter and rear totally diffused (PERT) cell; (v) passivated emitter and rear locally diffused (PERL) cell; (vi) backjunction Al alloyed rear emitter (“BJ-Alp⁺”) cell; (vii) backjunction PERT cell; (viii) bifacial cell; (x) interdigitated back contacted emitter wrap through (BC EWT) cell; (xii) heterojunction (HJ) cell.
during the metallization process similar to the formation of the Al-BSF for p-type cells and therefore requires additional process steps. On the other hand, screen printing can be employed to create an Al-p+ emitter at the rear side [Fig. 26 (vii)]. It is important to note, however, that elaborate cleaning steps are required to remove the Al and passivate the emitter. Obviously, passivation of the emitter is more straightforward when using boron diffusion or ion implantation processes.204

Al2O3-based passivation schemes have been employed for various types of solar cells listed in Fig. 26. An overview of important results is presented in Table II. Note that not all efforts could be included, given the accelerating activity in the field.

A. p-type Si cells

The first p-type PERC solar cell featuring Al2O3 surface passivation was reported in 2008 by Schmidt et al.205 It was demonstrated on cell level that the passivation performance of Al2O3 can be on par or superior to annealed thermally grown SiO2. An effective surface recombination velocity of ~70 cm/s was deduced from the internal quantum efficiency measurements for Al2O3 with a PECVD SiO2 capping layer and local rear contacts. The SiO2 capping films can be applied on top of the thin Al2O3 films to improve the rear reflection properties. Efficiencies of 20%–20.6% were reported, which were later increased up to 21.4% (Jsc = 40.7 mA/cm², Voc = 664 mV, FF = 79.4%) in a follow-up experiment.182 As expected, the Al2O3-passivated PERC cells did not suffer from parasitic shunting (by the formation of an inversion layer), as can be the case when SiNx is applied on the rear. By direct comparison, it was furthermore concluded that Al2O3 synthesized by sputtering led to a lower Voc and η compared to ALD Al2O3 films, which is consistent with the differences in passivation quality as deduced from effective lifetime measurements.182 Very similar efficiencies of up to 21.5% have been reported for PERC cells by Saint-Cast et al.188 The passivation by PECVD or plasma ALD Al2O3 led to similar solar cell performance. Moreover, the rear reflection properties for single layer Al2O3 with a thickness of ~100 nm were equivalent to those of SiO2 or Al2O3/SiO2 stacks. The high open-circuit voltages >675 mV clearly demonstrate the excellent rear surface passivation properties of the Al2O3 films.188 The front side of the PERC cells in Refs. 188 and 205 exhibited high-efficiency n+ emitters of 100 and 120 Ω/sq, respectively. In Ref. 205, the emitter surface was very lightly oxidized (“tunnel oxidation,” leading to ~1.5 nm SiO2) to improve the front side contact resistance and therewith the fill-factor (FF) of the cells. Ziehike et al. have recently demonstrated that a few ALD cycles of Al2O3 on top the n+ emitter also had a positive impact on the cell efficiency and reproducibility.206 However, when more than two ALD cycles were employed, a decrease in FF and η was observed, which the authors ascribed to a decrease in tunneling probability. A similar front and rear passivation scheme was used by Petermann et al. for thin 43 μm epitaxial Si layer solar cells in combination with the porous Si layer transfer process.207 Partially due to the improved surface passivation, they were able to improve the efficiency of this type of solar cells from 16.9% to 19.1%. It is important to note that the laboratory-type PERC cells discussed before were based on high-quality FZ Si (B-doped, 0.5 Ω cm, ~4 cm²) with an evaporated Al backcontact. Either

