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“Zero-charge” SiO$_2$/Al$_2$O$_3$ stacks for the simultaneous passivation of $n^+$ and $p^+$ doped silicon surfaces by atomic layer deposition

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A B S T R A C T

To achieve high conversion efficiencies, advanced silicon solar architectures such as interdigitated back contact solar cells demand that defects at both the $n^+$ and $p^+$ doped Si surfaces are passivated simultaneously by a single passivation scheme. In this work, corona charging experiments show that the fixed charge density $Q_f$ is a key parameter governing the passivation of both surface types. Alternatively, $Q_f$ can be controlled from strongly negative to even positive values by carefully tuning the SiO$_2$ interlayer thickness in SiO$_2$/Al$_2$O$_3$ stacks prepared by atomic layer deposition (ALD). This control in $Q_f$ allows for a superior passivation of $n^+$ Si surfaces by SiO$_2$/Al$_2$O$_3$ stacks compared to a single layer Al$_2$O$_3$. For instance, for SiO$_2$ interlayer thicknesses of ~3–14 nm, the recombination parameter of an $n^+$ Si surface having a high surface doping concentration $N_s$ of $2 \times 10^{20}$ cm$^{-3}$ was reduced from $J_{0n} = 81 \text{ fA/cm}^2$ to $J_{0n} = 50 \text{ fA/cm}^2$. Simulations predict that the SiO$_2$/Al$_2$O$_3$ stacks outperform Al$_2$O$_3$ passivation layers particularly on $n^+$ Si surfaces having a moderate $N_s$ in the range of $10^{18}$–$10^{20}$ cm$^{-3}$. On $p^+$ Si surfaces, $J_{0p} \leq 54 \text{ fA/cm}^2$ was achieved for all SiO$_2$ interlayer thicknesses investigated (i.e., 1–14 nm). The SiO$_2$/Al$_2$O$_3$ stacks presented in this work are compatible with SiN$_x$ capping and subsequent high-temperature firing steps, which are typically used in solar cell processing. Furthermore, the results were successfully reproduced in an industrial ALD batch reactor using a low-temperature process. This makes ALD SiO$_2$/Al$_2$O$_3$ stacks a promising candidate for the simultaneous passivation of $n^+$ and $p^+$ Si surfaces in solar cells.

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1. Introduction

A high level of surface passivation is a prerequisite to achieve crystalline silicon solar cells with high conversion efficiencies. Less than a decade ago, it was reported that Al$_2$O$_3$ films prepared by atomic layer deposition (ALD) provide superior passivation of $p$ and $p^+$-type Si surfaces, which was technologically challenging at that time [1–3]. The excellent passivation by Al$_2$O$_3$ can be related to a very low interface defect density $D_0$ ($< 10^{11}$ cm$^{-2}$) on Si, which is essential for chemical passivation. Furthermore, a high negative (fixed) charge density $Q_f$ in the order of $10^{12}$–$10^{13}$ cm$^{-2}$ (depending on synthesis method) is present at the interface [4], which reduces the minority carrier (i.e., electron) concentration near the Si surface, providing field-effect passivation. Even an ultrathin film of Al$_2$O$_3$ of less than 2 nm was found to be sufficient to passivate the Si surface, when combined with a-SiN$_x$:H (in short SiN$_x$) as anti-reflection coating (ARC) and/or capping layer [5,6]. The high levels of surface passivation provided by Al$_2$O$_3$ allow for solar cells with high conversion efficiency, including $p$-type concepts (e.g., PERC or Al–LBSF cells [7,8]) as well as $n$-type concepts such as PERL cells [9]. Due to superior uniformity and passivation performance, ALD of Al$_2$O$_3$ is currently piloted in industry [10].

