

ON THE DEGRADATION OF CZ-SILICON SOLAR CELLS

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ABSTRACT: The present work aims at the analysis and technological reduction of the metastable defect responsible for the degradation of efficiencies of solar cells fabricated from Cz-silicon under illumination or forward bias. Lifetime measurements on Cz-silicon wafers show a clear correlation between the oxygen and boron content and the defect concentration. Additionally, oxygen-doped FZ-wafers have been analyzed: While phosphorus- and oxygen-doped FZ-silicon and oxygen-free boron-doped FZ-silicon show no degradation effect, boron- and oxygen-doped FZ-silicon exhibits the same metastable defect behavior as boron-doped Cz-silicon in the absence of other contaminations. This is in coincidence with the recent suggestion that B_iO_i could be the responsible defect. We demonstrate that the defect concentration can be reduced significantly by high-temperature processes. Either a thermal oxidation or a solar cell process, both optimized for Cz-silicon at Fraunhofer ISE, increase the stable lifetime after degradation by a factor of 2 to 3.

Keywords: Czochralski - 1: Defects - 2: Recombination - 3.

1. INTRODUCTION

Efficiencies well above 20%, including the international record value of 22%, achieved from a broad range of different Cz-Si materials have demonstrated the potential of Cz-silicon [1]. However, the degradation of the initial cell efficiency induced by illumination or carrier injection to a stable final state is still a problem [2, 3]. Spectral response measurements have clearly shown that the degradation of efficiency is due to a reduction of carrier lifetime and diffusion length, respectively.

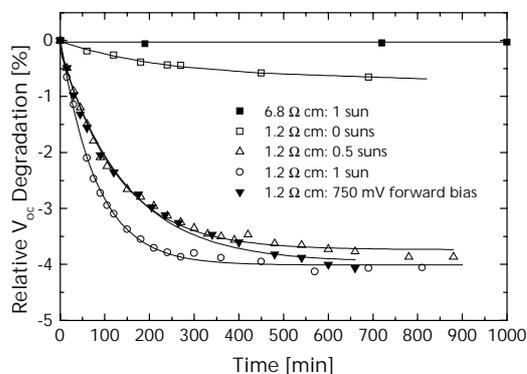


Figure 1: Relative loss in open circuit voltage of Cz solar cells for different base resistivities and degradation conditions. Note: The degradation of the cells without additional illumination may be caused by the repeated measurement of the IV-curve.

Since both, illumination and application of a forward bias, result in a lifetime degradation, the responsible defect is not activated by photons but by excess carriers. As can be seen in Fig. 1 the degradation is only observed for low-resistivity materials while cells fabricated from higher resistivity material do not degrade.

The initial lifetime and cell efficiency, respectively, can be recovered by an annealing step at 200°C in room ambient (see Fig. 2). Thus, the cycle degradation-anneal is fully reversible.

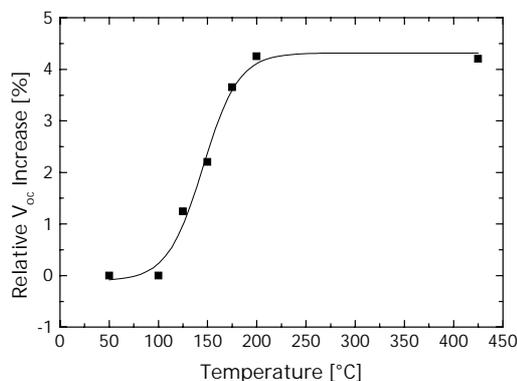


Figure 2: Anneal of Cz cells at different temperatures.

The aim of this work is the analysis of the underlying metastable defect. Over 30 different Cz-materials from various manufacturers are investigated. Since the open circuit voltage even of high-efficiency solar cells has only a limited sensitivity on changes of the diffusion length, the main investigation is performed with contactless lifetime measurements.

Of course, not only the identification of the defect structure is of interest: In the second part of this work we describe an effective way of reducing the defect density responsible for the lifetime decrease.

