Degradation of carrier lifetime in Cz silicon solar cells

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Abstract

The lifetime degradation induced by light illumination or carrier injection which is observed in Czochralski-grown silicon (Cz-Si) leads to a significant decrease of solar cell efficiency. Thus, the reduction of this effect has a high potential for the improvement of Cz-Si solar cells. In the present work both, the analysis of the underlying defect and its technological reduction are discussed. A clear correlation of the Cz-specific metastable defect with the oxygen and boron concentration in Cz-Si has been observed. Especially, recently performed lifetime measurements on oxygen-free boron-doped p-type MCz silicon and gallium-doped oxygen-contaminated Cz-silicon, both of which show no degradation, confirm this hypothesis. While the quantitative correlation between the defect concentration and boron is linear, the increase of the defect concentration induced by the interstitial oxygen concentration is superlinear, i.e. it follows a potential law of power approximately 5. Beyond the defect analysis, two different ways to reduce the metastable defect concentration are discussed. A proper material choice by substituting or reducing one of the major components of the metastable defect can completely avoid the degradation effect. The excellent performance of oxygen-free MCz-Si and gallium-doped Cz-Si is reflected in the achieved record efficiencies of 22.7% and 22.5%, respectively. In standard boron-doped oxygen-contaminated p-type Cz-Si a strong reduction of the metastable defect concentration can be achieved by a high-temperature process step resulting in an improvement of the stable bulk lifetime by a factor of 2–4. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

Monocrystalline silicon grown with the Czochralski-method (Cz-Si) is still the leading substrate for photovoltaic cells: 50% of all PV-cells in 1997 were fabricated

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from Cz-Si, ranking before multicrystalline silicon with 34% [1]. Since an important cost factor for the cell production is the starting material itself, two ways can be followed for a more cost-effective photovoltaic energy production: (1) cheaper substrates or (2) an improved cell technology leading to a higher conversion efficiency. For Cz-Si the second way seems to be more promising since the potential for a further cost reduction of the material is very limited. Especially, the reduction of the Cz-specific lifetime degradation [2–6] could easily lead to an efficiency improvement of around one percent absolutely. This Cz-Si specific lifetime degradation is induced by carrier injection or illumination. After an illumination of about 12 h AM1.5 (depending on the doping level), the lifetime is reduced exponentially to a stable end value. This lifetime degradation can be completely reversed by an anneal step of around 200°C in room ambient.

This article gives a survey of the correlation of the underlying metastable defect with doping type and concentration and Cz-specific impurities. In the second part, two different solutions to reduce or even avoid the lifetime degradation are given.

2. Components of the Cz-specific defect

Observations described in the literature [4–7] and obtained during a recent joint research on the light degradation of Cz-Si [8] have drawn quite a complete picture of the symptoms of the metastable defect:

(1) Boron-doped p-type FZ silicon free of interstitial oxygen and other contaminations shows no lifetime degradation.

(2) Boron-doped p-type FZ silicon intentionally contaminated with oxygen ($\rho_{\mathrm{base}} = 6.3 \, \Omega \, \mathrm{cm}$, $[\mathrm{O_i}] = 5.4 \times 10^{17} \, \mathrm{cm^{-3}}$) shows a degradation behavior very similar to the one observed in boron-doped p-type Cz-silicon, although no other contaminations are present in these FZ wafers [6].

(3) Phosphorus-doped n-type FZ silicon intentionally contaminated with oxygen ($[\mathrm{O_i}] = 4.2 \times 10^{17} \, \mathrm{cm^{-3}}$) as in (2) shows no lifetime degradation [6].

(4) Phosphorus-doped n-type Cz silicon shows no degradation [4,5].

(5) Oxygen-free boron-doped p-type MCz silicon shows no degradation (see Section 4.1) [7].

(6) Gallium-doped oxygen-contaminated Cz silicon shows no degradation (see Section 4.3) [5,7].

These observations justify the hypothesis that boron and oxygen are the major components of the metastable defect underlying the Cz-specific lifetime degradation.

