

A 3-state defect model for light-induced degradation in boron-doped float-zone silicon

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We report on a light-induced bulk defect activation and subsequent deactivation in boron doped float-zone silicon that can be described by a 3-state model. During treatment at elevated temperature and illumination, a sample first converts from an initial high lifetime state into a degraded low lifetime state and then shows a recovery reaction leading to a third

high lifetime state that is then stable under degradation conditions. Furthermore, it is shown that reverse reactions into the initial state appear to be possible both from the degraded as well as the regenerated state. An injection dependent analysis of lifetime data yields a defect capture cross section ratio of ~ 20 suggesting a positively charged defect.

1 Introduction Light-induced degradation (LID) may severely limit the bulk charge carrier lifetime τ_b in crystalline silicon [1] which poses a problem to devices relying on stable high τ_b such as sensors or solar cells. Examples are LID in multicrystalline (mc) silicon [2–4] and boron-oxygen (BO) related degradation in Czochralski-grown (Cz) monocrystalline silicon [5]. Float-zone (FZ) silicon, on the other hand, is usually supposed to be characterized by a stable and high τ_b . However, reports about instabilities of τ_b in FZ silicon are becoming more frequent [6–8].

In this study, a degradation and recovery of τ_b is reported in boron-doped FZ samples treated at elevated temperature and illumination. It will be shown that a 3-state defect model, as used e.g. for BO degradation, appears to be a promising approach for the description. In addition, evidence for different reaction pathways between the three states, particularly reverse reaction paths, is provided.

2 Experimental All samples shown here were made out of a single boron doped FZ wafer with specific resistivity $2 \Omega \text{ cm}$, diameter 150 mm, and thickness 250 μm . The wafer first received a cleaning in a solution of H_2O_2 and H_2SO_4 (1:4) at 80 °C followed by a dip in HF. Afterwards, the wafer was split in halves which were coated with hydrogenated silicon nitride ($\text{SiN}_x\text{:H}$) on both sides. Finally,

both halves received a short high temperature step in a fast-firing belt furnace at a measured peak sample temperature of $\sim 835 \text{ °C}$ to activate the passivation. Samples of edge length 5 cm were cut out using a laser and stored in darkness until sample treatment began.

The samples were treated on hotplates either in darkness or at an illumination intensity of 1 sun equivalent. For the repeated measurement of effective lifetime τ_{eff} in dependence of injection level Δn , the sample treatment was shortly paused and a measurement of the photoconductance decay (PCD) was carried out using a Sinton Instruments lifetime tester (WCT-120) at 30 °C. All lifetime data were corrected for Auger and radiative recombination according to the parameterization of Richter et al. [9].

3 Results

3.1 Evolution of effective lifetime As can be seen in Fig. 1(a), a sample treated at 80 °C and ~ 1 sun equivalent illumination intensity shows a strong degradation leading to a minimum of τ_{eff} after ~ 1 h. For longer treatment times, a recovery of τ_{eff} can be observed. A combination of corona charging series, capacitance voltage measurements and repassivation of the sample surface in similarly processed samples leads to the conclusion that the degradation is caused in the bulk of a sample. These measurements are

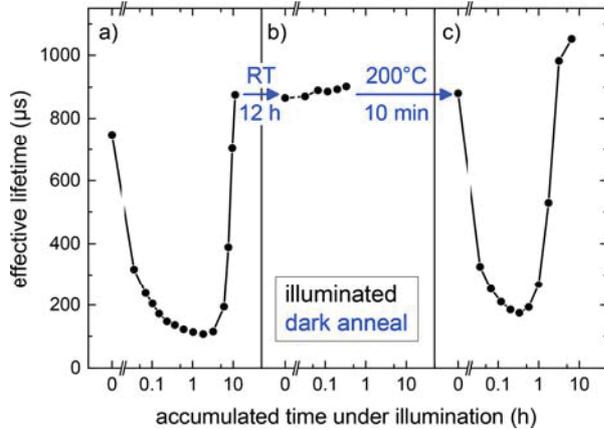


Figure 1 Measurement of τ_{eff} during treatment at 80 °C and ~ 1 sun equivalent illumination intensity (a) starting with a fresh sample, (b) after storage in darkness at room temperature (RT) over night, and (c) after 10 min at 200 °C in darkness. All measurements were evaluated at an injection level of $\Delta n = 7 \times 10^{14} \text{ cm}^{-3}$. Lines only serve as guide to the eye.