Despite the excellent results on $p$-type Si, on heavily doped $n^+$ Si surfaces the passivation of Al$_2$O$_3$ is compromised, as the minority carrier (i.e., hole) concentration at the surface is increased by the negative $Q_f$ of the Al$_2$O$_3$ [11,12]. On lowly doped $n$-type Si, Al$_2$O$_3$ generally passivates the surface well, as it induces strong near-surface inversion. However, inversion layers are associated with a lifetime reduction at low injection levels ($\Delta n < 10^{15}$ cm$^{-3}$), which is within the operating regime of solar cells [13–15]. Secondly, besides affecting the surface passivation, inversion layers potentially act as undesired conduction pathways to metal contacts. Such a pathway (sometimes referred to as parasitic shunting) affects the performance of solar cells via the fill-factor, short-
circuit current and open-circuit voltage [16]. All of these unfavorable effects occur not only when n or n⁺-type Si surfaces are passivated by the negative charge dielectric Al₂O₃, but they also take place when p or p⁺-type Si surfaces are passivated by a dielectric containing a positive charge density, such as SiNₓ.

In conventional diffused-junction Si solar cells, the n⁺ and p⁺ doped surfaces are located at each side of the cell, and hence can be passivated independently by a dielectric having the right charge polarity. However, in more advanced solar cell architectures such as interdigitated back-contact (IBC) cells, or in even more advanced axial Si nanowire cells [17], the n⁺ and p⁺ doped Si surfaces are adjacent and preferably passivated simultaneously by one film or film stack. Hence, the aim of this work is to achieve the passivation of both n⁺ and p⁺ Si surfaces via a low-temperature and industrially viable deposition process. To this end, we propose the use of a passivation scheme without significant Qᵣ, while providing very low Dᵣ, rather than relying on a fixed charge density to reduce one of the two charge carrier types at the surface, such as a “zero-charge” passivation approach could rely on high surface doping concentrations of the n⁺ and p⁺ Si regions, which reduces the minority carrier concentration at the surface and in this way suppresses surface recombination.

In literature, there are several ways reported to manipulate the passivation of n⁺ and p⁺ Si surfaces [18–22]. For instance, to reduce the negative Qᵣ of Al₂O₃, the films can be deposited at high deposition temperatures (i.e., 300–400 °C, e.g., 200 °C), although this adversely affects the level of chemical passivation [23]. Secondly, the negative Qᵣ of thin Al₂O₃ films can be reduced when it is combined with SiNₓ capping and a subsequent high-temperature firing step ≥ 800 °C [21,25]. Such Al₂O₃/SiNₓ stacks show promising results on both n⁺ and p⁺ Si surfaces with various sheet resistances, irrespective of whether the Al₂O₃ films are deposited by PE-CVD [18], or ALD [21,22]. Nonetheless, these stacks exhibit a significant negative Qᵣ of n = (1–2) × 10¹² cm⁻² [18,21,25], which is likely still affecting the passivation of n⁺ Si surfaces. Alternatively, it is known already for a long time that an interfacial SiO₂ layer strongly reduces the fixed charge density of Al₂O₃ layers [26,27]. In fact, various interlayers can be used to reduce the Qᵣ of Al₂O₃ layers to virtually zero. This includes SiO₂ layers prepared by ALD [13,28] and by plasma-enhanced chemical vapor deposition (PECVD) [20], thermally-grown SiO₂ [29], but also other materials such as HF₂O₂ [30]. Moreover, when SiO₂ is combined with other capping layers, such as in SiO₂/SiNₓ or SiO₂/Al₂O₃/SiNₓ stacks, very low charge densities can be obtained [7,29,31], although this strongly depends on the SiO₂ thickness and process conditions [7,29]. To achieve passivation of n⁺ and p⁺ Si surfaces, for example wet-chemical or PE-CVD SiO₂ films in combination with PE-CVD SiNₓ capping layers [19,22], and PE-CVD SiO₂/Al₂O₃ stacks with varying SiO₂ film thicknesses have been studied [20]. SiO₂/Al₂O₃ stacks which are fully prepared by ALD are very promising candidates as “zero-charge” passivation schemes for n⁺ and p⁺ Si surfaces. It has been reported by Dingemans et al. [13] and Terlinden et al. [28] that those stacks exhibit excellent chemical passivation levels (e.g., Dᵤ values < 10¹¹ eV⁻¹ cm⁻²) at mid gap [32], while their Qᵣ can effectively be tuned from strongly negative up to zero or even positive values by carefully tuning the ALD SiO₂ thickness. It is hypothesized that for these stacks the SiO₂ interlayer acts as a (trap-assisted) electron tunnel barrier, preventing charge-injection from the c-Si base into the electron trap sites in the Al₂O₃ [13,28]. The Al₂O₃ plays a key role in the reduction of Si/SiO₂ interface defect states, which are effectively passivated by the diffusion of hydrogen from the Al₂O₃ film to the Si/SiO₂ interface during annealing [33]. ALD SiO₂/Al₂O₃ stacks have the advantage that they can be prepared at relatively low temperatures (e.g., 200 °C), are conformal even over high-aspect ratio structures and can be prepared in a single deposition run [13,28,34]. The ALD stacks can potentially be used in high-volume manufacturing for the simultaneous passivation of both sides of IBC cells or bifacial cells. Moreover, very promising results containing the passivation of both sides of PERC cells have recently been reported for stacks having 5 nm ALD SiO₂ films [35].

