Impact of compensation on the boron and oxygen-related degradation of upgraded metallurgical-grade silicon solar cells

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1. Introduction

Simultaneous presence of boron (B) and oxygen (O) in crystalline silicon (Si) is known to result in the existence of a strong recombination center – the boron–oxygen (BO) defect – which forms or is activated under excess carrier injection. In its active state, the BO defect dominates bulk recombination in B-doped cast or Czochralski (Cz)-grown Si, on which most of the photovoltaic industry is based. One would naturally expect that solar cells made with upgraded metallurgical-grade (UMG)-Si are more affected by the BO defect, due to larger B concentration in this material than in Siemens-purified Si. Recent studies, however, found that the BO defect density was proportional in p-type Si to the net doping, rather than to the total B concentration, meaning that it could thus be reduced by compensation [2–5]. This finding was more recently contradicted by a study of the BO defect density evaluated by lifetime measurements before and after degradation is systematically found proportional to the total boron concentration, showing that compensation cannot reduce light-induced degradation. This result is confirmed by a comparison of upgraded-metallurgical grade silicon solar cells having identical boron, oxygen and carbon but different compensation levels and in which the degradation is found more severe when the compensation is stronger.

Another lately debated issue is the composition of the BO defect complex. Guided by observations that the BO defect density depends on the net doping – or majority carrier density – Voronkov and Falster [10] proposed a model in which the defect complex is made with interstitial boron (B_i). The dependence of the BO defect density was thereby explained by the proportionality of the solubility of positively charged B_i to the hole concentration, during the last phase of crystal cooling.

Measurements in n-type compensated Si [11–13] and in Si co-doped with B and Ga [14] were nonetheless found inconsistent with the involvement of B_i but rather suggested the participation of substitutional B (B_s).

In addition, the BO-related lifetime degradation was found invariant with respect to the presence of interstitial silicon atoms [15,16]—which are themselves likely to influence the concentration of interstitial boron. Recent calculations also found that the
concentration of B, was too low to explain the observed lifetime degradation and that the calculated characteristics of the BO$_2$$_3$ complex were inconsistent with those measured by lifetime spectroscopy for the BO defect [17]. On the other hand, participation of B, in the BO defect complex remains very difficult to reconcile with the linearity of the defect density to the net doping [18].

In the present work, we aim at verifying the effect of compensation on the BO recombination center and clarifying the composition of the defect complex. In a first experiment, we study the BO-related lifetime degradation in Si samples with a wide range of dopant concentrations and compensation levels. We evaluate the oxygen-normalized effective BO defect density and find that it depends on the total boron concentration, demonstrating the involvement of substitutional boron in the defect complex. In a second experiment, we crystallize two different Cz ingots having identical B, O and C profiles but different compensation levels. Then, we fabricate solar cells with wafers from both ingots and measure their behavior under illumination. We find that the activation of the BO defect leads to stronger performance degradation in solar cells made with heavily compensated Si than with lightly compensated Si. This experiment unambiguously shows that compensation does not mitigate the impact of the BO defect on solar cells but on the contrary worsens it.

2. Experimental methods

2.1. Study of the lifetime degradation in compensated silicon wafers

This study was carried out on p-type Cz-Si samples co-doped with Ga and B, B and P or B, P and Ga. These samples originate from a batch of <100> oriented Si ingots which were crystallized using the Czochralski pulling technique. They were grown using electronic-grade (EG)-Si to which were added various concentrations of B, P and Ga. In each sample, $p_0$ was deduced from Hall effect measurement, assuming a Hall factor of $r_H = 0.75$ [19], $[B]$ was deduced from the sample’s position in the ingot, and from the initial concentration of B added into the Si melt, using Scheil’s equation [20]. Together with uncompensated B-doped, P-doped and Ga-doped controls, these samples were subsequently acid etched to remove saw damage, RCA cleaned, and underwent a phosphorus diffusion gettering at 820 °C to dissolve oxygen-related thermal donors and eliminate metallic impurities. This ensures that there is no or very little impact of FeB and FeGa pairs during the degradation experiment. Diffused regions were then removed by an additional acid etch and samples were RCA cleaned before being coated on both sides by hydrogenated Si nitride (SiN$_x$:H) at 235 °C, using plasma-enhanced chemical vapor deposition (PECVD).

