

**OF APPLES AND ORANGES:  
WHY COMPARING BO REGENERATION RATES REQUIRES  
INJECTION LEVEL CORRECTION**

Svenja Wilking, Sebastian Ebert, Cornelius Beckh, Axel Herguth, and Giso Hahn  
Department of Physics, University of Konstanz, 78464 Konstanz, Germany  
Phone (+49) 7531 883731, Fax: (+49) 7531 883895, e-mail: Svenja.Wilking@uni-konstanz.de

**ABSTRACT:** Different injection levels make the comparison of BO Regeneration kinetics in different Si wafers or solar cells difficult, *e.g.*, when samples made of different materials featuring different background lifetime levels are to be compared. A correction factor is presented that is able to compensate for these differences in injection level during Regeneration. This is used to investigate the influence of metallic impurities, interstitial oxygen and different dopants on BO Regeneration kinetics. It is found that a  $\text{POCl}_3$  gettering step only affects Regeneration if the overall H concentration within the wafer is low. Interstitial oxygen is found to be less detrimental to Regeneration than assumed previously. The influence of different dopants is shown in a process leading to a stable regenerated lifetime, and the measured Regeneration rates can be compared because of the applied injection correction. A numerical fit optimization method is presented to separate the influence of the different dopants. It is shown that net doping concentration  $p_0$  is not relevant for BO Regeneration whereas B as well as Ga slow down the Regeneration process. An explanation within the H-model of BO Regeneration is given.

**Keywords:** Czochralski, BO defects, Boron-Oxygen, degradation, regeneration, hydrogen

## 1 MOTIVATION

### 1.1 BO defects

Boron doped crystalline Si with high oxygen content, *e.g.*, Cz-Si, shows severe lifetime degradation under carrier injection due to boron-oxygen related(BO) defects [1-3]. The BO defects can be deactivated using the so-called Regeneration mechanism that is triggered by applying a combination of slightly elevated temperatures (typically 60-230°C) and carrier injection [4], applied on hydrogenated Si wafers or solar cells [5-7].

### 1.2 The H-model of BO-Regeneration

The explanations of BO Regeneration kinetics in this paper are based on the H-Model of BO Regeneration [7-9] assuming that the deactivation of recombination active BO defects is caused by their being passivated with hydrogen(H). This makes a high H concentration within the Si bulk desirable. H is usually bound at temperatures typically used for BO Regeneration (60-230°C) [10]. Hence, it has to be released from one of its bound states under carrier injection (*e.g.*, 1 sun illumination) to become atomic and mobile. BH pairs were suggested as a possible H source under Regeneration conditions [8] as they can be split more easily by carrier injection [11,12]. Additionally, carrier injection plays an important role concerning the charge states of hydrogen: The degraded BO defects [13] as well as atomic hydrogen in p-type Si [14] are both positively charged and would therefore suffer from coulombic repulsion. However, the minority charge states  $\text{H}^0$  and  $\text{H}^-$  form in higher concentrations under carrier injection [15] and may be able to interact with the degraded BO defects leading to the deactivation of their recombination activity.

Instead of this direct H-passivation of BO defects, H could also be catalytically involved in the BO Regeneration process. Based on the data available until now this cannot be excluded because a catalytic process could depend on the H concentration and charge state under Regeneration conditions in the same way as if direct H-passivation of BO defects is assumed. We point out that the injection correction presented in this paper is

independent of the model used to describe the physics of the BO Regeneration reaction.

### 1.3 Injection dependence of BO Regeneration rates

Herguth *et al.* showed already in 2008 that BO Regeneration is accelerated by increasing illumination intensity [16,17]. Very probably, this is due to different injection levels within the differently illuminated samples. Until now this fact has usually been ignored when the Regeneration kinetics of different samples has been compared: If they feature different effective minority carrier lifetimes this causes different injection levels despite constant illumination. Hence, Regeneration rates measured in different samples can only be compared directly if temperature and illumination intensity are kept constant and if anything affecting minority carrier lifetime (material, surface passivation and many processing steps) is the same for all samples. But unfortunately, varying all those parameters is key to understanding the physics of BO Regeneration as well as the possibilities of technological optimization of Regeneration processes. Thus, injection level effects have to be compensated for by adjusting the injection level within different samples during regeneration either experimentally using different illumination intensities or by correcting the effect of those differences mathematically.

Since the experimental solution is hardly feasible, the first part of this paper aims at presenting an empiric correction function that can be used to compensate for different injection levels during Regeneration treatment.

In the second part of the paper, the influence of different impurities on Regeneration kinetics is investigated. The new correction method is used to compare samples differing in the concentration of (1) metallic impurities, (2) interstitial oxygen and (3) dopants B, P and Ga. New data is presented and the results given in literature concerning this topic are discussed.

## 2 EXPERIMENTAL DETAILS

The material used for the different investigations is described in the respective sections of the paper. For all wafers a  $\text{POCl}_3$  gettering step is applied except for denoted reference samples. The diffused layer is removed thereafter in hot NaOH. After RCA cleaning, plasma enhanced chemical vapor deposition (PECVD)  $\text{SiN}_x\text{:H}$  is deposited on both sides (75 nm each). Finally, all samples are fired in a belt furnace ( $\sim 800^\circ\text{C}$  peak sample temperature) in order to activate the  $\text{SiN}_x\text{:H}$  surface passivation and to release H from the layer into the Si bulk.

