LIGHT-INDUCED DEGRADATION OF THE CARRIER LIFETIME IN N-TYPE CZOCHRALSKI-GROWN SILICON DOPED WITH BORON AND PHOSPHORUS

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ABSTRACT: The carrier lifetime in oxygen-rich boron-doped crystalline silicon degrades under illumination at room temperature, both in *p*- and *n*-type silicon. While this so-called light-induced degradation has been intensely studied in *p*-type silicon, the data base on *n*-type silicon is still sparse. In this work, the defect generation in dopant-compensated *n*-type silicon is investigated at different light intensities, revealing a considerable increase of the defect generation rate with increasing light intensity. Based on this finding, we propose that the defect generation rate constant is proportional to the square of the hole concentration. Since holes are minority carriers in *n*-type silicon, their concentration depends on the carrier lifetime and the generation rate of excess carriers. The lifetime in turn depends on the amount of recombination active defects, which increases during the course of degradation. The result is a complex time dependence of the effective defect concentration. Simulations based on this model yield excellent agreement with the experimental data. In addition, by comparison with existing data of the rate coefficients in *p*-type silicon, the defect is identified as the fast forming recombination-center observed in *p*-Si.

Keywords: Czochralski silicon, boron, phosphorus, lifetime, recombination, defects

1 INTRODUCTION

Degradation of the carrier lifetime in boron-doped oxygen-rich *p*-type silicon under illumination due to the formation of boron-oxygen-related recombination centers is a well-known and intensely studied phenomenon [1-9]. It was found to proceed in two stages: a fast one, proceeding on a time scale of seconds to minutes, and a slow one, proceeding on a time scale of hours [6,8,9]. The time dependence of the effective defect concentration follows a simple exponential function for both the fast and the slow stage and the defect generation rate constants were found to be proportional to the square of the doping concentration [5,9]. In addition, studies on (exclusively) boron-doped *p*-Si showed a proportionality of the saturation values of the effective defect concentrations to the substitutional boron concentration, as well as to the square of the interstitial oxygen concentration [3,7,8].

However, recent studies on compensated *p*-type Czochralski-grown silicon (Cz-Si) revealed that the dependence of the defect generation rate constant (of the slow forming defect) is actually on the square of the hole concentration, whereas the saturation value of the effective concentration of the slow forming defect is proportional to the hole concentration [10].

In contrast to the wide range of experimental data in *p*-type silicon, experimental data on LID in boron-doped *n*-type silicon is sparse. Bothe *et al.* reported on LID in B-doped oxygen-rich Float-zone silicon which was overcompensated through the formation of thermal donors [5], while Schutz-Kuchly *et al.* observed LID in *n*-type Cz-Si that was doped with both boron and phosphorus [11]. However, no detailed measurements of the progress of degradation were performed in either of these studies.

In this work, we present time-resolved lifetime measurements on boron- and phosphorus-doped *n*-type Cz-Si under illumination at different light intensities, revealing a strong increase of the degradation rate with increasing light intensity. Based on this finding, we propose that the defect generation rate constant is proportional to the square of the hole concentration. Since holes are minority carriers in *n*-type silicon, their concentration depends on both the generation rate of excess carriers and the carrier lifetime. The latter, in turn, depends on the concentration of recombination-active defects, which increases during the course of LID. This feedback results in a complex time dependence of the effective defect concentration during the course of degradation. Simulations which use the proportionality of the defect generation rate constant on the square of the hole concentration are found to yield excellent agreement with the experimental data.

Using the known rate coefficients of the fast and the slow stage of degradation in *p*-Si [9], we find that the defect responsible for LID observed in compensated *n*-Si is actually the fast forming center.

In addition, the effective defect concentration after complete degradation is determined in a number of samples with different net doping concentrations. Interestingly, no dependence of the saturation value of the effective defect concentration on the net doping concentration is observed. Instead, the effective defect concentration correlates with the boron concentration. As a result, we conclude that the fast forming defect is composed of a substitutional boron atom B_s and an interstitial oxygen dimer O_{2i}, as was already proposed in the past [9].

