Optimizing Emitter Diffusion Process for Atmospheric Pressure Dry Nanotextured Monocrystalline PERC

Ahmed Ridoy, Nabeel Khan, Bishal Kafle, Stefan Schmidt, Laurent Clochard, Marc Hofmann, and Jochen Rentsch

Abstract—In this article, we present an optimization of the emitter diffusion for nanotextured p-type monocrystalline silicon solar cells using atmospheric pressure dry etching (ADE) in conjunction with a post-ADE short acidic etch in a passivated emitter and rear cell (PERC) architecture. The optimization of the phosphorus oxychloride diffusion process was realized by first investigating the emitter sheet resistance and emitter recombination current density to achieve improved electrical properties and cell performances at a later stage. The optimization of the diffusion process enables an excellent homogeneity for emitter sheet resistance of 105 Ω/sq with minimized standard deviation of 3%, a decreased emitter saturation current density of ~120 fA/cm², a peak doping concentration of 2.2 × 10²⁰ cm⁻³ and depth of the highly doped surface region of 20 nm, still in the range that is required for good contact formation. By step optimization of the emitter formation of ADE textured PERC solar cells, an efficiency improvement of 0.6% could be reached leading to best conversion efficiency of 20.9%.

Index Terms—Atmospheric pressure dry etching (ADE), diamond-wire sawn (DWS), p-type monocrystalline silicon (mono-Si), POCl₃ emitter diffusion, POCl₃ emitter optimization, passivated emitter and rear cell (PERC).

I. INTRODUCTION

In recent years, low reflectivity nanotexturing processes sometimes referred as “black silicon” (B-Si), have generated large interest within the silicon-based photovoltaic industry, leading to higher solar cell performances [1]–[8]. The plasma-less fluorine-based atmospheric pressure dry etching (ADE) process [6]–[11] is one of the several other texturing methods that is being used to form nanotextured surface on silicon wafer, such as metal-assisted wet-chemical etching (MACE) [2], [3], reactive ion etching (RIE) [4], [5], laser-assisted texturing [12] and other plasma-less nanotexturing [13], [14].

It is a single-sided process with the ability to form low reflective texture independent of the base material (e.g., monocrystalline silicon [7], [9], multicrystalline silicon [8], [10], cast mono, kerf-less wafers etc.) and it provides interesting opportunity for its application as a universal texturing process in photovoltaic manufacturing facilities.

To date several phosphorus-based emitter optimization approaches, such as modifications in deposition temperature [6], [15], deposition duration [6], in situ oxidation [6], [15], [18], ion implementation doses [17] have been implemented on B-Si or nanotexture from ADE process [6], [15] and RIE process [16]–[18]. Furthermore, B-Si or nanotexture were sometimes combined with post-processes involving brief etching for surface modification prior to their following emitter optimization approaches, such as nanotexture from RIE process [17] and MACE process [2], [19], [20].

In order to reach their full potential, B-Si or nanotextured cells require an optimized emitter diffusion process to avoid excessive recombination [2], especially when using plasma enhanced chemical vapor deposition (PECVD) of silicon nitride (SiNₓ) as the sole front surface passivation layer.

In this article, as a continuous development of the integration of the ADE process into solar cell manufacturing technology, we will present optimization of the phosphorus oxychloride (POCl₃) emitter diffusion process applied on diamond-wire sawn (DWS) p-type monocrystalline silicon (mono-Si) passivated emitter and rear solar cell (PERC) type architecture: enabling excellent homogeneity of emitter sheet resistance over the textured surface and reaching higher cell efficiency. The experiment was divided into two steps: first, optimization of the emitter diffusion process on nanostructured surfaces; and second, solar cell fabrication process.

The article starts with a short introduction to the ADE process and its recent development through POCl₃-based emitter optimization process along with other relevant etching techniques responsible for the formation of B-Si or nanotextured surface. It is followed by a detailed discussion on the entire process of emitter optimization (e.g., workflow and process variation) and relevant characterization (e.g., emitter profile, sheet resistance, recombination current density). Afterward, the article moves on
to the discussion of the solar cell results [e.g., current-voltage (I–V) and quantum efficiency (QE) analyses] based on the application of the optimized emitter and its respective findings, followed by the summary and outlook of the work.

II. Emitter Optimization and Characterization

A. Workflow of Emitter Optimization

The workflow of the emitter optimization process is presented in Fig. 1.