thoroughly discussed in a separate publication [10] whereas the scope of the study at hand is to further analyze the bulk degradation.

According to Fig. 1(b), after storage in darkness over night at room temperature, no degradation is observed during an identical illuminated treatment at 80 °C but the sampling continues its recovery. However, annealing in darkness at 200 °C for 10 min and subsequent treatment at 80 °C and illumination (as in the previous steps) leads again to a degradation within minutes (c). This degradation is similar to (a) but slightly weaker and the recovery sets in earlier.

The treatment of another sample was interrupted before reaching the minimum (and subsequent recovery) in τ_{eff} as shown in Fig. 2(a). The sample was then annealed in darkness at 200 °C for 5 min. As can be seen in Fig. 2(b), τ_{eff} is close to the initial value after the annealing step and the sample degrades again when subjected to 80 °C and illumination. According to Fig. 2(c), this procedure can be repeated. The values of τ_{eff} show, however, a small decrease after each additional cycle that could not be reversed by a doubled annealing time of 10 min after (c). Comparing surface saturation current density (J_{0s}) values at $t = 0$ h shows that the small decreases are probably caused by a degradation of surface passivation quality [11].

3.2 Injection dependent analysis One possible cause of light-induced degradation is a contamination with iron resulting in FeB pairing in darkness and FeB dissociation under illumination [12]. However, FeB degradation does not seem to be an issue in our samples because illumination after some days of storage in darkness did not cause significant changes (especially no crossover in low injection) neither in an untreated nor in a partially degraded sample.

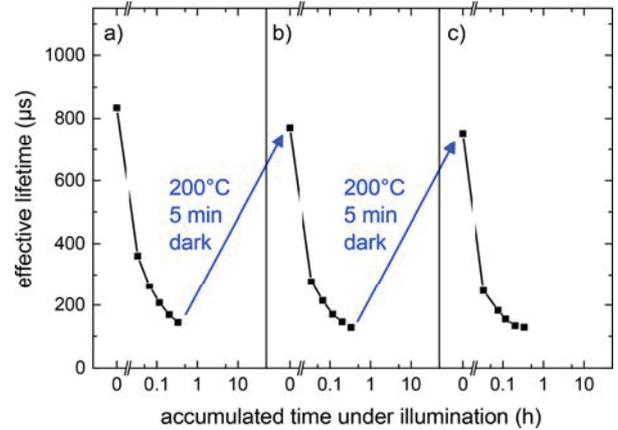


Figure 2 Measurement of τ_{eff} during treatment at 80 °C and ~ 1 sun equivalent illumination intensity (a) starting with a fresh sample, (b) after 5 min at 200 °C in darkness, and (c) after another 5 min at 200 °C in darkness. All measurements were evaluated at an injection level of $\Delta n = 7 \times 10^{14} \text{ cm}^{-3}$. Lines only serve as guide to the eye.

Figure 3 shows the changing injection dependency of τ_{eff} during the treatment shown in Fig. 1(a). Both before treatment and after long treatment times, the injection dependency is rather flat. After 1 h of treatment, however, τ_{eff} is strongly decreased, especially in low injection.

