

Lifetime-degrading boron-oxygen centres in p-type and n-type compensated silicon

V. V. Voronkov,^{1,a)} R. Falster,¹ K. Bothe,² B. Lim,² and J. Schmidt²

¹MEMC Electronic Materials, via Nazionale 59, 39012 Merano, Italy

²Institute for Solar Energy Research Hamelin (ISFH), Am Ohrberg 1, D-31860 Emmerthal, Germany

(Received 20 April 2011; accepted 7 June 2011; published online 22 September 2011)

Degradation of minority carrier lifetime under illumination occurs in boron-containing Czochralski silicon of both p- and n-type. In n-Si, the recombination centre responsible for degradation is found to be identical to the fast-stage centre (FRC) known for p-Si, where it is produced at a rate proportional to the squared hole concentration, p^2 . Holes in n-Si are the excess minority carriers—of a relatively low concentration; hence, the time scale of FRC generation is increased by several orders of magnitude when compared to p-Si. The degradation kinetics, which is non-linear, due to dependence of p on the current concentration of FRC, is well reproduced by simulations. The injection level dependence of the lifetime shows that FRC exists in 3 charge states (-1 , 0 , $+1$) possessing 2 energy levels. Comparison of n-Si samples of various electron concentrations shows that FRC emerges by the reconstruction of a latent B_sO_2 complex of a substitutional boron and an oxygen dimer (while the major recombination centre in p-Si denoted SRC was previously found to emerge by reconstruction of B_iO_2 defect involving an interstitial boron atom). A model of the B_sO_2 reconfiguration into FRC through an intermediate state accounts for the rate constant dependence on p , which is reduced to a p^2 proportionality, under certain conditions. © 2011 American Institute of Physics. [doi:10.1063/1.3609069]

I. INTRODUCTION

Czochralski-grown (CZ) boron-doped silicon is long known to suffer from a strong degradation of the minority carrier lifetime that occurs in the presence of excess carriers, particularly under illumination.^{1–3} This effect results in a significant efficiency loss in solar cells. Initially, the lifetime degradation was studied in boron-only doped CZ material.^{2–4} It was discovered³ that there are two lifetime-degrading recombination centres labelled fast-stage centre (FRC) and SRC; they correspond to a fast and a slow stages of degradation, respectively. The SRC is the major centre while FRC can be detected only after a short-time illumination. The saturated concentration of both centres³ is proportional to the boron concentration N_B and to the squared oxygen concentration C^2 . Hence, a natural attribution⁴ of each centre was to a B_sO_2 complex of a substitutional boron atom B_s and an oxygen dimer O_2 . An inspection of p-Si co-doped with boron and phosphorus revealed, however,^{5–7} that the SRC concentration is proportional to the hole concentration p rather than to N_B . This feature is consistent with identification of SRC as a B_iO_2 complex⁸ that involves an interstitial boron atom B_i rather than B_s and exists initially in a single-positive latent form (LCS), of a low recombination activity. In the presence of excess electrons, LCS is recharged from $+1$ into neutral state and then reconstructs into the recombination-active configuration, SRC, which is favourable in this charge state. The nature of FRC remained unclear; one possibility was that FRC is yet another configuration of the B_iO_2 defect.

Recently, lifetime degradation was found^{6,9} in boron-containing n-Si (co-doped with phosphorus and boron). In the present work, more data on this effect are obtained and analyzed; the lifetime-degrading centre in n-Si is proved to be FRC. A detailed study of lifetime degradation in n-Si provides an opportunity to understand the nature of FRC.

II. EXPERIMENTAL

The samples used for the lifetime degradation study were cut from a silicon crystal co-doped with phosphorus and boron. The oxygen concentration C was monitored both optically and by secondary ion mass spectroscopy (SIMS). It decreases in a range $(10 \text{ to } 8) \times 10^{17} \text{ cm}^{-3}$ from the seed to the tail. The initial boron concentration in the melt was $6 \times 10^{16} \text{ cm}^{-3}$. Since the boron segregation coefficient (about 0.9) is close to 1, the boron concentration does not change much along the crystal. The seed-end and the tail-end concentrations are 5.4×10^{16} and $7 \times 10^{16} \text{ cm}^{-3}$, respectively. On the contrary, due to a smaller segregation coefficient, the phosphorus concentration N_P shows a pronounced increase along the crystal. A small initial portion of the crystal is p-type, while the major portion is n-type, with a gradually increasing net doping $n = N_P - N_B$ and accordingly decreasing resistivity.

The value of n can be deduced from the measured four-probe resistivity $\rho = 1/[q \mu_n(N) n]$, where q is the electronic charge and $\mu_n(N)$ is the electron mobility controlled by the total concentration of charged scatterers, $N = N_P + N_B$. The mobility in compensated material is then identical to the mobility in phosphorus-only doped silicon with the phosphorus concentration equal to N . The $\mu_n(N)$ function is known by

^{a)}Electronic mail: vvoronkov@memc.it.