In order to investigate the correlation between the defect concentration and the boron and oxygen concentration we have analyzed more than 30 different Cz silicon types from different manufactures and with different oxygen and boron concentrations [6]. The defect concentration was determined using the extent of lifetime degradation by measuring the initial bulk lifetime, τ_0, after a 200°C anneal step and the final degraded lifetime, τ_d, after an illumination of AM1.5 for at least 30 h. Since the electron capture cross section of the defect is unknown it is only possible to

determine a normalized defect concentration, $N_t^*: = \sigma_n v_{th} N_t$. Assuming that (i) the metastable defect is completely deactivated after the anneal step and completely activated after the illumination step and (ii) all additional defects possibly contained in the material are not affected by the anneal/illumination cycle, N_t^* can be determined in the following way:

$$N_t^*: = \sigma_n v_{th} N_t = \frac{1}{\tau_d} - \frac{1}{\tau_0} = (\sigma_{res} v_{th} N_{res} + \sigma_n v_{th} N_t) - \sigma_{res} v_{th} N_{res}, \tag{1}$$

where σ_n and σ_{res} are the electron capture cross sections of the metastable defect and the residual defects, respectively, v_{th} is the thermal velocity while N_t and N_{res} are the concentrations of the metastable defect and residual defects, respectively.

Fig. 1 shows the influence of the boron concentration on the normalized defect concentration for Cz samples with nearly the same interstitial oxygen content, whereas Fig. 2 shows the influence of the interstitial oxygen concentration for samples within the same resistivity range. While the defect concentration is increased approximately linearly with the boron concentration, an increasing oxygen concentration increases the defect concentration more strongly. (The solid line in Fig. 2 follows an exponential law of power 5.)

Schmidt et al. [5] have suggested a model assigning the origin of the metastable defect to the $B_i O_i$ complex. The $B_i O_i$ defect was observed by Kimerling et al. [9] on electron-irradiated Cz-Si. The electron irradiation strongly increases the Si_i concentration and thereby the B_i concentration. Their DLTS measurements have shown that the DLTS-peak identified as the $B_i O_i$ defect ($E_c - E_t = 0.26$ eV) vanishes after an anneal in the temperature range from 150°C to 200°C. However, no reactivation of the defect by illumination or carrier injection was reported. Both, the metastable defect behavior and the correlation with boron and oxygen observed by the lifetime measurements reported here are in agreement with their results. However,
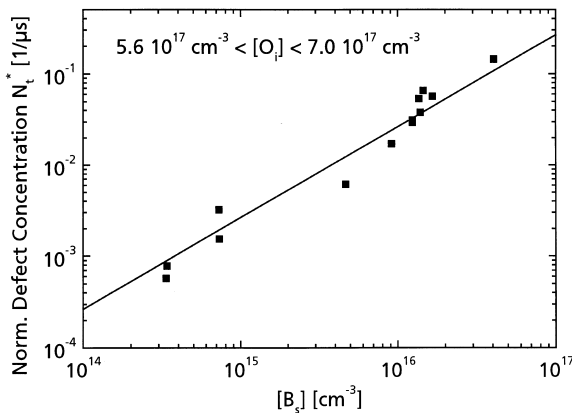

Fig. 1. Normalized defect concentration $N_t^*(: = 1/\tau_d - 1/\tau_0)$ vs. boron concentration for Cz samples with an interstitial oxygen concentration between 5.6 and 7.0×10^{17} cm^{-3}.
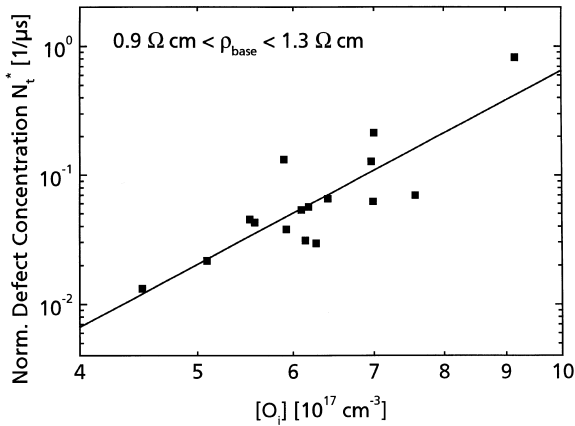
Fig. 2. Normalized defect concentration $N_t^*(:= 1/\tau_d - 1/\tau_0)$ vs. interstitial oxygen concentration for boron-doped Cz samples with base resistivities between 0.9 and 1.3 Ω cm.

a non-ambiguous correlation is not possible especially since the results reported in this article are obtained on non-electron-irradiated Cz-Si. Indeed, a recent result points at a different complex of boron with oxygen. From quasi-static injection-dependent lifetime measurements an energy level in the range of $E_v + 0.35\,\text{eV}$ to $E_c - 0.45\,\text{eV}$ was inferred [10], which excludes the B_iO_i pair defect. In addition, the fact that a super-linear dependence of the defect concentration on $[O_i]$ is observed (see Fig. 2) supports an unequal contribution of boron and oxygen to the complex formation.