From every material, the so processed lifetime samples undergo the whole Regeneration procedure consisting of (1) BO annealing, (2) complete BO degradation and (3) BO Regeneration at conditions specified within the respective sections. Illumination is done by a halogen lamp. After Regeneration, lifetimes are (4) stability checked and (5) a final BO annealing is done to exclude instable surface passivation. After each step and every few minutes during Regeneration, the effective minority carrier lifetime  $\tau_{\text{eff}}$  is measured and transformed into normalized defect concentrations  $N^*(t)$  using

$$N^*(t) = \frac{1}{\tau(t)} - \frac{1}{\tau_{\text{annealed}}} \quad (1)$$

with  $\tau(t)$  being the effective minority carrier lifetime at time  $t$  and  $\tau_{\text{annealed}}$  being the lifetime in the annealed BO state where it is not affected by BO defects.  $N^*(t)$  is fitted using a single exponential function

$$N^*(t) = k \cdot \exp(-R_R \cdot t) + N_0 \quad (2)$$

with constants  $k$  and  $N_0$ . This yields the characteristic Regeneration rate  $R_R$  that is used to compare the Regeneration kinetics of different samples.

The fact that  $N^*(t)$  can be fitted using a single exponential expression does not mean that the Regeneration rate is a constant during the whole Regeneration process. Even if the rate increases, *e.g.*, by factor 10 between the beginning and the ending of the Regeneration treatment, the extracted defect evolution can still be fitted by a single exponential function within measurement uncertainty. Hence, the measured Regeneration rate can either be a constant or an effective value representing a time dependent Regeneration rate. These considerations are equally valid for all samples, thus this effect does not affect the comparability of different samples regarding their (possibly effective) Regeneration kinetics.

## 3 RESULTS AND DISCUSSION

### 3.1 Correction of different injection levels

The injection level during the Regeneration treatment depends on external illumination intensity as well as recombination rate of the carriers within the Si bulk and/or at the Si surface. Hence, the injection level  $\Delta n$  increases with increasing generation rate  $G$  (being proportional to the illumination intensity  $I$ ) and with increasing effective lifetime  $\tau_{\text{eff}}$ . This means

$$\Delta n \sim G \cdot \tau_{\text{eff}} \sim I \cdot \tau_{\text{eff}} \quad (3)$$

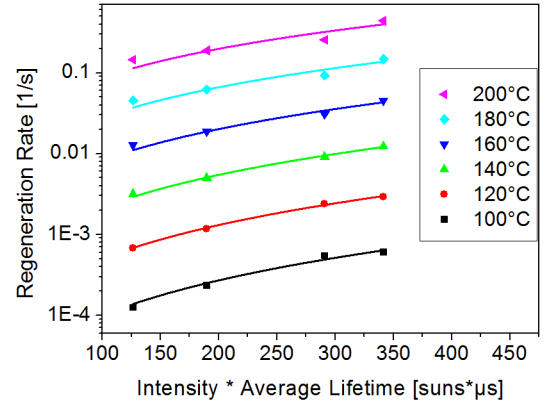
assuming the injection level being constant during the whole Regeneration process. This is virtually impossible because lifetime changes during the process. Because of the fact that this happens likewise in all samples, their kinetics can be compared anyway without any problems. But if samples differ in the degraded (*e.g.*, when samples feature different concentrations of B or O) or the annealed lifetime (*e.g.*, when samples feature different material quality or surface passivation),  $\Delta n$  is systematically shifted during the whole measurement. Thus, the average  $\Delta n_{\text{av}}$  is shifted as well. This automatically causes higher (higher  $\Delta n_{\text{av}}$ ) or lower (lower  $\Delta n_{\text{av}}$ ) Regeneration rates. Both cases are represented by an average lifetime

$$\tau_{\text{av}} = \frac{1}{2}(\tau_{\text{annealed}} + \tau_{\text{degraded}}) \quad (4)$$

Altogether,  $\Delta n_{\text{av}}$  can then be represented by

$$\Delta n_{\text{av}} \sim I \cdot \tau_{\text{av}} \quad (5)$$

For the empiric determination of factors correcting for different injection levels, Regeneration measurements are carried out on identically processed lifetime samples (Cz-Si, B doped, 1.5  $\Omega\text{cm}$ ) at different illumination intensities  $I$  (between 1.0 and 2.7 suns) and different temperatures  $T$  (100-200 $^\circ\text{C}$ ). All samples have an effective minority carrier lifetime of  $\sim 33 \mu\text{s}$  in the degraded and  $\sim 220 \mu\text{s}$  in the annealed state, hence the average lifetime is  $\tau_{\text{av}} = 126.5 \mu\text{s}$ . All samples were first BO-annealed (200 $^\circ\text{C}$ , 10 min, dark) and then degraded completely (40 $^\circ\text{C}$ , 0,1 suns,  $\sim 70$  h) before the start of the Regeneration measurement.



**Figure 1:** Regeneration rates measured at different injection levels and temperatures. The lines are parabolic fits.

Fig. 1 shows the measured Regeneration rates  $R_R$  plotted over  $I \cdot \tau_{\text{av}}$  (in  $\text{suns} \cdot \mu\text{s}$ ) with parabolic fits according to

$$R_R(I, \tau_{\text{av}}, T) = C \cdot (A(T) \cdot I + \tau_{\text{av}} \cdot I^2) \quad (6)$$

The y-intercept has to be zero because we assume that no Regeneration occurs without carrier injection. Fitting parameter  $A$  is temperature dependent according to

$$A(T) = 176 \text{ suns} \cdot \mu\text{s} \cdot \exp\left(\frac{T}{78 \text{ K}}\right) \quad (7)$$

with  $T$  being the temperature in K.

