Electrical characterization of the slow boron oxygen defect component in Czochralski silicon

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We investigated the light-induced degradation of compensated Czochralski grown n-type silicon and found a fast-forming and a slow-forming component similar to p-type silicon. A study by means of extended lifetime spectroscopy shows that the "slow" defect introduces two recombination-active energy levels in the silicon band gap. One level resembles the literature data from p-type silicon of a donor-like level at $E_{t1} = E_{CB} - (0.41 \pm 0.02\ \text{eV})$. The second level is found at $E_{t2} = E_{VB} + (0.26 \pm 0.02\ \text{eV})$ and exhibits a strong acceptor-like capture asymmetry. The two-level parameterization constitutes a unified model for the description of the injection dependent lifetime on both p- and n-type silicon and is physically more plausible than previous ones featuring multiple independent centers. A comparison to literature data demonstrates the improved description quality achieved with the new parameterization.

1 Introduction Owing to its strong economic impact the detrimental effect of light-induced degradation (LID) of silicon has been studied for decades and numerous studies, e.g. [1–14] and references in [14], have provided experimental insights as well as vivid discussion on the composition and attributes of the underlying defect. It is consensus that the effect appears in crystalline silicon containing significant amounts of both boron and interstitial oxygen and the assumed crystal defect is therefore addressed as boron-oxygen defect (BO-defect).

LID is usually studied by means of an effective defect concentration N_t^*, which is calculated from excess charge carrier lifetime measurements after defect activation by illumination and after annealing in the dark, a process known to revert BO-defects into a non-active state. Lifetime degradation in p-type Si was found to proceed in a two-stage exponential process indicating the formation of two defect components on different timescales: a fast-formed recombination center (FRC) formed within some 100 s and a slow-formed recombination center (SRC) formed over several 10 h [5]. Studies on compensated and non-compensated boron doped p-type Czochralski-grown (Cz) silicon found N_t^* of both components to be linearly

dependent on the net doping concentration $N_{net} = [B_s^-] - [P_s^+]$ and have a quadratic relation to the concentration of interstitial oxygen $[O_i]$ [2, 5, 6]. Thus, the BO-defect was believed to involve one substitutional boron atom and dimeric interstitial oxygen. Recombination activity of the BO-defect in p-type Si has been described by single-level Shockley–Read–Hall (SRH) parameterizations determined from lifetime spectroscopy on p-type silicon provided by Schmidt and Cuevas [1], Rein and Glunz [3, 4] and Bothe and Schmidt [5]. While these succeeded in describing the effects of LID in p-type with sufficient precision, deviations for certain doping ranges or injection conditions were observed and resolved with the debatable addition of independent shallow recombination centers [1, 4].

Further insight to the nature of BO-defects was obtained by the detection of LID in compensated n-type silicon [7]. Studies by Rougieux et al. [9] and Lim et al. [8] concluded from their results that the BO-defect in n-type Si forms slower than in p-type and in a single-step process, excluding formation of both FRC and SRC. Voronkov et al. [13] took the minority carrier nature of holes in n-type into account and found a kinetic model and developed a modified SRH parametrization for the fast BO-defect [13]. Pre-

vious research indicates that studies on boron doped p-type silicon allow easy assessment of trends, studies on compensated p-type silicon allow distinguishing between hole and boron influences and studies on compensated n-type silicon allow generalizing the results.

In this work we studied the LID in compensated n-type Si with widely varying material parameters. Our measurements provide experimental proof of the formation of both FRC and SRC in n-type silicon. From the injection dependence of the charge carrier lifetimes in compensated n- and p-type samples with widely varying doping a new SRH parametrization for the slowly formed defect is determined.

