CO-DIFFUSED APCVD BORON REAR EMITTER WITH SELECTIVELY ETCHED-BACK FSF FOR INDUSTRIAL N-TYPE SI SOLAR CELLS

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ABSTRACT: The employment of a B-doped atmospheric pressure chemical vapor deposited (inline belt APCVD) borosilicate glass is an elegant technology for industrially realizing a p+ emitter. By drive-in of B and a subsequent POCl₃ co-diffusion, p+ emitter and n+ front surface field (FSF) are established in a single process step. APCVD-SiOₓ is used to prevent the p+ emitter from being compensated during P diffusion. Its thickness needs to be adapted in order not to affect the p+ profile during POCl₃ diffusion while keeping it removable.

For rear junction solar cells, it is crucial to ensure low recombination activity at the front. Therefore, a selectively etched-back FSF is to be established in the solar cell. An adjusted etch-back solution increases n+ Rs to successfully and well controllably, accompanied by a drastic jₒFS reduction while simultaneously almost completely maintaining p+ Rp. A 43 Q/sq APCVD-AlOₓ passivated p+ emitter achieves jₒ of only 52 fA/cm². Total implied jₒE of a pseudo solar cell structure attains up to 695 mV.

The newly developed APCVD p+ emitter combined with the co-diffused and selectively etched-back FSF employed in an industrial n-type solar cell achieves 18.8% efficiency in a first experiment being still limited by a poor Ag/Al contact to the B-emitter.

Keywords: n-type, Boron, APCVD, Industrial, Selective

1 INTRODUCTION

Enhancing the energy conversion efficiency of solar cells is a fundamental approach to lower the cost of photovoltaic power. In this regard, n-type Si based devices have been proven to be a promising candidate, not only since record efficiencies above 25% have been attained by several manufactures recently [1-3]. Thus it is not surprising that the market share of n-type Si materials is expected to increase from today’s <10% to ~40% within the next ten years [4]. The higher tolerance of minority carrier lifetime to common impurities and the performance not suffering B-O complex related light-induced degradation allow such ultra-high efficiencies.

To benefit from these n-type Si bulk characteristics, an industrially applicable technology to create a low recombimative and well contactable p+ emitter is crucial. The p-n junction of n-type solar cells is frequently established by incorporation of B atoms into the Si wafer. The most common implementation is thermal diffusion of B from a liquid BBr₃ source [5].

An elegant alternative is the deposition of a capped B-doped silicon oxide layer (BSG), e.g. by plasma-enhanced chemical vapor deposition (PECVD) [6] or atmospheric pressure chemical vapor deposition (APCVD) [7,8]. By driving B into the Si wafer surface in a POCl₃ diffusion tube and a subsequent POCl₃ diffusion, p+ emitter and n+ back or front surface field (FSF/FSF) are established in a single process step, named co-diffusion. Furthermore, the separation of BSG deposition and drive-in step allows a structured doping source needed for local emitters in advanced solar cell concepts, such as the interdigitated back contact (IBC) cell.

Contrary to PECVD-BSG, the application of the doped layer including its sputtering by means of APCVD requires no vacuum and can hence be more cost-efficient. Thus, B-emitters created by APCVD can enable n-type solar cells to be industrially produced.

In the pursued cell concept, the B-emitter is located at the rear, ensuing several requirements and benefits:

- The B-emitter surface needs not be textured, leading to generally lower emitter saturation current densities jₒE due to a smaller crystal surface (e.g. [9]).
- For rear junction solar cells, it is crucial to ensure low recombination activity at the front. Therefore, a selectively etched-back FSF is to be established in the solar cell aiming at a jₒFS being even smaller than jₒE.
- Since FSF and Si base have the same polarity, generally higher fill factors can be attained.
- For front side metallization, the established Ag screen-print (small finger width, high conductivity, low contact resistivity) can be used.
- The metallization at the rear can be performed by full-area Al (e.g. PVD or screen-print) with local contacts as an alternative to Ag/Al screen-printed paste known to cause shunts of the p-n junction [10,11].