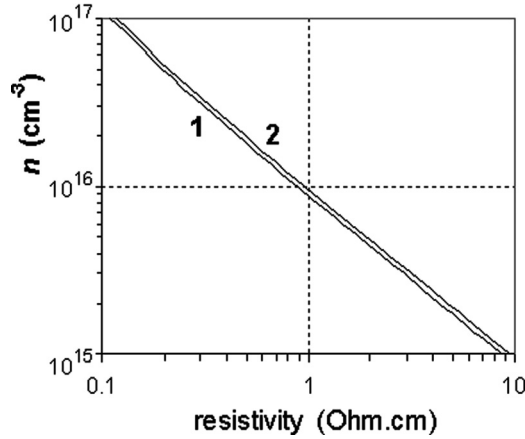


FIG. 1. Computed calibration curves, for conversion of resistivity into electron concentration, in compensated n-Si, for a specified boron concentration: curve 1: $N_B = 5.4 \times 10^{16} \text{ cm}^{-3}$ (seed-end) and curve 2: $N_B = 7 \times 10^{16} \text{ cm}^{-3}$ (tail-end).

the American Society for Testing and Materials (ASTM) F723-99 procedure for concentration-to-resistivity conversion. With specified values of N_B and n , the total concentration of scatterers is expressed as $N = n + 2 N_B$, and the resistivity of compensated material, $\rho(n, N_B) = 1/[q \mu_n(N) n]$, can be plotted as a function of n for any specified N_B . This gives a calibration curve $n(\rho, N_B)$. The two calibration curves shown in Fig. 1 are for two values of N_B : one at the seed end ($5.4 \times 10^{16} \text{ cm}^{-3}$) and the other at the tail end ($7 \times 10^{16} \text{ cm}^{-3}$). These curves are so close to each other that an average of the two curves can be used for the ρ to n conversion, independent of a sample location within the crystal. The phosphorus concentration can be then found as $N_P = n + N_B$. The compensation degree N_B/N_P for most samples ranged from 0.6 to 0.9. At a higher compensation degree (at low n/N_B), the material may become essentially non-uniform, which may lead to a reduced effective mobility¹⁰ and hence to some inaccuracy in the deduced n .

The sample surface was passivated by a plasma-enhanced chemical vapor deposited silicon nitride to reduce surface recombination. The degradation of the samples (150 micron thick) was performed by illumination by a halogen lamp for up to 2 weeks mostly at a power density of $P = 10 \text{ mW/cm}^2$ and sometimes at 40 mW/cm^2 . The sample temperature, controlled by natural cooling, was about 30°C and 50°C , respectively. The illumination was occasionally interrupted to measure the photoconductivity decay curve $p(t)$ after an applied pulse at the room temperature (RT). The reciprocal lifetime, $1/\tau_p = (-dp/dt)/p$, is obtained in a wide range of p , down to about 10^{12} cm^{-3} . The electron concentration n is incremented by illumination. From now on, the dark value of n will be denoted n_0 (the actual value is $n = n_0 + p$). The lifetime value used to monitor the degradation refers to a standard injection level, $p/n_0 = 0.1$.

III. RESULTS AND DISCUSSION

A representative evolution of the reciprocal lifetime of holes is shown in Fig. 2 for a sample of $n_0 = 3.3 \times 10^{16} \text{ cm}^{-3}$ illuminated at 10 and 40 mW/cm^2 (the curves 1 and 2,

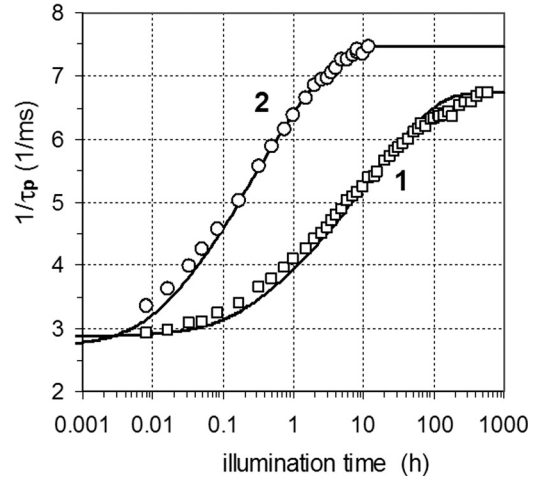


FIG. 2. Reciprocal hole lifetime in dependence of the illumination time, for samples of the highest electron concentration ($3.3 \times 10^{16} \text{ cm}^{-3}$), at two values of applied light power; curve 1: 10 mW/cm^2 and curve 2: 40 mW/cm^2 . The solid curves are obtained by simulation.

respectively). The features of the generation curves in Fig. 2 allow us to draw definite conclusions about the lifetime-degrading centres in n-Si, as discussed below.