2. INFLUENCE OF BORON AND OXYGEN

It is well known that the determination of bulk lifetimes requires a very low surface recombination velocity. Thus, all samples were surface passivated either with a silicon nitride layer [4] processed at low temperatures (375°C) at ISFH or a corona charged thermal oxide [5] processed at high temperatures (1050°C) at Fraunhofer ISE. For both passivation schemes extremely low S-values below 10 cm/s are achieved. This allows the exact determination even of high bulk lifetimes. The injection-dependent S-values for both passivation schemes were measured on high-lifetime FZ-wafers with comparable doping concentrations. These S-values were used to determine the bulk lifetimes of the Cz-samples from the measured effective lifetimes. The wafers were

measured with MW-PCD (microwave-detected photo-conductance decay) using an additional white bias light.

Since interstitial oxygen is one of the most prominent contaminations in Cz-silicon the influence of oxygen was investigated in an ideal system, i.e. an oxygen-doped FZ-wafer. Fig. 3 shows the results of time-dependent lifetime measurements on nitride passivated wafers. The defect was deactivated at the time $t = 0$ by a 200°C anneal (compare to Fig. 2). Then the wafers were degraded with white light of 50 mW/cm² intensity and measured repetitively during the degradation.

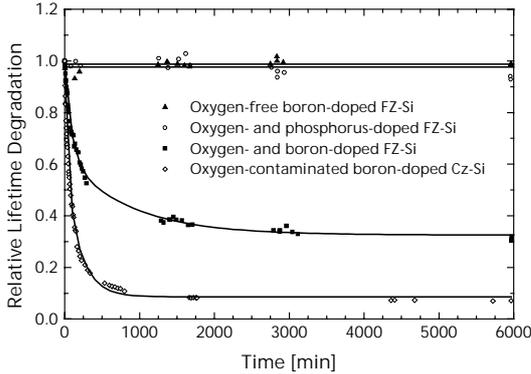


Figure 3: Lifetime degradation of oxygen-doped and oxygen-free p- and n-type FZ-silicon.

While the boron- and oxygen-doped FZ-wafer shows a lifetime degradation comparable to a boron-doped oxygen-contaminated Cz-wafer (also shown in Fig. 3), both, the oxygen-free boron-doped FZ-wafer and the phosphorus- and oxygen-doped FZ-wafer, shows no degradation. Together with the observation of Schmidt et al. [6] that there is no degradation for gallium-doped oxygen-contaminated p-type Cz-silicon the conclusion is justified that oxygen and boron are the components of the investigated defect.

For a quantitative investigation it is not useful to consider the absolute lifetime since this value is possibly influenced by other defects. Under the assumption that (i) the defect under investigation is totally deactivated after a 200°C anneal and (ii) totally activated after illumination with 1 sun light for at least 30 h and (iii) that additional defects in the different Cz-Si are not influenced by the anneal/degradation cycle, it is possible to determine the defect concentration in the following way: If we denote the initial lifetime measured directly after the anneal τ_0 and the final stable lifetime after degradation τ_d , then the following quantity is proportional to the metastable defect concentration.

$$1/\tau_d - 1/\tau_0 = (v_{th}\sigma N_t + v_{th}\sigma_{res} N_{res}) - v_{th}\sigma_{res} N_{res}$$

where v_{th} is the thermal velocity, σ is the capture cross section, N_t is the concentration of the metastable defect, and N_{res} is the concentration of the residual defects.

In the first experiment we investigated the defect reactivation behavior of Cz-materials with different oxygen and boron content listed in Tab. 1. Both, oxygen and boron concentration were measured on each separate sample, using FT-IR spectroscopy and resistivity measurements, respectively.

Table I: Measured material parameters (boron-doped Cz)

Material	ρ_{base} [Ω cm]	N_A [cm^{-3}]	O_i [cm^{-3}]
11	0.4	$4.25 \cdot 10^{16}$	$6.6 \cdot 10^{17}$
13	1.06	$1.42 \cdot 10^{16}$	$5.9 \cdot 10^{17}$
12	1.15	$1.30 \cdot 10^{16}$	$6.5 \cdot 10^{17}$
4	1.21	$1.23 \cdot 10^{16}$	$6.4 \cdot 10^{17}$
18	1.62	$9.04 \cdot 10^{15}$	$5.6 \cdot 10^{17}$
10	2.07	$6.95 \cdot 10^{15}$	$7.7 \cdot 10^{17}$
1	11.6	$1.18 \cdot 10^{15}$	$6.1 \cdot 10^{17}$

The sample surfaces were passivated with silicon nitride deposited at low temperatures in order to study the starting material. After an anneal at 200°C at $t=0$ the wafers were degraded by illumination with 0.5 suns. The reactivation of the defects shown in Fig. 4 follows an exponential time law:

$$\sigma v_{th} N_t(t) = (1/\tau_d - 1/\tau_0)(1 - e^{-t/\tau_{t-gen}})$$

This function is fitted to the measured data (solid lines in Fig. 4). The fit results are shown in Fig. 5.