2 Experiment Samples from different ingot positions of two n-type Cz crystals were used in this investigation. For one of the ingots upgraded metallurgical grade silicon feedstock by Elkem Solar Silicon® was used whereas the other was grown from electronic grade silicon feedstock co-doped with P and B. The different segregation coefficients of P and B result in a broad variation of the net doping concentration $n_0 = [P] - [B]$ from 1.1×10^{15} to 3.6×10^{16} cm^{-3} in the samples. Dopant concentration calculations from Scheil's equation were checked with dopant concentration and resistivity measurements [15]. FTIR measurements of the interstitial oxygen concentration $[O_i]$ with calibration factor 3.14×10^{17} atoms/cm^2 were conducted on samples cut from the crystal sides and interpolated to the wafer positions. The studied wafers featured moderate $[O_i]$ of $5-7 \times 10^{17}$ cm^{-3} representing a typical range for Cz silicon.

Lifetime samples were processed with a standard phosphorus diffusion gettering step followed by removal of the diffused region. A silicon-rich oxide/nitride stack was deposited by PECVD and subsequently activated in a short high temperature step with T_{peak} of 700 °C.

A set of p-type lifetime samples was prepared from various uncompensated boron doped Cz silicon crystals featuring [B] from 1.1×10^{15} to 1.4×10^{16} cm^{-3}. The wafers were gettered alike and passivated with aluminum oxide layers deposited by plasma-activated atomic layer deposition. FTIR measurements conducted on sister samples determined $[O_i]$ between 3.1 and 8.5×10^{17} cm^{-3}.

To study the LID in the samples we performed light soaking experiments on sample stages actively cooled to 25 ± 3 °C. Measurements of the injection dependent lifetime τ were done in order to monitor lifetime evolution over time. The samples were illuminated by halogen lamps and the lifetime measurements were conducted by means of QSSPC measurements, requiring interruption of the illumination. To exclude crucial influences of such interruptions or the white light illumination we performed further light soaking experiments with 790 nm cw laser illumination and *in situ* lifetime measurements in the first few hours with modulated photoluminescence (PL) measurements [16]. Later measurements were conducted *ex situ* due to experimental considerations.

Except for the laser light soaking experiment the lifetime measurements in this study were conducted with a Sinton Instruments WCT-120 QSSPC lifetime tester [17]. The mobility model used in the QSSPC evaluation cannot describe the material under investigation in this study properly due to the significant influence of compensation on the mobility. Following the suggestions by Forster et al. [12], we determined apparent doping concentrations reproducing the actual carrier mobility sum by using the recent mobility model by Schindler et al. [18]. This approach is exact for a single injection level but cannot avoid slight deviations in the lifetime in the order of a few percent due to the changing injection dependence of the mobility sum with doping.

3 Results

3.1 Degradation process After annealing in the dark for 30 minutes at 250 °C the samples exhibited good lifetimes in the range of 1–5 ms in dependence of their respective net doping, proving good surface passivation and crystal quality. Severe reduction of lifetimes was observed for all samples subjected to light soaking. This degradation was reversible by annealing in the dark and is therefore attributed to LID. The injection dependence of the lifetimes was found to change with proceeding degradation.

High temporal resolution in the early stage of LID was possible with *in situ* modulated PL measurements without relevant changes of the injection conditions. The resulting measurement curves clearly show a two-stage progression of the lifetime degradation, as demonstrated in Fig. 1.

3.2 Defect lifetime To assess the defect lifetime τ_{defect} the measured lifetimes τ_{eff} were corrected for the influences of recombination not related to LID taken to be equal to the lifetimes measured before light-soaking $\tau_{initial}$: $1/\tau_{defect} = 1/\tau_{eff} - 1/\tau_{initial}$. Lifetime curves with obvious artifacts (e.g. when $\tau_{eff} \geq \tau_{initial}$ in high injection due to uncertainties) were discarded or affected parts were cut off. Samples affected by severe handling damage (e.g. scratches or cracks) or featuring strong inconsistency of the n_0 determination were discarded, as well. The defect
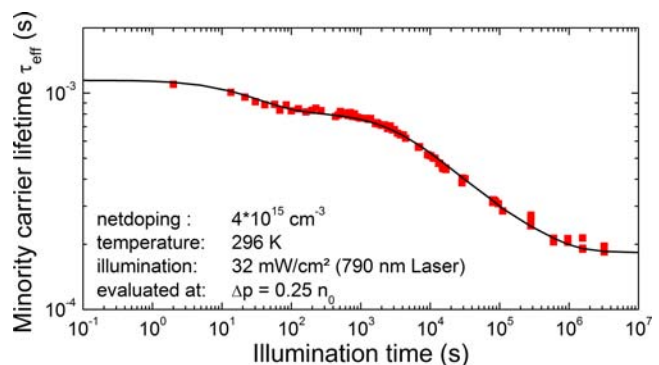

