Progress in the surface passivation of silicon solar cells

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PROGRESS IN THE SURFACE PASSIVATION OF SILICON SOLAR CELLS

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ABSTRACT: In order to increase the efficiency of silicon-wafer-based solar cells in production well above 20%, it is indispensable to improve the currently applied level of surface passivation at the front as well as at the rear of the cells. This paper focuses on two main challenges: (i) the low-temperature passivation of lowly doped p-type silicon surfaces at the cell rear and (ii) the passivation of highly boron-doped p' emitter surfaces as used at the front of solar cells on high-lifetime n-type silicon wafers. In the past, low surface recombination velocities (<20 cm/s) have been achieved on low-resistivity (~1 Ω·cm) p-type silicon using plasma-enhanced chemical-vapour-deposited (PECVD) silicon nitride (SiNx) as well as amorphous silicon (a-Si). However, the high density of fixed positive charges within the PECVD-SiNx layer induces an inversion layer at the rear of p-type Si cells, producing a detrimental parasitic shunting, which reduces the short-circuit current density by up to 3 mA/cm². The passivation quality of a-Si on the other hand is very temperature sensitive. More recently it has been shown that atomic-layer-deposited (ALD) aluminium oxide (Al2O3) provides an outstanding level of surface passivation, which can be attributed to its extremely high negative fixed charge density in combination with the very gentle deposition technique ALD, leading to low interface state densities. The application of these ALD-Al2O3 layers to the rear of p-type solar cells shows that this new passivation scheme is indeed suitable for high efficiencies and that due to the large negative fixed charge density no parasitic shunting occurs. We also demonstrate that ALD-Al2O3 seems to be the ideal passivation layer for boron-doped p' emitter surfaces. In a direct comparison with other passivation schemes, it is found that Al2O3 even outperforms optimized thermally grown SiO2 and opens the possibility of achieving very large open-circuit voltages up to $V_{oc} = 740$ mV.

Keywords: Silicon, Surface Passivation, Al2O3

1 INTRODUCTION

In high-efficiency laboratory silicon solar cells, surface recombination is very effectively suppressed by means of silicon dioxide (SiO2) grown in a high-temperature (≥900 °C) oxidation process [1]. Very low surface recombination velocities (SRVs) are in particular realized at the lightly doped rear surface, where the combination of a thermally grown SiO2 layer with an evaporated film of Al give – after an additional annealing treatment at ~400°C (the so-called ‘alneal’) – SRVs below 20 cm/s on un-metallized low-resistivity (~1 Ω·cm) p-type silicon wafers [2]. In addition, the SiO2/Al stack at the cell rear acts as an excellent reflector for near-bandgap photons, significantly improving the light trapping properties and hence the short-circuit current of the cell. One of the main reasons why high-temperature oxidation has not been implemented into the majority of industrial processes up to now is the high sensitivity of the a-Si passivation to high-temperature oxidation. In the case of an a-Si passivated cell rear, new problems arise from the high sensitivity of the a-Si passivation to thermal processes. More recently it was shown that thin films of aluminium oxide (Al2O3) grown by atomic layer deposition (ALD) provide an excellent level of surface passivation on low doped (~1 Ω·cm) p- and n-type silicon wafers [9,10,11] as well as on highly boron-doped p' emitters [12]. In the first part of this contribution, we compare the passivation properties of SiNx, a-Si and ALD-Al2O3 regarding the application to the rear of high-efficiency p-type silicon solar cells. The second part of the paper addresses the issue of passivating highly boron-doped p' emitters, which has been a main obstacle in the past for fabricating high-efficiency cells on high-lifetime n-type silicon wafers.
2 PASSIVATION OF UNDIFFUSED p-Si

Figure 1. Comparison of the injection-dependent effective SRVs \( S_{\text{eff}}(\Delta n) \) measured on 1-2 \( \Omega \text{cm} \) p-type float-zone silicon wafers passivated by (i) SiN, deposited by remote-PECVD [13], (ii) intrinsic a-Si deposited in a parallel-plate PECVD reactor [8], and (iii) Al\(_2\)O\(_3\) deposited by means of plasma-assisted ALD [14]. The lines are guides to the eye.

Figure 2. Measured effective SRV \( S_{\text{eff}} \) as a function of the Corona charge density \( Q_c \) and as a function of the Corona charge density \( Q_c \) for dielectric passivation layers of SiN, and Al\(_2\)O\(_3\). The lines are guides to the eye.

Figure 3. PERC-type solar cell structure used to demonstrate the applicability of an Al\(_2\)O\(_3\) rear surface passivation to high-efficiency solar cells.