2 EXPERIMENTAL DETAILS

In this study, we use compensated *n*-type Cz-Si wafers cut from an ingot which was doped with both boron and phosphorus. The resistivity ρ of the samples varied between 0.3 and 4.9 Ω cm. Processing steps include damage-etching, RCA-cleaning, and a phosphorus diffusion (50 min at 847°C) to remove any fast-diffusing metal impurities. The resulting n^+-layers on both sides of the wafer were removed by a short etch in KOH before passivation by plasma-enhanced chemical vapor-deposited silicon nitride [12].

Lifetime measurements were performed at 29°C using the photoconductance decay technique (PCD) and a Sinton WCT-120 lifetime tester. In order to study the

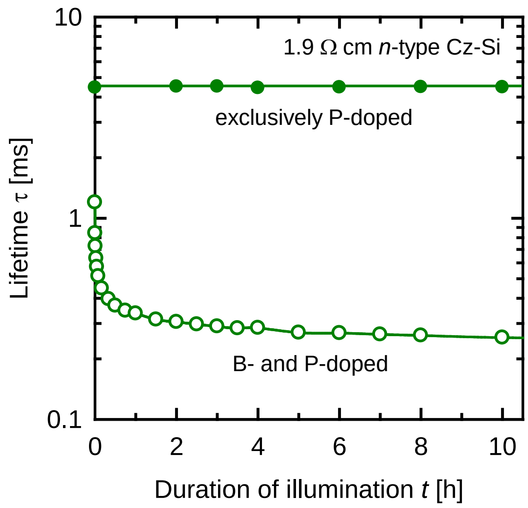

Figure 1: Lifetime τ in 1.9 Ω cm *n*-type Cz-Si plotted versus duration of illumination *t*. In exclusively P-doped *n*-Si (filled symbols) the lifetime is perfectly stable, whereas in dopant-compensated *n*-Si (open symbols) a significant degradation of the carrier lifetime is observed.

time dependence of the carrier lifetime τ during light-induced degradation, τ was extracted at a fixed injection level of $\Delta p = 0.1 \times n_0$. Note that the determination of the excess carrier density via conductance measurements is sensitive to the mobility, which in turn has already been found to be reduced in boron- and phosphorus-doped compensated Cz-Si [13,14]. We thus determined the majority- and minority-carrier low-injection mobilities in all samples and used the extracted data in the analysis of the lifetime measurements, noting that low-injection mobilities are appropriate for the injection level at which the carrier lifetimes are reported [10].

3 RESULTS AND DISCUSSION

An example of light-induced degradation of the carrier lifetime in compensated *n*-type Cz-Si is shown in Fig. 1. While the carrier lifetime in a 1.9 Ω cm *n*-type Cz-Si sample exclusively doped with phosphorus remains perfectly stable under illumination at room temperature, the carrier lifetime in the B- and P-doped sample significantly decreases. Note that only the first ten hours of illumination are shown and that the carrier lifetime in the dopant-compensated sample has not saturated at that point.

Looking at the time dependence of the effective defect concentration during the course of degradation, we seemingly observe significant differences in *p*- and *n*-type silicon. Figure 2 depicts the normalized defect concentration $y = N_t / N_{t.max}$ of two boron-doped Cz-Si samples, where the effective defect concentration N_t is defined as $N_t = \tau^{-1}(t) - \tau_0^{-1}$ that approaches a saturation value $N_{t.max}$.

One of the samples is exclusively doped with boron (blue triangles up) and has *p*-type conductivity, whereas the other sample has *n*-type conductivity and is doped with both boron and phosphorus (red triangles down). The (net) doping concentration of both samples is $p_0 = n_0 = 3 \times 10^{16}$ cm^{-3}. In *p*-type Cz-Si, the time dependence of the normalized defect concentration *y* during defect formation can be described by an exponential function of