2 EXPERIMENTAL

As preparative study prior to their integration into the solar cell process (Fig. 1), the creation of the APCVD boron emitter along with the co-diffused and selectively etched-back phosphorous FSF is investigated.

figure 1: Processing scheme for an industrial n-type solar cell with APCVD B-rear emitter, co-diffused selective P-FSF, and screen-printed contacts.

In order to prevent the p+ doped layer from being at least partly electrochemically compensated by the POCl₃ diffusion, the BSG is capped by undoped SiOₓ, both
deposited by an inline belt APCVD tool from SCHMID Thermal Systems, Inc. featuring three injectors. The capping layer ought to be thin to facilitate its removal after the high temperature annealing, but does then require being thick enough to prevent P atoms from diffusing into the B-emitter.

During the FSF etch-back process [12], the boron rich layer (BRL) on top of the rear p⁺ emitter, which forms during co-diffusion, is removed in the HF/HNO₃ etch-back solution. The composition of this solution has to be adjusted to the BRL thickness of the respective emitter and the desired etch-back depth of the FSF, aiming at a preferably small increase of emitter sheet resistance \( R_{\text{sheet}} \) during this process step.

In order to ensure very low saturation current density, two possible surface passivation schemes can be integrated into the solar cell process with reasonable additional effort:

- APCVD aluminum oxide (AlOₓ) with capping PECVD-SiNx for the rear B-emitter and PECVD-SiNx front side passivation.
- A stack of thermal SiO₂ and PECVD-SiNₓ passivating both sides of the solar cell.

Since metalization of the solar cells in this study is generated by screen-printed contacts, the aforementioned passivation stacks are characterized in the fired state.

All samples are subjected to a standard RCA cleaning before the BSG deposition. After co-diffusion in a POCl₃ tube furnace, the capping and BSG layers are removed in diluted HF. Prior to thermal oxidation or AlOₓ APCVD, the wafers are RCA cleaned.

2.1 \( R_{\text{sheet}} \) and \( j_0 \) investigation

\( R_{\text{sheet}} \) of the n⁺ and p⁺ layers is measured by the four-point probe method and therefore on substrates with the respective opposite doping type (struc. 1&3 in Fig. 2).

\( j_0 \) is determined using 10 Ωcm Cz Si substrates (135 µm thick) with an alkaline-etched surface and the respective doped layer on both sides (struc. 2&3 in Fig. 2). For \( j_0 \) and implied \( V_{\text{OC}} \) measurement of a structure similar to the solar cell, the n⁺ layer is applied at the front, the p⁺ layer at the rear (struc. 4 in Fig. 2).

2.2 n-type solar cells

The newly developed APCVD boron emitter combined with the co-diffused and selectively etched-back phosphorous FSF is then employed in an industrial bifacial n-type solar cell (Fig. 3) according to the processing sequence shown in Fig 1.

3 RESULTS & DISCUSSION

3.1 Co-diffused APCVD boron emitter

Varying capping layer thickness reveals a growing \( R_{\text{sheet}} \) increase of the p⁺ emitter after POCl₃ diffusion with decreasing capping thickness (Fig. 4). Furthermore, a thinner capping layer yields significantly higher \( j_{0E} \) values (Fig. 4).

ECV profiles of the B-emitters exhibit net surface doping concentrations which increase with capping layer thickness. Also, the B profiles feature a larger depth.

All findings can be explained by an increasing amount of P atoms with decreasing capping thickness which diffuse through the capping layer into the emitter, enhance recombination there, and derogate net p⁺ doping.

An adjusted etch-back solution raises \( R_{\text{sheet}} \) of the FSF successively and well controllably while almost completely maintaining \( R_{\text{sheet}} \) of the emitter at the rear (Fig. 5). Firstly, this results from the different etching efficacy of p and n-doped layers [9]. Furthermore, \( R_{\text{sheet}} \) of the p⁺ layer initially increases scarcely due to its relatively constant doping concentration and the absence of the kink and tail shape.

