ABSTRACT: Due to a different surface concentration and type of minority charge carriers compared to n⁺ emitters (on p-type substrates), novel surface passivation methods are required when using p⁺ emitters on n-type silicon for which a number of efficiency records have been achieved in recent years [1,2,3]. In this study emitter saturation current densities $j_0$ of two BBBr.diffused emitters passivated by a variety of dielectric stacks are compared using following processes: SiOₓ by dry thermal oxidation, direct and remote plasma enhanced chemical vapor deposited SiNx, atomic layer deposited Al₂O₃, SiOₓ remaining from the RCA standard cleaning process [4] yielding the lowest $j_0$ of 17.5 fA/cm² for a sample passivated by an Al₂O₃/SiNₓ stack. Furthermore, the $J_{0BSF}$ values of POCl₃ diffused n⁺ surfaces passivated by several passivation layers are determined as they are applied at the solar cell rear side. The resulting combined $j_0$ and $J_{0BSF}$ values $j_{0combined}$ are compared with IV characteristics of solar cells passivated by the corresponding passivation of emitter and BSF on front- and rear side. As passivation layers are additionally employed as antireflection coatings also the spectral reflectance of the investigated passivation stacks with optimized thickness was determined.

Keywords: Boron, c-Si, n-type, Passivation

1 INTRODUCTION

n-type silicon has received increasing interest as substrate material for solar cells since it features higher bulk charge carrier lifetimes than p-type doped silicon due to a lower impact of metal impurities like e.g. Fe [5]. In addition, solar cells from n-type Si material do not suffer from light induced degradation due to boron-oxygen complexes [6].

The different structure with p⁺-emitter on the front side and the n⁺-doped rear side requires a sophisticated way of surface passivation whose properties matches to minority charge carrier type and surface concentration on both front- and rear side, respectively. Therefore, in order to achieve highest solar cell efficiencies. Additionally, the front side passivation layer thickness needs to be optimized due to its further use as antireflection coating (ARC) requiring knowledge of the wavelength dependent refractive index n as well as the absorption coefficient k.

In this study, several promising dielectric layers and stacks are investigated as passivation on two different BBBr.diffused emitters with sheet resistivities of 50 Ω/sq and 100 Ω/sq (see also [7]): silicon nitride applied by direct plasma enhanced chemical vapor deposition (PECVD), stacks composed of atomic layer deposited (ALD) Al₂O₃ + remote-plasma enhanced chemical vapor deposition (r-PECVD) SiNx, SiOₓ by dry thermal oxidation + PECVD-SiNₓ and SiOₓ remaining from the RCA standard cleaning process (RCA-SiOₓ) + PECVD-SiNₓ. Additionally, passivation properties of PECVD-SiNₓ thermal SiOₓ + PECVD-SiNₓ and RCA2-SiOₓ + PECVD-SiNₓ are investigated on a 60 Ω/sq n⁺ POCl₃ diffused back-surface-field (BSF) and the combined saturation current densities $j_{0combined} = j_0 + J_{0BSF}$ are compared with IV characteristics of solar cells featuring the corresponding emitter/passivation combinations on front- and rear side, respectively.

2 EXPERIMENTAL

To investigate the electrical properties of the investigated passivation/emitter combinations, emitter saturation current densities are determined by the method of Kane and Swanson [8] at an injection level of $1 \times 10^{16}$ cm⁻³. For these samples, n-type float zone Si substrates with a base resistivity of 7.5 Ωcm, a thickness of 250 µm and an area of 50 × 50 mm² are used. Emitter as well as passivation layers are applied on both surfaces as required by the method. The samples are divided into three groups, group 1 and group 2 are for measuring $j_0$ of the passivated BBBr.emitters while the samples of group 3 are for determining $J_{0BSF}$ of the passivated POCl₃.diffused n⁺ BSFs. Group 1 and 3 are textured in an alkaline solution leading to pyramid textured surfaces with (111) orientation as also applied for solar cells, group 2 has (100) oriented planar surfaces.