A. Comparison of lifetime-degrading centres in n-Si and p-Si

In p-type silicon, the concentration $M(t)$ of the recombination centre (either FRC or SRC) increases exponentially and tends to a saturated value, M_{sat} . This corresponds to a linear kinetic equation

$$dM/dt = \beta(M_{\text{sat}} - M). \quad (1)$$

For FRC, the rate constant β is much larger than for SRC. For each centre, β is independent of the injected electron concentration n (if n is sufficiently high) and proportional³ to the squared hole concentration

$$\beta = g(p/10^{16} \text{ cm}^{-3})^2. \quad (2)$$

The rate coefficient g was reported³ to be about 0.1 s^{-1} for FRC, and 10^{-4} s^{-1} for SRC, at RT. It increases slightly upon increasing the illumination temperature. The activation energy is 0.23 eV for FRC and 0.475 eV for SRC. For a representative hole concentration, $p = 10^{16} \text{ cm}^{-3}$, the time scale of degradation at RT is about 10 s for FRC and 3 h for SRC.

Applying Eq. (1) and (2) to the results for n-type sample in Fig. 2, the following observations can be made:

- The kinetics are non-linear since the holes are now excess carriers, and p is not constant but depends on the concentration M of the recombination centres that are gradually produced. At $P = 10 \text{ mW/cm}^2$, p is initially about $5 \times 10^{14} \text{ cm}^{-3}$ decreasing down to $5 \times 10^{13} \text{ cm}^{-3}$ upon accumulation of recombination centres. The rate constant β is strongly reduced with time, and the degradation process is expanded over a wide range of duration, as indeed evident from Fig. 2.
- In n-type silicon, the concentration of holes is much lower than a representative value in p-Si (about 10^{16} cm^{-3}). The time scale of defect generation—for both FRC and SRC—

is accordingly strongly increased compared to p-Si: by a factor of 4×10^2 to 4×10^4 , depending on the duration. At an increased light power (curve 2 in Fig. 2), p is increased, and the degradation is accordingly accelerated.

Given such small values of p , the estimated time scale for SRC generation in n-Si is extremely long. At $P = 10$ mW/cm², it starts at 1000 h for the initial value of p and increases to 10^5 h later due to a degradation-induced reduction in p . It is thus concluded that SRC cannot be produced in n-Si within the illumination time (less than 10^3 h) used. On the other hand, the expected time scale of FRC generation, about 0.3 to 30 h at $P = 10$ mW/cm², is consistent with the data shown in Fig. 2 (curve 1). The solid curves in Fig. 2 are obtained by numerical solution of Eqs. (1) and (2) using the rate coefficient g known for FRC (the details are given below). A good fit to the data is a persuading proof in favor of FRC as the recombination centre responsible for the lifetime degradation in n-Si.

In short, the observed lifetime degradation in n-Si is entirely due to the recombination centre that was previously revealed in p-Si as the FRC.

B. Injection level dependence of the FRC-controlled lifetime

In n-Si, the reciprocal hole lifetime $1/\tau_p$ is composed of the contribution of FRC ($1/\tau_{pf}$) and a contribution of background recombination centres ($1/\tau_{p0}$). The latter (assumed to be unchanged by illumination) is measured before the degradation run. The FRC-controlled lifetime, τ_{pf} , is expressed as $1/(1/\tau_p - 1/\tau_{p0})$. Since both τ_p and τ_{p0} are known in dependence of the injection level, the FRC-controlled lifetime, τ_{pf} , can be plotted as a function of the p/n ratio. In Fig. 3, this dependence is shown for several samples of different electron concentration n_0 .

In p-Si, a similar plot for FRC (based on the reported³ injection level dependence of the lifetime after a short illumination) is just a straight line, as expected for recombination at a single deep energy level. For a deep level, the thermal emission of carriers can be neglected and the well

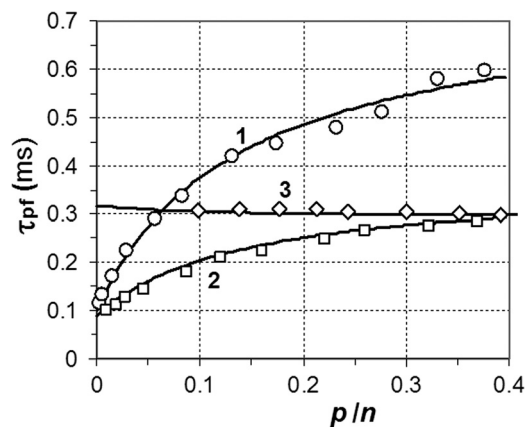


FIG. 3. Hole lifetime in n-Si samples in dependence of the p/n ratio. The samples 1 to 3 are of various electron concentrations: 3.3×10^{16} , 1.05×10^{16} and 1.85×10^{15} cm⁻³, respectively. The solid curves are calculated by Eq. (8) with the best-fit parameters.