Note that on \( n \)-type silicon with a resistivity of \( \sim 2 \) \( \Omega \text{cm} \) also very low SRVs of 4 cm/s have been measured over the entire relevant injection range [10,14]. Hence ALD-Al\(_2\)O\(_3\) is also excellently suited for passivating the rear of \( n \)-type silicon solar cells. In Section 4 the potential of all-Al\(_2\)O\(_3\) passivated \( n \)-type cells will be analysed in detail.
The use of electron-beam evaporation. A tunnel oxidation of 2 µm of Aluminium is evaporated on the entire cell rear of 2 mm and a metallization fraction of 4% is used. 20 photolithography mask resulting in a point contact pitchings are etched into the dielectric layers at the rear. A cm2 diffusion windows are photolithographically opened the PERC solar cell by remote-PECVD at 300°C. The cell batches. Using photolithography point contact open-ings are etched into the dielectric layers at the front. The remaining process steps are identical for all three stack consisting of a 30 nm Al 2O3 layer and a 200 nm methyl-aluminum [Al(CH3)3] exposure and an O 2 plasma. The subsequent annealing step as applied in the case of high-positive-ch arge dielectrics, such as SiN, with fixed positive charge densities >10 12 cm -2, it is not possible to quantify the exact rear surface passivation quality from comparison of the cell parameters given in Table 1, as these solar cells are largely limited by the front emitter. The average values of all 4 cells with SiO2 rear passivation show only a very small scatter, demonstrating the high reproducibility of the process. The average parameters of the cells with Al2O3, Al2O3/SiO2 and SiO2 rear passivation agree within the scatter ranges. In particular it is noticeable that the Jsc of the cells with Al2O3 and Al2O3/SiO2 rear surface passivation is not reduced compared to the SiO2-passivated cells. In the case of high-positive-charge dielectrics, such as SiN, with fixed positive charge densities >10^{12} cm^{-2}, it was reported that Jsc is reduced by 1-2 mA/cm² compared to the thermal SiO2 reference, due to the above-described parasitic shunting effect. This effect is not expected in the case of Al2O3 as it is a negative-charge-dielectric inducing an accumulation layer. The cell results summarized in Table 1 confirm the expected non-existence of the parasitic shunting for Al2O3-passivated as well as for Al2O3/SiO2-passivated rear surfaces. The best cell of the entire batch is obtained for the Al2O3/SiO2-passivated cell, resulting in an independently confirmed efficiency of η = 20.6%, a Voc of 660 mV and a Jsc of 39.0 mA/cm².

It is not possible to quantify the exact rear surface passivation quality from comparison of the cell parameters given in Table 1, as these solar cells are largely limited by recombination losses in the front emitter. Hence, we analyze the IQE in the wavelength range 800-1200 nm to determine the rear SRVs of the different rear surface passivation schemes. The symbols in Fig. 4 show the IQE as a function of wavelength λ of PERC cells.

<table>
<thead>
<tr>
<th>Rear side</th>
<th>Cell ID</th>
<th>Voc [mV]</th>
<th>Jsc [mA/cm²]</th>
<th>FF [%]</th>
<th>η [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thermal SiO2 (220 nm)</td>
<td>7_1</td>
<td>656</td>
<td>38.9</td>
<td>80.3</td>
<td>20.5</td>
</tr>
<tr>
<td>Average of 4</td>
<td></td>
<td>655±1</td>
<td>38.4±0.5</td>
<td>80.3±1.3</td>
<td>20.2±0.3</td>
</tr>
<tr>
<td>ALD-Al2O3 (130 nm)</td>
<td>3_3</td>
<td>655</td>
<td>38.7</td>
<td>78.9</td>
<td>20.0*</td>
</tr>
<tr>
<td>Average of 4</td>
<td></td>
<td>656±2</td>
<td>38.6±0.1</td>
<td>79.4±1.4</td>
<td>20.0±0.4</td>
</tr>
<tr>
<td>ALD-Al2O3 (30 nm)/PECVD-SiOx (200 nm)</td>
<td>2_4</td>
<td>660</td>
<td>39.0</td>
<td>80.1</td>
<td>20.6*</td>
</tr>
<tr>
<td>Average of 8</td>
<td></td>
<td>657±2</td>
<td>38.6±0.3</td>
<td>80.4±1.1</td>
<td>20.4±0.4</td>
</tr>
</tbody>
</table>