The pre-treatment includes a cleaning step in dilute HCl and a subsequent dip in a HF solution after which group 3 samples are directly subjected to a POCl₃ diffusion for a 60 Ω/sq n⁺ layer on both surfaces without any further cleaning step. Group 1 samples with textured surfaces are afterwards exposed to a H₂O₂/H₂SO₄ cleaning step (Piranha-cleaning) in order to remove organic residues from the texturing process followed by a RCA cleaning for both group 1 and group 2 samples. Directly after the final HF dip, the emitter of these samples is formed by BBBr.diffusion resulting in a 50 Ω/sq or 100 Ω/sq emitter.

For the solar cells 5 inch 2 Ωcm Cz-Si wafers are used as substrate material and etched to a thickness of approx. 130 µm in NaOH solution before the texturizing process in alkaline solution. The cleaning consists of an HCl step and a subsequent RCA cleaning prior to BBBr.diffusions for 50 Ω/sq and 100 Ω/sq emitters. Afterwards, a SiNₓ capping layer is applied on the front side to protect the emitter on the front side at the subsequent etch back of the emitter on the rear side in NaOH solution and the repeated texturizing of the rear side in alkaline solution for an improved electrical contact of the finger grid on the front side.
rear side, leading to a final cell thickness of approx. 100 µm. After cleaning in diluted HCl and HF, a POCl3 diffusion forms the BSF with a sheet resistivity of 60 Ω/sq prior to SiN$_x$ capping layer as well as the PSG being removed in a final HF dip.

The following passivation / ARC stacks or layers are investigated on $j_{0e}$ level:
- **ALD Al$_2$O$_3$ (5 nm and 15 nm) + r-PECVD SiN$_x$ (thickness optimized as ARC).** The remote plasma is expected to decrease the possible damage due to radiation or ions compared to a direct plasma source.
- **Dry thermal oxide at 900°C (7 nm and 15 nm) + PECVD SiN$_x$ (optimized thickness)**
- **Silicon oxide layer resulting from the second RCA step (thickness assumed to be 3 nm) + PECVD SiN$_x$ (optimized thickness)**
- **75 nm PECVD SiN$_x$ (only on planar samples)**

The solar cells are passivated on front/emitter side and rear side with following passivation layer combinations:
- **Al$_2$O$_3$ + r-PECVD SiN$_x$ on front side / PECVD SiN$_x$ on rear side**
- **Thermal SiO$_x$ + PECVD SiN$_x$ on front and rear side**
- **RCA SiO$_x$ + PECVD SiN$_x$ on front and rear side**

These combinations are also used for calculating the combined saturation currents $j_{0\text{combined}}$ of front- and rear side.

Metallization of the solar cells is maintained by screen printing of an AgAl paste on the front and an Ag paste on the rear side followed by co-firing in a 9-zone belt firing furnace. As the cells are designed as bifacial, a finger grid is printed on both sides instead of a full-area rear side metallization.

$j_{0e}/j_{0\text{BSF}}$ values are measured with a Sinton Lifetime Tester WCT-120 on both planar and pyramid textured samples, the complex refractive index (n- and k-values) is determined by ellipsometry using a J. A. Woollam device only on samples with planar surfaces. All parameters are measured after a high temperature step in a firing belt furnace at the same set peak temperatures as for the solar cells.

The SiN$_x$ layer thicknesses are optimized regarding best ARC properties applying a numerical calculation method using the determined n- and k-values of the layers as input parameters.

For the solar cell results the IV curve is measured on a constant light cell tester.

3 RESULTS

In Figure 1 and 2 the $j_{0e}$ values of the investigated layers and stacks are illustrated with a very low $j_{0e}$ of 17.5 fA/cm$^2$ for a 15 nm Al$_2$O$_3$ + SiN$_x$ stack as passivation layer on a 100 Ω/sq emitter and a planar surface. For most passivation layers, $j_{0e}$ is lower for 100 Ω/sq emitters than for 50 Ω/sq emitters which is expected to be caused by a higher recombination in the 50 Ω/sq emitter bulk and a simultaneously identical recombination at the surface, as both emitters feature similar surface doping concentrations but different profile depths. Furthermore, the results show an increased $j_{0e}$ for samples with textured surfaces which can be referred to the larger surface area of a pyramid textured compared to a planar surface and so to an enhanced surface recombination.

The differences between stacks with 5 nm Al$_2$O$_3$ and 15 nm Al$_2$O$_3$ or 7 nm SiO$_x$ and 15 nm SiO$_x$ are rather small, suggesting to further decrease the layer thickness, especially of Al$_2$O$_3$, and to examine if passivation quality can be maintained. This renders the opportunity to reduce the process duration and to further optimize light trapping when applying an Al$_2$O$_3$/SiN$_x$ stack with an Al$_2$O$_3$ thickness below 5 nm.