<table>
<thead>
<tr>
<th>Solar cell type</th>
<th>Passivation layer(s)</th>
<th>Cell efficiency (%)</th>
<th>Additional details</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>p-PERC (ii)</td>
<td>(Rear) ALD Al2O3 + SiO2, (Rear) thermal SiO2</td>
<td>20.1</td>
<td>Al evaporated contacts, 0.5 Ω cm FZ, 4 cm²</td>
<td>182, 205</td>
</tr>
<tr>
<td>p-PERC (ii)</td>
<td>(Rear) ALD Al2O3 + SiO2</td>
<td>21.3</td>
<td>Al rear, plated front contacts, 0.5 Ω cm FZ, 4 cm²</td>
<td>188</td>
</tr>
<tr>
<td>p-PERC (ii)</td>
<td>(Rear) PECVD Al2O3 + SiO2</td>
<td>21.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>p-PERC (ii)</td>
<td>(Front) ALD Al2O3 + SiN, ARC; (rear) Al2O3/SiN stack</td>
<td>19.7</td>
<td></td>
<td></td>
</tr>
<tr>
<td>n-PERT (iv)</td>
<td>(Front) Al2O3/SiN stack</td>
<td>19.4</td>
<td>43 μm thick, B-doped epitaxial Si, 0.5 Ω cm FZ, 4 cm²</td>
<td>207</td>
</tr>
<tr>
<td>n-PERT (ii)</td>
<td>(Rear) Al2O3/SiN stack</td>
<td>19.0</td>
<td>Screen-printed, 3 Ω cm Cz, 125 × 125 mm</td>
<td>208</td>
</tr>
<tr>
<td>n-PERT (ii)</td>
<td>(Rear) Al2O3/SiN stack</td>
<td>19.1</td>
<td>Screen-printed, 2–3 Ω cm FZ, 125 × 125 mm</td>
<td>184</td>
</tr>
<tr>
<td>n-PERT (vi)</td>
<td>(Front) Al2O3/SiN, stack</td>
<td>22.4</td>
<td>Local diffused rear side, 1.5 Ω cm FZ, 4 cm²</td>
<td></td>
</tr>
<tr>
<td>n-PERT (vi)</td>
<td>(Front) Al2O3/SiN</td>
<td>23.9</td>
<td>140 Ω/sq p+, 1 Ω cm FZ, 4 cm²</td>
<td>9, 19</td>
</tr>
<tr>
<td>n-IBC (x)</td>
<td>(Rear) Al2O3</td>
<td>19.0</td>
<td>Local n+ BSF (PassDop, Laser doping), 1 Ω cm FZ, 4 cm²</td>
<td>212</td>
</tr>
<tr>
<td>EWT (x)</td>
<td>(Rear) Al2O3/SiN, (Front) SiN</td>
<td>21.6</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

TABLE II. Selection of solar cell results with implemented Al2O3-based surface passivation schemes. The “solar cell types” in the first column refer to Fig. 26.
photolithography-based processes were used to create openings in the rear surface passivation scheme,\textsuperscript{205} or laser-fired-contacts (LFCs) were implemented.\textsuperscript{188}

Results on industrially feasible PERC cells, based on Cz-Si and screen-printed metallization, have also been reported (Table II). For these type of cells, a stack of Al$_2$O$_3$/SiN$_x$ is used on the rear, instead of single layer Al$_2$O$_3$. This is chiefly related to the high chemical stability of N-rich SiN$_x$ when covered by metal paste. Lauermann \textit{et al.} reported a \textasciitilde 0.7\% higher (absolute) efficiency for PERC cells (18.6\%) than for Al-BSF reference cells.\textsuperscript{208} 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 the references. These results demonstrate on a device level that the Al$_2$O$_3$/SiN$_x$ passivation scheme is sufficiently firing stable. Gatz \textit{et al.} reported an energy conversion efficiency of 19.0\% for large area Cz Si solar cells passivated by an Al$_2$O$_3$/SiN$_x$ stack.\textsuperscript{184} As expected, the $J_{sc}$ (38.9 mA/cm$^2$) and $V_{oc}$ (652 mV) were significantly higher than for the Al-BSF reference (\eta = 18.6\%, $J_{sc} = 37$ mA/cm$^2$, $V_{oc} = 636$ mV). Very recently, Vermang \textit{et al.} reported an efficiency of 19.1\% for a PERC cell with a triple-layer Al$_2$O$_3$/SiO$_x$/SiN$_x$ stack on the rear.\textsuperscript{209} Taken together, the PERC cells exhibited significantly lower FF values [e.g., 77.2\% (Ref. 208) and 75.1\% (Ref. 184)] than were obtained for the Al-BSF references (79.5\% and 78.7\%, respectively). An enhanced series resistance associated with the local (line or point) contacts is responsible for this difference. For PERC cells, the pitch and local contact size are critical parameters for optimizing the rear side, which involves a trade-off between a low contact resistance (narrow pitch and large contacts) and low surface recombination velocities (wide pitch and small contacts). Ongoing optimization of metal pastes for local contacts will contribute to further reductions in contact resistance. Apart from laser ablation (or etching) of the dielectric prior to metallization, another industrially feasible option is to use LFCs at the rear side where structuring is done after the application of the metal paste.\textsuperscript{201} An alternative rear side metallization process based on an open grid is used for the so-called PASHA cell (Passivated on all sides H-pattern), compare Fig. 26 (ix).\textsuperscript{210} Although the efficiency potential for these cells is somewhat lower than for PERC cells, the fabrication is simpler as the contacts are fired through the dielectric layer forming an effective BSF. A capping layer on Al$_2$O$_3$ is not necessary.

