LOW-TEMPERATURE SURFACE PASSIVATION

One intensively investigated low-temperature surface passivation alternative to thermal oxide is silicon nitride (SiNx) grown by plasma-enhanced chemical vapor deposition (PECVD) at \(2 \text{ to } 400 \text{ °C}\), which has proven to give comparably low SRVs as thermal SiO\(_2\) on low-resistivity p-type silicon [5,6]. However, when applied to the rear of PERC (Passivated Emitter and Rear Cell)-type solar cells the short-circuit current density is strongly reduced compared to the SiO\(_2\)-passivated cell rear [7]. This effect has been attributed to the large density of fixed positive charges within the SiNx layer, inducing an inversion layer in the crystalline silicon underneath the SiNx. The coupling of this inversion layer to the base contact leads to a significant loss in the short-circuit current density. This detrimental effect is known as ‘parasitic shunting’ [8]. Another alternative low-temperature passivation scheme resulting in comparable SRVs as annealed SiO\(_2\) is intrinsic hydrogenated amorphous silicon (a-Si) deposited by PECVD in the temperature range between 200 and 250°C [9]. Despite the fact that no parasitic shunting occurs 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.

ATOMIC-LAYER-DEPOSITED Al\(_2\)O\(_3\)

Recently, it was shown that thin films of aluminum oxide (Al\(_2\)O\(_3\)) grown by atomic layer deposition (ALD) provide an excellent level of surface passivation on low-resistivity p- and n-type silicon wafers [10,11]. Figure 1 shows a comparison of the injection-dependent effective SRVs measured on 1-2 \(\Omega\)cm p-type silicon wafers passivated by (i) SiNx deposited by remote-PECVD [12], (ii) intrinsic a-Si deposited in a parallel-plate PECVD reactor [9], and (iii) Al\(_2\)O\(_3\) deposited by means of plasma-assisted ALD [13]. The measurements are shown in the injection range between \(10^{12}\) and \(10^{15}\) cm\(^{-3}\), which is the most relevant range for the rear of one-sun silicon solar cells. Within this injection range it becomes obvious from Fig. 1 that the Al\(_2\)O\(_3\) passivation outperforms the well-optimized SiNx, as well as the a-Si passivation. Importantly, the Al\(_2\)O\(_3\) passivation results in a very weak injection level dependence in the injection range between \(10^{12}\) and \(10^{15}\) cm\(^{-3}\), and the effective SRV stays well below 10 cm/s even at low injection densities \(< 10^{13}\) cm\(^{-3}\). The strong injection level dependence of the effective SRV measured on SiNx-passivated p-Si surfaces can be attributed to recombination within the space charge region induced by the high fixed positive charge density within the SiNx layer [6].
Figure 2 shows the measured effective SRV as a function of the Corona charge density deposited onto dielectric passivation layers of SiN$_x$ and Al$_2$O$_3$. In the flat-band case when the deposited Corona charge density equals the fixed charge density within the dielectric layer, the recombination rate shows a maximum. From this maximum the charge density within the layer can be deduced. As can be seen from Fig. 2, the fixed charge density within the SiN$_x$ layer is positive and amounts to $Q_f = +2 \times 10^{12}$ elementary charges/cm$^2$, whereas the fixed charge density within the Al$_2$O$_3$ layer is negative and amounts to $Q_f = -1.3 \times 10^{13}$ cm$^{-2}$. The fixed negative charge density within the Al$_2$O$_3$ layer induces an accumulation layer at the $p$-type silicon surface in contrast to the SiN$_x$ layer inducing and inversion layer. As a consequence, the Al$_2$O$_3$ provides a very effective field-effect passivation without the additional contribution of recombination in the space charge region, which is the dominant recombination channel in the case of the SiN$_x$ passivation of $p$-type silicon surfaces at low injection densities [6]. In addition, due to the formation of an accumulation layer instead of an inversion layer at the $p$-type silicon surface, the above-mentioned parasitic shunting effect at the solar cell rear is not expected for an Al$_2$O$_3$-rear-passivated cell. In combination with its very high transparency for near-bandgap photons, ALD-deposited Al$_2$O$_3$ should hence be an optimal choice for a dielectric layer at the silicon solar cell rear. In this contribution, we present first results of PERC-type solar cells with Al$_2$O$_3$-passivated rear surface, demonstrating the large potential of atomic-layer-deposited Al$_2$O$_3$ films for future high-efficiency silicon solar cells.