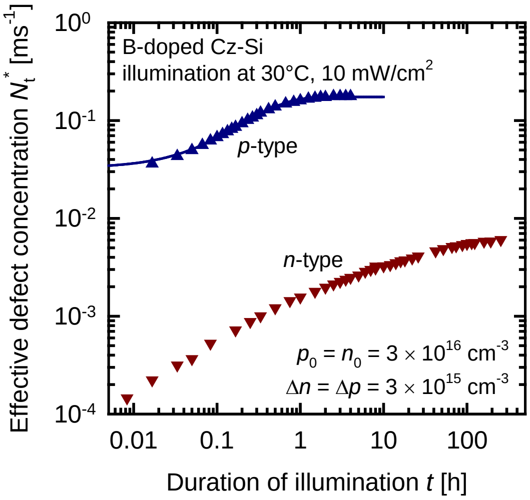

Figure 2: Time dependence of the normalized defect concentration *y* in two Cz-Si samples during illumination at 30°C and a light intensity of 10 mW/cm^2, plotted on a double-logarithmic scale. The blue triangles refer to a 0.5 Ω cm exclusively boron-doped *p*-type Cz-Si wafer, whereas the red triangles correspond to a 0.3 Ω cm compensated (B- and P-doped) *n*-type Cz-Si sample. The data of the *p*-type wafer can be fitted by an exponential function which yields the defect generation rate constant R_{gen}, as indicated by the solid blue line. No such fit is possible for the data of the *n*-type sample.

the form $y = 1 - \exp(-R_{gen}\, t)$, where R_{gen} is the defect generation rate constant, as indicated by the solid blue line. Such a simple fit is not possible for the data of the *n*-type sample, indicating a more complex rate equation for the recombination-active defect responsible for the lifetime degradation.

Interestingly, in *p*-type Cz-Si, the defect generation rate constant R_{gen} was found to be proportional to the square of the net doping concentration p_0^2 [10]. Since holes are minority carriers in *n*-type silicon, a dependence of R_{gen} on the hole concentration would result in a change of R_{gen} over the course of time, because the minority carrier concentration depends on both the generation rate of excess carriers and the carrier lifetime. The latter, in turn, depends on the concentration of recombination-active defects, which increases during the course of degradation. Consequently, the defect generation rate constant R_{gen} would decrease during LID, resulting in a non-linear rate equation for N_t.

Light-induced degradation was also studied at higher light intensity. An example is shown in Fig. 3, where the inverse lifetime τ^{-1} in a 0.3 Ω cm compensated *n*-type Cz-Si sample is plotted versus the duration of illumination *t*. The light intensity was set at 10 mW/cm^2 at a temperature of 30°C (green squares) as well as at 40 mW/cm^2 and 60°C (red circles). The solid lines represent theoretical calculations, as is explained in Section 4. The fact that the degradation proceeds much faster at the higher light intensity further supports the theory that the defect generation rate constant depends on the hole concentration.

Apart from the time dependence of the effective defect concentration during degradation, we also investigated the saturation value of N_t as a function of net doping concentration n_0. Interestingly, no dependence of

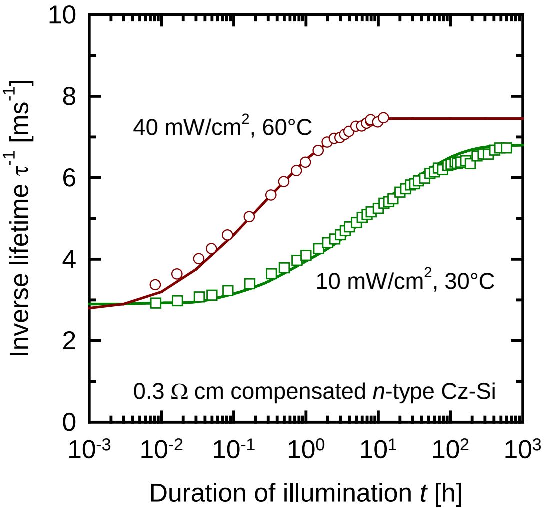

Figure 3: Reciprocal lifetime τ^{-1} as a function of duration of illumination t in a 0.3 Ω cm dopant-compensated n-type Cz-Si sample illuminated at 30°C and 10 mW/cm^2 light intensity (green squares) as well as at 60°C and 40 mW/cm^2 light intensity (red circles). The solid lines represent theoretical calculations. We observe very good agreement between experiment and theory.

$N_{t.max}$ on n_0 was observed. The implications of this finding for the underlying defect reaction are discussed in the next section.