Since there is only one free fitting parameter (“ $C$ ”), a corrected  $R_{R1}$  can be calculated from a single measured data point  $R_{R0}$  using

$$R_{R1} = R_{R0} \cdot \frac{A(T) \cdot I_1 \cdot \tau_{av,1} + (I_1 \cdot \tau_{av,1})^2}{A(T) \cdot I_0 \cdot \tau_{av,0} + (I_0 \cdot \tau_{av,0})^2} \quad (8)$$

where subscript 0 denotes the measured values and subscript 1 the corrected ones. This may not be valid in high injection. An uncertainty of ~25% is to be added to the measurement uncertainty of the uncorrected value. More data would be needed to minimize this additional uncertainty.

A correction like this one should always be applied when the BO Regeneration rates of samples featuring different average injection levels are to be compared. Reasons for these differences can be, *e.g.*, different illumination intensities during Regeneration, different surface recombination velocities due to different surface passivation or different bulk lifetime due to different material composition. Comparing Regeneration rates of samples illuminated by different intensities is the most obvious case where an injection level correction is required. Differences in the effective minority carrier lifetime are less obvious and will be discussed in the following sections.

### 3.2 Application I: Correction of different surface recombination velocities

The samples presented in this section were all made from the same material but differ in surface passivation layer (SiN<sub>x</sub>:H vs. a stack of thermal SiO<sub>2</sub> and SiN<sub>x</sub>:H) as well as in the presence of a diffused emitter layer (50Ω/□) that has been etched off in some of the samples.

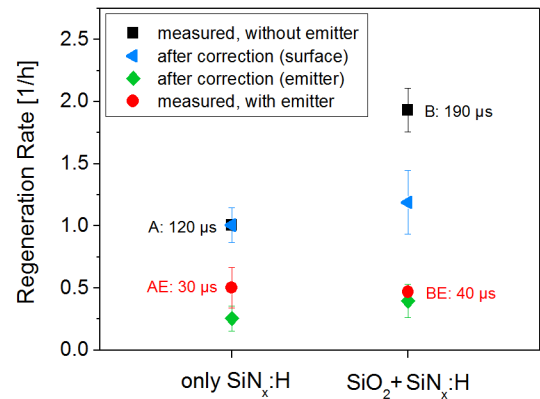
**Table I:** Samples used to investigate the influence of different surface passivation and the presence of an emitter layer on BO Regeneration kinetics.

| Sample              | A                   | AE                  | B                                      | BE                                     |
|---------------------|---------------------|---------------------|--|--|
| Surface Passivation | SiN <sub>x</sub> :H | SiN <sub>x</sub> :H | SiO <sub>2</sub> + SiN <sub>x</sub> :H | SiO <sub>2</sub> + SiN <sub>x</sub> :H |
| Emitter Layer       | no                  | yes                 | no                                     | yes                                    |

After BO-annealing and degradation, all samples undergo a Regeneration procedure at 130°C, 1.2 suns. The measured Regeneration rates are between 0.4 h<sup>-1</sup> and 1.9 h<sup>-1</sup> (see Figure 2 for details), thus they differ by more than factor 4. At first glance, one could reason that samples covered by a stack of silicon oxide and silicon nitride regenerate faster than samples featuring only silicon nitride passivation. In addition, the presence of an emitter layer seems to slow down the process. But are these differences in the Regeneration rate really caused by the presence of the SiO<sub>2</sub> interlayer or by the emitter being somehow involved in the Regeneration of BO defect? Or can everything be explained by the simple fact that the different sample structures cause different injection levels during Regeneration though illumination intensity was kept constant?

Indeed, the highest background lifetime (not affected by BO defects) as well as the highest Regeneration rate are found in the samples B (without emitter layer, passivated by a stack of SiO<sub>2</sub> + SiN<sub>x</sub>:H) ( $\tau_{av} = 190 \mu\text{s}$ ,  $R_R = 1.9 \text{ h}^{-1}$ ). What if these samples had the same average lifetime as samples A (without emitter layer, passivated only by SiN<sub>x</sub>:H)? Applying the correction function (8) to the measured  $R_R$  using the average lifetime values given

in Figure 2 reduces  $R_R$  to the same value (within measurement uncertainty) that has been measured in samples A ( $\tau_{av} = 120 \mu\text{s}$ ,  $R_R = 1.1 \text{ h}^{-1}$ ). Thus, the higher  $R_R$  measured in samples B can be explained by the injection level being higher compared to samples A – despite constant illumination intensity. Further applying the correction function (8) using the average lifetime values of samples AE and BE, respectively, results in further reduced  $R_R$ . The rates that have been deduced by injection correction from samples A and B (Fig. 2, green diamonds) are identical to the measured values in samples AE and BE. There may be small systematic differences, but more data is needed to investigate if there is a small real effect of an emitter layer in Regeneration kinetics or if all differences can be explained by the obvious different background lifetime caused by recombination active defects within the emitter layer.