After deposition, samples were annealed in the dark at 200 °C under air ambient during 30 min, in order to annihilate the boron-oxygen defect. The effective lifetime was then measured using inductively-coupled photo-conductance decay [21], immediately after annealing ($r_0$) and after different times $t$ of illumination under a 10 mW/cm$^2$ halogen lamp at 25–27 °C.

A fit to Dannhauser and Krause’s mobility sum measurements [22–24] is commonly used to convert photo-conductance data into excess carrier density for injection-dependent lifetime measurements [21]. This fit is accurate in uncompensated Si [25] but overestimates the mobility sum in compensated Si [26]. To account for that lower mobility in our samples, we adjust the doping used as input in the fit to Dannhauser and Krause’s mobility so that it yields the same low-injection mobility sum as we previously measured in our compensated samples (see [27]).

As illustrated in Fig. 1, the effective lifetime degraded under illumination in all samples except for those which did not contain B, in which it remained stable. This proves that the surface passivation quality of the SiN$_x$:H layer did not change throughout the experiment. The observed degradation in samples containing B can thus be attributed to a decrease of the bulk lifetime. After complete degradation, i.e. after saturation of the measured lifetime to its final value $\tau_{deg}$, the effective BO defect density is calculated using the following expression:

$$N_B^f = \frac{1}{\tau_{deg}} - \frac{1}{\tau_0}$$

(1)

in which $\tau_{deg}$ and $\tau_0$ are taken at a fixed injection level of $\Delta n = 0.1 \times p_0$. It is well known that the effective defect density after complete degradation $N_{B, sat}$ displays a quadratic dependence on $[O_i]$ [28]. This dependence is thought to be due to the participation of oxygen dimers which are themselves present in a concentration proportional to $[O_i]$ squared [29]. Since we intend to study the impact of dopants on the BO defect density, a more relevant parameter to focus on is,

$$N_{BC} = \frac{N_{B, sat}}{[O_i]^2}$$

(2)

This oxygen-normalized parameter reflects the influence of defect components (such as [B] or $p_0$) not directly related to $[O_i]$. To evaluate $N_{BC}$ in our samples, SiN$_x$:H layers were etched off in hydrofluoric acid after the degradation experiment and $[O_i]$ was measured by Fourier transform infrared spectroscopy (FTIR).

2.2. Study of the degradation of compensated Si solar cells

2.2.1. Feedstock preparation

For this study, we used 30 kg of PHOTOSIL UMG-Si [30–32]. The starting metallurgical-grade (MG)-Si was produced by FerroPEM, with careful selection of raw materials, i.e. silica and carbon, enabling to limit the initial impurity concentration. A first segregation treatment was applied during solidification of this MG-Si straight away after carbothermic reduction, decreasing the concentration of phosphorus and metallic impurities. The resulting material was then transferred to the PHOTOSIL facilities where it was purified according to the standard PHOTOSIL process [30–32], involving a plasma treatment to remove B and segregations to remove P and metallic impurities. After purification, the Si feedstock contains 0.25 ppmw of B and 0.60 ppmw of P.

![Figure 1](image-url)
2.2.2. Crystallization

This lot of 30 kg of PHOTOSIL UMG-Si was divided into two batches of 15 kg, considered as identical in terms of impurity concentration. These two batches were used to grow two different \(< 100 \rangle\)-oriented Si ingots of about 160 mm in diameter using the Czochralski crystallization technique. Both crystals were pulled with an average rate of \(v = 0.7\) mm/min, a crystal rotation rate of \(w_{\text{cryst}} = 1.26\) rad s\(^{-1}\) and an inverse rotation of the crucible with a rate of \(w_{\text{cruc}} = 0.84\) rad s\(^{-1}\) under an Ar pressure of 20 Torr.

