ABSTRACT: We investigate the impact of high-temperature processes on phosphorus-doped n-type Czochralski-grown silicon (Cz-Si) wafers. Wafers from five ingots are subjected to high-temperature process sequences with different temperatures, times, and gas atmospheres. The process sequences are specifically chosen to represent different routes for the fabrication of high-efficiency n-type Cz-Si solar cells. As POCl₃ diffusion is known for its effective gettering of metal impurities, it is preferably used as the last high-temperature step. However, our results show that other process sequences, e.g. with BBr₃ diffusion as last high-temperature step, enable high charge carrier lifetimes in the range of a few milliseconds as well. For some materials and process sequences, ring-shaped defect structures are observed while for others increased charge carrier lifetimes by a factor up to 2.6 are found compared to their initial values prior to high temperature processing.

Keywords: n-type, silicon, high-temperature processes, lifetime, precipitates, oxygen, POCl₃ diffusion, BBr₃ diffusion, nitrogen
With thermal processes

<table>
<thead>
<tr>
<th>Process</th>
<th>Description</th>
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<tbody>
<tr>
<td>alkaline cleaning</td>
<td>Wet-chemical cleaning</td>
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<tr>
<td>First high-temperature tube furnace process</td>
<td>PSU/BGS/SiO₂ etching</td>
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<td>Second high-temperature tube furnace process</td>
<td>Measurement of μ delights</td>
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Reference (Ref) without thermal processes

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<tr>
<th>Process</th>
<th>Description</th>
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<tbody>
<tr>
<td>Initial measurement of μ delights with thermal donors</td>
<td>None</td>
</tr>
<tr>
<td>alkaline cleaning</td>
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</tr>
<tr>
<td>PSU/BGS/SiO₂ etching</td>
<td>PSU/BGS/SiO₂ etching and KOH etching</td>
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Pyramid formation in alkaline solution and wet-chemical cleaning, the wafers are subjected to one or two selected high-temperature processes such as BBr₃, POCl₃, or N₂ tube furnace processes at different T_peak and T_ref (see Table I). In between those two processes, the possibly formed phosphosilicate glasses (PSG), borosilicate glasses (BSG) or SiO₂ layers (depending on the used processes) are removed in HF solution. The two subsequently carried out high-temperature processes are referred to as “process 1 + process 2” (e.g., “BBr₃ + O₂ low”). The double-sided highly-doped regions after the initial POCl₃/BBr₃ diffusion are neither removed nor coated by diffusion barrier layers for the second high-temperature process. One reference group per material is not subjected to any high-temperature process.

After the high-temperature sequences, all surface oxide layers are removed in HF solution and the diffused and textured surfaces are subsequently etched back and smoothened in KOH solution (silicon removal of about 10 um from each side resulting in a final wafer thickness W ≈ 150 μm, also for the reference group). The used high-temperature processes dissolve any thermal donors which might have existed before. To determine information about the content of thermal donors per material, another measurement of \( \rho_{\text{Base}} \) is performed at this stage of the experiment.

Following wet-chemical cleaning, the alkaline saw-damage etched surfaces are passivated with a layer stack consisting of silicon-rich oxynitride (SiRiON) [7] and silicon nitride (SiNₐ) deposited by PECVD. After activating the passivation layers in a fast firing furnace at a set peak temperature of 700°C, the effective charge carrier lifetime \( \tau_{\text{eff}} \) is measured by QSSPC at five positions over each wafer and spatially resolved PL images are recorded. As all wafers are identically wet-chemically etched and passivated, we assume the surface recombination velocity to be very similar for all wafers. Therefore, we conclude that all correlations found for the measured effective lifetimes can be related to the silicon bulk.

The base resistivities \( \rho_{\text{Base}} \) of the five n-type Cz-Si ingots investigated in this work are shown in Fig. 2 with and without thermal donors. Thermal donors can be correlated to the oxygen content of the Cz-Si [8]. For Mat1, \( \rho_{\text{Base}} \) is determined to be \( \rho_{\text{Base}} \approx 1.6 \, \Omega \text{cm} \) with and without thermal donors. Thus, the thermal donors within this material is marginal. In contrast, \( \rho_{\text{Base}} \) for Mat3 increases from \( \rho_{\text{Base}} \approx 4.2 \, \Omega \text{cm} \) with thermal donors to \( \rho_{\text{Base}} \approx 11.1 \, \Omega \text{cm} \) without thermal donors, which comes along with a high content of thermal donors. The different materials have been chosen such that the investigation includes materials with different amounts of thermal donors to examine if they affect the material properties after exposure to different high-temperature processes.