**Figure 2:** Regeneration rates (black squares) measured in lifetime samples passivated with SiN<sub>x</sub>:H (samples A & AE, left) or with a stack of thermal SiO<sub>2</sub> and SiN<sub>x</sub>:H (samples B & BE, right). The average lifetime values are given. The injection correction shows the reason for the different rates: If samples B had an average lifetime of 120 μs (as samples A) they would feature the same Regeneration rate as samples A (blue triangles: rates after correction to  $\tau_{av} = 120 \mu\text{s}$ ). If the average lifetime was 30 μs or 40 μs, respectively, as measured in the samples with emitter, the Regeneration rate would be even lower (green diamonds: rates after correction to  $\tau_{av} = 30 \mu\text{s}$  (A) or 40 μs (B)). The values calculated by injection correction from the values measured without emitter (measured: A & B, black squares; after correction: green diamonds) coincide with the measured values (AE & BE, red circles) within measurement uncertainty.

### 3.3 Application II: Correction of different bulk lifetimes

#### 3.3.1 Interstitial oxygen

Si containing more oxygen normally has lower background lifetime (measured in the annealed BO state) than samples containing less oxygen. In addition to that, lifetime in the degraded BO state decreases by increasing  $[O_i]$  [18]. Since  $R_R$  is extracted from a single exponential fit to  $N^*(t)$ , the lifetime values at the beginning of the Regeneration process strongly affect the calculated  $R_R$ : Lower lifetime in the degraded state automatically results in reduced  $R_R$  due to the lower injection level in samples containing high  $[O_i]$ . Hence, the degraded as well as the annealed lifetime differ for samples that differ in  $[O_i]$  and one has to pay attention to the fact that the same

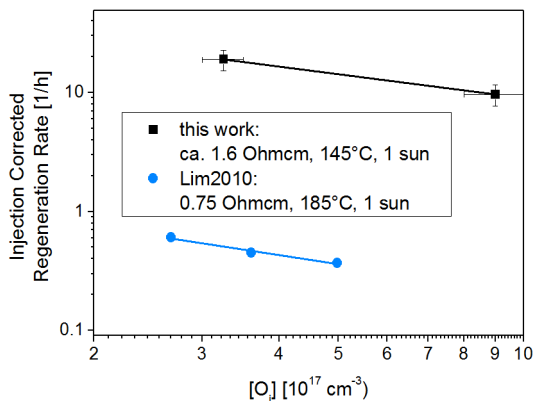
illumination intensity leads to different injection levels during Regeneration.

Lim *et al.* showed in [19] that interstitial oxygen  $O_i$  decelerates BO Regeneration with  $R_R \sim [O_i]^{-1.5 \pm 0.2}$ . This is the measured result without any injection correction. Now, the injection correction (8) is applied using the lifetime values published in [19] (see Table ) and the injection corrected Regeneration rates are shown in (Fig. 3). Plotting the corrected Regeneration rates over  $[O_i]$  on double logarithmic scale reveals a slope of  $0.8 \pm 0.1$  meaning  $R_R \sim [O_i]^{-0.8 \pm 0.1}$ . Hence, interstitial oxygen is less detrimental than previously assumed.

We can confirm this by our own data (black squares in Fig. 3) also yielding a slope of  $-0.8 \pm 0.2$ . Considering the huge measurement uncertainty due to limited access to Cz silicon differing in  $[O_i]$  the real influence of  $[O_i]$  on BO Regeneration kinetics could be even weaker. More data is needed to quantify this influence.

**Table II:** Lifetime values and Regeneration rates  $R_{R,meas}$  measured on samples featuring different oxygen content (taken from [20]) as well as the Regeneration rates corrected to  $\tau_{av} = 200 \mu s$  (last column).

| $[O_i]$<br>( $10^{17} \text{ cm}^{-3}$ ) | $\tau_{max}$<br>( $\mu s$ ) | $\tau_{min}$<br>( $\mu s$ ) | $\tau_{av}$<br>( $\mu s$ ) | $R_{R,meas}$<br>( $\text{h}^{-1}$ ) | $R_{R,corr}$<br>( $\text{h}^{-1}$ ) |
|--|-----------------------------|-----------------------------|----------------------------|-------------------------------------|-------------------------------------|
| 2.67                                     | 690                         | 90                          | 390                        | 1.18                                | <b>0.60</b>                         |
| 3.61                                     | 575                         | 55                          | 315                        | 0.71                                | <b>0.45</b>                         |
| 4.98                                     | 405                         | 30                          | 218                        | 0.40                                | <b>0.37</b>                         |



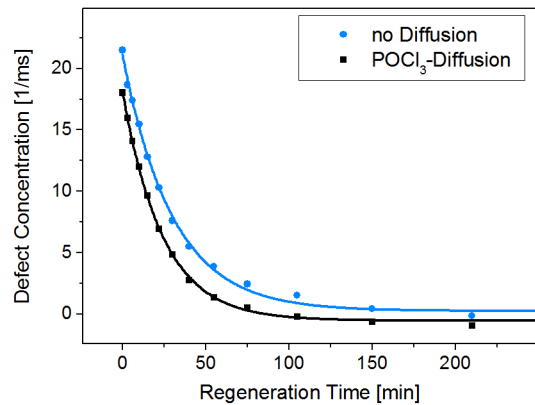
**Figure 3:** Regeneration rates corrected for injection level differences of samples featuring different oxygen concentrations. Both linear fits reveal a slope of  $-0.8$ .