known Shockley–Read expression for the electron lifetime^{11,12} is simplified to

$$\tau_{nf} = [1 + (\alpha_n/\alpha_p)(n/p)]/(\alpha_n M), \quad (3)$$

where α_n and α_p are the capture coefficients of an electron and a hole at the recombination level (a capture coefficient is the product of a capture cross section and the thermal velocity). The capture ratio deduced from the measured dependence³ of τ_{nf} on n/p is $\alpha_n/\alpha_p = 65$. This large value implies that electrons are captured by an attractive (positive) centre. In other words, the FRC recombination level in p-Si is a donor level (+1/0). At this point, it is convenient to supply the capture coefficients with a superscript that indicates explicitly the charge state of the centre that captures a carrier: α_n^+ will be used instead of α_n and α_p^0 instead of α_p . A large capture ratio for the donor level, $Q_d = \alpha_n^+/\alpha_p^0 = 65$, leads to a pronounced increasing dependence of τ_{nf} on n/p .

The injection level dependence of the lifetime in n-Si is quite different: according to Fig. 3, τ_{pf} is not a linear function of p/n and the type of the dependence is essentially different for samples of various n_0 . A strong injection level dependence for the highest n_0 (curve 1 in Fig. 3) suggests that the holes are captured by attractive (negative) centre. The capture ratio deduced below is $\alpha_p^-/\alpha_n^0 = 86$. Hence, there are three charge states of FRC (−1, 0, +1) and accordingly two energy levels of this defect: a donor level (+1/0) operating in p-Si (with the capture ratio $Q_d = \alpha_n^+/\alpha_p^0 = 65$) and an acceptor level (−1/0) manifested in n-Si (with the capture $Q_a = \alpha_p^-/\alpha_n^0 = 86$). The non-linear curves of Fig. 3 can be explained by recombination at a two-level centre. The lifetime for this case is obtained similar to^{11,12} using the quasi-steady state balance equations for the concentrations m^- , m^0 and m^+ of all the charge states of the defect (with $m^+ + m^0 + m^- = M$)

$$dm^+/dt = -\alpha_n^+ n m^+ + \alpha_p^0 p m^0 = 0, \quad (4)$$

$$dm^-/dt = -\alpha_p^- (p m^- - p_a m^0) + \alpha_n^0 (n m^0 - n_a m^-) = 0. \quad (5)$$

In Eq. (5) for the acceptor level, thermal emission of holes and electrons (by 0 and −1 states, respectively) is included. The emission is described through the parameters p_a and n_a that have the meaning of carrier concentrations in the dark with the Fermi level coincident with the acceptor level.¹³ For instance,

$$p_a = g_a N_v \exp(-E_a/kT), \quad (6)$$

where N_v is the state density in the valence band, and E_a is the acceptor level referenced from the top of this band; g_a is a degeneracy factor, on the order of 1. Thermal emission is important only if the level is sufficiently close to either the valence or conduction band—otherwise both p_a and n_a are very low in comparison to the actual carrier concentrations. In Eq. (4) for the donor level, thermal emission is neglected since this level is deep³—somewhere above the mid-gap.

It is now assumed that the acceptor level of FRC lies in the lower half of the gap—below the donor level (which means that FRC is a so called “negative-U” centre); then, n_a in Eq. (5) can be neglected. This assumption allows for a

good fit of the data shown in Fig. 3. The recombination rate G is the flux of electrons to the centre, $\alpha_n^+ n m^+ + \alpha_n^0 n m^0$ (or equivalently, the net flux of holes, $\alpha_p^-(p m^- - p_a m^0) + \alpha_p^0 p m^0$). The resulting expression for G (the same for p-Si and n-Si) is

$$G = \alpha_n^+ \alpha_p^- M n p (\alpha_n^0 n + \alpha_p^0 p) / [\alpha_n^+ \alpha_n^0 n^2 + \alpha_p^- \alpha_p^0 p^2 + \alpha_n^+ \alpha_p^- n p + \alpha_p^- \alpha_n^+ n p_a] \quad (7)$$

In case of n-Si, the reciprocal hole lifetime is defined as G/p

$$1/\tau_{pf} = (\alpha_p^- M)(1+yQ_0)/[1+yQ_a(1+y/Q_d)+Q_a p_a/n], \quad (8)$$

where $y=p/n$. The capture ratios Q_d and Q_a were defined above, and $Q_0 = \alpha_p^0/\alpha_n^0$. In the denominator of Eq. (8), the term y/Q_d will be neglected since Q_d is large and $y < 1$.