4 DEFECT MODEL

As already mentioned above, light-induced degradation in B-doped p-Si proceeds in two stages, "fast" and "slow". In the traditional defect model for the slow stage of boron-oxygen-related degradation, the recombination-active defect is composed of one substitutional boron atom B_s and an interstitial oxygen dimer O_{2i} [15,16]. This model was based on the numerous experimental results obtained on (exclusively) boron-doped p-type Cz-Si.

Recent studies on boron- and phosphorus-doped (i.e., compensated) p-type Cz-Si, however, revealed results that could not be explained with the traditional B_sO_{2i} model, leading to the proposal of a new defect model, in which the defect is composed of one interstitial boron atom B_i and an interstitial oxygen dimer O_{2i} [17]. In this model, the defect B_iO_{2i} forms during ingot cooling, resulting in a fixed concentration of B_iO_{2i} at room temperature. However, the initial form of the defect is not (or very weakly) recombination-active (the so-called "latent" form, LC). Only under illumination, or rather through the injection of excess carriers, the defect is recharged and subsequently reconstructed into its recombination-active form (SRC) [17].

Note that the proposed recharging and subsequent reconstruction of the defect is in excellent agreement with the experimental finding of Schmidt and Bothe [7] that the defect generation rate constant is proportional to the illumination intensity at very low intensities (below 1 mW/cm^2) but independent of the illumination intensity at higher intensities [18]. In addition, we recently presented experimental data on the lifetime recovery through annealing in darkness in compensated p-Si. We found that the recovery time constant is proportional to the hole concentration, which is in accord with the proposed recharging and reconfiguration of the (slow forming) recombination-active center (SRC) to its latent form (LC) in the B_iO_{2i} model [19].

While a lot of experimental and theoretical work was done on the slow forming defect (SRC), the nature of the fast forming defect (FRC) has been less clear. Bothe and Schmidt [9] reported the defect generation rate constant of FRC to be proportional to the square of the doping concentration, while the saturation value of the effective defect concentration was found to be proportional to the doping concentration as well as to the square of the interstitial oxygen concentration. As a consequence, FRC was also associated with B_sO_{2i} however, the formation mechanism differed from that proposed for SRC [9].

Given that the experimental data on FRC so far has been obtained on exclusively B-doped p-Si and with regard to the new insights into the nature of SRC provided by the experiments on compensated p-Si, however, it seems prudent to question the nature of FRC as well.

Unfortunately, due to the short time scale in which the fast stage of degradation proceeds in p-Si, a conclusive investigation in compensated material has proven difficult.

Looking at light-induced degradation in compensated n-type silicon, however, might solve this problem. As already mentioned above, the time dependence of the effective defect concentration during degradation in n-Si is quite complex. In addition, an increase in illumination intensity was found to significantly increase the speed of degradation. This suggests that the defect generation rate constant depends on the hole concentration, especially since such a dependence is also observed in p-Si (most likely both for SRC and FRC).

The rate equation of the effective defect concentration N_t is thus given by:

$$dN_t/dt = r(T)\, p^2\, (N_{t.max} - N_t), \qquad (1)$$

where $r(T)$ is the temperature-dependent rate coefficient, p is the hole concentration and $N_{t.max}$ is the saturation value of N_t.

In n-type Cz-Si, holes are minority carriers. As a consequence, p depends on the generation rate of excess carriers G and the minority carrier lifetime τ:

$$p = G\,\tau. \qquad (2)$$

The minority carrier lifetime in turn depends on the amount of recombination-active defects already produced:

$$1/\tau = \Sigma\, \alpha_p\, N_t/[1 + (\alpha_p\, p)/(\alpha_n\, n)], \qquad (3)$$

where, α_p and α_n are the capture coefficients [20,21].

Inserting Eqs. (2) and (3) into Eq.(1) yields a non-linear equation for $N_t(t)$, which needs to be solved numerically. Accordingly, a complicated time dependence of the effective defect concentration during degradation is obtained. As already shown in Fig. 2, such a behavior is indeed observed in boron-doped n-type Cz-Si, and using Eq.(1), the time dependence of the effective defect concentration during degradation can be well described, as is shown in Fig. 3 by the solid lines.