*Calibrated measurement at Fraunhofer ISE CalLab.
with the three different rear passivation schemes, measured at a fixed bias light intensity of 0.3 suns. The solid lines in Fig. 4 show the fits to the measured data. To model the IQE(λ) dependence we use the software LAS-SIE [16,17], which combines the extended IQE evaluation by Basore [18] with the improved optical model developed by Brendel [19]. The bulk lifetime is assumed to be limited by Auger recombination, resulting in a bulk diffusion length of Lb = 1500 µm for the 0.5 Ωcm p-type silicon material used in this work [20]. As we assume the intrinsic upper limit for the bulk lifetime, the SRVs determined from the IQE analysis are upper limits as well. Table 2 summarizes the rear SRVs S_r and the internal rear reflectances R_r extracted from the IQE analysis. All three rear structures are equally effective reflectors for near-bandgap photons (R_r = 91%). The rear SRV (including recombination at the metal contacts) of the reference cell with alaneled SiO2 amounts to S_r = 90 ± 20 cm/s. The extracted S_r for the cell with single-layer Al2O3 rear passivation is the same as for the SiO2-passivated reference cell, showing that ALD-deposited Al2O3 performs as good as aluminium-annealed high-temperature-grown SiO2. A further reduction in the S_r is obtained for the Al2O3/SiOx stack, resulting in an S_r of only (70 ± 20) cm/s, which we attribute to the hydrogenation of interface states at the Al2O3/Si interface during deposition of the hydrogen-rich SiOx layer.

The effective SRV of a point-contacted rear is given by Fischer’s equation [17]

\[ S_r = \frac{D_s}{W} \left[ \frac{p}{2W} \arctan \left( \frac{2W}{p} \sqrt{\frac{\pi}{f}} \right) \right]^{11} - \exp \left( -\frac{W}{p} \right) + \frac{S_{\text{ass}}}{1 - f} \]

where D_s is the electron diffusion coefficient, W the wafer thickness, p the contact pitch, f the metallization fraction and S_{ass} and S_{pass} are the SRVs on the metallized and on the passivated areas of the rear. According to Eqn. (1) the minimum SRV S_{min} for a point-contact rear with perfect passivation in the non-metallized area (i.e., S_{ass} = 0) is given by the first summand on the right-hand side of Eqn. (1). For our cell structure we determine S_{min} = 73 cm/s (D_s = 23 cm²/s, W = 290 µm, p = 2000 µm, f = 4%, S_{ass} ≥ 10⁵ cm/s). As the S_r of (70 ± 20) cm/s extracted from the IQE analysis is practically identical to the S_{min} calculated using Eqn. (1), we conclude that recombination in the passivated area of the cell rear can be completely neglected. Note that, although a slightly better passivation is obtained in the case of the Al2O3/SiOx stacks, the rear SRV of the single-layer Al2O3-passivated cells is also mainly determined by recombination at the metal contacts. The IQE results clearly prove that atomic-layer-deposited Al2O3 is a very effective new dielectric passivation layer for high-efficiency silicon solar cells.

### 3 PASSIVATION OF B-DOPED p'-EMITTERS

Emitter saturation current densities J_0e of borondoped p' emitters were extracted from QSSPC measurements of the effective lifetime as a function of the injection density using the method of Kane and Swanson [21,12]. High-resistivity (20-90 Ωcm) shiny-etched n-type silicon wafers with a thickness of ~260 µm were used as base material. BBr3 diffusions were performed on both sides of the wafers in the temperature range 895-1010°C [22]. After etching off the boron glass, the drive-in was performed by a thermal oxidation at 1050°C [22]. All oxide-passivated samples received a 40-min forming gas anneal at 400°C before the QSSPC measurements. The sheet resistance of the p' emitters was determined from four-point probe measurements [23].

Figure 5 shows the measured emitter saturation current densities J_0e of the boron-diffused p' emitters as a function of their sheet resistance. After boron diffusion all samples were thermally oxidized and forming gas annealed. The open blue triangles in Fig. 5 show the result-
ing $J_{0e}$ values ranging from 85 fA/cm$^2$ at a sheet resistance of 30 Ω/sq down to only 30 fA/cm$^2$ at 100 Ω/sq. However, as has been shown in a recent study [24], this very good passivation quality is highly unstable and after approximately two years of storage in the dark the $J_{0e}$ of the oxide-passivated $p^+$ emitters degraded to ~300 fA/cm$^2$ (filled blue triangles in Fig. 5). The fact that SiO$_2$-passivated boron-doped $p^+$ emitters are unstable has also been observed on high-efficiency $n$-type PERL silicon solar cells with $p^+$ front emitter [25].