Figure 1 Lifetime evolution of a sample under laser illumination. The line serves as guide-to-the-eye.

lifetime curves of n-type samples in early stages of degradation exhibited injection dependent lifetimes in qualitative accordance with the FRC parameterization given in [14]. The same approach was applied to curves measured after long-term degradation and failed to provide qualitative resemblance. This indicates the formation of defects exhibiting different injection dependence than FRC. We attribute those to SRC, obtaining $1/\tau_{\mathrm{defect}} = 1/\tau_{\mathrm{FRC}} + 1/\tau_{\mathrm{SRC}}$. The influence of the FRC was corrected for, using the parameterization by Voronkov et al. [14] with the concentration $N_{\mathrm{t}}^{*}{}_{\mathrm{FRC}}$ determined from the measured lifetime evolution using a kinetic degradation model. Measurements on p-type samples were corrected accordingly using the FRC parameterization from [5].

4 Lifetime spectroscopy The resulting set of τ_{SRC} curves was studied in terms of SRH statistics. The notations in this section and the assumed lifetime equations follow the suggestion by Murphy et al. [19].

It is possible to reproduce multiple curves for n-type silicon in acceptable quality with a parameterization describing a single-level defect as was presented in [20]. However, such parameterizations cannot describe the whole set of n-type lifetime curves in decent quality and fail to explain lifetime curves not following straight lines when plotted versus the ratio of minority to majority carriers. This is a general feature of single-level defects following SRH statistics [19]. Examples can be found in [20] and are shown in Fig. 2 (dashed lines).

This implies that SRC is either composed of two (or more) independent defect centers or one defect center with multiple defect states in the band gap. The assumption of multiple independent defect centers is considered less plausible. To explain the experimental findings, such independent defect centers would have to be formed simultaneously (independent of sample or process parameters) while still introducing very different recombination channels, i.e. deep and shallow levels in the band gap. Therefore we studied the injection dependent curves by means of a two-level defect. Recombination activity of such defects can be described in analogy to single-level defects with SRH statistics. The minority charge carrier lifetime then depends on the energetic positions E_{t1} and E_{t2} in the band gap, the concentration N_{t} and four charge carrier capture coefficients α_{n1}, α_{p1}, α_{n2} and α_{p2}. For n-type silicon with electron concentration n_0 the hole lifetime $\tau_{\mathrm{h,n\text{-}type}}$ was derived in the appendix of [19] to be

$$\tau_{\mathrm{h(n\text{-}type)}} = \frac{1 + \left(\dfrac{\dfrac{Q_1 n_1 (1-Y)}{n_0} + Y}{Q_1 + \dfrac{p_1(1-Y)}{n_0}} \right) + \left(\dfrac{1 + \dfrac{p_2(1-Y)}{Q_2 n_0}}{\dfrac{n_2(1-Y)}{n_0} + \dfrac{Y}{Q_2}} \right)}{N_{\mathrm{t}} \left(\dfrac{\alpha_{\mathrm{n1}}}{Q_1 + \dfrac{p_1(1-Y)}{n_0}} + \dfrac{\alpha_{\mathrm{p2}}}{\dfrac{n_2(1-Y)}{n_0} + \dfrac{Y}{Q_2}} \right)} \,. \quad (1)$$