In previous work dealing with the passivation of n⁺ and p⁺ Si surfaces, the influence of the fixed charge density on the passivation was not fully addressed yet. In this work, first the influence of the charge density on the passivation of these surfaces is investigated via corona charging experiments. The results serve as a benchmark for the next part of the paper, where we will carefully tune the SiO₂ interlayer thickness to control the fixed charge density of ALD SiO₂/Al₂O₃ stacks and will study its applicability as passivation scheme of both n⁺ and p⁺ Si surfaces. Next, the role of surface doping concentration on the passivation properties will be discussed. Finally, we will study the compatibility of ALD SiO₂/Al₂O₃ films as “zero-charge” passivation scheme with typical Si solar cell processing, such as the compatibility with SiNₓ capping layers and high-temperature processing steps.

2. Experimental

Symmetrical n⁺/p/n⁺ lifetime samples were made by POCl₃ diffusions in an industry-scale tube furnace process (Tempress systems TS81003) on double-side chemically polished, p-type Czochralski-grown (Cz) Si (100) wafers. In another tube of the furnace, symmetrical n⁺/n/p⁺ lifetime samples were fabricated using BBr₃ as precursor, on Cz n-type wafers with a random-pyramid textured surface. After diffusion, the surface doping concentration of the n⁺/p⁺ sample was increased by a short wet etch [36]. The resulting (active) doping profiles were determined from electrochemical capacitance–voltage (ECV) profiling (see Fig. 1) using a WEP wafer profiler CVP21 table-top unit. Note, that the doping profile of the boron-doped samples can be affected by the texture of the surface, and a heavier doping level can be expected at the pyramid tips [37]. The sheet resistance and the homogeneity of the doped regions were measured using a Signatone four-point probe, in combination with a Keithley 2400 Source Measurement Unit.

After glass removal, the samples received a short dip in diluted HF (1%, 1 min). Subsequently, SiO₂/Al₂O₃ stacks and Al₂O₃ films were deposited on both sides of the samples by plasma-enhanced ALD in an Oxford Instruments OpAL™ reactor at 200 °C in a single deposition run, H₂Sil(N(C₂H₅)₂)₂ and Al(CH₃)₃ were used as metal-organic precursors and O₂ plasma as oxidant. More details on the ALD processes can be found elsewhere [34]. A schematic display of the passivated lifetime samples is given in Fig. 2. To activate the passivation, the stacks were either annealed for 10 min at 400 °C in N₂, or capped with 70 nm SiNₓ, followed by an industrial firing step (~800 °C for 1 s). The SiNₓ was prepared by in-line PE-CVD reactor (MAIA, Roth and Rau), equipped with a microwave plasma source. As deposited, the SiNₓ has a refractive index of n = 2.05 at 633 nm.

A lifetime tester (Sinton WCT 100) was used for quasi-steady state photoconductance decay (QSS-PC) and transient-PC measurements. Using QSS-PC the recombination parameter J₀ was derived at high injection levels of Δn ~ (0.4–6.2) × 10¹⁶ cm⁻³ using the method of Kane and Swanson [38], which allows the extraction of J₀ from lifetime measurements via

\[
\frac{1}{\tau_{\text{eff}}} - \frac{1}{\tau_{\text{Auger}}} = \frac{1}{\tau_{\text{SH}}} + \frac{J_0}{n_0 \Delta n \tau_{\text{Auger}}} \frac{q n W}{\Delta n} \tag{1}
\]
end, the symmetrically doped lifetime samples were passivated by the (bulk) Auger lifetime, $\tau_{\text{Auger}}$ the Shockley–Read–Hall (SRH) lifetime of the bulk, $n_i$ the intrinsic carrier concentration, $q$ the elementary charge, $W$ the wafer thickness and $N_d$ the base doping concentration. Importantly, it was verified that the method of Kane and Swanson could be used for all samples in this work, as straight lines were observed for the Auger-corrected inverse lifetime plots. Note, that $j_0$ values of the $p^+/n^+$ doped samples were divided by a factor of 1.7 to account for the increase in surface area due to the surface texture of these samples.