Apart from PERC cells based on Cz-Si, excellent results were reported recently by Q-Cells for industrially manufactured multicrystalline Si (mc-Si) cells with improved front and rear side. Using a rear surface passivation stack (materials undisclosed) and LFCs, Engelhart and co-workers demonstrated record efficiencies of up to 19.5\% (mc-Si) and 20.2\% (Cz-Si).\textsuperscript{203,211} The authors estimated that the improvement in $J_{sc}$ due to enhanced rear reflection ($\Delta J_{sc}$ \sim 1 mA/cm$^2$) was almost as important as the reduction in electronic rear side recombination ($\Delta J_{sc}$ \sim 1.2 mA/cm$^2$) for the mc-Si cells ($J_{sc} = 38.9$ mA/cm$^2$, $V_{oc} = 652$ mV, FF = 76.7\%). These solar cell results demonstrate clearly that rear side surface passivation is not only useful for monocrystalline Si cells but has also significant potential for cells based on lower quality Si substrates, which was previously unexpected. Moreover, these developments suggest that the performance gap between industrially produced Cz-Si cells and cheaper mc-Si cells can be reduced by the implementation of new technologies. Finally, it is important to point out that a fair comparison between various surface passivation schemes should also address the solar cell performance under low-illumination conditions.\textsuperscript{211}

B. \textit{n}-type Si cells

Al$_2$O$_3$-based passivation was first tested for \textit{n}-type Si solar cells in a PERL cell design. An Al$_2$O$_3$/SiN$_x$ stack was used on the front side boron emitter (\textasciitilde 140 $\Omega$/sq).\textsuperscript{19} Hoex \textit{et al.} demonstrated that Al$_2$O$_3$-passivated boron emitters with comparable sheet resistance lead to ultralow $J_0$ of \textasciitilde 10 fA/cm$^2$.\textsuperscript{137} For the PERL cell, Benick \textit{et al.} reported record efficiencies of, at that time, 23.2\% (or 23.4\% after adjustment of the AM1.5 spectrum).\textsuperscript{19} In subsequent work, the efficiency was even improved further to 23.9\%.\textsuperscript{9} Internal quantum efficiencies of approximately 100\% were obtained for the front side, in combination with $V_{oc}$ values \textasciitilde 700 mV. These results underline the passivation properties of Al$_2$O$_3$ for highly doped \textit{p}-type surfaces on a device level. The PERL cell, featuring local \textit{n}$^+$ BSFs fabricated using photolithography processes, presents a complex cell concept involving many different process steps. To simplify the formation of the \textit{n}$^+$ BSF, a novel process was developed at Fraunhofer ISE where a phosphosilicate containing passivation layer (called PassDop) is locally opened by a laser under the simultaneous diffusion of P atoms into Si. Using this process, promising efficiencies of 22.4\% have already been demonstrated.\textsuperscript{212} A next step toward industrial feasibility is the use of screen-printed metallization.