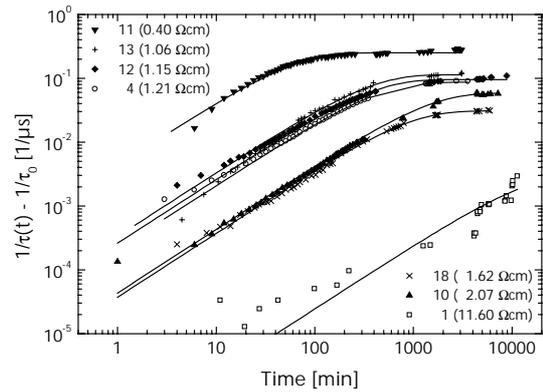


Figure 4: Time dependent defect reactivation for different Cz-materials (see Tab. 1) under 50 mW/cm² illumination.

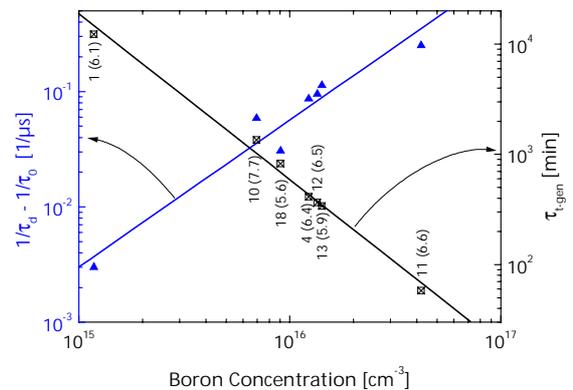


Figure 5: $1/\tau_d - 1/\tau_0$ (proportional to the total defect concentration) and τ_{t-gen} from the fits in Fig. 4. The labels denote the material type (see Tab. 1) and the interstitial oxygen concentration in [$10^{17} cm^{-3}$].

Obviously the total defect concentration is a clear function of the boron concentration. Additionally, the

impact of oxygen can be observed: Although material 10 has a lower boron concentration than material 18, its defect concentration is higher due to its higher oxygen concentration. However, the defect generation rate $1/\tau_{t-gen}$ increases monotonically with increasing boron concentration since the reaction kinetics are determined by the highly mobile interstitial boron.

In order to study the influence of the interstitial oxygen concentration quantitatively, samples of approximately the same boron concentration were chosen. Fig. 6 shows the defect concentration and $1/\tau_d - 1/\tau_0$, respectively, of samples with base resistivities between $0.9 \Omega \text{ cm}$ and $1.3 \Omega \text{ cm}$ which received a high-temperature (1050°C) passivation by a corona-charged thermal oxide.

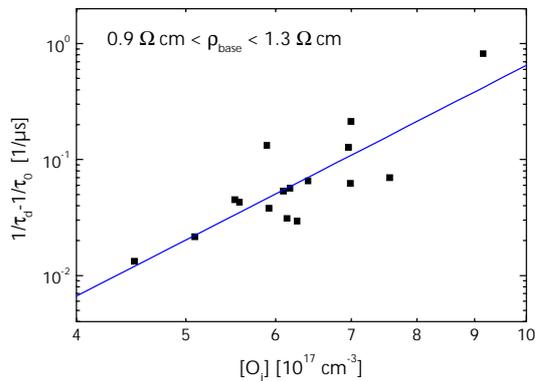


Figure 6: $1/\tau_d - 1/\tau_0$ (proportional to the total defect concentration) vs. the interstitial oxygen concentration for boron-doped Cz-samples with base resistivities between $0.9 \Omega \text{ cm}$ and $1.3 \Omega \text{ cm}$.