Corona charging measurements were carried out by depositing (positive) corona charges on both sides of the lifetime samples which were passivated by Al$_2$O$_3$. The charges were deposited by applying a DC-bias (± 11 kV) between a tungsten needle and a grounded plate to ionize air molecules. After charge deposition step lifetime measurements were performed. Additionally, the deposited density of corona-charges $Q_{\text{corona}}$ was derived from Kelvin probe potential measurements, using a Trek electrostatic voltmeter. Note that the deposited charge density on the Al$_2$O$_3$ surface was found to be stable for days, even when placing the charged surfaces directly onto a grounded metal.

3. Results

3.1. The influence of fixed charges on the passivation of $n^+$ and $p^+$ Si

Before investigating the passivation quality of SiO$_2$/Al$_2$O$_3$ stacks, it is illustrative to demonstrate the effect of fixed charges on the passivation of both $n^+$ and $p^+$ doped Si surfaces. To this end, the symmetrically doped lifetime samples were passivated by a single-layer of Al$_2$O$_3$, after which lifetime measurements and positive corona charging on both sides were carried out in a step-wise fashion. In this way, the net charge density $Q_{\text{net}}$ was varied from being strongly negative (i.e., $Q_{\text{net}} = -5 \cdot 10^{12}$ cm$^{-2}$), which corresponds to $Q_{f}$ of the (ALD) Al$_2$O$_3$ films [39] to positive values of $+5 \cdot 10^{12}$ cm$^{-2}$.

In Fig. 3a, the results of $n^+/p^+$ samples are given. Prior to deposition, the level of surface passivation provided by the Al$_2$O$_3$ results in $J_{\text{on}}$ = 79 fA/cm$^2$. When changing the net charge density via corona charging towards a more positive $Q_f$, $J_{\text{on}}$ decreases. The decrease in $J_{\text{on}}$ can be understood as the more positive fixed charge will reduce the minority carrier (i.e., hole) concentration at the surface. A similar trend was observed in Ref. [11] for corona charging experiments on highly $n$-doped surfaces passivated by Al$_2$O$_3$. However, note that also opposite trends are observed in case of lowly doped $n$-type Si surfaces passivated by Al$_2$O$_3$. [39]. There, positive corona charging first results in an increase of surface recombination. For such lowly doped surfaces, an inversion layer is formed near the Si surface by the negative $Q$ of Al$_2$O$_3$, after which the surface is gradually moved to depletion and consequently accumulation by positive corona charging. Therefore, we can conclude that the highly-doped $n^+$ Si surfaces used in this work were not in inversion, not even for the highest negative fixed charge densities. For high positive $Q_{\text{net}}$ = $4.9 \times 10^{12}$ cm$^{-2}$, the reduction of $J_{\text{on}}$ saturated at $J_{\text{on}}$ = 50 fA/cm$^2$, behavior which is observed more often for such high charge doses [11,40]. Simulations using the free-ware program EDNA [41], using Fermi–Dirac statistics, the Auger parameterization from Richter et al. [42] and the band-gap narrowing model of Schenk [43], indicate that the Auger limit of the $n^+$ region is $J_{\text{on}}$,Auger = 16 fA/cm$^2$. This significant difference $\Delta J_{\text{on}}$ of 34 fA/cm$^2$ can indicate the presence of other recombination processes in the $n^+$ doped region, potentially due to SRH recombination via inactive phosphorus precipitates [44,45].

On the $p^+/n^+$ doped samples in Fig. 3b, the opposite behavior in Fig. 3a is obtained when depositing positive corona charges, and a strong increase in $J_{\text{op}}$, can be observed. On the $p^+$ Si surface a negative $Q_f$ provides strong field-effect passivation, enabling very low $J_{\text{op}}$ = 32 fA/cm$^2$ for Al$_2$O$_3$. EDNA simulations indicate that this value within error equal to the (lower) limit set by Auger recombination, i.e., $J_{\text{op}}$,Auger = 35 fA/cm$^2$.