A very elegant method to improve the poor passivation quality of thermally grown SiO$_2$ on $p^+$ emitters has recently been proposed [26,27]. This method makes use of the excellent passivation quality of SiO$_2$ on $n$ surfaces by implementing an additional phosphorus diffusion at the surface of the $p^+$ emitter. The resulting $n^+/p^+$ junction at the surface can be well passivated as the excellent passivation properties of oxide on the $n^+$ surface are exploited. The described new passivation method has already been applied in the “buried emitter solar cell” [26,28] currently under development at ISFH.

The black open squares in Fig. 5 show the $J_{0e}$ values after etching off the SiN stacks deposited by PECVD (open circles) [24] and (v) ALD-Al$_2$O$_3$ [12]. To our knowledge this is the best passivation realized so far on boron-doped $p^+$ emitters. A very high open-circuit voltage of 704 mV and an efficiency of 23.2% have in fact recently been realized using the above ALD-Al$_2$O$_3$ passivation scheme on the front boron-doped $p^+$ emitter of an $n$-type cell, whereas the rear was thermally oxidised [31]. As an additional advantage, Al$_2$O$_3$ as a large-bandgap material (~9 eV) is perfectly transparent for solar radiation. Hence, double layers consisting of a 10 nm thick a-Si film deposited at 230°C and a 60 nm thick SiN$_x$ film deposited at the same temperature. The a-Si/SiN$_x$ stacks were subsequently annealed at 350°C for 5 min to improve their passivation quality [24]. Despite the remarkably low deposition temperature, the a-Si/SiN$_x$ stack passivates as effectively as the best high-temperature SiO$_2$ and is also perfectly stable, as has been shown in a recent study [24]. The main disadvantage of the a-Si/SiN$_x$ stack regarding the application to the front $p^+$ emitter is the increased absorption within the a-Si layer, reducing the short-circuit density of the solar cell.

The filled red triangles in Fig. 5 show the measured $J_{0e}$ values after stripping off the a-Si/SiN$_x$ stacks, depositing Al$_2$O$_3$ by plasma-assisted ALD at 200°C and annealing the samples for 30 min at 425°C [12]. The $J_{0e}$ values of the Al$_2$O$_3$-passivated $p^+$ emitters range from ~50 fA/cm$^2$ measured at a sheet resistance of 30 Ω/sq down to only 6 fA/cm$^2$ at 150 Ω/sq [12]. The $J_{0e}$ values shown in the figure are perfectly stable, as has been shown in a recent study [24]. We have also studied the stability of the Al$_2$O$_3$ passivation under UV illumination. The experiments mimic 2 years outdoor conditions.

![Figure 5](image.png)

**Figure 5.** Measured emitter saturation current density $J_{0e}$ of B-diffused $p^+$ emitters as a function of sheet resistance. Surfaces are passivated by (i) forming-gas-annealed thermal SiO$_2$ (open blue triangles), (ii) thermal SiO$_2$ after 2 years of storage in the dark (closed blue triangles), (iii) PECVD-SiN$_x$ (open squares), (iv) a-Si/SiN$_x$ stacks deposited by PECVD (open circles) [24] and (v) ALD-Al$_2$O$_3$ [12].

![Figure 6](image.png)

**Figure 6.** Perfect stability of Al$_2$O$_3$-passivated B-doped $p^+$ emitters under UV illumination. The experiments mimic 2 years outdoor conditions.
outdoor conditions. The results of this experiment are shown in Fig. 6. The Al₂O₃ passivation is found to be perfectly stable and shows no degradation at all during UV exposure.

4 ALL-Al₂O₃ PASSIVATED CELLS

Using the measured recombination parameters of Al₂O₃-passivated p⁺ emitters and on undiffused Al₂O₃-passivated n-type Si surfaces we calculate the 1-sun efficiency and \( V_{oc} \) limits for all-Al₂O₃ passivated n-type silicon solar cells. For these calculations we assume an n-type silicon wafer with a base resistivity of 1 \( \Omega \) cm and Lambertian light trapping. The lowermost curve (black squares) shows that the bulk recombination lifetime \( \tau_b \) is assumed to be limited by Coulomb-enhanced Auger recombination, and we use a widely accepted parameterization as a function of the carrier densities [33].

![Figure 7](image-url)

**Figure 7.** Calculated limiting (a) 1-sun efficiency \( \eta \) and (b) open-circuit voltage \( V_{oc} \) as a function of cell thickness \( W \) for a 1-µm n-type silicon base assuming Lambertian light trapping. Black squares: only bulk recombination via Coulomb-enhanced Auger; red circles: additional surface recombination at the Al₂O₃-passivated p⁺ emitter and Al₂O₃-passivated n-Si base; blue triangles: additional contact recombination and front-grid shading.