### 3.3.2 Phosphorus gettering

Lim *et al.* presented in [21] that a  $\text{POCl}_3$  gettering step accelerates BO Regeneration by a factor 5 from  $R_R = 0.02 \text{ h}^{-1}$  without diffusion to  $R_R = 0.11 \text{ h}^{-1}$  after  $\text{POCl}_3$  diffusion. This is still valid after the correction of injection level differences during Regeneration according to (8). The measurement was done at  $135^\circ\text{C}$ , 0.7 suns. Our samples regenerated at  $130^\circ\text{C}$ , 0.6 suns (Fig. 4) seem to contradict these results. When comparing the Regeneration rates of samples that had received a  $\text{POCl}_3$  gettering step ( $R_R \approx 2.5 \text{ h}^{-1}$ ) with undiffused reference samples ( $R_R \approx 2.0 \text{ h}^{-1}$ ), only slightly different Regeneration rates are found.

However, there is another striking difference between both investigations: The Regeneration conditions are very

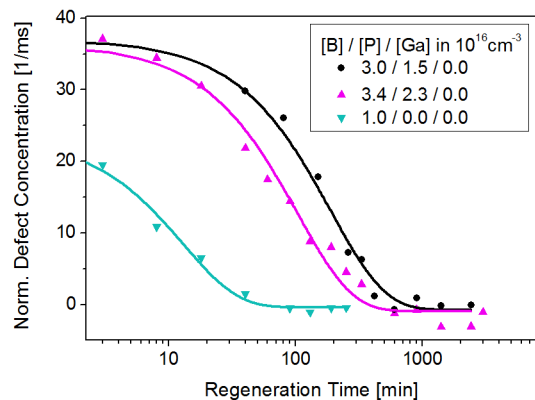
similar but the Regeneration rates showed by Lim *et al.* are a factor 100 lower than the ones presented here. This is very probably due to lower H content within the wafers because they did not receive a high temperature firing step. On the other hand, different metallic impurities that can be partly removed by a  $\text{POCl}_3$  gettering step are known to trap H in Si. Hence, they can reduce the amount of H available during BO Regeneration and therefore decelerate the Regeneration process. Comparing the two data sets ([21] and this paper) suggests that H trapping by metallic impurities is especially harmful to BO Regeneration if the overall H concentration within the wafer is low.

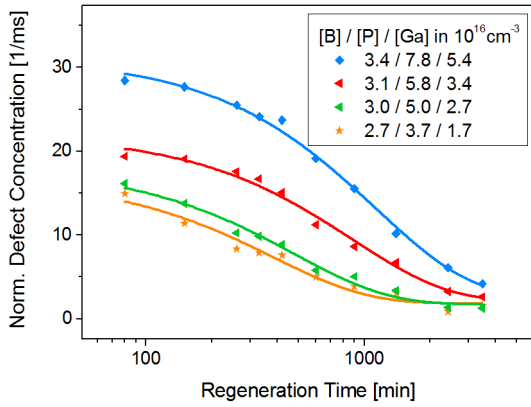


**Figure 4:** Evolution of the normalized BO defect concentration during Regeneration at  $130^\circ\text{C}$ , 0.6 suns for lifetime samples after a  $\text{POCl}_3$ -gettering step has been applied (black squares) or not (blue circles). They show almost the same Regeneration kinetics.

### 3.3.3 Dopants in compensated Si

Lim *et al.* showed in [22] that the BO Regeneration rate decreases with increasing B concentration. Compensated p-type silicon has then been used to determine whether this is an effect of the net doping or the absolute B concentration [22,23]. No clear answer has been found yet and it is not clear whether the measured difference in the Regeneration rates really originates from different net dopings / B concentrations or if it could also be an injection effect caused by differences in the background lifetime that automatically come with different dopant concentrations.

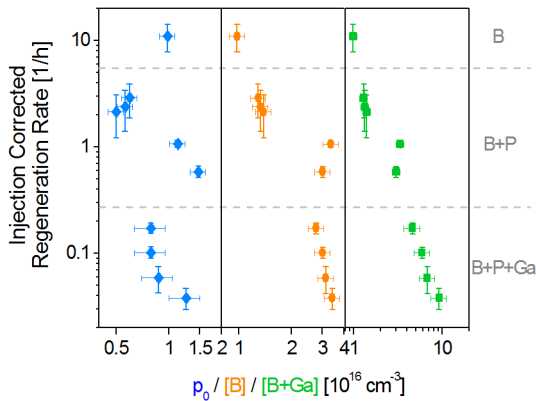




**Figure 5:** Evolution of the normalized BO defect concentration during Regeneration at 130°C, 1.1 suns for samples containing different amounts of B, P and Ga.

Here, we present data on the BO Regeneration kinetics of p-type Cz wafers doped with differing amounts of B, P and Ga. Details are given in Fig. 5. [B] was determined in the uncompensated samples by four point probe resistivity measurements. [B], [P] and [Ga] in the co-doped wafers were calculated from their ingot position using Scheil's equation. [O<sub>i</sub>] was determined using FTIR spectroscopy with the calibration factors by Borghesi *et al.* [24]. The concentrations are [O<sub>i</sub>] =  $(6.2 \pm 0.6) \cdot 10^{17} \text{ cm}^{-3}$  in all compensated samples and [O<sub>i</sub>] =  $(8.0 \pm 0.2) \cdot 10^{17} \text{ cm}^{-3}$  in the uncompensated ones. These slight differences were not mathematically corrected because they affect the measured Regeneration rates by less than 20%; thus they are not relevant in this study. Some of the results shown here has already been published in [25].