The first crystal, which we will refer to as Cz\#U1, was grown without addition of any dopants aside from those already contained in the UMG-Si. The second ingot, called Cz\#U2, was grown using the same crystallization process except that we added 1.4 ppmw of P and 85 ppmw of Ga into the crucible before melting of the Si. The addition of P enables to reduce the net doping while the addition of Ga serves to maintain fully p-type ingot. Note that without the addition of Ga, adding P into the Si melt would reduce the \(p\)-type fraction of the ingot and thus the ingot yield. After crystallization, both ingots were shaped into 125 \(\times\) 125 mm\(^2\) pseudo-square bricks and the resistivity and carrier lifetime profiles were measured respectively by Eddy current and \(\mu\)W-PCD along the length of each brick.

2.2.3. Solar cells fabrication and characterization

Both ingots were then cut by a slurry wire saw into wafers with a thickness of about 200 \(\mu\)m. Hall effect measurements were carried out on 2 \(\times\) 2 cm\(^2\) samples cut into wafers taken from different heights along each ingot.

Industrial type screen printed solar cells with full area phosphorous front side diffusion and Al back contact were fabricated at ISC Konstanz with 40 wafers of each one of the two ingots, evenly distributed along their lengths. Uncompensated B-doped EG-Si control wafers were processed simultaneously—10 wafers with a resistivity of 1.5 \(\Omega\) cm and 10 wafers with a resistivity of 3.0 \(\Omega\) cm.

The current–voltage (I–V) characteristics of these solar cells were then measured using a flash I–V tester before degradation and after 60 h under illumination at a temperature of 60 °C. The temperature was chosen to be high enough to ensure complete degradation after only 60 h under illumination (see Fig. 2), but still low enough so that significant annihilation [28] or permanent deactivation [33,34] of the BO defect is not expected to occur.

3. Results and discussion

3.1. BO defect density in compensated Si wafers

To observe separately the potential influences of \([B]\) or \(p_0\) on \(N_{\text{BC}}\) we selected among our samples groups with equal \(p_0\) and other groups with equal \([B]\). To study the influence of \([B]\), we found two groups of samples with iso-\(p_0\): one with 7 samples having \(p_0 = (2.0 \pm 0.3) \times 10^{16}\) cm\(^{-3}\) and one with 3 samples with \(p_0 = (5.7 \pm 0.4) \times 10^{16}\) cm\(^{-3}\). Plotting \(N_{\text{BC}}\) against \([B]\) in these two groups (Fig. 3(a)) reveals a clear correlation between these two quantities. To study the influence of \(p_0\), we found two groups of 4 samples, the first one with \([B] = (1.7 \pm 0.06) \times 10^{17}\) cm\(^{-3}\) and the second one with \([B] = (3.6 \pm 0.6) \times 10^{16}\) cm\(^{-3}\). In Fig. 3(b), we see an increase of \(N_{\text{BC}}\) with \(p_0\) in samples with \([B] = (1.7 \pm 0.06) \times 10^{17}\) cm\(^{-3}\) and no clear trend in samples with \([B] = (3.6 \pm 0.6) \times 10^{16}\) cm\(^{-3}\).

The clear correlation between \(N_{\text{BC}}\) and \([B]\) unambiguously indicates the participation of substitutional boron \(B_s\) in the BO defect complex, since there is no other means through which \([B]\) can influence \(N_{\text{BC}}\). We have proposed in Ref. [14], as an alternative explanation to the involvement of \(B_s\) in the complex, that \([B]\) or \([O_i]\) could be reduced due to the presence of Ga. This could have justified, keeping \(B_0\), as the defect complex, the lower values for \(N_{\text{BC}}\) in Si co-doped with Ga and B than in uncompensated B-doped Si with the same \(p_0\). Such a proposition can be discarded in the views of the present results, since in samples co-doped with B, P and Ga and in which \(p_0 < [B]\), \(N_{\text{BC}}\) is still measured to be proportional to \([B]\). The only remaining plausible interpretation for the variation of \(N_{\text{BC}}\) with \([B]\) which we observe here is hence the participation of \(B_s\) in the BO complex.

