Zero-charge” SiO2/Al2O3 stacks for the simultaneous passivation of n+ and p+ doped silicon surfaces by atomic layer deposition


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To achieve high conversion efficiencies, advanced silicon solar cell 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 \( Q_f \) can be controlled from strongly negative to even positive values by carefully tuning the SiO₂ interlayer thickness in SiO₂/Al₂O₃ stacks prepared by atomic layer deposition (ALD). This control in \( Q_f \) allows for a superior passivation of n⁺ Si surfaces by SiO₂/Al₂O₃ stacks compared to a single layer Al₂O₃. For instance, for SiO₂ interlayer thicknesses of ~3–14 nm, the recombination parameter of an n⁺ Si surface having a high surface doping concentration \( N_s \) of \( 2 \times 10^{19} \) cm\(^{-3} \) was reduced from \( J_{0,n} = 81 \) fA/cm\(^2\) to \( J_{0,n} = 50 \) fA/cm\(^2\). Simulations predict that the SiO₂/Al₂O₃ stacks outperform Al₂O₃ passivation layers particularly on n⁺ Si surfaces having a moderate \( N_s \) in the range of \( 10^{18}–10^{19} \) cm\(^{-3} \). On p⁺ Si surfaces, \( J_{0,p} \leq 54 \) fA/cm\(^2\) was achieved for all ALD SiO₂ interlayer thicknesses investigated (i.e., 1–14 nm). The SiO₂/Al₂O₃ stacks presented in this work are compatible with SiNx 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 SiO₂/Al₂O₃ 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 Al₂O₃ 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 Al₂O₃ can be related to a very low interface defect density \( D_{it} \) (< 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 Al₂O₃ of less than 2 nm was found to be sufficient to passivate the Si surface, when combined with a-SiNₓ:H (in short SiNₓ) as anti-reflection coating (ARC) and/or capping layer [5,6]. The high levels of surface passivation provided by Al₂O₃ 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 Al₂O₃ is currently piloted in industry [10].

Despite the excellent results on p-type Si, on heavily doped n⁺ Si surfaces the passivation of Al₂O₃ is compromised, as the minority carrier (i.e., hole) concentration at the surface is increased by the negative \( Q_t \) of the Al₂O₃ [11,12]. On lowly doped n⁺ Si, Al₂O₃ 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 (\( \Delta \tau < 10^{-15} \) 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 shunt) 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 SiN.

In conventional diffusion-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 Qf, while providing very low D0. Rather than relying on a fixed charge density to reduce one of the two charge carrier types at the surface, such 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 natively present fixed charge density of dielectrics and dielectric stacks, and some of them have been studied to address the simultaneous passivation of n+ and p+ Si surfaces [18–22]. For instance, to reduce the negative Q 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 Q of thin Al2O3 films can be reduced when it is combined with SiN, capping and a subsequent high-temperature firing step ≥ 800 °C [21,25]. Such Al2O3/SiN 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 [15], or ALD [21,22], Nonetheless, these stacks exhibit a significant negative Q 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 Q of Al2O3 layers to virtually zero. This includes SiO2 layers prepared by ALD [13,28] and by plasma-enhanced chemical vapor deposition (PE-CVD) [20], thermally-grown SiO2 [29], but also other materials such as HfO2 [30]. Moreover, when SiO2 is combined with other capping layers, such as in SiO2/SiN or SiO2/Al2O3/SiN stacks, very low charge densities can be obtained [7,29,31], although this strongly depends on the SiO2 thickness and process conditions [7,29,29,31]. To achieve passivation of n+ and p+ Si surfaces, for example wet-chemical or PE-CVD SiO2 films in combination with PE-CVD SiN, 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., Dv values < 1011 eV−1 cm−2 at mid gap [32]), while their Qf 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 electron-injection from the c-Si base into the electron trap sites in the Al2O3 [13,28]. The Al2O3 layers play 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 of 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 SiN, capping layers and high-temperature processing steps.

2. Experimental

Symmetrical n+/p/n+ lifetime samples were made by POCi3 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 p+/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 p+/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 CV2P1 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 OpALTM reactor at 200 °C in a single deposition run. H2Si(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 SiN, followed by an industrial firing step (~800 °C for 1 s). The SiN was prepared by in-line PE-CVD reactor (MAIA, Roth and Rau), equipped with a microwave plasma source. As deposited, the SiN has a refractive index of n = 2.05 at 633 nm.

A lifetime tester (Sinton WCT 100) was used for quasi-steady state photocconductance 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

\[
\frac{1}{\tau_{\text{eff}}} - \frac{1}{\tau_{\text{Auger}}} = \frac{1}{\tau_{\text{SH}}} + J_0 \frac{(N_n + \Delta n)\Delta n}{q\mu_W^2 W}
\]  

(1)
end, the symmetrically doped lifetime samples were passivated by a single-layer of Al₂O₃, 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., \( Q_{\text{net}} = -5 \times 10^{12} \text{ cm}^{-2} \)), which corresponds to \( Q_f \) of the (ALD) Al₂O₃ films \([39]\) to positive values of \( +5 \times 10^{12} \text{ cm}^{-2} \).