Passivation stacks consisting of RCA SiO$_x$ + SiN$_x$ exhibit the highest $j_{0e}$ values except for the pure SiN$_x$ layer which is only measured on planar surfaces. However, the difference of RCA SiO$_x$ + SiN$_x$ passivated samples to samples passivated with thermal SiO$_x$ + SiN$_x$ is rather small on textured.

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**Figure 1:** $j_{0e}$ values of BBr$_3$ diffused samples with planar surfaces and different surface passivations

**Figure 2:** $j_{0e}$ values of BBr$_3$ diffused samples with textured surfaces and different surface passivations

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$j_{0\text{BSF}}$ values illustrated in Figure 3 reveal a clearly advanced passivation performance when using a stack consisting of thermal SiO$_x$ + SiN$_x$ compared to a SiN$_x$ single layer. Obviously, a thin interface layer of RCA SiO$_x$ does not have a similar influence on the passivation properties as thermal SiO$_x$. Compared to the $j_{0e}$ values in Figure 1 and 2, the $j_{0\text{BSF}}$ values in Figure 3 are much higher emphasizing the importance of a sophisticated rear side passivation.

For comparing different cell concepts distinguished by their front and rear side design, the saturation current densities of the emitter side and the corresponding BSF side are combined and yields the saturation current...
densities \( j_{\text{combined}} \) illustrated in Figure 4. Each saturation current density was determined on symmetric samples.

In this calculation, saturation current density of a solar cell base and that caused by an increased recombination at the not passivated area under the metal contacts is not included, as these two saturation current densities are just a constant offset to the overall \( j_0 \) values independent of surface passivation layout.

The results reveal the lowest combined saturation current densities to be attained for samples passivated with thermal SiO\(_2\) + SiN\(_x\) on front and rear, despite the not optimal saturation current density on the emitter side. Highest combined saturation current densities are determined for RCA SiO\(_2\) + SiN\(_x\) passivation on both sides which is mainly due to the contribution of the \( j_{\text{BSF}} \). For the same reason, the \( j_{\text{combined}} \) of samples with Al\(_2\)O\(_3\) + SiN\(_x\) emitter passivation is higher due to the high \( j_{\text{BSF}} \) of the PECVD SiN\(_x\) passivated BSF.

The IV characteristics of the solar cells featuring a 50 \( \Omega \)/sq emitter in Table I confirm the trend of the combined saturation current densities in Figure 4. The highest efficiency of 18.0% is measured for cells with a thermal SiO\(_2\) + SiN\(_x\) passivation followed by the solar cells with Al\(_2\)O\(_3\) + SiN\(_x\) passivation. SiO\(_2\) and Al\(_2\)O\(_3\) layer thicknesses have only a negligible influence. Both \( j_{\text{SC}} \) and \( V_{\text{OC}} \) and thus cell efficiency are very low for solar cells passivated by RCA SiO\(_2\) + SiN\(_x\) which also corresponds to the results of the combined saturation current density illustrated in Figure 4.

A different trend is observed for solar cells with 100 \( \Omega \)/sq emitter in Table II with a maximal efficiency of 17.0% for Al\(_2\)O\(_3\) + SiN\(_x\) passivation. The efficiency loss for cells with a thermal SiO\(_2\) + SiN\(_x\) compared to an Al\(_2\)O\(_3\) + SiN\(_x\) passivation is mainly due to a much lower \( V_{\text{OC}} \). As neither the used AgAl pastes nor the firing parameters (except the peak temperatures) are optimized for these cells, a possible explanation for the voltage drop can be found in metallization issues when contacting the very shallow 100 \( \Omega \)/sq emitter.