The emitter optimization step involved both p-type and n-type of wafers: boron-doped p-type wafers (0.8 Ω cm ≤ ρ_	ext{base} ≤ 1.2 Ω cm) and phosphorus-doped n-type wafers with relatively high base resistivity (5 Ω cm ≤ ρ_	ext{base} ≤ 7 Ω cm).

All wafers went through saw-damage etching (SDE) using an anisotropic alkaline process. Three pairs of p-type and n-type wafers were created, so that each pair could go through three different etching processes.

1) B-Si nanotexture using an ADE tool [9] to create low reflectivity sub-micron structures on the front side and flat SDE on the rear side.

2) Reference alkaline texture, with random pyramids on both sides.

3) Reference flat wafers, with SDE process on both sides.

In this article, the ADE textured wafers exhibited a surface inhomogeneity that led to a varying surface reflection at the wavelength of 600 nm ranging from R_{600} ≈ 3%–5% to in few surface areas R_{600} ≈ 8%–10%. In order to decrease the surface roughness, the wafers subsequently went through a short isotropic acidic HF/HNO₃-based post-processing, increasing the surface reflectivity to a range between R_{600} ≈ 10%–12% and in few areas R_{600} ≈ 16%–18%, with the majority of the wafers within the range of R_{600} ≈ 10%–12%. This range is comparable to the alkaline textured wafers, which is important for later comparisons of subsequent diffusion results. To verify this, each p-type ADE textured wafer was measured for surface reflection (R_{600}) at 5 locations. Each n-type ADE textured wafer was also measured for emitter recombination current density (j_{0e}) at 5 locations, each measuring spot being approximately 3–4 cm in diameter.

A spectral representation of surface reflection (R) profiles along with their corresponding R_{600} and weighted surface reflection (R_w) values for ADE nanotextured surface and ADE texture with HF/HNO₃-based short isotropic acidic post-processed surface (an average one) in comparison to alkaline textured surface is presented in Fig. 2. Additionally, surface morphologies of ADE texture and postprocessed ADE texture using cross-section views in scanning electron microscope (SEM) are also presented in Fig. 3.

The p-type wafers were prepared for emitter characterization, such as emitter dopant profiling using electrochemical capacitance voltage (ECV) technique [22] and emitter sheet resistance (R_{sh}) measurements using four-point probe (4pp) method [22]. On the other hand, the n-type wafers were prepared only to analyze the j_{0e} by investigating carrier lifetime using quasi-steady state photoconductance (QSSPC) technique [23]–[25]. For the ADE textured wafers, being single-sided in nature, the j_{0e} for the flat wafers were used to account for the contribution from the flat rear side of the ADE wafers. All n-type wafers were passivated using a combination of plasma oxide layer followed by SiNₓ.

Emitter diffusion recipes optimized for standard alkaline texture (diffusion A) and three modified recipes (diffusion B, C, D) were applied within an industrial POCl₃-based tube diffusion furnace, followed by chemical edge isolation including phosphosilicate glass (PSG) etching. As reference, alkaline textured and saw-damage etched flat surface samples of the same bulk material were also prepared. Resulting emitters were characterized for all three surfaces—ADE, alkaline, and flat.
TABLE I
EMITTER VARIATIONS FOR EMITTER DIFFUSION

<table>
<thead>
<tr>
<th>Emitter diffusion</th>
<th>Diffusion recipe parameters</th>
<th>Drive-in step</th>
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<tbody>
<tr>
<td></td>
<td>Deposition step</td>
<td>Drive-in step</td>
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<tr>
<td></td>
<td>Temp. (T$_{dep}$)</td>
<td>Time (t$_{dep}$)</td>
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<tr>
<td>Diffusion A</td>
<td>higher</td>
<td>fixed</td>
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<tr>
<td>Diffusion B</td>
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<td>Diffusion C</td>
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<tr>
<td>Diffusion D</td>
<td>lower</td>
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B. Emitter Variation

Process parameters important for the emitter diffusion process were varied, such as gas flux, temperature and duration of the PSG deposition step and of the drive-in step as presented in Table I [26]. During this experiment, we mostly demonstrated the influences of temperature and duration combinations of the deposition step ($T_{dep}$) and the drive-in step ($t_{drive-in}$) in oxygen atmosphere, respectively, while keeping the gas flux constant, for $T_{dep}$ has major influence on the total dopant concentration while the depth of the p-n junction is defined mostly by $t_{drive-in}$ [26].

C. Emitter Profiles

Emitter doping profiles ($N$) of ADE wafers with different emitters diffused were measured by the ECV technique as shown in Fig. 4.