The experimental curves $\tau_{pf}(y)$ for the samples shown in Fig. 3—as well as for other samples are well reproduced by Eq. (8) with $Q_a = 86$, $Q_0 = 7.4$, and $p_a = 2.2 \times 10^{14} \text{ cm}^{-3}$. The combination $\alpha_p^- M$ was fitted individually for each sample.

The FRC acceptor level is now found to be at 0.28 eV above the valence band, by Eq. (6); an uncertainty—due to an unknown degeneracy factor—is about ± 0.03 eV. The thermal emission of holes by FRC^0 plays an important role: without the emission term p_a in Eq. (8), the predicted function $\tau_{pf}(y)$ would be the same for all the samples—which is not the case. At high electron concentration, $n_0 > Q_a p_a = 2 \times 10^{16} \text{ cm}^{-3}$, Eq. (8) predicts a pronounced increase in the lifetime upon increasing y from 0 to 1: by a factor of $(1+Q_a)/(1+Q_0) \approx 10$. At one particular electron concentration, $n_0 = p_a Q_a(1+Q_0)/(Q_a-Q_0) = 2 \times 10^{15} \text{ cm}^{-3}$, Eq. (7) shows no injection level dependence. At smaller n_0 , the injection level dependence of τ_p would be decreasing. Indeed, for a sample of the lowest available n_0 ($1.85 \times 10^{15} \text{ cm}^{-3}$, the curve 3 in Fig. 3), there is a slight decrease in τ_{pf} upon increasing the injection level.

Why does the electron lifetime in p-Si, when controlled by the same two-level FRC defect, correspond to recombination at only donor level of this defect? In this case, the expression for the reciprocal electron lifetime, G/n , following from Eq. (7), reads

$$1/\tau_{nf} = (\alpha_n^+ M)(1+x/Q_0)/[1+xQ_d(1+x/Q_a)+p_a/p], \quad (9)$$

where $x=n/p < 1$. The capture ratios Q_a and Q_0 —deduced above from the data on n-Si are both large. In addition, $p_a \ll p$ for p-Si. Eq. (9) is thus simplified and reduced to Eq. (3). The main reason for this simplification is a small capture ratio $\alpha_n^0/\alpha_p^0 = 1/Q_0$. Accordingly, the capture of electrons by the recharged centre (FRC^0) can be neglected in comparison to capturing by FRC^+ . Hence, only the donor level of FRC is essential for the recombination in p-Si.

C. Simulation of the degradation kinetics in n-Si

The boron-oxygen defect responsible for FRC is assumed to exist initially in a latent form (LCF) and to reconstruct into FRC configuration in the presence of excess carriers, according to the kinetic equations (1) and (2).

A detailed re-configuration model, which accounts for the dependence of the rate constant β on p , will be discussed below, after the nature of the defect is established. The most essential point of the model is that re-configuration occurs through a transient configuration denoted TCF—intermediate between LCF and FRC. The forward rate $\text{LCF} \rightarrow \text{TCF}$ is proportional to p^2 , but at very low p a backward transition $\text{TCF} \rightarrow \text{LCF}$ becomes important and reduces the overall rate by a factor

$$f = p/(p+a), \quad (10)$$

where the coefficient a may depend on n_0 . Therefore, the rate constant β in Eq. (1) should be generally modified by replacing it with βf . The additional factor f turns out to be close to 1 in the beginning of a degradation run becoming only somewhat reduced (typically to about 0.3) toward the end. This factor therefore is not of a crucial importance, yet it helps to improve the fit quality.

To solve the non-linear equation (1) for the FRC concentration, $M(t)$, the hole concentration p should be expressed through M by the balance equation of production and recombination of electron-hole pairs

$$J/d = G = p/\tau_p = p(1/\tau_{p0} + 1/\tau_{pf}), \quad (11)$$

where J is the number of pairs produced per unit area and time, and d is the sample thickness. The light is absorbed within a narrow near-surface layer, but the carriers are fast spread by diffusion over the sample depth. For $d = 150 \text{ }\mu\text{m}$, the homogenization time by diffusion, $(d/\pi)^2/D_h$, where D_h is the hole diffusivity, is about $2 \text{ }\mu\text{s}$ —much shorter than the lifetime. The number of pairs produced per unit volume is J/d . When using Eq. (11), a scaling ratio $S = J/P$ between the carrier production rate J and the light power density P should be specified. Approximately, J is equal to P divided by the average photon energy, which leads to $S \approx 2.5 \times 10^{15}$ (if J is in $\text{cm}^{-2} \text{ s}^{-1}$ and P is in mW/cm^2). The factor S should be tuned individually for every illumination run since the actual value of P may deviate somewhat from the nominal value of 10 or 40 mW/cm^2 . The tuned value of S was found to be scattered within $\pm 20\%$ around the above-mentioned seed value.