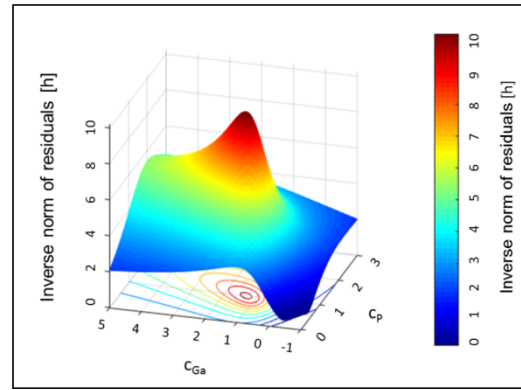
Regeneration is done at 130°C, 1.1 suns. All lifetimes are stable after Regeneration (tested at 45°C, 0.2 suns); thus no accidental BO annealing has occurred. The measured Regeneration rates are corrected for injection differences according to equation (8). The resulting rates  $R_R$  are shown in Fig. 6, plotted over the net doping concentration  $p_0$  (left), over the boron concentration [B] (middle) and over the total acceptor concentration [B + Ga] (right).



**Figure 6:** Regeneration rates corrected for injection differences plotted over the net doping  $p_0$  (left), over the boron concentration [B] (middle) and over the total acceptor concentration [B + Ga] (right). Each part contains p-type samples doped with B (upper part), with B + P (middle) and with B + P + Ga (lower part).

Lim *et al.* have shown in [22] that  $R_R$  should form a straight line when plotted over the most relevant entity in double logarithmic scaling. Fig. 6 shows that this is definitely not the case if  $p_0$  is chosen as x-axis.  $R_R$ ([B]) rather resembles a straight line. The best match is found when  $R_R$  is plotted over the total acceptor concentration [B + Ga]. This means that additionally to B, Ga has negative impact on BO Regeneration as well. In fact, no Regeneration is found in samples containing more than  $10^{17} \text{ cm}^{-3}$  Ga.

Due to the limited data set it is not clear whether choosing other entities as x-axis would lead to similar results. *E.g.*, P could also affect  $R_R$  and B and Ga may not be harmful to the same extent. Since the samples compensated with P also contain higher [B] than the uncompensated ones and those additionally doped with Ga feature even higher [B] and [P], it is difficult to separate the effects of the respective dopants.



**Figure 7:** Inverse norm of residuals of the linear fits resulting from different combinations of weighting factors  $c_P$  and  $c_{Ga}$  for [P] and [Ga] relative to [B]. The dark red region corresponds to the highest inverse norm of residuals and thus to the lowest deviation between fit and data points.

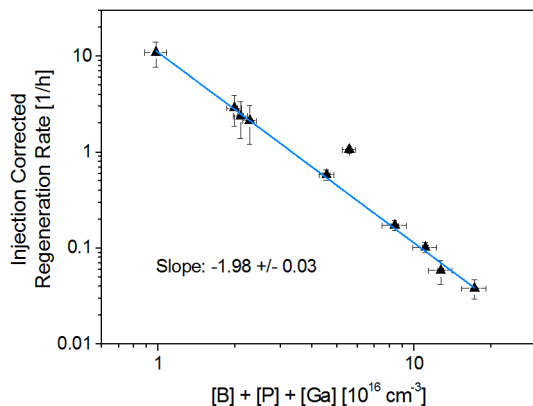
This problem is addressed using a fit optimization approach. It is known that all Regeneration rates should form a straight line when plotted in double logarithmic scaling [5]. Hence, we try to find the best function  $X$  which is the entity that will be plotted on the x-axis.  $X$  consists of a linear combination of [B], [P] and [Ga]:

$$X = [B] + c_P \cdot [P] + c_{Ga} \cdot [Ga] \quad (8)$$

$c_P$  and  $c_{Ga}$  are weighting factors representing how detrimental P and Ga are relative to B. Due to the limited number of data points no possible quadratic effects are considered here. If the optimal combination of  $c_P$  and  $c_{Ga}$  is found, the norm of residuals of a linear fit on  $R_R(X)$  on double logarithmic scaling is minimized; the inverse norm of residuals is maximized (see Fig. 7).

We find that the best fit results from a combination of  $c_P = 1.0 \pm 0.3$  and  $c_{Ga} = 1.3 \pm 0.5$ . The uncertainty interval (10% deviation from the optimum) hence includes the case of all three dopant being equally harmful to BO Regeneration. This is shown in Fig. 8 giving a slope of  $-1.98 \pm 0.03$ . Thus,  $1/R_R$  depends quadratically on the sum of all dopant concentrations. In the best case shown in Fig. 6 ( $R_R$  plotted over [B + Ga]), the fit uncertainty is a factor 10 higher. The single data point that does not fit in a straight line has been ignored

during the fit optimization procedure although the reasons for its strange position are unclear.



**Figure 8:** Fit resulting from an optimized weighting factor combination representing a similar impact of B, P and Ga.

Due to the large uncertainty concerning  $c_p$  and  $c_{Ga}$ , more data is needed to come to a definite conclusion about how harmful P and Ga are for BO Regeneration. In fact, the weighting factors within the interval  $0 \leq c_p \leq 1$  and  $1 \leq c_{Ga} \leq 2$  lead to less than 10% deviation from the optimal fit. Thus in the most extreme case it is even possible that P does not affect BO Regeneration at all while Ga could be clearly more harmful than B.