τ_{eff} can be described by the sum of a time dependent defect concentration $N_{\text{def}}(t)$ and a constant defect background lifetime τ_{bg} :

$$\frac{1}{\tau_{\text{eff}}(t)} = c \cdot N_{\text{def}}(t) + \frac{1}{\tau_{\text{bg}}} \quad (1)$$

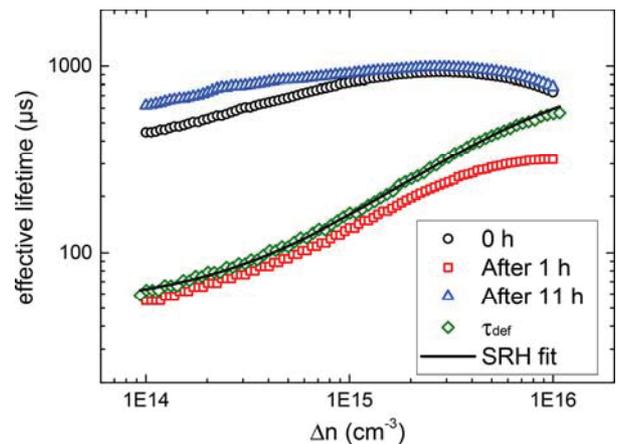


Figure 3 Changes in injection dependence of τ_{eff} during treatment at 80 °C and ~ 1 sun equivalent illumination intensity. Measurement data are taken from the treatment shown in Fig. 1(a). They are already corrected by Auger and radiative recombination according to [9] and therefore only reflect recombination via defect levels in the bulk or at the surface. The values of τ_{def} (green) were calculated by comparing data from the untreated (black) and degraded (red) state. Subsequently, a SRH fit of τ_{def} was conducted and is shown as a black line.

A comparison of τ_{eff} at two different times of treatment yields the corresponding change in defect concentration ΔN_{def} and can be used to define a defect related lifetime τ_{def} as follows:

$$\frac{1}{\tau_{\text{def}}(t)} := c \cdot \Delta N_{\text{def}}(t) = \left(\frac{1}{\tau_{\text{eff}}(t)} - \frac{1}{\tau_{\text{eff}}(t_0)} \right). \quad (2)$$

We use the theory of Shockley, Read and Hall (SRH) [13, 14] under the assumption of a single deep defect level to determine the characteristic capture cross section ratio σ_n/σ_p of electrons and holes. A fit of τ_{def} resulting from the data before and after 1 h of treatment as shown in Fig. 3 yields a σ_n/σ_p ratio of ~ 20 , suggesting a positively charged defect in our FZ samples. This value was calculated assuming stable surface passivation and stable defect background. This seems to be justified because the comparison of data at different treatment times (up to 3 h) either with data before treatment (black) or after recovery (blue) leads to a rather constant σ_n/σ_p ratio of 20 ± 2 .

4 Discussion For defects that express both degradation and recovery at the same treatment conditions, a 3-state defect model as proposed in Fig. 4 is a promising approach to explain the observed behaviour.

A prominent example of a 3-state model is the one used in the description of BO related degradation in Cz silicon [15]. In this model, a defect evolves from an annealed state A into a degraded state B and subsequently recovers into a supposedly stable regenerated state C when subjected to appropriate temperature and illumination conditions. The charge carrier lifetime of the macroscopic sample is then defined by a defect pool in which different defect states are occupied to a certain degree. For example, a partially degraded sample refers to a mixture of some defects being in state A and some in state B. The continuous change in lifetime corresponds to a redistribution within the defect pool.

Additionally, it is known that reverse reactions from B to A and from C to A (possibly via B) occur during elevated temperature treatment and become observable espe-

cially in darkness when other reaction pathways are inactive. The FZ samples in the present study have been subjected to similar temperature and illumination treatments and possible reaction pathways can now be identified.

From Fig. 2(a) it can be concluded that non-degraded samples (state A, high lifetime) evolve towards a degraded state B (low lifetime) when subjected to an elevated temperature and illumination treatment. A temperature step at 200 °C in darkness seems to lead back to the non-degraded state A, because afterwards a sample degrades very similarly compared to an untreated sample. If treated at elevated temperature and illumination for a longer time, however, a regeneration reaction occurs as seen in Fig. 1(a), leading towards a regenerated state C (high lifetime).