In Eq. (11), both τ_{p0} and τ_{pf} depend on p . For τ_{p0} , this dependence is relatively weak and it is taken from the experiment. For τ_{pf} , the analytical expression (8) is used, with the best-fit parameters listed above. The lifetime depends on the combination $Y(t) = \alpha_p^- M(t)$, which represents the FRC concentration. The simulation procedure consists of solving the balance equation (11) at a current value of $Y(t)$ and integrating the kinetic equation (1), with a modified rate constant, for the variable Y

$$dY/dt = -\beta f(Y_{\text{sat}} - Y). \quad (12)$$

where $Y_{\text{sat}} = \alpha_p^- M_{\text{sat}}$ is the saturated value of Y .

The rate coefficient g in Eq. (2) for the rate constant β was fixed at a value known³ for FRC in p-Si: 400 h^{-1} at $30 \text{ }^\circ\text{C}$ (at 10 mW/cm^2) and 650 h^{-1} at $50 \text{ }^\circ\text{C}$ (at 40 mW/cm^2). The fitting of the calculated degradation curves, of the type shown in Fig. 2, consists only in a slight tuning of the scaling

ratio S and in a proper choice of the parameter a in Eq. (10). The best fit is achieved at $a \approx 2 \times 10^{14} \text{ cm}^{-3}$. The calculated curves are shown in Fig. 2 by the solid lines. Similarly, calculated curves for other samples, of smaller n_0 , also provide a good reproduction of the data. The only exception is the sample of the lowest $n_0 = 1.85 \times 10^{15} \text{ cm}^{-3}$, where a discrepancy between the computed and experimental curves is significant. A possible reason may be a strong compensation of phosphorus by boron for this sample ($n_0 \ll N_P$), which may lead to a strong non-uniformity.

D. The nature of FRC

The FRC concentration in p-Si is proportional to the reciprocal lifetime $1/\tau_{\text{nf}}$ taken at a standard injection level, according to Eq. (3). This however does not apply to n-Si since, according to Eq. (8), the lifetime depends not only on M but also on n_0 . In this case, one should use the combination $Y = \alpha_p^- M$, expressed through τ_{pf} and n_0 by Eq. (8). The saturated value of this combination, $Y_{\text{sat}} = \alpha_p^- M_{\text{sat}}$, is plotted in Fig. 4 for samples of different n_0 . The saturated FRC concentration (which is identical to the initial concentration of latent defect, LCF) is known³ to be proportional to the squared oxygen concentration, C^2 . To exclude an effect of oxygen variation along the crystal, Y_{sat} was corrected—multiplied by a factor $(C_0/C)^2$, where C_0 corresponds to the seed-end sample. The oxygen concentration was determined by SIMS for each sample.

The proportionality to p of the grown-in concentration of B_iO_2 defect in p-Si comes⁸ from the single-positive charge of B_i . This concentration becomes negligible in intrinsic material. In n-Si, the charge state of B_i changes¹⁴ to -1 , and the B_iO_2 concentration increases in proportion to n_0 . A lack of correlation between Y_{sat} and n_0 (Fig. 4) implies that FRC (unlike SRC) is not a B_iO_2 defect. On the other hand, an alternative attribution of FRC—to B_sO_2 —is quite consistent with the data of Fig. 4. In this case, Y_{sat} is expected to be proportional to the boron concentration N_B , which increases from the seed to the tail by only 30%—which is insignificant in comparison to the scatter of the data in Fig. 4.

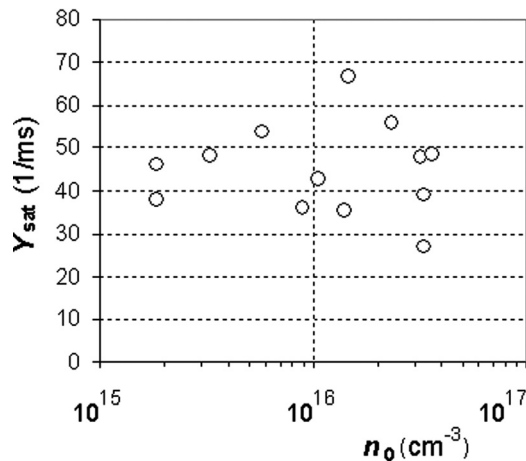


FIG. 4. Saturated effective concentration of FRC, $Y_{\text{sat}} = \alpha_p^- M_{\text{sat}}$, corrected for a variation in the oxygen concentration, in dependence of the electron concentration n_0 , that increases along the crystal, from the seed-end to the tail-end.