Considering these possibilities, different conclusions can be drawn from this finding. Based on the data presented here it is not clear whether P has negative or positive or no impact at all. Additionally, almost all information that is available on the behavior of P in Si comes from studies in n-type Si and it is not clear if these results can be used to explain experimental data from compensated p-type Si. Thus we refrain here from speculating about the possible influence of P on the Regeneration process (see [9] for a detailed discussion including the influence of P on the net dopant concentration, therefore on the quasi Fermi level under illumination and therefore on the  $H^-$  concentration during Regeneration) and focus on the negative impact of Ga additionally to B. The following hypotheses are based on the assumption that the influence of Ga is due to the same physical reasons that the influence of B. We also assume that mobile H atoms are involved in the BO Regeneration process with the concentration of mobile H during Regeneration limiting the Regeneration rate. To be more exact, the concentration of the minority charge state  $H^-$  (or possibly  $H^0$ ) is assumed to determine the actual Regeneration rate [9,26].

Based on this, Ga could influence BO Regeneration kinetics in two different ways either by reducing its concentration or its mobility. First, the fact that H is typically bound at the temperatures used for Regeneration treatments [10] (here:  $130^\circ\text{C}$ ) means that it needs to be released from a bound state due to the carrier injection applied during Regeneration. BH pairs were found to be a possible H source under Regeneration conditions because they feature a relatively low dissociation energy ( $1.28 \pm 0.03 \text{ eV}$ ) that is even lowered under carrier injection [8,27]. The dissociation energy of GaH pairs is higher in the dark ( $1.40 \pm 0.03 \text{ eV}$ ) [8]. No studies on how this value may change under carrier injection have

been done yet but the GaH pair may stay more stable than BH. In this case the forming of GaH pairs (e.g., during cool down from a high temperature step) would reduce the amount of H that can later become mobile during Regeneration.

This may explain why more Ga could be more detrimental to BO Regeneration than B but it cannot explain the negative impact of B: changes in the concentration of B could hardly affect the amount of H available during Regeneration (see [9] for details). Hence, the impact of the concentration of acceptor atoms may rather be due to their influence on the H mobility during Regeneration: they may be temporary H traps that can reduce the effective H mobility and therefore the frequency at which H atoms encounter BO defects they can interact with. Assuming this mechanism, anything being able to trap hydrogen will reduce the Regeneration rate: Acceptor atoms compete directly with the equally positively charged BO defects in the degraded state and can thus directly reduce the amount of  $H^-$  atoms available for BO passivation. Atoms binding to other H charge states ( $H^+$  or  $H^0$ ) would reduce the overall concentration of atomic H. Because of the fact that there is an equilibrium distribution of H charge states at a given temperature and injection level [15], this would reduce the  $H^-$  concentration and thus the Regeneration rate indirectly. (The H charge state relevant for BO Regeneration could also be  $H^0$  [26] that may be able to interact with almost any impurity leading to direct negative impact of these impurities on BO Regeneration kinetics.)

Combining those aspects we conclude that impurities being able to reduce the mobility of the H species relevant for BO Regeneration (possibly  $H^-$ ) under Regeneration conditions reduce the BO Regeneration rate, e.g., by temporary trapping. Impurities like Ga could additionally trap H and thus reduce the amount of mobile H available for BO Regeneration.

More data is needed to decide which processes dominate during BO Regeneration. Regeneration measurements at different temperatures on differently doped material could reveal interesting information on how the activation characteristics of BO Regeneration depend on material properties. Regeneration studies on Si co-doped with B and Ga (without P) would be especially informative.

#### 4 SUMMARY

It has been explained why the comparison of Regeneration rates measured in different samples requires experimental or mathematical correction of the injection level that can vary even if the external illumination intensity during Regeneration is kept constant. The proposed correction function includes variations that come from different background lifetimes within the silicon bulk (measured in the annealed BO state) as well as different lifetimes in the degraded BO state due to variations in the concentration of B or  $O_i$ . The injection level correction has been applied to allow the investigation how interstitial oxygen, phosphorus gettering steps and different dopants affect BO Regeneration kinetics. It has been found that the impact of  $O_i$  on BO Regeneration may be less detrimental than previously assumed. Apparently, gettering steps are only beneficial if poorly hydrogenated silicon is used for

investigating BO Regeneration kinetics. The possible role of different dopants is very complex and a numerical method has been presented that can be used to discriminate the influences of different impurities being present at the same time. Additionally to B, Ga was found to slow down BO Regeneration kinetics and may be even more harmful than B. Further data is needed to quantify the influence of P reliably.

## 5 ACKNOWLEDGEMENTS

We would like to thank ApollonSolar for providing the compensated material and Stanislav Stoyanov for characterizing most of the lifetime samples. Parts of this work have been funded by the German Federal Ministry of Economic Affairs and Energy (0325450A, 0325581, 0325877C).