As mentioned in the introduction, these conclusions are in contradiction with those of several studies published by different groups [2–5]. It is however worth noting that in those studies, the influence of oxygen was generally neglected. In a typical B and P compensated Cz- or cast-Si ingot such as those that were investigated in Ref. [2–5], \([O_i]\) and \(p_0\) both decrease with the solidified fraction while \([B]\) slightly increases. Disregarding the quadratic dependence of the BO defect density on \([O_i]\) may thus have lead previous authors to erroneously attribute variations of \(N_{\text{BC}}\) to a correlation with \(p_0\) whereas those variations were actually resulting from changes in \([O_i]\). In contrast, the impact of oxygen is systematically taken into account in the present study by using the oxygen-normalized effective defect density.

Another point that should be stretched is that previous studies were carried out on samples in which \([B]\) did not vary much or in which compensation was relatively weak, leading to small differences between \([B]\) and \(p_0\). This made the distinction between a dependence on \(p_0\) or \([B]\) difficult, especially considering the large measurement errors. Our study, however, includes samples with a wide range of \([B]\) (from \(10^{15}\) cm\(^{-3}\) to \(2 \times 10^{17}\) cm\(^{-3}\)) and in which the difference between \(p_0\) and \([B]\) is significant (the ratio \(p_0/[B]\) ranges from about 0.1 in highly-compensated samples to about 10 in samples co-doped with Ga and B).

3.2. Doping and lifetime profiles along UMG-Si ingots

As can be seen on Fig. 4(a), the net doping is significantly lower along most of ingot Cz\#U2 than along Cz\#U1. This is due to compensation by larger concentration of P atoms in this ingot, while \(p\)-type conductivity is maintained along the entire crystal length due to the presence of Ga. This lower net doping leads to a higher resistivity, with an average of 2.5 \(\Omega\) cm along the first 70% of ingot Cz\#U2 against 1.2 \(\Omega\) cm for ingot Cz\#U1 (Fig. 4(b)).
Because both ingots Cz#U1 and Cz#U2 are grown with the same crystallization process, in the same conditions and with the same Si feedstock, they have identical impurity profiles apart from P and Ga which were added in Cz#U2. This means that two wafers taken from the same position in ingot Cz#U1 and Cz#U2 have the same B, O and C concentrations, but different $p_0$. This will enable us to study in the next section the impact of reducing $p_0$ by compensation on light-induced degradation of solar cells without varying other parameters affecting the BO defect.

The carrier lifetime measured along both bricks is shown in Fig. 5. Because of the smaller majority carrier density in Cz#U2, the measured lifetime is about 3 times higher in this ingot than in Cz#U1. This illustrates well the positive outcome of compensation on carrier lifetime before light-induced degradation, which was previously reported and analyzed by several groups[35–37]. Note that despite the bricks were not exposed to intentional illumination before lifetime measurements, a fraction of the BO defects may already be in the active state, due to exposure to room light during handling of the bricks. Considering the weak intensity of room light and the short exposure time, we however assume that this fraction is very small.

![Fig. 3. Normalized effective BO defect density plotted as a function of the total boron concentration (a) or as a function of the majority carrier density (b). Solid line is a fit to experimental data on B-doped Si from Ref. [28]. Dashed line corresponds to the same fit divided by a correction factor of 2 to account for the BO defect density reduction expected in P-diffused Si (see Ref. [40]). Samples co-doped with B and P are represented by triangles, samples co-doped with B and Ga are represented by circles and samples co-doped with B, P and Ga are represented by stars.](image)

![Fig. 4. (a) Majority carrier density measured by Hall effect (dots) and calculated using Scheil's equation and considering incomplete ionization of dopants (lines) along UMG-Si ingots Cz#U1 and Cz#U2. (b): Resistivity measured by 4-point probe (dots) and calculated (lines) along UMG-Si ingots Cz#U1 and Cz#U2. The resistivity was calculated from the majority carrier density – determined using Scheil's equation for the dopants concentrations and taking incomplete ionization into account – and the majority carrier mobility calculated with a version of Klaassen's model modified to yield accurate values in compensated Si (see Ref. [41]).](image)

![Fig. 5. Carrier lifetime measured by μW-PCD along ingots Cz#U1 and Cz#U2.](image)
3.3. I–V characteristics