Diffusion B, having a relatively low deposition temperature, shows relatively low peak doping concentration ($N_{sur, B}$ $\approx$ 2.2 $\times$ $10^{20}$ cm$^{-3}$) with relatively low depth of highly doped surface region ($d_{high,B}$ $\approx$ 20 nm). Diffusion C, having an increased drive-in duration, increases the depth of the emitter as it allows phosphorus atoms more time to diffuse into the silicon substrate at elevated temperature, causing increased depth of the highly doped surface region ($d_{high,C}$ $\approx$ 27 nm) with relatively higher peak concentration ($N_{sur, C}$ $\approx$ 2.9 $\times$ $10^{20}$ cm$^{-3}$). Diffusion D was performed using a combination of low deposition temperature (same as diffusion B) and a longer drive-in duration (same as diffusion C), hence, lower depth of highly doped surface region ($d_{high,D}$ $\approx$ 20 nm) and lowered peak doping concentration ($N_{sur, D}$ $\approx$ 1.8 $\times$ $10^{20}$ cm$^{-3}$). Therefore, for diffusion D, the phosphorus surface concentration is lower than in diffusion B due to longer drive-in time, which drives phosphorus deeper and converts more highly doped silicon into silicon oxide (SiO$_x$), whereas, the emitter depth is lower than in diffusion C due to lower deposition temperature, which leads to smaller total phosphorus dose.

D. Emitter Sheet Resistance

The locally measured $R_{sh}$ by the 4pp technique is shown in Fig. 5.

In comparison, $R_{sh}$ is relatively higher in diffusion B than in diffusion D for each corresponding wafer group due to the shorter drive-in time. Longer drive-in time drives the dopants further, deepens the emitter and results in lower $R_{sh}$. Diffusion C shows relatively lower $R_{sh}$ than both diffusion B and D, because of higher phosphorus concentration and deeper emitter. The standard deviation of $R_{sh}$ for ADE wafers in diffusion B is lower ($\sigma$ $\approx$ 3.1%) than in diffusion D ($\sigma$ $\approx$ 4.0%), indicating a better emitter homogeneity. As shown in Fig. 4, diffusion B provides relatively lower dopant concentration for ADE wafers, hence, presumably less inactive phosphorus atoms.

The emitter sheet resistance measured for ADE textured wafers is lower than alkaline textured wafers for all diffusion variations, mostly due to the higher surface area of the ADE textured wafers enabling higher accumulation of phosphorus from the gas atmosphere than the alkaline textured wafers, in consistency to [27].
E. Emitter Recombination Current Density

The $j_{0e}$ was measured by investigating carrier lifetime using QSSPC, on the passivated $n$-type wafer groups as shown in Fig. 6. Diffusion B leads to the lowest $j_{0e}$ for all types of wafer surfaces. Diffusion C leads to the highest $j_{0e}$. Therefore, $j_{0e}$ shown in Fig. 6 follows the expected dependency on $R_{sh}$ shown in Fig. 5. However, the recombination current is much larger for the ADE textured wafers, even for comparable $R_{sh}$, as shown in Fig. 7, which requires further investigation.

F. Lifetime-Calibrated Photoluminescence (PL)

Differences in $j_{0e}$ can be better explained through the lifetime-calibrated PL images presented in Fig. 8 [28]–[30].

The alkaline textured wafers show a lot less damage/scratches than the other groups, and are more uniform, possibly due to less manual handling and deeper etching. While looking at the reference flat wafers from all different diffusions, it seems that the lifetime of the minority charge carriers in diffusion B is higher than the rest of the three diffusions (A, C, D). The nearest comparison for the flat wafer from diffusion B (wafer f2) seems to be the flat wafer from diffusion D (wafer f4).

On the other hand, PL for any given wafer type from diffusion C exhibit lower lifetime than their respective wafer types of all other diffusion variations (A, B, D), which could either be due to a deeper emitter compared to diffusion B and diffusion D or due to higher phosphorus concentration than diffusion B and diffusion D or could also be a combined effect of both these factors.

III. CELL BATCH

Based on the emitter profile, emitter sheet resistance, emitter recombination current density and lifetime-calibrated PL images of the ADE wafers, diffusion B provides lower dopant concentration and losses. Therefore, diffusion B was applied to make passivated emitter and rear cell (PERC) type solar cells on ADE texture, along with the originally optimized emitter for alkaline texture.

A. Workflow of Cell Fabrication

The workflow of the cell fabrication process is presented in Fig. 9.