The factors n_1, n_2, p_1 and p_2 represent the SRH densities defined by E_{t1} and E_{t2}. We assume one SRC defect level at 0.41 eV below the conduction band edge with a capture coefficient ratio of $Q = \alpha_{\mathrm{n}}/\alpha_{\mathrm{p}}$ known from p-type silicon [3, 4]. The remaining unknown factors have strong influence on the lifetime as seen in Eq. (1) and can vary over orders of magnitude. Therefore we performed extensive parameter sweeps in analogy to the defect parameter solution surface (DPSS) approach for single-level defects by Rein [4]. Every parameter combination was assessed by the quality of the best fit (based on a weighed least-squares deviation) to the measurements with effective defect concentration $N_{\mathrm{t}}^{*} = N_{\mathrm{t}} \alpha_{\mathrm{n1}}$ as free fitting parameter. Determination of absolute values of the capture coefficients and concentrations is not possible solely from lifetime measurements, as discussed in detail in [4].

We found the resulting parameterization to describe p-type measurement data better than the parameterization by Rein et al. [4], as demonstrated in Fig. 2A. Figure 2B gives examples of the parameterization on n-type samples.

Thus, we included the p-type SRC data to the analysis and thereby increased sensitivity of the fitting procedure to parameters related to electron capture. The resulting parameterization confirms the energetic position $E_{\mathrm{t1}} = E_{\mathrm{CB}} - (0.41 \pm 0.02 \text{ eV})$ and locates the second energy level at $E_{\mathrm{t2}} = E_{\mathrm{VB}} + (0.26 \pm 0.02 \text{ eV})$. This combination of energetic positions does not allow determination of an absolute value of the capture ratio Q_2 due to the small sensitivity of the lifetime to α_{p2} for small values of Q_2. Good agreement within measurement uncertainties is achieved for the 18 measurement curves in the data set with $\alpha_{\mathrm{n2}} = 0.55 \alpha_{\mathrm{p1}}$ and the least extreme limit of the capture asymmetry ratio of $Q_2 = 2.55 \times 10^{-3}$ (i.e. $\alpha_{\mathrm{p2}} = 215 \alpha_{\mathrm{p1}}$).
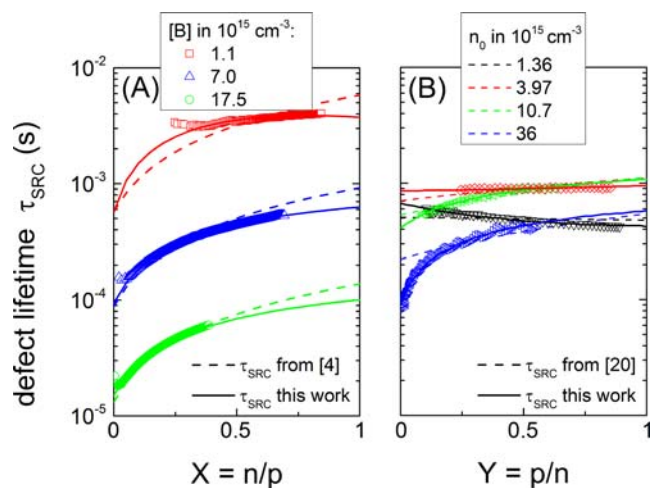

Figure 2 Choice of typical lifetime measurements described with the new parameterization. (A) Comparison with the parameterization from [4] on p-type samples with varying [B]. (B) One- and two-level parameterizations on compensated n-type samples of various n_0.