Interestingly, the recombination parameter of the $p^+/n^+$ sample is much more sensitive to the total fixed charge density than the $n^+/p^+$ sample, as is evident from the drastic increase in $J_{\text{op}}$ to ~490 fA/cm$^2$ at $Q_{\text{net}}$ = $5.7 \cdot 10^{12}$ cm$^{-2}$. This higher sensitivity to $Q_f$ of $J_{\text{op}}$, compared to $J_{\text{on}}$, can be explained by two
Considering the fact that in an actual solar cell, the surface surfaces should be passivated by a single passivation scheme. Qf properties such as (boron-) surface doping concentration (provided that the interface surfaces in a case without $N_s$ regions as compared to the phosphorus doped surfaces (i.e., relatively low surface doping concentration of the boron-doped in a separate publication. Nonetheless, we can state here that the recombination rate is rather complex, and will be treated in detail the exact interplay between the highly doped region and the surface surface recombination, which has not been discussed so far. The doping profile have an influence on the surface recombination, which has not been discussed so far. The exact interplay between the highly doped region and the surface recombination rate is rather complex, and will be treated in detail in a separate publication. Nonetheless, we can state here that the relative low surface doping concentration of the boron-doped regions as compared to the phosphorus doped surfaces (i.e., $N_n=9 \cdot 10^{19}$ cm$^{-3}$ versus $\sim 2 \cdot 10^{20}$ cm$^{-3}$, respectively) plays a key role in the increased sensitivity of $J_{0p}$. A route to further reduce the recombination at $p^+$ Si surfaces in a case without fixed charges is therefore to increase the surface doping concentration (provided that the interface properties such as $Q_f$ and $D_n$ are independent of surface doping level), as will be further discussed in Section 3.3. The boron surface doping concentration could for instance be increased by etching of the boron-depletion region (BDR) which is typically present near the surface [36].

Finally, it is interesting to look at a case where $n^+$ and $p^+$ Si surfaces should be passivated by a single passivation scheme. Considering the fact that in an actual solar cell, the surface recombination also scales with the surface areas of the $n^+$ and $p^+$ region, i.e., $A_{p^+}$ and $A_{n^+}$ respectively, we have evaluated several different cases using the interpolation of the corona charging results of Fig. 3a and b. In case of equal area fractions $A_{n^+}=A_{p^+}=A_{S}=(1:1)$, which, for instance, would be the case when both front and back-side of a bifacial solar cell are passivated at once, a value of $Q_{net}=-4 \cdot 10^{12}$ cm$^{-2}$ would result in the lowest average $J_0$. For $p$-type based IBC cells, it is common that $A_{p^+}$ at the back side to prevent electrical shading, (or conversely, $A_{n^+}$ for $n$-type Si based IBC cells [50]). As can be seen from Fig. 3c, the optimum charge density in terms of $J_0$ shifts from $Q_{net}=-4 \cdot 10^{12}$ cm$^{-2}$ for $A_{n^+}=A_{p^+}=(1:1)$, towards $Q_{net}=0$ for the fraction $A_{n^+}=2 \cdot A_{p^+}$ (1:20).

To summarize, it can be concluded that the fixed charge density is an important parameter when optimizing the simultaneous passivation of $n^+$ and $p^+$ doped Si surfaces. The optimum charge density will in practice vary from case to case, and is dependent on the doping profile and the area fractions of the $n^+$ and $p^+$ doped regions. In particular on $p^+$ Si surfaces, the passivation shows a strong dependence on the charge density, most likely due to a moderate level of chemical passivation and a relative low surface doping concentration (i.e., below $< 10^{20}$ cm$^{-3}$).