Interestingly, using the known rate coefficient $r(T)$ of 0.3 h^{-1} for the slow forming center [9], one finds that under an illumination intensity of 10 mW/cm^2 (green squares in Fig. 3) the slow stage of degradation is expected to be extremely long, and in particular much longer than the 500 h observed in Fig. 3 [20,21].

Using the rate coefficient for the fast forming center (~300 h^{-1} [9]), on the other hand, one finds an expected time frame of 0.3 to 30 h [20,21], which is in good agreement with the experimental data. We thus conclude that the light-induced degradation observed so far in compensated *n*-type silicon is due to the fast forming defect FRC.

Note that due to the much longer time intervals in which LID occurs in compensated *n*-type silicon, a detailed study of the fast forming boron-oxygen related defect is much easier in *n*-Si than in *p*-Si, particularly (presumably) without the "interfering" presence of the slow forming defect. Using injection-dependent carrier lifetime data, for example, it is found that FRC exists in three charge states and possesses two energy levels, as is presented in detail in Refs. [20] and [21].

Studying FRC in compensated *n*-type silicon also enables a closer look at its chemical composition. In exclusively boron-doped *p*-type silicon, the saturated effective defect concentration was found to be proportional to the substitutional boron concentration and to the square of the interstitial oxygen concentration. Accordingly, the defect was proposed to be composed of one substitutional boron atom B_s and an interstitial oxygen dimer O_{2i} [9].

However, exclusively boron-doped *p*-Si does not allow a distinction between the boron concentration and the net doping concentration. Consequently, it is also conceivable that the saturated effective defect concentration of FRC is actually proportional to the net doping concentration instead of the boron concentration, as was found to be case for the slow forming defect SRC [10].

Looking at the experimental findings obtained in this work, we see no dependence of the saturated effective defect concentration on the net doping concentration. Instead, the saturated effective defect concentration is very similar for all investigated samples, even though the net doping concentration varies by more than one order of magnitude.

This suggests that the dependence of the saturated effective defect concentration is indeed on the boron concentration. Since all wafers were cut from the same ingot, the boron concentration is expected to be comparable in all of them, as the segregation coefficient of boron is 0.85. Furthermore, a more detailed analysis shows that the effective concentration of FRC measured in the compensated *n*-Si samples can be well predicted by using known data from *p*-Si, as well as the boron and oxygen concentrations measured in the samples [20,21].

5 CONCLUSIONS

Light-induced degradation in dopant-compensated *n*-type Cz-Si was investigated in samples with varying resistivities and under varying light intensities and temperatures. A simultaneous increase of both the light intensity and the temperature resulted in a noticeably accelerated degradation of the lifetime. In addition, the time dependence of the lifetime degradation in compensated *n*-Si was found to be quite complex – as opposed to *p*-Si, where the time dependence can be described by a simple exponential function.

We explain these findings as follows: the formation rate of the recombination center is determined by the amount of holes *p* present in the material. In *p*-type silicon, *p* does not change notably during illumination at moderate light intensities and the rate equation for the effective defect concentration is linear. In *n*-type silicon, however, holes are minority carriers. Thus, *p* depends both on the light intensity and on the carrier lifetime τ. The minority carrier lifetime, on the other hand, depends on the concentration of recombination-active defects. As a consequence, the defect formation rate constant in *n*-type silicon increases with increasing light intensity and decreases with time (if the light intensity remains constant), resulting in a complex time dependence of τ^{-1} on *t*. Simulations of the time dependence of the effective defect concentration using such a proportionality yield excellent agreement with the experimental data.

Using the rate coefficients for the slow and the fast stage of light-induced degradation obtained in *p*-type silicon, we identify the fast forming defect (FRC) as the defect responsible for LID observed so far in compensated *n*-Si.

The saturated effective defect concentration shows no dependence on the net doping concentration in compensated *n*-type Cz-Si. In contrast, comparable saturated effect defect densities were found in all investigated samples. Consequently, we propose that FRC is composed of one substitutional boron atom B_s and an interstitial oxygen dimer O_{2i}, as was already suggested in the past. The concentration of this defect is expected to be proportional to the boron concentration, which is in accord with the experimental finding of similar saturated effective defect concentrations in the investigated *n*-type samples. Since all samples were cut from the same ingot, the boron concentration is comparable in all samples, due to the high segregation coefficient of boron (0.85).

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