According to Fig. 1(b), state C appears to be rather stable during a continued treatment. Subjecting a sample in state C to a treatment at 200 °C in darkness, however, partially destabilizes a regenerated sample, bringing it back towards state A: it degrades again starting from a high lifetime level comparable to the untreated sample when subjected to an elevated temperature and illumination treatment as shown in Fig. 1(c). The slightly weaker degradation amplitude and faster recovery in Fig. 1(c) could be related to an incomplete destabilization due to a rather short annealing time at 200 °C. It cannot be ruled out that the transition from state C towards state A corresponds to a two-step reaction via state B.

It is interesting to note that the defect under investigation in FZ silicon reacts to very similar treatment conditions compared to BO defects in Cz silicon. It is nevertheless unlikely that the cause of degradation is the same. On the one hand, σ_n/σ_p is known to have a value of ~ 10 for the slowly forming BO defect and a value of ~ 100 for the fast forming defect center [16] which do both differ significantly from the value of ~ 20 determined in our FZ samples.

Additionally, it has been shown in great detail that the strength of BO degradation depends strongly on the oxygen content of a sample. The upper limit of oxygen concentration in the FZ material used here is given by the supplier as 10^{16} cm^{-3} . This would lead to a BO degraded lifetime of around 70 ms for 2 Ω cm material according to the parameterization of Bothe et al. [17] that was determined using Cz silicon, far too high to explain the observed lifetime changes in FZ silicon. It appears, however, possible that regeneration of our FZ samples and regeneration of BO degraded samples share a common mechanism. This, e.g., could be a hydrogen passivation of the defect which is often suspected in BO regeneration [18, 19].

The defect discussed here could be related to a defect described by Grant et al. [6] that occurs in as-grown p-type but not in n-type FZ silicon. Their value of σ_n/σ_p of ~ 26 is rather close to our value of ~ 20 and the observations in [6] agree well with transitions between states A and B. However, a state C has not been described in the cited study. This could be related to different passivation methods used which might change sample properties. E.g., our samples are expected to feature a rather high hydrogen content due

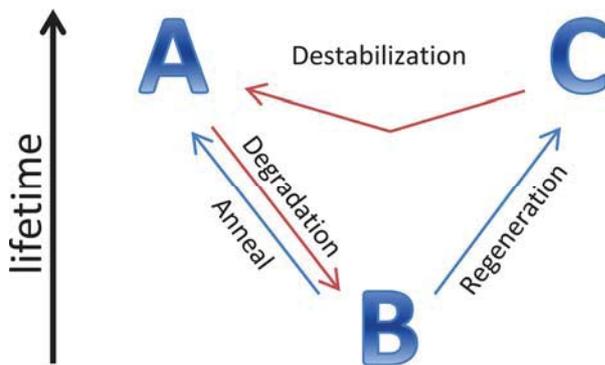


Figure 4 Illustration of the proposed 3-state defect model and associated reaction pathways for charge carrier lifetime degradation and regeneration in boron-doped FZ silicon.

to the $\text{SiN}_x\text{:H}$ layer and the fast firing step whereas the samples in [6] should rather have a low hydrogen content. Consequently, a hydrogen passivation of the defect appears to be possible in our samples whereas it might not be possible in the samples described in [6].

5 Conclusion In this study, a degradation and subsequent recovery of bulk lifetime τ_b was observed in boron-doped float-zone silicon during treatment at elevated temperature and illumination. This was attributed to a defect switching from an initial state A into a degraded state B and subsequently into a regenerated state C. Additionally, it has been shown that reverse reactions seem to occur during a temperature treatment in darkness. These reverse reactions to the initial state A appear to be possible both from the degraded state B as well as from the regenerated state C. An injection dependent analysis was used to differentiate the defect from FeB and BO related degradation and the capture cross section ratio σ_n/σ_p was determined to be ~ 20 , suggesting a positively charged defect.

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