3. Dynamics of the Cz-specific defect

In addition to the total extent of degradation, we have analyzed the dynamics of the reactivation of the metastable defect [6]. Again the normalized defect concentration was determined following Eq. (1). The defect reactivation can be described excellently by the following exponential law:

$$N_t^*(t) = N_t^*(0)(1 - e^{-t/\tau_{t-gen}}),\tag{2}$$

with $N_t^*(0) = \dfrac{1}{\tau_d} - \dfrac{1}{\tau_0},$ (3)

It was observed that the defect reactivation rate $1/\tau_{t-gen}$ increases with increasing boron concentration (see Table 1).

4. Reduction of lifetime degradation by proper material choice

A major task besides the determination of the origin of the Cz-specific defect as discussed in the previous sections is also its avoidance or reduction. Since boron and

Table 1
Normalized defect concentration and reactivation rate (illumination 0.5 suns) for different boron-doped Cz-Si

Material	N_A (cm^{-3})	O_i (cm^{-3})	N_t^* (µs)	$\tau_{t\text{-gen}}$ (min)
11	4.25×10^{16}	6.6×10^{17}	0.251	58
13	1.42×10^{16}	5.9×10^{17}	0.113	339
12	1.30×10^{16}	6.5×10^{17}	0.0954	365
4	1.23×10^{16}	6.4×10^{17}	0.0865	412
18	9.04×10^{15}	5.6×10^{17}	0.0307	824
10	6.95×10^{15}	7.7×10^{17}	0.0586	1355
1	1.18×10^{15}	6.1×10^{17}	0.003	12275

interstitial oxygen were identified as the components of the defect, one possible way is the avoidance of one of these two elements in the starting material. Several possibilities are available:

4.1. Usage of material with very low concentrations or even free of interstitial oxygen, as MCz-Si or FZ-Si

While the usage of expensive FZ-Si is only feasible for high-efficiency cells, MCz-Si could easily increase the performance of Cz-Si cells due to its very low interstitial oxygen content. We have passivated MCz samples fabricated by Shin–Etsu with both, SiN_x and a corona-charged SiO_2 [11], the first deposited at low temperatures (350°C) and the second grown at high temperatures (1050°C). In both cases, high-lifetime FZ-references have revealed excellent surface recombination velocities of below 10 cm/s. Effective lifetimes of more than 1 ms on all investigated MCz materials were measured for both states, before and after a high-temperature process. No degradation was observed. Since the oxygen concentration of these materials is very low (< 1 ppma), it is not necessary to modify the standard high-efficiency process sequence for FZ-Si, since a precipitation of oxygen and other detrimental effects related with interstitial oxygen are very unlikely.

Confirmed efficiencies up to 22.3%[1] ($V_{oc} = 686.3$ mV) have been demonstrated on an MCz-Si (1.2 Ω cm, [O_i] = 0.54 ppma) [7]. This result could be increased up to 22.7% ($V_{oc} = 689.4$ mV) on another MCz-material (5.2 Ω cm, [O_i] = 0.99 ppma) in the mean time.

4.2. Usage of n-type Cz-Si

Although, in principle, the usage of n-type Cz-Si is possible, considerable efforts would be necessary to change the common solar cell technology (e.g. formation of p^+-emitters).

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[1] Note: All efficiences reported in this article are obtained by aperture area measurements, thus, fingers and busbar lie within the illuminated area.

4.3. Substitution of boron by other acceptors as gallium in p-type Cz-Si

This approach has been pursued in a recent research activity [7,8] on material grown by Shin–Etsu. Lifetimes above 1 ms before and after a high-temperature process (see Section 4.1) were determined on high-resistivity material (5.2 Ω cm) with a high interstitial oxygen concentration (13.7 ppma). Even if the doping concentration was significantly higher (0.77 Ω cm) the lifetime was excellent (700 μs). Since no degradation was observed for all investigated material types, this approach seems to be very promising. The only disadvantage of this approach is the low segregation coefficient of gallium in silicon, resulting in a higher resistivity variation over the crystal length compared to boron doping.