In Fig. 3a, the results of \( n^+ / p^+ / n^+ \) samples are given. Prior to deposition, the level of surface passivation provided by the Al₂O₃ results in \( J_{\text{ann}} = 79 \text{ fA/cm}^2 \). When changing the net charge density via corona charging towards a more positive \( Q_f, J_{\text{ann}} \) decreases. The decrease in \( J_{\text{ann}} \) 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 \( n^+ \)-type Si surfaces passivated by Al₂O₃. However, note that also opposite trends are observed in case of lowly doped \( n^+ \)-type Si surfaces passivated by Al₂O₃ \([39]\). 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 \( Q_f \) of Al₂O₃, 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 \( Q_{\text{net}} = 4.9 \times 10^{12} \text{ cm}^{-2} \), the reduction of \( J_{\text{ann}} \) saturated at \( J_{\text{ann}} = 50 \text{ fA/cm}^2 \), 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 \( J_{\text{ann}-\text{Auger}} = 16 \text{ fA/cm}^2 \). This significant difference \( \Delta J_0 \) of 34 fA/cm² 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 \( p^+ / n^+ / p^+ \) 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 \( J_{\text{op}} = 32 \text{ fA/cm}^2 \) for Al₂O₃. EDNA simulations indicate that this value within error equal to the (lower) limit set by Auger recombination, i.e., \( J_{\text{op}}<\text{Auger} = 35 \text{ fA/cm}^2 \).

Interestingly, the recombination parameter of the \( p^+ / n^+ / p^+ \) sample is much more sensitive to the total fixed charge density than the \( n^+ / p^+ / n^+ \) sample, as is evident from the drastic increase in \( J_{\text{op}} \), to \( \sim 490 \text{ fA/cm}^2 \) at \( Q_{\text{net}} = 5.7 \times 10^{12} \text{ cm}^{-2} \). This higher sensitivity to \( Q_f \) of \( J_{\text{op}} \), compared to \( J_{\text{ann}} \), can be explained by two
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., $A_{n^+}$ and $A_{p^+}$, respectively, we have evaluated several different cases using the interpolation of the corona charging results of Fig. 3b and d. In case of equal area fractions $A_{n^+} = A_{p^+} = 1:1$, 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 $Q_{\text{corona}} = -5 \times 10^{12}$ cm$^{-2}$ would result in the lowest average $J_0$ for $p$-type based IBC cells, it is common that $A_{n^+} \times A_{p^+}$ at the back side to prevent electrical shading, (or conversely, $A_{n^+} \times A_{p^+}$ 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 $Q_{\text{corr}} = -4 \times 10^{12}$ cm$^{-2}$ for $A_{n^+} = A_{p^+} = 1:1$, towards $Q_{\text{corr}} = 0$ for the fraction $A_{n^+} = 20 \times A_{p^+}$ (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} \text{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 of 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 ~5 \times 10^{12} \text{cm}^{-2} for Al2O3 only to Q = (4 \pm 2) \times 10^{13} \text{cm}^{-2} for SiO2/Al2O3 stacks with 12–16 nm thick SiO2 interlayer [28]).

In Fig. 3d, J_0, of the n^+/p^− samples passivated by single layer Al2O3 or SiO2/Al2O3 stacks are shown for varying SiO2 interlayer thickness. For all cases where ALD SiO2 was present (i.e., 1–14.4 nm), the recombination parameter J_0, 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 J_0, 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 J_0, was observed for SiO2 films with thicknesses > 3.6 nm. The lowest values of J_0, correspond well to the final J_0, 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 J_0, under these circumstances.

On p^+/n^− samples, J_0, 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 J_0, can be explained by the reduction in negative Q, and accompanying loss in field-effect passivation. It is notable that the maximal J_0, values obtained for SiO2/Al2O3 stacks (i.e., J_0, = 54 fA/cm^2 for all ALD SiO2 thicknesses investigated) are significantly lower than the charged samples passivated by Al2O3, having J_0, = 95 fA/cm^2 for Q_corona ~ 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 D_q [34]. Further evidence for this improved chemical passivation can be found on the n^+ Si surface, where the J_0, 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 Q_corona = 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 A_p, = A_n (1:1), having a significantly lower average J_0 as compared to single layer Al2O3 film (J_0, = 44 versus 55 fA/cm^2, respectively). For A_p, > A_n, 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 N_s ~ 2 \times 10^{20} \text{cm}^{-2}. Using the device simulation package Atlas [51], the J_0, 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_m, and S_p are being the fundamental surface recombination velocities for electrons and holes respectively are independent of the surface doping concentration. For S_m and Q of ALD Al2O3 films this was recently experimentally proven for boron-doped surfaces having N_s in the range of 9 \times 10^{15}–3 \times 10^{17} \text{cm}^{-3} [53]. The simulations allow for the identification of the different contributions to the total recombination of the highly-doped region J_0, that is the contribution of Auger, surface, defect and radiative recombination

\[ J_0, = J_{Auger} + J_{surface} + J_{SiO2} + J_{radiative} \] (2)