### Table I: IV characteristics of bifacial n-type solar cells with 50 \( \Omega \)/sq emitter and 60 \( \Omega \)/sq BSF for different passivation layers (labeled layers correspond to the front side passivation)

<table>
<thead>
<tr>
<th>( j_{\text{SC}} ) [mA/cm(^2)]</th>
<th>( V_{\text{OC}} ) [mV]</th>
<th>( \eta ) [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>5 nm Al(_2)O(_3) + SiN(_x)</td>
<td>37.1</td>
<td>623</td>
</tr>
<tr>
<td>15 nm Al(_2)O(_3) + SiN(_x)</td>
<td>36.4</td>
<td>623</td>
</tr>
<tr>
<td>RCA SiO(_2) + SiN(_x)</td>
<td>30.5</td>
<td>601</td>
</tr>
<tr>
<td>7 nm SiO(_2) + SiN(_x)</td>
<td>37.3</td>
<td>631</td>
</tr>
<tr>
<td>15 nm SiO(_2) + SiN(_x)</td>
<td>36.7</td>
<td>632</td>
</tr>
</tbody>
</table>

### Table II: IV characteristics of bifacial n-type solar cells with 100 \( \Omega \)/sq emitter and 60 \( \Omega \)/sq BSF for different passivation layers (labeled layers correspond to the front side passivation)

<table>
<thead>
<tr>
<th>( j_{\text{SC}} ) [mA/cm(^2)]</th>
<th>( V_{\text{OC}} ) [mV]</th>
<th>( \eta ) [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>5 nm Al(_2)O(_3) + SiN(_x)</td>
<td>36.3</td>
<td>620</td>
</tr>
<tr>
<td>15 nm Al(_2)O(_3) + SiN(_x)</td>
<td>37.1</td>
<td>617</td>
</tr>
<tr>
<td>RCA SiO(_2) + SiN(_x)</td>
<td>32.3</td>
<td>594</td>
</tr>
<tr>
<td>7 nm SiO(_2) + SiN(_x)</td>
<td>36.8</td>
<td>603</td>
</tr>
<tr>
<td>15 nm SiO(_2) + SiN(_x)</td>
<td>37.4</td>
<td>610</td>
</tr>
</tbody>
</table>

In general, a further increase of cell efficiency is expected for an advanced passivation of the solar cell rear side as well as an optimized metallization.

The measurements of the complex refractive index by means of ellipsometry in a wavelength range between 290 nm and 1000 nm (results not illustrated here) show that thermal SiO\(_2\) and Al\(_2\)O\(_3\) are fully transparent in the entire wavelength range. Both PECVD and r-PECVD SiN\(_x\) absorb at wavelengths below 400 nm and 450 nm,
respectively, with an increasing absorption coefficient towards shorter wavelengths. All layers exhibit only slight changes of the n- and k-values caused by the firing step.

Figure 5 illustrates the spectral reflectance of the investigated layers in the relevant wavelength range of 290 nm to 1200 nm which in general is very low for all passivation layers. Stacks of Al$_2$O$_3$ + SiN$_x$ have a minimum at a smaller wavelength compared to the other stacks exhibiting a lower reflectance over the higher wavelength range. The visible color of all layers is dark blue to black with a purple shade at the Al$_2$O$_3$ + SiN$_x$ samples.

4 CONCLUSIONS

The results presented in this work emphasize Al$_2$O$_3$ + SiN$_x$ stacks to be best suited to passivate BBr$_3$ diffused emitters yielding a very low emitter saturation current density of 17.5 fA/cm$^2$. However, the high recombination velocity on the SiN$_x$ passivated POCl$_3$ diffused BSF on the rear side limits the performance of the cells. Maximum efficiencies of 18.0% are achieved employing a 50 Ω/sq emitter and a thermal SiO$_x$ + SiN$_x$ passivation stack on both surfaces despite a possible parasitic shunting of the p-n junction described by Dauwe [9] due to the positive fixed charges in the passivation layer. Furthermore, a firing step does not deteriorate the passivation properties of the investigated layers as the emitter saturation current densities still exhibit sufficiently low values.

As spectral reflectance measurements reveal, a very low reflectance over the relevant wavelength region can be achieved using the investigated layers with optimized thickness.

5 ACKNOWLEDGEMENTS

The authors would like to thank L. Kraus and L. Mahlstaedt for their processing assistance. The research leading to these results has received funding from the EU 7$^{th}$ Framework Programme (FP7/2007-2013) for the Collaborative Project (CP) ‘20plµs’ with the full title: ‘Further development of very thin wafer based c-Si photovoltaics’ under grant agreement n° 256695. The content of this publication is the responsibility of the authors.

6 REFERENCES