An excellent solar cell performance with confirmed efficiencies up to 22.5% (689.8 mV) on the 5.2 Ω cm material mentioned above was achieved in our lab [7]. In addition to these 4 cm^2 cells, we have processed 10×10 cm^2 cells on Ga-doped material with confirmed efficiencies of up to 20.2% [12]. To our knowledge, this is the highest efficiency achieved on Cz-Si on such a large cell area up to now.

4.4. Reduction of boron doping concentration in p-type Cz-Si (e.g. from 1 Ω cm up to 7 Ω cm)

It was already demonstrated that this approach results in very high efficiencies, up to 22.0% [13], but since the lower doping concentration does not allow a simple ohmic back contact, a back surface field is obligatory.

4.5. Other approaches

Schmidt et al. have suggested another approach [5]: the use of very highly doped p-type Cz-Si (e.g. 0.1 Ω cm). They justify this with one single lifetime measurement and the observation of Kimerling et al. [9] that the concentration of $B_i O_i$ observed with DLTS in electron-irradiated Cz is reduced for a very high B_s concentration due to a preferred formation of $B_i B_s$ pairs. In a first experiment, we could not confirm this result: Solar cells fabricated on boron-doped 0.1 Ω cm Cz wafers demonstrated an extremely fast efficiency degradation (within 10 min, compare with Table 1) of 1% absolutely. Of course this approach should be discussed on the basis of a more comprehensive set of experimental data.

5. Reduction of lifetime degradation by optimized processing

In addition to a proper material choice a reduction of the metastable defect concentration during the cell process should be discussed. In the IC-technology exists a well-known technique for the reduction of the interstitial oxygen concentration: the formation of a denuded zone [14]. Unfortunately, this technique is not suitable for the solar cell technology since it is combined with the formation of oxide precipitations under the denuded zone which reduce the carrier lifetime strongly [15].

We have already demonstrated that a high-temperature step which is optimized for Cz-Si can significantly reduce the extent of degradation and increase the stable lifetime after degradation, respectively [3,6]. Recently, the thermal oxidation process necessary for masking oxides and passivation layers was studied comprehensively by experimental design methods. The ramp-up, oxidation and ramp-down parameters were varied and the effect on the carrier lifetime was studied on different Cz materials with different interstitial oxygen and boron concentrations. An FZ-reference wafer was added in order to control the passivation quality of the resulting oxide. The Cz materials under investigation had initial lifetimes ranging from 3 μs up to 12.7 μs, i.e., no "academic" hyperpure material was chosen.

It was possible to distinguish between two principal effects. If the ramping conditions were chosen in a wrong way the bulk lifetime was reduced strongly independent of the plateau conditions. If the ramping conditions were chosen properly an increase of the stable bulk lifetime and a reduction of the extent of degradation, respectively, were observed. For properly chosen ramping parameters an improvement was obtained within the whole oxidation parameter range, but best results were obtained for temperatures above 1000°C.

Fig. 3 visualizes the strong influence of the process parameters on the stable lifetime after an illumination of 30 h. In addition to the measured bulk lifetimes, calculated cell efficiencies which could be achieved with the corresponding lifetimes are given.

The initial lifetime before the process of 12.7 μs can be either decreased down to 0.8 μs (6.3% of the initial lifetime) or increased up to 54 μs (425 % of the initial lifetime). Speaking in terms of efficiencies, this means a decrease from 18.7% down to 14.9% or an increase up to 20.3%!

For properly chosen ramping parameters an improvement of τ_d was obtained within the whole oxidation parameter range. However, the highest improvement of τ_d compared to the initial value of the unprocessed material (see Fig. 4) and the strongest reduction of N_t^* (see Fig. 5) were obtained for temperatures around 1050°C.
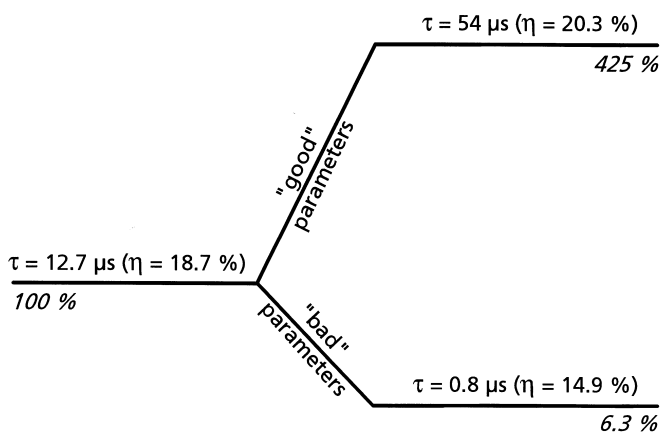