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Figure 2: Sample structures for \( R_{\text{sheet}} \) and \( j_0 \) investigation of p⁺ emitter and n⁺ FSF.

\( j_0 \) and implied \( V_{\text{OC}} \) are determined from photoconductance decay measurement evaluated at an injection level of \( \Delta n = 3\times10^{15} \text{ cm}^{-3} \) (high level injection mode) [13] using a Sinton lifetime tester.

Since sample type 1 and 2 are simultaneously subjected to the etch-back process, the \( j_0 \) values can be assigned to the respective \( R_{\text{sheet}} \).

Figure 3: Industrial n-type bifacial solar cell with APCVD B-emitter (AlOₓ/SiNx passivation) and selective FSF (SiNx passivation).

Figure 4: \( R_{\text{sheet}} \) and \( j_{0E} \) of a p⁺ emitter (passivation by annealed AlOₓ) after co-diffusion in a POCl₃ diffusion tube for different capping layer thicknesses.

Figure 5: \( R_{\text{sheet}} \) and \( \Delta \text{R}_{\text{sheet}} \) of a n⁺ emitter after POCl₃ diffusion with decreasing capping thickness.
In order to examine a potential influence of the initial high temperature (>900°C) B drive-in upon the n+ layer due to residual P atoms in the POCl3 tube, two sample types are processed with the FSF created by the complete B drive-in + POCl3 diffusion process and by the POCl3 diffusion only (Fig. 5).

Along with the increased FSF $R_{sheet}$ during the etch-back, $j_{0FSF}$ is reduced drastically (Fig. 6) as intended therewith. Especially for $R_{sheet} \leq 100 \, \Omega/\text{sq}$, $j_{0FSF}$ is further reduced (30-50 fA/cm$^2$) by enhancing passivation with a SiO$_2$/SiNx stack instead of a single SiNx layer (Fig. 6). A passivation consisting of SiO$_2$/SiNx instead of APCVD-AlOx capped by SiNx further reduces $j_{0E}$ by ~50 fA/cm$^2$. Besides a possible better passivating quality of SiO$_2$, this may be caused by a variation of the emitter doping profile, i.e. a reduction of surface doping density during high temperature thermal oxidation yielding less recombination.

The corresponding effective carrier lifetimes measured on sample structure 2 reach values of up to ~800 µs (B drive-in + POCl3) or ~1200 µs (POCl3 only), respectively. This can be regarded as the lower bound of the base carrier lifetime indicating that the Si substrate material is not considerably impaired by the high temperature processes in the POCl3 diffusion tube.

At the same time, $j_{0E}$ of the p' emitter remains virtually constant with increasing etch-back depth after an initial steep decrease by ~30 fA/cm$^2$ (Fig. 7). This drop may be caused by the removal of the BRL, which otherwise shields the actual emitter surface from being passivated. The more or less constant $j_{0E}$ behavior is in correlation with the moderate ascent of emitter $R_{sheet}$ during etch-back (cf. Fig. 5). A passivation consisting of SiO$_2$/SiNx instead of APCVD-AlOx capped by SiNx is expected from optimizing co-firing parameters, since a 43 Ω/sq p' emitter passivated by annealed APCVD-AlOx achieves a $j_{0E}$ of only 52 fA/cm$^2$ (cf. Fig. 4, see also sec. 3.2). Moreover, using AlOx instead of SiO$_2$ as passivation of the p' layer is beneficial because it can be deposited in the same industrial-type inline APCVD tool as employed for BSG deposition. Contrary to thermal oxidation, RCA pre-clean may be substituted, for instance, by less costly ozone cleaning.