3.3.1. Before degradation

Measured I–V characteristics of fabricated solar cells are shown in Fig. 6. Before degradation, solar cells made with wafers from Cz#U2 have on average slightly better $J_{sc}$ and slightly worse $V_{oc}$ than Cz#U1. The slightly better $J_{sc}$ for Cz#U2 illustrates the positive impact of increasing compensation on the minority carrier diffusion length. Because the lifetime enhancement due to compensation outweighs the reduction in minority carrier mobility, the minority carrier diffusion length increases with compensation [9], and so does $J_{sc}$. On the other hand, the lower $V_{oc}$ for ingot Cz#U2 than for Cz#U1 illustrates that in the expression of $V_{oc}$ (Eq. (3)), the reduction in $p_{0}$ due to compensation slightly outweighs the increase in $\Delta n$ resulting from the carrier lifetime improvement.

\[ V_{oc} \approx \frac{kT}{q} \ln \left( \frac{\Delta n + (\Delta n + p_{0})}{n_{i}^{2}} \right) \tag{3} \]

Overall, the differences in $J_{sc}$ and $V_{oc}$ between Cz#U1 and Cz#U2 cancel each other out and both ingots yield – before light-induced degradation – similar solar cell conversion efficiencies $\eta$ of respectively 17.94% and 17.92% on average. This result shows that by using Ga co-doping, it is possible to tolerate a much higher P concentration (2 ppmw in Cz#U2 instead of 0.6 ppmw in Cz#U1) in the Si feedstock, without compromising neither the ingot yield nor the solar cells performance. Such a finding is very positive because it shows that compensation engineering offers the potential to strongly release the specifications on P concentration, of which the reduction represents an important cost element of UMG-Si purification. Also note that the gap between the average efficiency of EG-Si and UMG-Si solar cells is less than 0.3%, showing that UMG-Si is an appropriate material for making high-efficiency solar cells.

3.3.2. After degradation

Fig. 7 shows the efficiency of 6 pairs of solar cells taken from equivalent positions along ingots Cz#U1 and Cz#U2 before and after light-induced degradation. Before light-induced degradation, solar cells from both ingots have similar efficiency. After activation of the BO defect, the efficiency degrades in both ingots, but the degradation is significantly stronger in ingot Cz#U2, down to 16.4% on average against 17.0% in Cz#U1. This shows that compensation does not mitigate light-induced degradation of UMG-Si solar cells but, on the contrary, worsens it. This result is in good agreement with our previous finding that the BO defect density depends on the total boron concentration rather than on the net doping. Indeed, both ingots Cz#U1 and Cz#U2 having the same [B] and [O] profiles, they also have the same BO defect density profile. Since the BO recombination center is a deep level with a capture cross section for electrons which does not differ strongly from that for holes [38] (capture cross section ratio of about 10 for the BO defect against around 700 for interstitial iron [39]), its recombination activity does not vary much with the majority carrier density [37]. This means that carrier lifetime after degradation depends only on the BO defect density and should therefore be the same in ingots Cz#U1 and Cz#U2. On the other hand, due to stronger compensation in Cz#U2, the majority carrier density and the minority carrier mobility are lower in this ingot. This leads to lower open-circuit voltage and short-circuit current in solar cells made with wafers from Cz#U2. If the BO defect density was, on the contrary, proportional to the net doping, carrier lifetime should be about twice longer in Cz#U2 than in Cz#U1 which should thus
counterbalance the lower minority carrier mobility and majority carrier density, thereby yielding similar efficiencies for both ingots.

4. Conclusion

In summary, we have shown through the analysis of the lifetime degradation in samples with a wide variety of doping and compensation levels that the BO defect density is in general proportional to the total boron concentration, rather than to the net doping. Such dependence implies the participation of substitutional boron in the defect complex and means that light-induced degradation cannot be mitigated by compensation. This finding is confirmed by a comparison between two UMG-Si Cz ingots having identical B, O and C profiles but different compensation levels. Because both ingots have identical carrier lifetime profiles after degradation the lower majority carrier density and minority carrier mobility in the heavily compensated ingot lead to lower open-circuit voltage, short-circuit current and hence conversion efficiency. This experiment unambiguously shows that whatever the nature of the BO defect, its impact cannot be diminished by compensation.

References


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fion is