The defect concentration is a strong function of the interstitial oxygen concentration. Although there is some scatter in the data points, one can clearly conclude that the increase is superlinear. The solid line in Fig. 6 follows a potential law of order five.

An analogous investigation was performed for the influence of boron. Now samples with interstitial oxygen concentration between 5.6 and $7 \cdot 10^{17} \text{ cm}^{-3}$ were selected.

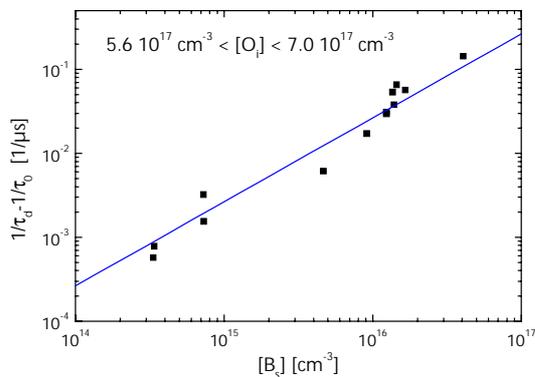


Figure 7: $1/\tau_d - 1/\tau_0$ (proportional to the total defect concentration) vs. boron concentration for Cz-samples with an interstitial oxygen conc. between 5.6 and $7 \cdot 10^{17} \text{ cm}^{-3}$.

There is a linear relationship between the defect and the boron concentration (solid line in Fig. 7). The defect concentration and the lifetime degradation, respectively, of

materials with high base resistivity is very low. This explains why no efficiency degradation was observed for solar cells made from this material group (see Fig. 1). Comparing the defect concentrations of nitride- (see Fig. 5) and oxide-passivated samples (see Fig. 7), the same linear correlation to boron is observed. However, the defect concentration of the samples which received a high-temperature step is shifted to lower values.

3. REDUCTION OF DEFECT CONCENTRATION

As already mentioned in a previous publication [3] the bulk lifetime of Cz-silicon cannot only be increased temporarily, but it is also possible to increase the stable lifetime after degradation, τ_d , permanently by high-temperature steps. In order to investigate this effect we have treated wafers of different resistivity and oxygen content (see Tab. 1) with an oxidation at 1050°C and a complete RP-PERC solar cell process [1]. Then we compared the measured lifetime and effective defect concentration with the initial values of the unprocessed wafers.

The oxidation was performed at 1050°C for 35 min under oxygen with an addition of DCE (Dichlorethylen) and a subsequent post-oxidation anneal at the same temperature under argon for 20 min, resulting in a 105 nm thick oxide. The RP-PERC process sequence includes the same oxidation scheme and several additional high-temperature steps. In both processes we used ramps which were optimized for Cz-silicon. While the lifetimes of the initial and oxidized wafers were determined using MW-PCD, the diffusion lengths of the cells before and after the degradation were determined from spectral response measurements. In order to calculate L_b and τ_b , respectively, from the measured L_{eff} , the rear surface recombination velocity S_{back} has to be known. S_{back} was determined from FZ-cells processed in parallel assuming an Auger-limited lifetime in the FZ-base. The values in Fig. 8 and 9 represent the average of three batches of solar cells.

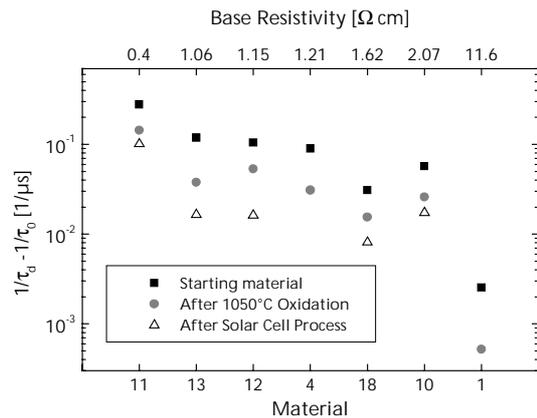


Figure 8: $1/\tau_d - 1/\tau_0$ (proportional to the total defect conc.) for different Cz-materials (see Tab. 1) and process steps.

Fig. 8 shows the effective defect concentration of the different materials. It is obvious that the defect concentration is strongly reduced by the thermal oxidation and even more by the solar cell process. This reduction of the defect concentration should result in an increase of the absolute final lifetime after degradation, τ_d , which is the essential value for the performance of Cz solar cells.