### 3.2. Passivation of $n^+$ and $p^+$ Si surfaces by ALD SiO$_2$/Al$_2$O$_3$ stacks

It is clear that the control in fixed charge density and polarity provides an additional parameter to optimize the passivation of both $n^+$ and $p^+$ Si surfaces. Next, we will investigate the possibility to optimize this passivation by precisely tuning the ALD SiO$_2$ interlayer thickness of the SiO$_2$/Al$_2$O$_3$ stack between 0 and 14.4 nm. It has been hypothesized, that an ALD SiO$_2$ interlayer of...
2–4 nm thickness prevents the charge-injection from the Si into trap sites in the Al2O3 layers [28]. Therefore, the negative Q of SiO2/Al2O3 stacks rapidly decreases towards virtually zero for these SiO2 thicknesses. It should be noted that also some positive charge formation in the SiO2 film can occur (this is a “bulk” charge, instead of “interface” charge as is the case for Al2O3 films). However, this charge density is relatively low (10^13 cm^-2) for ALD SiO2 films and is therefore only partly contributing to the nullification of Q of the SiO2/Al2O3 stacks [28]. Yet, due to these positive bulk charges in the SiO2 film, the overall charge polarity of the SiO2/Al2O3 stacks becomes slightly positive for increasing ALD SiO2 thicknesses (i.e., Q changes from 10^13 to 10^12 cm^-2 for all ALD SiO2 thicknesses with 12–16 nm thick SiO2 interlayer [28]).

In Fig. 3d, Jn vs. of the n+/p- samples passivated by single layer Al2O3 or SiO2/Al2O3 stacks are shown for varying SiO2/Al2O3 interlayer thickness. For all cases where ALD SiO2 was present (i.e., 1–14.4 nm), the combination parameter Jn - was reduced when compared to single-layer Al2O3 films. For instance, SiO2/Al2O3 stacks having an ultra-thin ALD SiO2 interlayer of 3.6 nm thickness, results in the significant improvement in Jn - as compared to single layer Al2O3 from 81 to 50 fA/cm^2. This improvement is in line with the expected transition from negative to positive charges, as a negative Q was undesirable for the passivation of n+ Si surfaces, as also the corona charging experiments have pointed out. Interestingly, no further decrease in Jn - was observed for SiO2 films with thicknesses > 3.6 nm. The lowest values of Jn - correspond well to the final Jn - values after positive corona charging of 50 fA/cm^2. This further supports the hypothesis that recombination in the n+ doped region itself is limiting Jn - under these circumstances.

On n+/p- samples, Jp+ gradually increases with increasing ALD SiO2 thickness from 32 fA/cm^2 for single-layer Al2O3 to 52 fA/cm^2 for 14.4 nm ALD SiO2 (Fig. 3e). This increase in Jp+ can be explained by the reduction in negative Q and accompanying loss in field-effect passivation. It is notable that the maximal Jp+ values obtained for SiO2/Al2O3 stacks (i.e., Jp+ < 54 fA/cm^2 for all ALD SiO2 thicknesses investigated) are significantly lower than the charged samples passivated by Al2O3, having Jp+ = 95 fA/cm^2 for Qn ~ 0 cm^-2. This could indicate that the introduction of ALD SiO2 stacks also improves the chemical passivation compared to single-layer Al2O3, as is also observed in literature by a slight decrease in Dq [44]. Further evidence for this improved chemical passivation can be found on the n- Si surface, where the Jn - values obtained from SiO2/Al2O3 stacks (for 3.6–14.4 nm ALD SiO2) are lower than what would be expected on the basis of corona charging of Al2O3 passivated samples with Qn = 0.

To simulate the (average) recombination parameter in case both surface types would be passivated by SiO2/Al2O3 stacks, the results of n+ and p+ Si are combined in Fig. 3f. The results show an optimal ALD SiO2 thickness of 2–5 nm in case An = Ap = (1:1), having a significantly lower average Jn - compared to single layer Al2O3 film (Jp+ = 44 versus 55 fA/cm^2, respectively). For Ap > An+, the optimal SiO2 thickness becomes less critical and ~3–12 nm SiO2 is preferred.