**ALD-PASSIVATED SOLAR CELLS**

Figure 3 shows the PERC-type solar cell structure used in this study to demonstrate the applicability of Al$_2$O$_3$ rear surface passivation to high-efficiency silicon solar cells and Fig. 4 shows the corresponding process flow diagram. As starting material used is (100)-oriented boron-doped float-zone (FZ) silicon with a thickness of 310 µm and a resistivity of 0.5 Ω·cm. After damage etching of ~10 µm/side and wet chemical cleaning, an SiO$_2$ layer is grown on both wafer surfaces in a wet oxidation process at 1000°C. Subsequently, 2×2 cm$^2$ diffusion windows are photolithographically opened on one wafer side and the silicon surface within the windows is textured with random pyramids in a KOH/isopropanol solution. A single-step phosphorus emitter is diffused from a POCl$_3$ source, resulting in an $n^+$-emitter with a sheet resistance of...
Table 1: One-sun parameters measured under standard testing conditions of 290 µm thick PERC-type silicon solar cells with three different rear surface passivations: (i) thermal SiO₂ (220 nm), (ii) ALD-Al₂O₃ (130 nm) and (iii) ALD-Al₂O₃(30 nm)/PECVD-SiO₂(200 nm). All cells were fabricated on 0.5-Ωcm FZ p-Si wafers. The aperture cell area is 4 cm².

<table>
<thead>
<tr>
<th>Rear side</th>
<th>Cell ID</th>
<th>Vₜ [mV]</th>
<th>Jₛ [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)/</td>
<td>2_4</td>
<td>660</td>
<td>39.0</td>
<td>80.1</td>
<td>20.6*</td>
</tr>
<tr>
<td>PECVD-SiO₂ (200 nm)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></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.

100 Ω/square, and the phosphorus glass is removed by a short HF dip. At this point of the process, the cell batch is split up into three batches, of which each one receives a different rear surface passivation: (i) one batch of cells keeps the thermally grown SiO₂, (ii) the second one is coated by a 130 nm Al₂O₃ film and (iii) the third batch is passivated by a stack consisting of a 30 nm Al₂O₃ layer and a 200 nm thick PECVD-SiO₂ layer deposited in a Plasmalab 80+ parallel-plate reactor (Oxford Instruments) at 425°C. The Al₂O₃ films are deposited by plasma-assisted ALD in a commercial ALD reactor (FlexAL[15], Oxford Instruments) at a deposition temperature of 200°C [15]. The plasma-assisted ALD Al₂O₃ process is split up into two self-limiting reactions consisting of a tri-methyl-aluminum [Al(CH₃)₃] exposure and an O₂ plasma. The subsequent annealing step as applied in the study of Hoex et al. [11] is omitted in this case as adequate post-deposition annealing steps are already present in the process flow shown in Fig. 4. The SiO₂ layer is deposited in a continuous PECVD process using silane (SiH₄) and di-nitrogen oxide (N₂O) as process gases. The remaining process steps are identical for all three cell batches. Using photolithography point contact openings are etched into the dielectric layers at the rear. A photolithography mask resulting in a point contact pitch of 2 mm and a metallization fraction of 4% is used. 20 µm of Aluminium is evaporated on the entire cell rear using electron-beam evaporation. A tunnel oxidation of the n⁺-emitter is performed at 500°C for 10 min, resulting in an ~1.5 nm thick oxide layer [16]. The 20 µm thick Al front metal grid is then evaporated through a shadow mask onto the tunnel oxide. Finally, a surface-passivating SiNx antireflection coating is deposited onto the front of the PERC solar cell by remote-PECVD at 300°C [5]. Before characterization all solar cells receive an additional 1-min 300°C anneal in air, which slightly improves the fill factor and the open-circuit voltage. The aperture area of all solar cells fabricated in this study is 4 cm² and the entire front metallization, including the busbar, is within the active cell area.
Table 2: Effective rear surface recombination velocity $S_r$ and internal rear reflectance $R_r$ extracted from the IQE measurements shown in Fig. 5.

<table>
<thead>
<tr>
<th>Rear side</th>
<th>Rear surface recombination velocity $S_r$ [cm/s]</th>
<th>Internal rear reflectance $R_r$ [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thermal SiO$_2$ (220 nm)</td>
<td>90 ± 20</td>
<td>91 ± 1</td>
</tr>
<tr>
<td>Al$_2$O$_3$ (130 nm)</td>
<td>90 ± 20</td>
<td>90 ± 1</td>
</tr>
<tr>
<td>Al$_2$O$_3$(30 nm)/SiO$_2$(200 nm)</td>
<td>70 ± 20</td>
<td>91 ± 1</td>
</tr>
</tbody>
</table>