The processed wafers were mono-Si grown by the Czochralski process, boron-doped $p$-type pseudosquare wafers with edge length of 156.75 mm, diameter of 210 mm, initial wafer thickness of $\approx 190 \mu m$ and base resistivity of $0.8 \Omega \text{cm} \leq \rho_{\text{base}}$.
The precursors were at first saw-damage etched using an anisotropic alkaline process, followed by nanotexturing using an ADE tool [9] to create low reflectivity B-Si submicron structures on the front side. The ADE wafers then went through a short isotropic acidic postprocess to decrease the surface roughness and increase the surface reflectivity ($R_{600} \approx 10\%$), leading the ADE textured wafers primarily with lowest reflection to a surface reflectivity comparable to the alkaline textured wafers.

The precursors went through all subsequent process steps typically applied to fabricate PERC architecture starting with rear surface passivation with 6 nm of aluminium oxide (AlO$_x$) by fast atomic layer deposition followed by a low-temperature annealing/outgassing process [31]. Afterward, the precursors received another dielectric coating of SiN$_x$ by applying PECVD [75 nm on front surface as antireflection coating (ARC) and 150 nm on rear surface as capping-layer]. After surface passivation, local contact opening of rear passivation layer is performed using a laser. Finally, the precursors were metalized using silver (Ag) paste to create the front contact in the form of fingers and busbars, and aluminum (Al) paste to create the rear contact by covering most of the rear surface. Before printing of rear contact, an Ag/Al paste was applied as well for solder pads to allow module integration. In the final step, both the ADE and the reference alkaline textured precursors of each emitter variation were divided into two groups in order to apply two different firing temperatures set at 850 °C and 870 °C. Finally, the cells were characterized for $I-V$ and QE analyses.

B. Surface Reflection

Reflection at the wavelength of 600 nm ($R_{600}$) of the acidic post-processed ADE wafers in each diffusion experiment is shown in Fig. 10. It can be seen that the reflection on the ADE wafers vary largely in this particular batch, therefore, this plot will assist in better understanding and effective comparison of the $I-V$ analyses of the ADE cells.

C. Current-Voltage Analyses

ADE textured wafers and reference alkaline textured wafers were prepared for both, diffusion A and diffusion B with PERC architecture and were characterized for $I-V$ analyses as presented in Fig. 11(a)–(d) as open-circuit voltage ($V_{oc}$), short-circuit current density ($J_{sc}$), fill factor (FF), and cell efficiency ($\eta$), respectively.
Open-circuit voltage ($V_{oc}$) is affected by the emitter recombination current, which depends on surface recombination, i.e., by surface defects and Auger recombination. Lower surface reflection of postprocessed ADE wafers, shown as yellow and blue squares in Fig. 10, corresponds to a deeper texture (higher density of surface defects), which increases surface recombination, hence, lowers $V_{oc}$, corresponding to the yellow and blue squares shown in Fig. 11(a). Phosphorus surface concentration for ADE textured wafers was found higher than alkaline textured wafers due to higher surface area [21], expected to lead to higher surface recombination, resulting in lower $V_{oc}$ for ADE textured cells with lowest reflectivity and/or highest surface doping concentration. This particular batch suffered from strong reflectivity variations, both within a single wafer surface, and also wafer to wafer. Both $V_{oc}$ and $J_{sc}$ results are very dependent on the specific reflectivity of the sample. $V_{oc}$ levels comparable to the reference were mostly achieved with average reflectivity $> 14\%$.

Overall, in terms of $V_{oc}$, cells with diffusion B yield higher efficiency than cells with diffusion A. The lowest and highest reflective ADE cells with diffusion B show higher $V_{oc}$ (at both firing temperatures) than the corresponding ADE cells with diffusion A.

The short-circuit current density ($J_{sc}$) of the ADE cells are improved in diffusion B compared to diffusion A. As indicated by yellow and blue squares in Fig. 10 and (b). For low reflectance wafers, higher $J_{sc}$ was expected. However, $J_{sc}$ was the lowest for lowest reflectance wafers. Associated with lowest $V_{oc}$, it suggests that the current for these cells is not limited by the reflection, but by the surface and emitter recombination [10].

ADE cells show higher FF overall than the alkaline reference cells as shown in Fig. 11(c), which is partly linked to lower $R_{sh}$ of ADE, as shown in Fig. 5. The FF is not much influenced by the diffusion process temperature or firing temperature variations applied.