3 RESULTS

3.1 Base resistivity with and without thermal donors

The base resistivities \( \rho_{\text{Base}} \) of the five n-type Cz-Si materials investigated in this work are shown in Fig. 2 with and without thermal donors. Thermal donors can be correlated to the oxygen content of the Cz-Si [8]. For Mat1, \( \rho_{\text{Base}} \) is determined to be \( \rho_{\text{Base}} \approx 1.6 \, \Omega \text{cm} \) with and without thermal donors. Thus, the content of thermal donors within this material is marginal. In contrast, \( \rho_{\text{Base}} \) for Mat3 increases from \( \rho_{\text{Base}} \approx 4.2 \, \Omega \text{cm} \) with thermal donors to \( \rho_{\text{Base}} \approx 11.1 \, \Omega \text{cm} \) without thermal donors, which comes along with a high content of thermal donors. The different materials have been chosen such that the investigation includes materials with different amounts of thermal donors to examine if they affect the material properties after exposure to different high-temperature processes.

3.2 Experiment 1: material variation

Fig. 3a) shows the effective charge carrier lifetimes \( \tau_{\text{eff}} \) measured by QSSPC at an injection level \( \Delta n = 10^{15} \text{cm}^{-3} \) for the five materials and five different high-temperature process sequences after firing. The reference group “Ref” processed without any high-temperature steps is also stated. It is evident that the materials Mat3 and Mat4 with higher \( \rho_{\text{Base}} \) show higher \( \tau_{\text{eff}} \) throughout the experiment due to less recombination active centres.

For easier interpretation, we calculate the lifetime factor \( \beta \) by dividing \( \tau_{\text{eff}} \) per material and process sequence by the effective charge carrier lifetime \( \tau_{\text{eff,Ref}} \) measured for the reference group per respective material:

\[
\beta = \frac{\tau_{\text{eff}}}{\tau_{\text{eff,Ref}}} \tag{1}
\]

Fig. 3b) shows \( \beta \) for all groups.

Compared with \( \tau_{\text{eff,Ref}} \) the measured \( \tau_{\text{eff}} \) increases for all materials after a single POCl₃ diffusion by 1.6 ≤ \( \beta \) ≤ 2.4 or after sequential BBr₃ + POCl₃ diffusions by 1.2 ≤ \( \beta \) ≤ 2.6. Mat1 shows \( \tau_{\text{eff}} \) up to \( \tau_{\text{eff}} \approx 3 \, \text{ms} \) after single POCl₃ diffusion and Mat3 and Mat4 even up to \( \tau_{\text{eff}} \approx 6 \, \text{ms} \).

With BBr₃ diffusion being the second process (sequences: POCl₃ + BBr₃ and O₂ low + BBr₃), \( \tau_{\text{eff}} \) is on the
same level as the group Ref independent of whether there has been a POCl3 diffusion or process O2 low before BBr3 diffusion. The factor $\beta$ is found to be $\beta \approx 1$ for most of the materials or even $\beta \approx 1.3$ for Mat1 and Mat5.

Only the process sequence BBr3 + O2 low significantly reduces $\tau_{\text{eff}}$ by $0.3 \leq \beta \leq 0.7$ compared with group Ref. This degradation might be correlated with the O2 low process as for all other combinations with BBr3 diffusion the factor $\beta$ is found to be $\beta \geq 1$ (see discussion above). A more detailed discussion will follow when discussing the PL images.

In the literature, it is reported that BBr3 diffusion might lead to a significant degradation of $\tau_{\text{eff}}$ [9]. Here, we demonstrate that our optimized BBr3 diffusion process is suitable for sequential diffusion processes. In combination with POCl3 diffusion, $\tau_{\text{eff}}$ is at least the same as for group Ref, no matter which process order is used. When using sequential diffusion processes with POCl3 first and then BBr3, the phosphorus atoms can be driven-in even deeper during the BBr3 diffusion. Our results indicate that both orders of the two diffusion processes are suitable for cell manufacturing, but for cell concepts that heavily rely on high bulk lifetimes, such as back contact back junction cells, POCl3-last processing does appear to be advantageous.