For a 1-sun silicon solar cell we assume a perfectly passivated emitter and rear surface, i.e. \( J_{sc} = 0 \) and \( S_r = 0 \) in Eq. (2). The cell thickness \( W \) is varied between 1 and 1000 µm. The bulk recombination lifetime \( \tau_b \) is assumed to be limited by Coulomb-enhanced Auger recombination, and we use a widely accepted parameterization as a function of the carrier densities [33].

![Figure 8](image-url)

**Figure 8.** The all-Al₂O₃ passivated n-type silicon solar cell has an efficiency limit of 26.1% including bulk, surface and contact recombination as well as shading losses.

**Table 3. Calculated limiting 1-sun efficiency \( \eta \) and open-circuit voltage \( V_{oc} \) as a function of cell thickness \( W \) for a 1-Ωcm n-type silicon base assuming Lambertian light trapping.**

<table>
<thead>
<tr>
<th>Losses</th>
<th>( \eta_{\text{max}} ) (%)</th>
<th>( V_{oc @ \eta_{\text{max}}} ) (mV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>bulk</td>
<td>28.5</td>
<td>770</td>
</tr>
<tr>
<td>bulk + Al₂O₃</td>
<td>27.5</td>
<td>740</td>
</tr>
<tr>
<td>bulk + Al₂O₃ + contacts</td>
<td>26.1</td>
<td>720</td>
</tr>
</tbody>
</table>

Figure 7 and Table 3 show the calculated efficiency limit and the corresponding \( V_{oc} \) for three different cases. The uppermost curve (black squares) shows that Coulomb-enhanced Auger recombination limits the efficiency of a silicon solar cell to an ultimate efficiency of 28.5% for a cell thickness of ~50 µm. The red curve (circles) includes recombination in the Al₂O₃-passivated boron-diffused p⁺ emitter as well as recombination at the undiffused Al₂O₃-passivated cell rear. For Al₂O₃-passivated p⁺ emitters we have measured a \( J_{sc} \) value of 6 fA/cm² and for undiffused n-type silicon a SRV of \( S_r = 4 \) cm/s. These additional recombination channels reduce the efficiency limit to 27.5% for a cell thickness between 100 and 300 µm. Moreover, the all-Al₂O₃ passivated cell permits open-circuit voltages of up to 755 mV for a cell thickness between 1000 µm and 3000 µm. The latter case corresponds to the cell structure shown in Fig. 8. Under the contacts we assume that heavy diffusions reduce the contact recombination. The front p⁻ diffusion beneath the metal contacts has a sheet resistance of 30 Ω/sq and a
Atomic layer deposition (ALD) of Al₂O₃ has been identified as an ideal new passivation scheme for passivating undiffused p- and n-type silicon surfaces as well as for the passivation of boron-doped p⁺ regions. Our calculations of efficiency and Voc limits of n-type Si solar cells show that all-Al₂O₃ passivated cells have an efficiency limit of 27.5% at a Voc of 740 mV. Including contact recombination and optical shading with realistic assumptions the efficiency limit drops to 26.1% at a Voc of 720 mV.

In addition to the outstanding surface passivation provided by ALD-deposited Al₂O₃, the deposition process itself is also beneficial from an application point of view. In contrast to the conventionally applied PECVD, ALD consists of two self-limiting half-reactions, which implies several important advantages: (i) ALD gives highly conformal coatings, which allows to deposit and passivate e.g. deep trenches or even pores in silicon, (ii) pin-hole and particle-free deposition is achieved, (iii) ALD is a self-limiting process uniform films can be deposited over large areas with mono-layer growth control and (iv) very low impurity concentrations of deposited films and hence very high film quality is achieved. The main disadvantage of ALD for photovoltaic applications is its relatively low deposition rate. However, this disadvantage can be overcome by depositing ultrathin (2-30 nm) ALD-Al₂O₃ films and capping them with a thicker film of e.g. PECVD-SiO₂, SiNₓ or SiC [36]. Apart of the advantageous optical properties of these stacks, we have demonstrated that the passivation quality of such ALD/PECVD stacks can even be superior to that of single layers of Al₂O₃ [11], which we attribute to the hydrogenation of interface states at the Al₂O₃/Si interface during deposition of the hydrogen-rich PECVD layer. Combination of ALD and PECVD might hence be a key technology for future industrial high-efficiency solar cells.

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