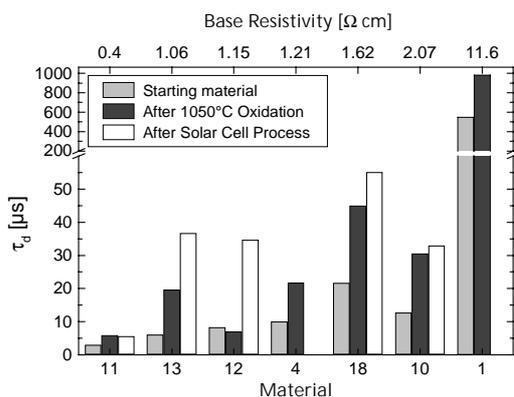


Figure 9: Absolute lifetimes after degradation for different Cz-materials (see Tab. 1) and process steps.

The trend of Fig. 8 is clearly reflected in Fig. 9: the final lifetime after degradation is increased by the thermal oxidation and the solar cell process, respectively. On average the stable lifetime was increased by a factor of 2 to 3 by the high-temperature processes! For example, the lifetime of the low-resistivity sample 13 ($N_A=1.4 \cdot 10^{16} \text{ cm}^{-3}$) is increased from 6.1 to 36.8 μs . For a 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 nicely correlates with a stable efficiency after 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.

In a second experiment we investigated the influence of the duration of the high-temperature oxidation at 1050°C using the same ramps. Prolonged high-temperature times of 1h, 3h, 5h, and 15h did not further improve lifetime. This underlines the importance of the temperature scheme of the ramps used in our processes.

4. DISCUSSION

The lifetime measurements and the solar cell results have demonstrated a clear correlation of the investigated Cz-defect with the interstitial oxygen and boron concentration. Especially, the results obtained on the oxygen-doped FZ-wafers with no additional defects have consolidated this conclusion. Schmidt et al. [6] have suggested a model where the complex B_iO_i is the metastable defect. This model is based on deep-level transient spectroscopy (DLTS) investigations on electron-irradiated boron-doped Cz-Si by Kimerling et al. [7]: They observed a defect energy level of $E_C - E_t = 0.26 \text{ eV}$ attributed to B_iO_i . This defect level could be annihilated by an anneal in the temperature range from 150°C to 200°C and is transferred to a defect level $E_V + E_t = 0.29 \text{ eV}$ correlated to B_iC_s . The metastable lifetime behavior and the correlation of the defect concentration with oxygen and boron observed in this work are in good correlation with their results. However, Kimerling et al. have performed their measurements on electron-irradiated Cz-samples in order to increase the defect concentration. DLTS measurements on our un-irradiated samples showed no significant signal [8] even on the material type 11 with the highest defect concentration.

However, it is known from earlier DLTS investigations [9] that the electron capture cross section of the B_iO_i complex has an extremely high capture cross section for electrons of $3 \cdot 10^{-13} \text{ cm}^2$. Assuming this capture cross section, the defect concentration of material 11 would be approximately $5 \cdot 10^{10} \text{ cm}^{-3}$. This value is one order of magnitude lower than the DLTS detection limit for a material with the respective doping concentration (see Tab. 1).

5. CONCLUSION

The results of lifetime measurements presented in this paper have demonstrated a clear correlation between the metastable Cz-defect and the elements boron and oxygen. In addition to a quantitative study of this correlation on over 30 different Cz-materials, experiments were carried out on oxygen-doped FZ-silicon. While oxygen- and phosphorus-doped and oxygen-free boron-doped FZ-silicon showed no degradation effect, boron- and oxygen-doped FZ-silicon showed the same metastable defect behavior as boron-doped Cz-silicon in the absence of other contaminations. Thus, our experimental results support the suggestion that the B_iO_i is the responsible metastable defect although no direct observation of the defect was possible up to now.

In a technological study we have demonstrated that the defect concentration and the stable lifetime after degradation can be increased by high-temperature processes. Both, a thermal oxidation and a solar cell process, optimized for Cz-silicon at ISE, have decreased the defect density significantly. The stable lifetime after degradation could be increased by a factor of 2 to 3.

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