Single POCl3 diffusion as well as POCl3-last processing lead to highest $\beta$ values in this investigation. This might be correlated to a high gettering effect initiated by POCl3 diffusion. In n-type silicon, impurities as Co, Cr, Ni and Fe might be recombination active and reduce $\tau_{\text{eff}}$ [10]. Phosphorus gettering is known to reduce these impurities in silicon wafers [11–14]. However, it is
not clear which type of impurity is relevant for the n-type wafers used in our investigation.

However, all materials show the same trends for the different process combinations. Most of the materials and most of the process sequences show $\tau_{\text{eff}} > 1$ ms and $\beta \geq 1$. Mat4 shows the lowest $\beta$ for all process sequences compared with the other materials. In comparison with Mat1, Mat2, and Mat5, the content of thermal donors is much higher (see Fig. 2). Thus, the thermal donors might affect $\tau_{\text{eff}}$ for Mat4. However, the high content of thermal donors for Mat3 does not seem to affect $\tau_{\text{eff}}$.

In Fig. 4, PL images for the five materials after the high-temperature processes, as indicated in Fig. 3, are shown for one representative wafer per group after firing. Lines with lower PL intensity parallel to the wafer edges are caused by an insufficient saw-damage etching. Other scratches are attributed to wafer handling. The group Ref without any high-temperature processing is also shown in the very right column.

As already discussed, the process combination BBr$_3$ + O$_2$ low shows a degradation of $\tau_{\text{eff}}$ for all materials (Fig. 3). This can also be seen from the PL images. Wafers processed with BBr$_3$ + O$_2$ low show a dark area with lower PL intensity for all materials (Fig. 4). These dark structures might originate from an interaction of boron dopants and silicon interstitials injected by the O$_2$ low oxidation causing lower $\tau_{\text{eff}}$ compared with the reference group Ref. As these dark structures are visible in every material, they might be attributed to the process sequence and not to the material properties.

Mat2 and Mat3 show slight ring structures for the process sequence POCl$_3$ + BBr$_3$, and Mat3 also for the sequence O$_2$ low + BBr$_3$. Such ring structures are typically formed by oxygen precipitate formation [15]. These ring structures seem not to cause a significant degradation of $\tau_{\text{eff}}$ for Mat2. The QSSPC measurement performed in the wafer’s center results in a similar $\tau_{\text{eff}}$ as the measurements performed at the other four positions. The wafers from Mat3 behave different. The QSSPC measurement in the wafer’s center shows about 10% lower $\tau_{\text{eff}}$ compared to the measurement at the other four positions for both sequences with BBr$_3$-last processing.

In general, Mat3 with high content of thermal donors behaves similar as Mat1 with marginal content of thermal donors. Only for the process sequences with BBr$_3$-last processing small ring defects and a slight degradation of $\tau_{\text{eff}}$ occur in the wafer’s center for Mat3. But these ring defects are also visible for Mat2 which does hardly contain any thermal donors. Hence, thermal donors do not seem to significantly influence the materials’ properties after exposure to specific high-temperature processes.

3.3 Experiment 2: high-temperature process sequence variation

For Mat1 and Mat2, the influence of the order of high-temperature processes with higher or lower temperature first as well as the applied gas atmosphere on $\tau_{\text{eff}}$ is investigated in more detail. The used process sequence is the same as in Fig. 1 and the measured $\tau_{\text{eff}}$ after firing are shown in Fig. 5a). Again, we calculate the lifetime factor $\beta$ as given in Eq. (1); see Fig. 5b).

Again, it is obvious that the POCl$_3$ diffusion process being the second high temperature process shows an increased $\tau_{\text{eff}}$ compared with the reference group Ref. The factor $\beta$ is calculated to be $\beta = 2.6$ and $\beta = 1.8$ for Mat1 and Mat2, respectively, when O$_2$ high is the preceding high-temperature process. These $\beta$ values are very similar as those calculated for Mat1 and Mat2 after a single POCl$_3$ diffusion (see section 3.2). But when N$_2$ high is the preceding high-temperature process before POCl$_3$ diffusion, the process combination POCl$_3$ + BBr$_3$ shows a degradation of $\tau_{\text{eff}}$, which is similar as those calculated for Mat1 and Mat2 after a single POCl$_3$ diffusion process. This can also be seen from the PL images.
diffusion, $\beta$ is reduced to $\beta = 1.3$ for both materials. Thus, the process $O_2$ high seems advantageous compared to $N_2$ high within the process sequence with following POCl$_3$ diffusion.