3.3. Role of surface doping concentration

Besides being dependent upon the relative areas of both regions, the optimal SiO2 thickness in ALD SiO2/Al2O3 stacks to passivate both n+ and p+ surfaces is also dependent upon the doping concentrations of both surfaces. Note that in this work, corona charging indicated that the n+ doped surfaces are depleted. Apparently, the high negative Q of the Al2O3 is insufficient to induce inversion on these highly doped surfaces, having a phosphorus surface concentration of Np~2.10^20 cm^-3. Using the device simulation package Atlas [51], the Jn - values belonging to Gaussian-shaped n+ doping profiles having different surface doping concentrations and a fixed depth of 0.1 μm were calculated. Note that the commonly reported effective surface recombination velocity S_eff typically varies with surface doping concentration [52]. However, S_eff was not required as input parameter for the Atlas simulations. Instead, the simulations are based on the assumption that the interface input parameters Q, S_n and S_p (being the fundamental surface recombination velocities for electrons and holes respectively) are independent of the surface doping concentration. For S_n and Q of ALD Al2O3 films this was recently experimentally proven for boron-doped surfaces having Np in the range of 9·10^15–3·10^19 cm^-3 [53]. The simulations allow for the identification of the different contributions to the total recombination of the highly-doped region Jn - , that is the contribution of Auger, surface, defect and radiative recombination.

\[
J_n = J_{n,\text{Auger}} + J_{n,\text{surface}} + J_{n,\text{Sti}} + J_{n,\text{radiative}}
\] (2)

The results for Jn_surface are presented in Fig. 4. It can be seen that for moderate surface doping concentrations (Np~10^17 cm^-3), low Jn_surface values are obtained for all Q_i values investigated. However, in case of a negative Q_i the near surface region is strongly inverted which is why Al2O3 single layers will likely passivate very well. Nevertheless, as it is mentioned in Section 1, inversion conditions are undesirable in solar cells due to inversion layer recombination and potential parasitic shunting [15]. For higher n+ Si surface doping concentrations within the range of 10^18–10^20 cm^-3, Jn_surface is severely increased for dielectrics having a strong negative Q (such as for Al2O3), which is in line with the experimental observations by others [11,12,21]. This strong surface recombination occurs when the n+ surface transitions from depletion to inversion, and the concentrations of electrons and holes at the surface (n and p, respectively) satisfy the condition \(p \varepsilon p=\sigma n \mu n\) [54]. Interestingly, the simulations predict that for this particular surface doping range excellent passivation can be maintained in case of Q_i = 0. Therefore, a strong gain in passivation for SiO2/Al2O3 stacks compared to single layer Al2O3 can be expected in the range of surface doping 10^18–10^20 cm^-3. This may
be very relevant when SiO₂/Al₂O₃ stacks are used to passivate a lightly doped n⁺ Si front surface of e.g., an IBC cell.

Although moderate doping concentrations are often desirable to ensure a low Auger recombination (i.e., a low $J_{\text{Auger}}$), it is insightful to consider the effects of very high surface doping concentrations $N_d > 10^{20}$ cm⁻³ on $J_{\text{Auger}}/\text{surface}$. Interestingly, the Atlas simulations show a strongly reduced $J_{\text{Auger}}/\text{surface}$ for all fixed charge densities investigated. This effect can be understood as the high surface doping levels reduce the minority carrier (i.e., hole) concentration at the surface. For these very low $J_{\text{Auger}}/\text{surfaces}$ values, it can be expected from Eq. (2) that surface recombination will become negligible compared to the other recombination mechanisms in the highly doped region, such as Auger and SRH recombination. The results from the simulations can explain the excellent passivation results on highly-doped n⁺ Si surfaces by PE-CVD Al₂O₃/SiNₓ stacks, which are obtained despite of their negative $Q_d$ of $(1-2) \times 10^{12}$ cm⁻² [18], which now can (partly) be attributed to the very high phosphorus surface doping concentration used ($N_d \sim (4-6) \times 10^{20}$ cm⁻³).

Overall, it can be expected that SiO₂/Al₂O₃ stacks will outperform Al₂O₃ passivation schemes in a wide range of phosphorus surface doping concentrations from $\sim 5 \times 10^{17}$ to $\sim 10^{20}$ cm⁻³ due to the absence of a negative $Q_d$, which is the range of practical interest for most solar cell applications.