Another approach, which is compatible with industrial processing, consists of a full-area \textit{n}$^+$ diffusion. [Fig. 26 (iv)]. Richter \textit{et al.} demonstrated efficiencies of 20.8\% for this concept using an Al$_2$O$_3$/SiN$_x$ stack on the front side \textit{p}$^+$ emitter (90 $\Omega$/sq) in combination with screenprinting technology.\textsuperscript{111} The \textit{p}$–$\textit{n} junction can also be formed at the rear side by the formation of an \textit{Al}$^+$ \textit{p}$^+$ emitter and efficiencies up to 19.8\% have been reported.\textsuperscript{214} It is evident that both cells are limited by the properties of the rear side, which does not comprise dielectric passivation. Therefore, to further improve the energy conversion efficiency, a passivated rear with local contacts can be implemented similar to \textit{p}-type PERC cells. In a preliminary study, SiN$_x$ and SiON$_x$/SiN$_x$ stacks have been evaluated for the passivation of the rear \textit{n}$^+$ BSF.\textsuperscript{215} In combination with a stack comprising 0.5 nm Al$_2$O$_3$ and 70 nm SiN$_x$ on the front side, a significantly enhanced $V_{oc}$ of 671 mV was obtained, which represented an increase of \textasciitilde 15 mV compared to the cell with fully metalized BSF. At Q-Cells, the potential of concept (viii) was evaluated (Fig. 26). As the \textit{p}$–$\textit{n} junction is moved to the rear side, the front side can be manufactured similarly to conventional industrial \textit{p}-type cells. First results already demonstrated a promising efficiency of 20.2\% for large area Cz cells using industrially feasible techniques (passivation materials not disclosed).\textsuperscript{216}

In addition to the PERL and PERT cells, various other \textit{n}-type cell designs have the potential of high efficiencies and can
therewith exploit the benefits of n-type Si over p-type Si base material. Bifacial cells [Fig. 26 (ix)] have attracted considerable attention due to the simplicity of the rear side, which does not require any structuring or local opening of the passivation layer. Efficiencies of 19.5% have been reported for industrially produced cells by Yingli in collaboration with Energy Center Netherlands.215 Although promising, to our knowledge no results have been reported for n-type bifacial cells with Al2O3 passivation as yet. Another concept compatible with very high efficiencies is the so-called interdigitated backcontacted (IBC) cell design, which has been commercialized by Sunpower. Exceptionally high efficiencies up to 24.2% have been realized.219 Low recombination on the front side—obtained by effective surface passivation and/or the implementation of an FSF—and in the Si bulk are crucial as the minority carriers generated near the front side have to diffuse to the rear p–n junction. At the rear side, a passivation scheme compatible with both n+ and p–type Si is required. Moreover, depending on cell design, the passivation scheme needs to ensure excellent electrical insulation as the oversized metal contacts (of the n+ BSF) need to be isolated from the emitter underneath. Gong et al. reported that higher implied Voc values were obtained when using Al2O3 instead of SiO2/SiNx on the Al-p+ emitters, but this was not yet corroborated on the solar cell level.218 Reichel et al. have reported efficiencies up to 23% for IBC cells, but no details were given concerning the rear side passivation.219 IBC cells with a screen-printed Al-p+ emitter have been reported by Bock et al. For these cells with Al2O3 passivation on the rear side, efficiencies of 19% were obtained with significant room for improvement up to 21.3%, as suggested by device simulations.220 Another backcontacted cell concept is the so-called emitter wrap through (EWT) cell. In this cell concept, the requirements on the bulk lifetime and front side recombination are less strict than in the IBC concept. Therefore, a separate diffusion for the front side is not necessary for the EWT cells. Kiefer et al. reported a cell efficiency of 21.6% for EWT cells using Al2O3/SiNx passivation on the front and rear side p+ emitter.221 Low Jsc of 60 and 35 fA/cm² were reported for the textured and planar p+ emitter (~50 Ω/sq) surfaces. For the n+ BSF, the Al2O3/SiNx layers were deposited on top of a thermally grown SiO2 layer. Note that Sun et al. employed such an SiO2/Al2O3 stack at the rear of p-type PERC cells and reported excellent passivation properties and η = 20.1%.222 The SiO2/Al2O3 stack system leads to a high level of chemical passivation (Sec. VI B). Moreover, the absence of significant negative fixed charge density in the SiO2/Al2O3 is expected to be beneficial for the passivation of n+ surfaces.