## 6 REFERENCES

- [1] H. Fischer and W. Pschunder, "Investigation of photon and thermal induced changes in silicon solar cells," in *Photovoltaic Specialists Conference, 10 th, Palo Alto, California, 1974*, pp. 404–411.
- [2] J. Knobloch, S. Glunz, D. Biro, W. Warta, E. Schäffer, and W. Wetzling, "Solar cells with efficiencies above 21% processed from czochralski grown silicon," in *5th IEEE Photovoltaic Specialists Conference, 1996*. IEEE, 1996, pp. 405–408.
- [3] J. Schmidt and K. Bothe, "Structure and transformation of the metastable boron-and oxygen-related defect center in crystalline silicon," *Physical review B*, vol. 69, no. 2, p. 024107, 2004.
- [4] A. Herguth, G. Schubert, M. Kaes, and G. Hahn, "A new approach to prevent the negative impact of the metastable defect in boron doped Cz silicon solar cells," in *2006 IEEE 4th World Conference on Photovoltaic Energy Conference, 2006*.
- [5] K. Muenzer, "Hydrogenated silicon nitride for regeneration of light induced degradation." in *24th EU PVSEC, Hamburg, Germany, 2009*.
- [6] G. Krugel, W. Wolke, J. Geilker, S. Rein, and R. Preu, "Impact of hydrogen concentration on the regeneration of light induced degradation," *Energy Procedia*, vol. 8, pp. 47–51, 2011.
- [7] S. Wilking, A. Herguth, and G. Hahn, "Influence of hydrogen on the regeneration of boron-oxygen related defects in crystalline silicon," *Journal of Applied Physics*, vol. 113, no. 19, p. 194503, 2013.
- [8] S. Wilking, C. Beckh, S. Ebert, A. Herguth, and G. Hahn, "Influence of bound hydrogen states on bo-regeneration kinetics and consequences for high-speed regeneration processes," *Solar Energy Materials and Solar Cells*, vol. 131, pp. 2–8, 2014.
- [9] S. Wilking, "Das Wasserstoff-Modell der Bor-Sauerstoff-Regeneration," Ph.D. dissertation, University of Konstanz, to be published.
- [10] S. Pearton, J. Corbett, and T. Shi, "Hydrogen in crystalline semiconductors," *Applied Physics A*, vol. 43, no. 3, pp. 153–195, 1987.
- [11] T. Zundel and J. Weber, "Boron reactivation kinetics in hydrogenated silicon after annealing in the dark or under illumination," *Physical Review B*, vol. 43, no. 5, p. 4361, 1991.
- [12] C. Seager and R. Anderson, "Two-step debonding of hydrogen from boron acceptors in silicon," *Applied physics letters*, vol. 59, no. 5, pp. 585–587, 1991.
- [13] S. Rein and S. Glunz, "Electronic properties of the metastable defect in boron-doped czochralski silicon: Unambiguous determination by advanced lifetime spectroscopy," *Applied Physics Letters*, vol. 82, no. 7, pp. 1054–1056, 2003.
- [14] A. Tavendale, D. Alexiev, and A. Williams, "Field drift of the hydrogen-related, acceptor-neutralizing defect in diodes from hydrogenated silicon," *Applied Physics Letters*, vol. 47, no. 3, pp. 316–318, 1985.
- [15] C. Herring, N. Johnson, and C. G. Van de Walle, "Energy levels of isolated interstitial hydrogen in silicon," *Physical Review B*, vol. 64, no. 12, p. 125209, 2001.
- [16] A. Herguth, G. Schubert, M. Käs, and G. Hahn, "Investigations on the long time behavior of the metastable boron–oxygen complex in crystalline silicon," *Progress in Photovoltaics: Research and Applications*, vol. 16, no. 2, pp. 135–140, 2008.
- [17] A. Herguth and G. Hahn, "Kinetics of the boron-oxygen related defect in theory and experiment," *Journal of Applied Physics*, vol. 108, no. 11, p. 114509, 2010.
- [18] K. Bothe, R. Sinton, and J. Schmidt, "Fundamental boron–oxygen-related carrier lifetime limit in mono- and multicrystalline silicon," *Progress in photovoltaics: Research and Applications*, vol. 13, no. 4, pp. 287–296, 2005.
- [19] B. Lim, K. Bothe, and J. Schmidt, "Impact of oxygen on the permanent deactivation of boron–oxygen-related recombination centers in crystalline silicon," *Journal of Applied Physics*, vol. 107, no. 12, p. 123707, 2010.
- [20] B. Lim, F. Rougieux, D. Macdonald, K. Bothe, and J. Schmidt, "Generation and annihilation of boron-oxygen-related recombination centers in compensated p-and n-type silicon," *Journal of Applied Physics*, vol. 108, no. 10, p. 103722, 2010.
- [21] B. Lim, K. Bothe, and J. Schmidt, "Deactivation of the boron–oxygen recombination center in silicon by illumination at elevated temperature," *physica status solidi (RRL)-Rapid Research Letters*, vol. 2, no. 3, pp. 93–95, 2008.
- [22] B. Lim, A. Liu, D. Macdonald, K. Bothe, and J. Schmidt, "Impact of dopant compensation on the deactivation of boron-oxygen recombination centers in crystalline silicon," *Applied Physics Letters*, vol. 95, no. 23, p. 232109, 2009.
- [23] B. Lim, "Boron-oxygen related recombination centers in crystalline silicon and the effects of dopant-compensation," Ph.D. dissertation, University of Hannover, 2011.

- [24] A. Borghesi, B. Pivac, A. Sassella, and A. Stella, "Oxygen precipitation in silicon," *Journal of Applied Physics*, vol. 77, no. 9, pp. 4169–4244, 1995.
- [25] S. Wilking, M. Forster, A. Herguth, and G. Hahn, "From simulation to experiment: Understanding BO-regeneration kinetics," *Solar Energy Materials and Solar Cells*, vol. 142, pp. 87–91, 2015.
- [26] M. Gläser and D. Lausch, "Towards a quantitative model for BO-regeneration by means of charge state control of hydrogen," *Energy Procedia*, vol. 77, pp. 592–598, 2015.
- [27] T. Zundel and J. Weber, "Dissociation energies of shallow-acceptor-hydrogen pairs in silicon," *Physical Review B*, vol. 39, no. 18, p. 13549, 1989.