The results for J_{surface} are presented in Fig. 4. It can be seen that for moderate surface doping concentrations (N_s ~ 10^{17} \text{cm}^{-3}), low J_{surface} values are obtained for all Q values investigated. However, in case of a negative Q, 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^{19}–10^{20} \text{cm}^{-3}, J_{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_i and p_i respectively) satisfy the condition \(\sigma_{ni} n_i = \sigma_{pi} p_i\) [54]. Interestingly, the simulations predict that for this particular surface doping range excellent passivation can be maintained in case of Q = 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^{19}–10^{20} \text{cm}^{-3}. This may...
be very relevant when SiO$_2$/Al$_2$O$_3$ 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 $J_{Auger}$), it is insightful to consider the effects of very high surface doping concentrations $N_i > 10^{20}$ cm$^{-3}$ on $J_{Auger}$. Interestingly, the Atlas simulations show a strongly reduced $J_{Auger}$ for all fixed charge densities investigated. This effect can be understood as the high surface doping levels reduce the minority carrier (i.e., hole) concentrations investigated. This effect can be understood as the high surface doping levels reduce the minority carrier concentrations.

The results from the simulations can explain the excellent passivation of n$^+$ Si surfaces by PE-CVD Al$_2$O$_3$/SiN$_x$ stacks, which are obtained despite of their negative $Q_f$ of $(1-2) \times 10^{12}$ cm$^{-2}$ [18], which now can (partly) be attributed to the very high phosphorous surface doping concentration used ($N_i \sim (4-6) \times 10^{20}$ cm$^{-3}$).

Overall, it can be expected that SiO$_2$/Al$_2$O$_3$ stacks will outperform Al$_2$O$_3$ passivation schemes in a wide range of phosphorous surface doping concentrations from $\sim 5 \cdot 10^{17}$ to $\sim 10^{20}$ cm$^{-3}$ due to the absence of a negative $Q_f$, which is the range of practical interest for most solar cell applications.

3.4. Aspects related to application of ALD SiO$_2$/Al$_2$O$_3$ stacks in solar cells

In solar cells, typically thin (~2–5 nm) Al$_2$O$_3$ passivation layers are combined with SiN$_x$ 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 SiN$_x$ capping and subsequent firing, various passivation schemes are compared on n$^+$/p$^+$ lifetime samples in Fig. 5. The passivation schemes include single layer Al$_2$O$_3$ and SiO$_2$/Al$_2$O$_3$ stacks with or without SiN$_x$ capping, and in addition to this, also results from a batch ALD reactor are shown. Interestingly, the passivation of n$^+$ Si surfaces by thin Al$_2$O$_3$ films capped by SiN$_x$ in combination with a firing step (Fig. 5b) leads to a reduced $J_{Auger}$, as compared to the thicker reference Al$_2$O$_3$ films without SiN$_x$ 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 $Q_f$ as was observed by Richter et al. for similar passivation schemes after firing [21]. Here, we show that even though Al$_2$O$_3$ films capped by SiN$_x$ can provide excellent passivation of the n$^+$ Si surfaces, its passivation could be even further improved by having a thin (3 nm) ALD SiO$_2$ interlayer. Moreover, the ALD SiO$_2$/Al$_2$O$_3$ films capped by SiN$_x$ of Fig. 5b yield similar results compared to their reference samples of Fig. 5a. Hence, these initial findings indicate that the application of a SiN$_x$ capping layer and a high temperature firing step do not significantly affect the passivation level offered by the SiO$_2$/Al$_2$O$_3$ stacks.

The results of Fig. 5b, which were obtained using a single-wafer ALD reactor, could be successfully reproduced by depositing the Al$_2$O$_3$ and SiO$_2$ 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 SiO$_2$/Al$_2$O$_3$ stacks were deposited in a single deposition run without unloading the samples in between. In the batch ALD reactor, O$_2$ was used as oxidant in the ALD processes, whereas O$_3$ 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 SiO$_2$/Al$_2$O$_3$ stacks via carefully tuning the amount of ALD SiO$_2$ cycles, a strongly improved passivation on highly-doped n$^+$ Si compared to single layer Al$_2$O$_3$ films could be achieved. Simultaneously, due to a high level of chemical passivation, a low $J_{Auger}$ and p$^+$ Si could be maintained. Simulations predict that SiO$_2$/Al$_2$O$_3$ stacks have the potential to outperform Al$_2$O$_3$ in a wide range of phosphorous surface doping concentrations, most prominently in the range of $10^{18}$–$10^{20}$ cm$^{-3}$. In general, at highly-doped surfaces the condition for maximal surface recombination (i.e., $\sigma_n \cdot n_i \approx p_i \cdot \sigma_p$) is less likely to be met for “zero-charge” passivation schemes.

Initial feasibility studies on the compatibility of the SiO$_2$/Al$_2$O$_3$ stacks with conventional Si solar cell steps, such as capping by a SiN$_x$ layer and a subsequent high temperature firing step, yielded similar results in terms of $J_{Auger}$. 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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