However, most of the process sequences with the high-temperature process at low temperature first and the process at high temperature second yield $1.3 < \beta < 2.6$, only the sequence $N_2$ high + $N_2$ low shows a reduced $\tau_{\text{eff}}$ with $\beta \approx 0.7$ for both materials. The reason for this is not clear yet and further investigations are necessary.

Mat2 shows reduced $\tau_{\text{eff}}$ after process sequences with the higher temperature last (either $O_2$ or $N_2$ gas atmosphere). The factor $\beta$ is found to be $0.6 < \beta < 0.9$ for Mat2 while $1.2 < \beta < 1.6$ for Mat1. The origin can be found in ring-like structures as apparent from the PL images in Fig. 6. For Mat2, $O_2$ high as well as $N_2$ high cause dark ring structures when being the second high-temperature process. The PL intensity in the ring area is even lower for $O_2$ high than for $N_2$ high. This is not only valid when POCl$_3$ is the first process but also for the groups with $O_2$ low + $O_2$ high or $N_2$ low + $N_2$ high (PL images not shown). As already mentioned, such ring structures are typically formed by oxygen precipitate formation [15]. But no ring structures are visible when $O_2$ high is the first process followed by either POCl$_3$ diffusion or $O_2$ low.

Furthermore, a lot of point-like structures appear especially for Mat1 after the process sequences featuring $N_2$ high as first process, as can be seen in the PL images in Fig. 7a) for representative wafers of material Mat1. The point-like structures are obvious for the sequences $N_2$ high + POCl$_3$ as well as $N_2$ high + $N_2$ low. These point-like structures might be attributed to oxide stacking faults [16]. But as $\beta = 2.6$ for Mat1 and the process sequence $N_2$ high + POCl$_3$, these point-like structures seem not to necessarily reduce $\tau_{\text{eff}}$. When changing the process order to $N_2$ low + $N_2$ high, no point-like structures are visible.

Fig. 7b) shows the enlargement of the area marked in Fig. 7a). The PL images are taken as-cut, after process $N_2$ high, after POCl$_3$ diffusion and finally after passivation and firing. It is obvious that the point-like structures occur right after the $N_2$ high process. They stay at the same positions after POCl$_3$ diffusion as well as after passivation and firing. This indicates that the point-like structures can be related to the silicon bulk and not to the surface. The reason for these point-like structures as well as their impact on $\tau_{\text{eff}}$ need to be further investigated.

4 SUMMARY AND CONCLUSION

The present work shows the impact of high-temperature processes at different temperatures, times, and gas atmospheres on n-type Czochralski-grown silicon wafers. Symmetric sample for lifetime measurements have been processed from wafers from five different ingots with different base resistivities and different contents of thermal donors. The high-temperature processes include BBr$_3$, POCl$_3$, $O_2$, or $N_2$ tube furnace processes, which are typically used for fabrication of high-efficiency n-type silicon solar cells.

The five materials react very differently to the high-temperature process sequences. Some process sequences have a positive impact on the effective charge carrier lifetimes $\tau_{\text{eff}}$ of these wafers, while other wafers show reduced $\tau_{\text{eff}}$. The five materials react very differently to the high-temperature process sequences. Some process sequences have a positive impact on the effective charge carrier lifetimes $\tau_{\text{eff}}$ of these wafers, while other wafers show reduced $\tau_{\text{eff}}$.

POCl$_3$-last processing has a positive impact on $\tau_{\text{eff}}$ for all materials. This might be related to a POCl$_3$ gettering that reduces recombination active impurities in the silicon wafers. After single POCl$_3$ diffusion, this results in $3 \text{ ms} \leq \tau_{\text{eff}} \leq 6 \text{ ms}$ for all investigated materials.

Our optimized BBr$_3$ diffusion process is suitable for sequential diffusion processes. In combination with POCl$_3$ diffusion, $\tau_{\text{eff}}$ is at least the same as for the reference group (no high-temperature processing), no matter which process order is used.

For process sequences with a moderate temperature in the first and a high temperature in the second process, some of the investigated wafers show ring structures, which likely originate from oxygen precipitate formation. These materials do not show any ring structures when changing the order of the high-temperature processes. Besides ring structures, also point-like structures are observed for some wafers which are subjected to process sequences with pure $N_2$ gas atmosphere at 1000°C as first process. These point-like structures might be attributed to oxide stacking faults, but they seem not to necessarily reduce $\tau_{\text{eff}}$.

An appropriate order of the high-temperature processes enables final charge carrier lifetimes that maintain or even exceed the values initially measured without any high-temperature processing.

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REFERENCES