The absolute value of Y_{sat} can be predicted using the published data³ for saturated τ_{nf} in p-Si. The effective FRC concentration, $X = \alpha_n^+ M$, is expressed by Eq. (3). The saturated concentration X_{sat} —proportional to N_B and C^2 in boron-only doped samples of Ref. 3—is then specified

$$X_{\text{sat}} = \alpha_n^+ M_{\text{sat}} = (28 \text{ ms}^{-1})(N_B/10^{16} \text{ cm}^{-3})(C/10^{18} \text{ cm}^{-3})^2. \quad (13)$$

If FRC is B_sO_2 , then the saturated concentration in n-Si, $Y_{\text{sat}} = \alpha_p^- M_{\text{sat}}$, is given by the right-hand part of Eq. (13) multiplied by the rescaling ratio α_p^-/α_n^+ that is expressed through the already known parameters: $\alpha_p^-/\alpha_n^+ = Q_a/(Q_0 Q_d) = 0.18$. The predicted value of Y_{sat} is then

$$Y_{\text{sat}} = \alpha_p^- M_{\text{sat}} = (5 \text{ ms}^{-1})(N_B/10^{16} \text{ cm}^{-3})(C/10^{18} \text{ cm}^{-3})^2. \quad (14)$$

With $N_B = 5.4 \times 10^{16} \text{ cm}^{-3}$ and $C = 10^{18} \text{ cm}^{-3}$, Eq. (14) gives $Y_{\text{sat}} = 27 \text{ ms}^{-1}$, which is not much different from the experimental values of Fig. 4. This strongly supports the identification of FRC as a B_sO_2 defect.

E. A model for B_sO_2 reconfiguration from LCF to FRC

A B_sO_2 defect in its grown-in LCF is most likely single-negative, in both p-Si and n-Si, since the oxygen dimer is definitely a neutral species.¹⁴ A proportionality of the reconfiguration rate constant to p^2 in p-Si can be understood, assuming that LCF possesses donor and acceptor levels, both well below a typical position of the Fermi level (Fig. 5). The concentration of a minor charge state 0 is defined by Eq. (5) now applied to LCF. Since the characteristic concentration p_a is now very large, the concentration ratio is controlled by capture and backward emission of holes, being independent of n

$$m^0/m^- = p/p_a. \quad (15)$$

Similarly, the m^+/m^0 ratio is equal to p/p_a . Here, all the quantities refer to the LCF defect and should have been marked, for example, by a subscript L; this subscript is however

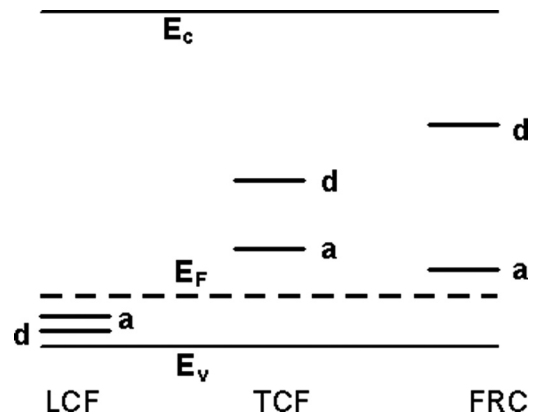


FIG. 5. Schematic position of the donor and acceptor levels (marked d and a) for the B_sO_2 defect in the latent configuration (LCF), the transient configuration (TCF), and the recombination-active configuration (FRC). The broken line shows the Fermi level for a representative hole concentration in p-Si, about 10^{16} cm^{-3} .

omitted to simplify the notations. If LCF can reconfigure into FRC only through the $+1$ state, then the proportionality of the degradation rate constant to p^2 is understood, since the fraction of the “active” $+1$ state is equal to $p^2/(p_a p_d)$.

The next important step is to assume that LCF^+ reconstructs not directly to FRC but first to a transient configuration, TCF, that exists in the dark in the $+1$ state (in p-Si)—and thus has a donor level above the Fermi level (Fig. 5). The position of the acceptor level of TCF can be above the donor level or below it, as shown in Fig. 5; in the latter case, the only essential point is that the average of the two levels be above the Fermi level to ensure the dominance of the $+1$ state of TCF in p-Si. The final transition from TCF to FRC is now assumed to proceed through TCF^0 . In p-Si this state of TCF appears only due to recharging TCF^+ into TCF^0 by excess electrons. The free energy diagram corresponding to the assumptions made is shown schematically in Fig. 6. The forward flux from LCF to TCF (starting from a minor charge state, LCF^+) is characterized by the rate constant β that is now expressed explicitly through the free energy barrier F between LCF^+ and TCF^+

$$\beta = [p^2/(p_a p_d)] \nu \exp(-F/kT), \quad (16)$$

where ν is the attempt frequency for overcoming the barrier. The TCF produced exist in $+1$ and 0 states. TCF^0 reconstructs forward with a rate constant ω controlled by the free energy barrier between TCF^0 and FRC^0 in Fig. 6. TCF^+ reconstructs backwards with a rate constant ω_p controlled by the free energy barrier between TCF^+ and LCF^+ in Fig. 6. The ratio of the two probabilities—for a TCF to go forward and to go backwards—is $(\omega m^0)/(\omega_p m^+)$. The concentration ratio m^0/m^+ is defined by the balance equation (4) now applied to the donor level of TCF. This ratio is equal to Q_{dt} (n/p) where the capture ratio Q_{dt} is analogous to Q_d for FRC. The overall rate constant β_p for LCF to FRC reconfiguration in p-Si is equal to β multiplied by the probability for TCF to go forward