A solar cell with annealed SiO$_2$ rear surface passivation is characterized by an efficiency of $\eta = 20.5\%$, an open-circuit voltage of $V_{oc} = 666$ mV and a short-circuit current density of $J_{sc} = 38.9$ mA/cm$^2$. The analysis of the internal quantum efficiency (IQE) shows that the $V_{oc}$ is limited by the front emitter. The average values of all 4 cells with SiO$_2$ rear passivation show only a very small scatter, demonstrating the high reproducibility of the process. The average parameters of the cells with Al$_2$O$_3$, Al$_2$O$_3$/SiO$_2$ and SiO$_2$ rear passivation agree within the scatter ranges. In particular it is noticeable that the $J_{sc}$ of the cells with Al$_2$O$_3$ and Al$_2$O$_3$/SiO$_2$ rear surface passivation is not reduced compared to the SiO$_2$-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 $J_{sc}$ is reduced by 1-2 mA/cm$^2$ compared to the thermal SiO$_2$ reference, due to the above-described parasitic shunting effect [7,8]. This effect is not expected in the case of Al$_2$O$_3$ 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 Al$_2$O$_3$-passivated as well as for Al$_2$O$_3$/SiO$_2$-passivated rear surfaces. The best cell of the entire batch is obtained for the Al$_2$O$_3$/SiO$_2$-passivated cell, resulting in an independently confirmed efficiency of $\eta = 20.6\%$, a $V_{oc}$ of 660 mV and a $J_{sc}$ of 39.0 mA/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 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. 5 show the IQE as a function of wavelength $\lambda$ of PERC cells with the three different rear passivation schemes, measured at a fixed bias light intensity of 0.3 suns. The solid lines in Fig. 5 show the fits to the measured data. To model the IQE($\lambda$) dependence we use the software LASSIE [17,18], which combines the extended IQE evaluation by Basore [19] with the improved optical model developed by Brendel [20]. The bulk lifetime is assumed to be limited by Auger recombination, resulting in a bulk diffusion length of $L_b = 1500$ µm for the 0.5 cm p-type silicon material used in this work [21]. 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 of the reference cell with annealed SiO$_2$ amounts to $S_r = (90 \pm 20)$ cm/s. The extracted $S_r$ for the cell with single-layer Al$_2$O$_3$ rear passivation is the same as for the SiO$_2$-passivated reference cell, showing that ALD-deposited Al$_2$O$_3$ performs as good as aluminum-annealed high-temperature-grown SiO$_2$. A further reduction in the $S_r$ is obtained for the Al$_2$O$_3$/SiO$_2$ stack, resulting in an $S_r$ of only $(70 \pm 20)$ cm/s, which we attribute to the hydrogenation of interface states at the Al$_2$O$_3$/Si interface during deposition of the hydrogen-rich SiO$_2$ layer.

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

$$S_r = \frac{D_w}{W} \left[ \frac{p}{2W/\sqrt{rf}} \left\{ \arctan \left( \frac{2W}{p} \sqrt{n/f} \right) \right\}^{-1} - \exp \left( -\frac{W}{p} \right) + \frac{D_w}{fWS_{\text{met}}} \right] + \frac{S_{\text{pass}}}{1 - f},$$

where $D_w$ is the diffusion coefficient of minority carriers, $W$ is the thickness of the silicon layer, $f$ is the front surface recombination velocity, $n$ is the effective refractive index of the cell, $r$ is the reflectivity of the front surface, $S_{\text{pass}}$ is the surface recombination velocity at the front surface, and $f$ is the fraction of the incident light that is absorbed in the silicon layer.
where $D_e$ is the electron diffusion coefficient, $W$ the wafer thickness, $p$ the contact pitch, $f$ the metallization fraction and $S_{\text{met}}$ and $S_{\text{pass}}$ are the SRVs on the metallized and on the passivated areas of the rear. According to Eqn. (1) the minimum SRV $S_{\text{min}}$ for a point-contact rear with perfect passivation in the non-metallized area (i.e., $S_{\text{pass}}=0$) is given by the first summand on the right-hand side of Eqn. (1). For our cell structure we determine $S_{\text{min}} = 73$ cm/s ($D_e = 23$ cm/s, $W = 290$ μm, $p = 2000$ μm, $f = 4\%$, $S_{\text{met}} \geq 10^3$ cm/s), clearly demonstrating that in the case of the Al₂O₃/SiOₓ stack, 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.

**CONCLUSIONS**

The excellent silicon surface passivation by atomic-layer-deposited Al₂O₃, which had up to now only been demonstrated by lifetime measurements, has successfully been transferred to the device level for the first time.

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) as 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, as shown in this study, 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-SiOₓ. Apart from the advantageous optical properties of these stacks, we have demonstrated that the passivation quality of such ALD-Al₂O₃/PECVD-SiOₓ stacks can even be superior to that of single layers of Al₂O₃, which we attribute to the hydrogenation of interface states at the Al₂O₃/Si interface during deposition of the hydrogen-rich SiOₓ layer. The same beneficial effect can be observed for other hydrogen-rich PECVD-deposited films, such as SiNₓ or SiCₓ. Combination of ALD and PECVD might hence be a key technology for future industrial high-efficiency solar cells.

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