Finally, heterojunction (HJ) cells critically rely on an excellent level of surface passivation, typically realized by using undoped a-Si:H thin films below the p- and n-doped a-Si:H films [Fig. 26 (xii)]. The latter concept is used in the successful Heterojunction with Intrinsic Thin Layer cells commercialized by Sanyo.11,84 Note that HJ technology can also be combined with the IBC concept for realizing high Voc and Jsc.81 It is expected that the passivation properties of Al2O3 films can be exploited for HJ cells using innovative approaches and cell designs. For example, Al2O3 could be applied on a front side (diffused) p+ emitter for cells with an n+ heterojunction at the rear side.9

VIII. CONCLUDING REMARKS

In this article the fast-growing activities relating to Al2O3 thin films applied for the passivation of Si surfaces since 2006 have been reviewed. The appearance of Al2O3 as a very effective passivation material was not anticipated in the field, where surface passivation schemes had primarily been based on Si-containing films (e.g., SiO2, a-SiNₓ, and a-Si:H). Compared to these other materials, a distinguishing characteristic of the Al2O3 films is field-effect passivation induced by negative fixed charges. Nonetheless, the very low defect densities (D is < 10¹¹ eV⁻¹ cm⁻²) induced by the films are also essential for the low surface recombination velocities that have been reported for p, p+, and n-type Si. Depending on sheet resistance, Al2O3 may even contribute to sufficiently low emitter saturation current densities for n+ Si, although SiO2/Al2O3 stacks without negative charges are likely preferable.

Atomic layer deposition is also novel in the field of c-Si photovoltaics. Because of its precise thickness control, ALD is ideally suited for engineering the Si surface and tailoring the properties of nanolayer surface passivation schemes. For example, ultrathin SiO2 interlayers have been used to control the fixed charge density associated with Al2O3. In addition, the application of just a few ALD Al2O3 cycles, prior to a-SiNx deposition, was demonstrated to be already sufficient to improve the passivation properties of p+ emitters. Other enticing possibilities for the future may include the use of ALD for ultrathin pinhole-free inversion, barrier and tunneling layers, selectively doped films, and stacks in combination with transparent conductive oxides. This may contribute to developments regarding novel low-recombination contact and metallization schemes.

The use of ALD is no longer limited to ultrathin films of only a few nanometers. With the availability—and further development—of spatial ALD and large-scale batch reactors, ALD may soon be a technologically and cost-effective deposition process for the PV industry. The industry at large has been relying on the successful screen-printed Al-BSF technology for the last few decades, but it is expected that the PERC-type solar cells featuring dielectric rear side passivation will become a prominent technology in the next few years. Subsequently, and partially concurrently, higher efficiency n-type Si cells featuring passivation on the front and rear sides will play an increasingly important role. It has been demonstrated that Al2O3, deposited either by ALD or PECVD, and in combination with an a-SiNx:H capping layer, provides a metallization-stable solution for both p- and n-type Si cells. Nonetheless, the integration of the (novel) technologies (i.e., cleaning, deposition, contacting methods) in industrial process flows can still pose challenges. In addition, methods to monitor the passivation quality during manufacturing have to be developed. Appropriate tests (e.g., accelerated aging) to determine the long-term
field performance of surface passivation films are also not available yet.

In the broader field of photovoltaics, surface passivation schemes based on ALD Al\textsubscript{2}O\textsubscript{3} may be a natural choice for field performance of surface passivation films are also not available yet. schemes based on ALD Al\textsubscript{2}O\textsubscript{3} may be a natural choice for the large-scale adoption of sustainable energy sources, we hope that the technology described in this paper will contribute significantly to improving the conversion efficiency of industrial solar cells and further reducing the price of solar electricity on the short term.

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