Fig. 3. Influence of process parameters of a thermal oxidation at 1050°C on the stable bulk lifetime. The efficiencies in the brackets are calculated from the measured bulk lifetimes for a simple high-efficiency cell.
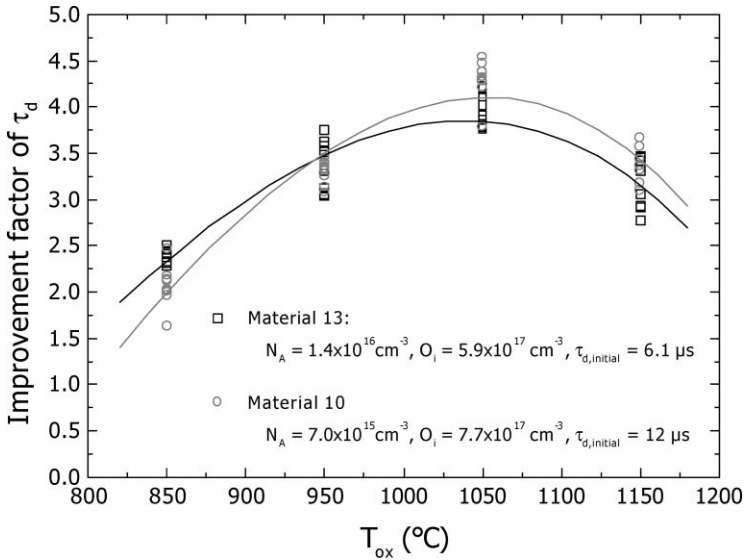
Fig. 4. Improvement factor of the stable lifetime, τ_d, compared to the initial value before processing induced by a thermal oxidation with optimized ramping conditions at different oxidation temperatures, T_{ox}. The specifications (doping concentration, interstitial oxygen concentration and initial lifetime of the unprocessed material) of the boron-doped Cz-Si are given in the graph.
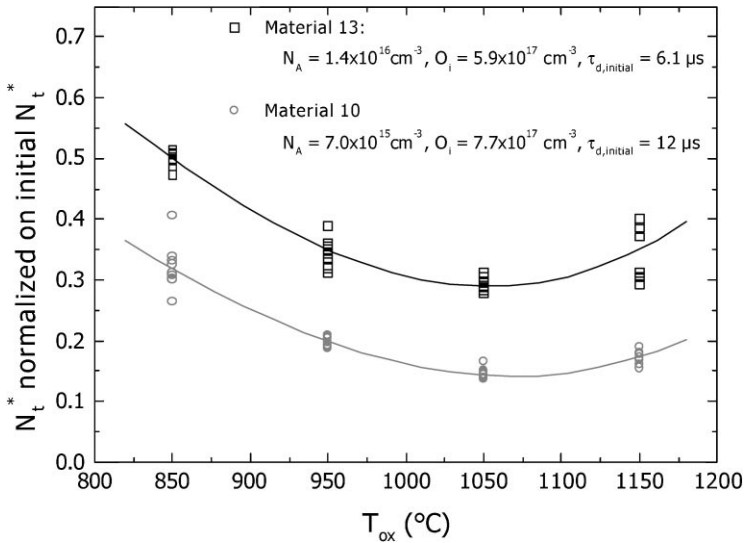

Fig. 5. Reduction of the normalized defect concentration, N_t^*, compared to the initial value before processing induced by a thermal oxidation with optimized ramping conditions at different oxidation temperatures, T_{ox}. The specifications (doping concentration, interstitial oxygen concentration and initial lifetime of the unprocessed material) of the boron-doped Cz-Si are given in the graph.

The similarity of the dependence on the oxidation temperature of both, τ_d and N_t^*, indicates that the improvement of the stable lifetime is mainly induced by the reduction of the concentration of the metastable defects or in other words by the reduction of degradation.

Using the optimized high-temperature processes it was possible to achieve an improvement of the starting material on many different Cz materials. Fig. 6 shows the reduction of the normalized defect concentration by a thermal oxidation and by the complete solar cell process for boron-doped Cz-Si with very different specifications.

Fig. 7 shows the improvement of the stable lifetime by a thermal oxidation and by the complete solar cell process for the same boron-doped Cz-Si as in Fig. 6.