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A room temperature approximation for net doping concentrations exceeding 2×10^{15} cm^{-3} is given by Eq. (2):

$$\tau_{h, \text{n-type}} \approx \frac{1 + \left(\dfrac{\dfrac{Q_1 n_1 (1-Y)}{n_0} + Y}{Q_1} \right) + \dfrac{Q_2}{Y} \cdot \left(1 + \dfrac{p_2 (1-Y)}{Q_2 n_0} \right)}{N_t^* \left(1 + \dfrac{0.54}{Y} \right)},$$

$$(2)$$

$$\tau_{e, \text{p-type}} \approx \frac{1 + \left(\dfrac{\dfrac{Q_1 n_1 (1-X)}{p_0} + 1}{Q_1 X} \right) + \dfrac{p_2 (1-X)}{p_0}}{N_t^* \left(\dfrac{1}{X} + 0.54 \right)}.$$

5 Discussion

5.1 Parameterization The injection dependence of SRC in p-type Si can be described with a deep donor level reasonably well for doping concentrations exceeding 5×10^{15} cm^{-3} and low to medium injection conditions. Such defect level cannot by itself describe injection dependence in most n-type samples as it predicts vanishing injection dependence for n-type. Implementation of an independently recombination active shallow defect level improves description of p-type measurements and allows for description of n-type measurements. However, a fixed set of two defects cannot provide good description of different samples featuring very different doping concentrations.

In resemblance to the FRC as described by Voronkov et al. [14], we achieved excellent fit quality for SRC on a multitude of samples with the assumption of a single two-level defect. This description is also physically more convincing, multiple independent centers would imply defects of different electronic structure to be created with the same characteristic formation kinetics. Another explanation would be SRC being a defect of an extent capable of inducing multiple independent recombination centers at once. This option cannot be ruled out but appears unlikely, as there have been no reports of any experimental trace of such an extended defect in materials affected by LID. On the other hand, many defects of different composition introducing multiple energetic levels into the silicon bulk are known from literature, e.g. in [21].

To assure the validity of our parameterization we applied it to describe lifetime measurement data from literature for compensated material obtained by Rougieux et al. [9]. The resulting high fit quality is presented in Fig. 3 along with a comparison of our parameterization to the two-defect parameterization of [1] which was proposed for n-type silicon by Rougieux et al. The comparison shows how the two-defect parameterization does describe certain n_0 but results in wrong injection dependencies for others,
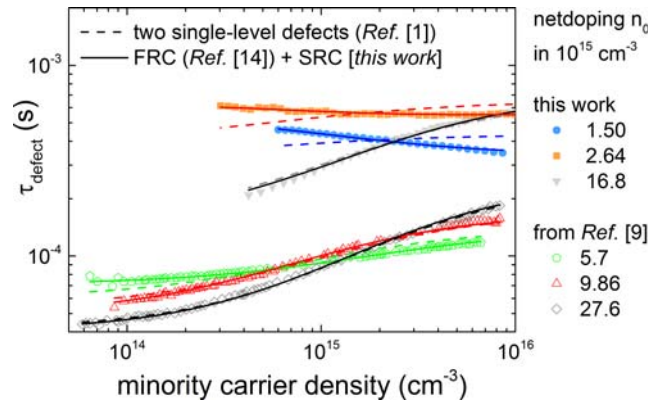

Figure 3 Comparison of the parameterization according to Ref. [1] using two single-level defects to the two-component-two-level parameterization derived in this work.

while the two-level parameterization provides decent fits for all samples.

5.2 Electronic structure of SRC The parameters of the found two-level description presented above allow assessment of the electronic properties of the underlying defect. The capture constants α_{n2} and α_{p2} of the defect level E_{t2} exhibit a strong asymmetry favoring the capture of holes, implying the level to mark an acceptor-like charge transition. Although being less asymmetric the same argumentation holds for level E_{t1} identifying it as the energetic equivalent of a donor-like transition. The energetic position of the defect´s acceptor transition is positioned below the donor transition level, indicating that it might be a negative-U defect, resembling the findings of Voronkov et al. for the FRC [14].

6 Summary A thorough study of the injection dependent lifetime of SRC was performed. It resulted in a parameterization capable of describing lifetimes of both n- and p-type materials and demonstrating the defect to induce two energetic levels into the silicon band gap. This verifies that the same defect is active in both doping types and provides valuable further insights into the nature of the defect.

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