Asymmetric $j_{0}$ samples featuring a structure similar to the final solar cell (struc. 4 in Fig. 2) yield $j_{0FSF}$ values saturating for a FSF etched-back to ≥100 Ω/sq at about ~60 fA/cm$^2$ (Fig. 8). $j_{0FSF}$ of the AlOx/SiNx−SiNx passivated samples is not consistent with the addition of $j_{0E}$ (Fig. 7) and $j_{0FSF}$ (Fig. 6), since measurement uncertainty for high $j_{0}$ values is greater. Additionally determined implied $V_{OC}$ of the same samples indicate the potential of the solar cell. The SiO$_2$/SiNx passivated samples attain values of up to 695 mV.
3.2 n-type solar cells

As a proof of concept, initial bifacial n-type solar cells (cf. Fig. 3) are manufactured employing a ~70 Ω/sq B-emitter. In Tab. I, the IV characteristics of the best solar cells with AlOx/SiNx – SiNx or SiO2/SiNx – SiO2/SiNx passivation scheme, respectively, are compared.

Table I: IV characteristics of the best bifacial n-type solar cells featuring AlOx/SiNx – SiNx or SiO2/SiNx – SiO2/SiNx passivation scheme.

<table>
<thead>
<tr>
<th>Passivation Scheme</th>
<th>Voc (mV)</th>
<th>Jsc (mA/cm²)</th>
<th>FF (%)</th>
<th>η (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>AlOx/SiNx – SiNx</td>
<td>655</td>
<td>38.5</td>
<td>73.9</td>
<td>18.6</td>
</tr>
<tr>
<td>SiO2/SiNx – SiO2/SiNx</td>
<td>647</td>
<td>38.4</td>
<td>75.8</td>
<td>18.8</td>
</tr>
</tbody>
</table>

Voc of the SiO2/SiNx passivated solar cell is 8 mV lower whereas FF is ~2%abs higher. Correspondingly, specific contact resistivity of the Ag/Al contact to the B-emitter with SiO2/SiNx passivation is reduced by 9 mΩcm² yielding a series resistance decrease by 0.6 Ωcm² compared to the AlOx/SiNx passivation.

Optimal firing temperature of the solar cells with SiO2/SiNx passivation is ~40 K higher. Implied Voc values of comparable pseudo solar cells without metallization exhibit their maxima (677 mV for AlOx/SiNx, 675 mV for SiO2/SiNx) each at the same firing temperature as the solar cells indicating AlOx to be less firing stable. Furthermore, the SiO2/SiNx passivated solar cells feature a ~0.1 µm deeper emitter profile (due to the additional high temperature oxidation) which is less susceptible to shunting by Al spikes and may also account for the better contact [14]. Nevertheless, the higher firing temperatures impair passivation quality more heavily.

4 CONCLUSION & OUTLOOK

In order to prevent a p⁺ emitter from APCVD-BSG from being compensated by P in a POCl3 co-diffusion, a SiOx capping layer is deposited also by APCVD. The p⁺ Rshunt increase after POCl3 co-diffusion is more pronounced with diminishing capping layer thickness while Jsc increases significantly because more P atoms derogate net p⁺ doping of the B-emitter.

For rear junction solar cells, it is crucial to ensure low recombination activity at the front. Therefore, a selectively etched-back FSF is to be established in the solar cell. An adjusted etch-back solution increases n⁺ Rshunt successively and well controllably, accompanied by a drastic Jsc reduction, while simultaneously almost completely maintaining p⁺ Rshunt at the rear.

No considerable Si substrate impairment due to the high temperature processes in the POCl3 diffusion tube could be ascertained. A 43 Ω/sq APCVD-AlOx passivated p⁺ emitter achieves a Jsc of 52 fA/cm². Total implied Voc of a pseudo solar cell structure attains up to 695 mV.

The newly developed APCVD p⁺ emitter combined with the co-diffused and selectively etched-back FSF has been employed in industrial bifacial n-type solar cells. Efficiencies of up to 18.8% have been attained, mainly limited by a poor Ag/Al contact to the B-emitter.

Further investigations are aimed at reducing contact resistivity and the implied Voc to Voc discrepancy by the appropriate adaption of the B-emitter profile.

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6 REFERENCES