On an average the stable lifetime was increased by a factor of 2–3 by the high-temperature processes! For example, the lifetime of the low-resistivity sample shown in the second set of columns ("1.06/5.9") is increased from 6.1 to 36.8 µs. For an RP-PERC solar cell this improvement in lifetime would result in a V_{oc} increase from 606 to 636 mV and an efficiency improvement from 17.3% to 19.4 %, respectively! This correlates well with a stable efficiency after a degradation of 19.2% achieved on this material type. Thus, our investigation has shown that an optimized high-temperature process is not detrimental even to solar-grade Cz-silicon, but it can increase the bulk lifetime even if no phosphorus gettering is involved.

Note that the optimized ramp conditions are not only important for standard boron-doped Cz-Si but also for other oxygen-contaminated Cz-materials. Only nearly oxygen-free MCz will tolerate other process parameters.
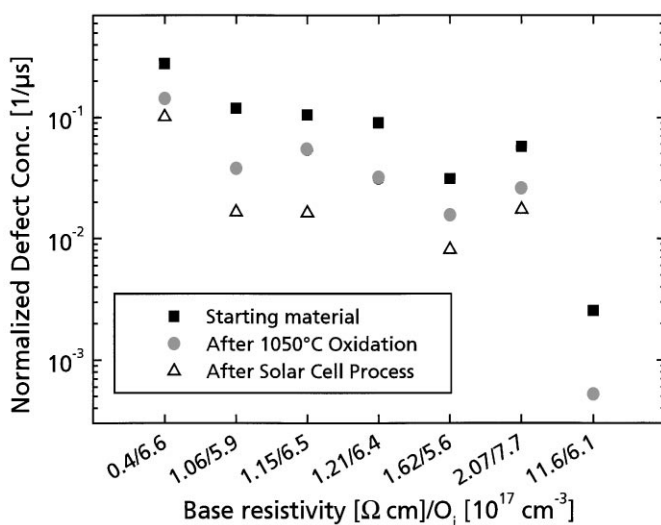

Fig. 6. Normalized defect concentration, N_t^*, for different boron-doped Cz materials and process steps.
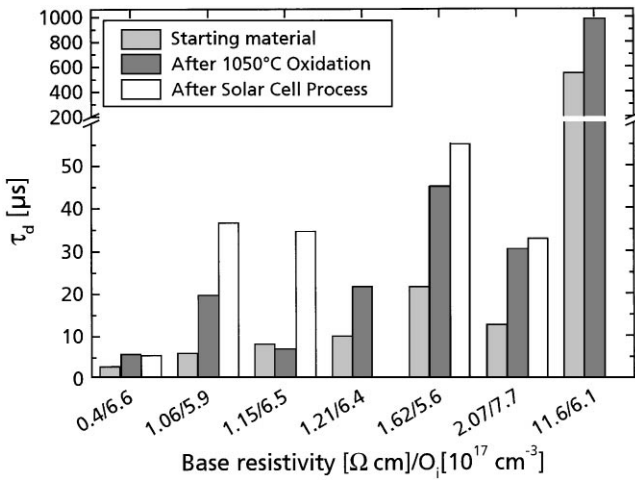
Fig. 7. Stable lifetimes after degradation, τ_d, for different boron-doped Cz materials and process steps.

6. Conclusion

The minority carrier lifetime degradation induced either by light illumination or carrier injection is *clearly correlated with boron and oxygen*. While the quantitative correlation between the defect concentration and boron is linear, the increase of the defect concentration induced by the interstitial oxygen concentration is superlinear, i.e. it follows a potential law of power approximately 5. Also, the rate of the defect reactivation by light is strongly increased especially by an increasing boron concentration.

Possibilities to reduce the metastable defect concentration are discussed:

One way could be a *proper material choice*. The *substitution or reduction of boron* as the dopant was already quite successful: With lowly doped Cz-Si (7 Ω cm) cell efficiencies of 22.0% have been obtained, while gallium-doped Cz-Si has even yielded a value of 22.5%. On a large cell area (100 cm²) a record efficiency of 20.2% was achieved on gallium-doped Cz-Si. In both cases, no degradation was observed. The *reduction of interstitial oxygen* in boron-doped Cz-Si using the MCz method was also very successful, and resulted in cell efficiencies of 22.7%.

The second way is the reduction of the metastable defect concentration in conventional p-type Cz silicon by *high-temperature process steps*. With an oxidation step optimized for Cz silicon it was possible to increase the stable bulk lifetime significantly. On the other hand, a process with non-optimized parameters resulting in the same thermal oxide could totally deteriorate the material.

Acknowledgements

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