3.4. Aspects related to application of ALD SiO₂/Al₂O₃ stacks in solar cells

In solar cells, typically thin (~2–5 nm) Al₂O₃ passivation layers are combined with SiNₓ capping layers, which serve as anti-reflection coating when on the front side or as dielectric mirror when on the rear side of the solar cell. Furthermore, to "fire" the (printed) metal contacts through the passivation layers, a very short (~1 s) high temperature anneal at 800 °C (firing step) is typically performed. To study the compatibility of the ALD passivation layers of this work with SiNₓ capping and subsequent firing, various passivation schemes are compared on n⁺/p⁺ lifetime samples in Fig. 5. The passivation schemes include single layer Al₂O₃ and SiO₂/Al₂O₃ stacks with or without SiNₓ capping, and in addition to this, also results from a batch ALD reactor are shown. Interestingly, the passivation of n⁺ Si surfaces by thin Al₂O₃ films capped by SiNₓ, in combination with a firing step (Fig. 5b) leads to a reduced $J_{\text{AR}}$, compared to the thicker reference Al₂O₃ films without SiNₓ capping and firing (Fig. 5a). This can possibly be explained by a reduction in terms of $D_k$ in combination with a reduction of negative $Q_d$, as was observed by Richter et al. for similar passivation schemes after firing [21]. Here, we show that even though Al₂O₃ films capped by SiNₓ can provide excellent passivation of the n⁺ Si surfaces, its passivation could be even further improved by having a thin (3 nm) ALD SiO₂ interlayer. Moreover, the ALD SiO₂/Al₂O₃ films capped by SiNₓ of Fig. 5b yield similar results compared to their reference samples of Fig. 5a. Hence, these initial findings indicate that the application of a SiNₓ capping layer and a high temperature firing step do not significantly affect the passivation level offered by the SiO₂/Al₂O₃ stacks.

The results of Fig. 5b, which were obtained using a single-wafer ALD reactor, could be successfully reproduced by depositing the Al₂O₃ and SiO₂ layers in a batch ALD reactor (see Fig. 5c). This reactor was designed specifically for high-volume manufacturing. Note that in the batch ALD reactor, the passivation layers were deposited on both sides of the lifetime samples at the same time. Moreover, the SiO₂/Al₂O₃ stacks were deposited in a single deposition run without unloading the samples in between. In the batch ALD reactor, O₂ was used as oxidant in the ALD processes, whereas O₃ plasma was used in the single wafer reactor. Despite the differences in reactor geometry and oxidants used, both ALD processes yielded very similar passivation results as can be seen when comparing Fig. 5b with 5c. This demonstrates the robustness and scalability of the ALD processes.

4. Conclusions

In this work, the simultaneous passivation of n⁺ and p⁺ Si surfaces has been investigated. Corona charging experiments on lifetime samples clearly demonstrate that the fixed charge density is a key parameter controlling the passivation of both surface types. It was shown, that by precisely controlling the $Q_f$ in SiO₂/Al₂O₃ stacks via carefully tuning the amount of ALD SiO₂ cycles, a strongly improved passivation on highly-doped n⁺ Si compared to single layer Al₂O₃ films could be achieved. Simultaneously, due to a high level of chemical passivation, a low $J_{\text{AR}}$, and $p^+$ Si could be maintained. Simulations predict that SiO₂/Al₂O₃ stacks have the potential to outperform Al₂O₃ in a wide range of phosphorus surface doping concentrations, most prominently in the range of $10^{16}$–$10^{18}$ cm⁻³. In general, at highly-doped surfaces the condition for maximal surface recombination (i.e., $\sigma_n \cdot n_d \approx \sigma_p \cdot p_d$) is less likely to be met for “zero-charge” passivation schemes.

Initial feasibility studies on the compatibility of the SiO₂/Al₂O₃ stacks with conventional Si solar cell steps, such as capping by a SiNₓ layer and a subsequent high temperature (firing) step, yielded similar results in terms of $J_{\text{AR}}$. Moreover, after successful upscaling of the ALD process from a single-wafer ALD reactor to an industrial batch ALD reactor, similar passivation results were achieved.

In conclusion, this work reveals the opportunities for ALD based passivation schemes to passivate n⁺ and p⁺ Si surfaces either separately or even simultaneously in a single deposition run. These results are particular relevant for the passivation of the back side of IBC solar cells, but are also of interest for the passivation of both sides of a diffused-junction solar cell at once. Further research is currently ongoing to demonstrate the concept of a “zero-charge” passivation scheme on solar cell level.
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