ADE cells with diffusion B on average show higher conversion efficiencies than the ADE cells with diffusion A as shown in Fig. 11(d). The best performing ADE textured cell for diffusion B is 20.9% efficient (fired at 850 °C) and the lowest performing ADE textured cell for diffusion B is 19.2% efficient (fired at 870 °C).

The lower temperature diffusion process (diffusion B) seems more favorable to the ADE cells. This lower temperature setting is required to reach emitter sheet resistance values above 100 $\Omega$/sq. Also the lower firing temperature (850 °C) seems more favorable to the ADE cells. Altogether, lower temperature settings lead to better cell results while using the ADE textured samples.

D. Quantum Efficiency Analysis

ADE cells and reference alkaline cells for both, diffusion A and diffusion B were measured for QE analysis, where each cell represents the sample with highest weighted reflection ($R_w$) within their respective groups as shown in Fig. 12. The QE measurement was performed locally on the cells with a measurement area of $2 \times 2$ cm$^2$.

Within the region of shorter wavelength, 350–650 nm, ADE cells from group B have slightly lower reflections than those of group A. Furthermore, internal quantum efficiency (IQE) of group B in that short wavelength region is higher than group A, correlating to the higher sheet resistance ($R_{sh}$) obtained with diffusion B, as shown in Fig. 5. This could confirm that diffusion B has lessened Auger recombination by reducing inactive phosphorus contents for ADE textured wafers. The improvement from diffusion B on ADE textured wafers leads to an IQE that roughly matches this of the reference alkaline textured wafer (diffusion A).

ADE cells towards the beginning of the spectrum have higher reflection and lower IQE compared to alkaline cells from the same diffusion group. It could result from a more porous and rough surface texture of the ADE wafers, which eventually contributed to large variance in surface reflection, as shown in Fig. 10.

Within the region of longer wavelength, alkaline cells exhibit lower reflection and higher IQE, mostly due to the texture size matching of the incident light’s wavelength.

IV. SUMMARY

In this article, we report on the optimization of POCl$_3$ diffusion process on ADE nanotextured wafers in conjunction with a short acidic post-process and apply the results to $p$-type monocrystalline silicon PERC cells.

Nanotextured surfaces, resulting from their enlarged surface area, usually accumulate larger amount of phosphorus dopants during POCl$_3$ diffusion, which results in higher doping, thus could lead to Auger recombination in the emitter. This was dealt with by lowering the PSG deposition temperature, resulting in lowered dose of phosphorus dopants in the emitter. It was found in this article, to decrease the emitter recombination current density ($j_{0e}$) by more than 12%. On the other hand, a diffusion process operating at longer dopant drive-in time increased the emitter profile depth, while also improving the emitter sheet resistance ($R_{sh}$) and the emitter recombination current density ($j_{0e}$) on ADE nanotextured surfaces. It resulted in $R_{sh}$ and $j_{0e}$ values of $\sim$105 $\Omega$/sq and $\sim$120 fA/cm$^2$ respectively. Despite a large distribution of surface reflection of the ADE samples, the
optimized emitter shows excellent homogeneity for emitter sheet resistance, in the range that is desired for good conductivity.

A lower PSG deposition temperature processing is therefore more favorable for the ADE textured cells, since this surface exhibits an increased ability to react with the doping gas atmosphere. Reducing both deposition step temperature and firing temperature lead to improved cell performances reducing even further might be beneficial.

ADE textured cells with the optimized emitter reached on average efficiency gain of 0.6%abs compared to the non-optimized emitter, with peak cell efficiency reaching to 20.9% absolute. ADE textured cells show higher fill factor than the alkaline reference cells, and suffered mostly from lower current for all cells, combined with lower $V_{oc}$ for the ADE cells of lower reflectivity. Alkaline reference cells led to a peak efficiency of 21.4%. The optimized diffusion recipe lead to a noticeable IQE improvement of the ADE textured cells, roughly matching the IQE of the reference process.

This particular ADE batch suffered from strong reflectivity variations. Hence, ADE reflectance was modified to approach that of the reference alkaline texture. Nevertheless, for ADE surfaces, $f_{oc}$ remains higher, whereas, IQE in short wavelength region remains lower than those of the reference texture, despite achieving $R_{sh}$ values above 100 Ω/sq. The emitter recombination and lower IQE limitations of ADE texture need to be overcome. For further experiment, the analysis of the results would be facilitated by using a more uniform batch and uniformly textured wafers.

Furthermore, the ADE cell current could be enhanced by reducing front surface recombination through reduced surface roughness, enabling improved surface passivation.

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