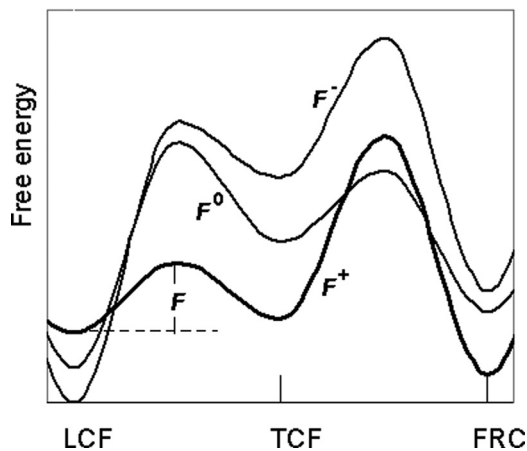


FIG. 6. Free energy diagram for reconfiguration of the latent defect (LCF) into the recombination centre (FRC) through the metastable transient configuration (TCF). Positions of F^+ profile (for the $+1$ charge state) and F^- profile (for the -1 charge state), with respect to F^0 (for the neutral charge state) correspond to a representative hole concentration of 10^{16} cm^{-3} in p-Si. A transition from LCF^+ to TCF^+ is characterized by a free energy barrier F indicated in the diagram.

$$\beta_p = \beta n / (n + h_p p / Q_{dt}), \quad (17)$$

where the parameter $h_p = \omega_p / \omega$, and β is defined by Eq. (16). At low injection level the rate constant β_p is proportional to n while at sufficiently high injection level it becomes identical to β and independent of n —just proportional to p^2 . A similar dependence on p and n holds also for the rate constant of SRC.^{15,16} At low n , the degradation kinetics becomes non-linear since n depends on the current concentration of SRC.

A peculiarity of the $\text{LCF} \rightarrow \text{FRC}$ transition in n-Si is due to the population of charge states of TCF: here, the $+1$ state is negligible since n/p is high, and the dominant states are 0 and -1 . A backward reconstruction $\text{TCF}^- \rightarrow \text{LCF}^-$ proceeds with the rate constant ω_n controlled by the free energy barrier for this transition in Fig. 6. The probability ratio for the forward and backward transitions is $(\omega m^0)/(\omega_n m^-)$. The concentration ratio m^0/m^- is defined by the balance equation (5) applied to the acceptor level of TCF. This is equal to $p/(p_{at} + n/Q_{at})$, where p_{at} and Q_{at} are analogous to p_a and Q_a for FRC. The overall rate constant β_n for LCF to FRC transition in n-Si is then

$$\beta_n = \beta p / [p + h_n (p_{at} + n/Q_{at})], \quad (18)$$

where $h_n = \omega_n / \omega$. At a sufficiently high injection level of holes, the rate constant is identical to β and proportional to p^2 . At low p , there is an additional factor f of a type given by Eq. (10), with $a = h_n (p_{at} + n/Q_{at})$. A dependence of the rate constant on p then becomes stronger: proportional to p^3 . The fitting procedure described above shows that a is independent of n_0 . This means that $p_{at} \gg n/Q_{at}$. In other words, the recharging from TCF^0 into TCF^- occurs by the thermal emission of holes rather than by the capture of electrons. The acceptor level of TCF is thus located relatively close to the valence band.

IV. SUMMARY

Minority lifetime degradation observed in boron-containing p-Si and n-Si Czochralski samples has revealed a striking difference between these two materials.

- In p-Si, two kinds of lifetime-degrading centres emerge during illumination: FRC (found after a very short illumination) and SRC (dominant during subsequent illumination). The major centre, SRC, was previously identified as a B_iO_2 complex involving an interstitial boron atom B_i .
- In n-Si, only FRC is generated within the actual illumination time since the time scale for production of both centres is greatly increased—due to a lower hole concentration—and becomes enormously long for SRC.

The injection level dependence of the lifetime shows that FRC exists in 3 charge states and possesses 2 energy levels, a donor one and an acceptor one. Both levels contribute into recombination in n-Si, but only the donor level is essential in p-Si.

The accumulation kinetics of FRC in the course of illumination of n-Si samples is well reproduced by simulations, taking into account that the hole concentration depends on the current FRC concentration. The saturated FRC concentration

in n-Si was found to be independent of the electron concentration and well predicted by the data for p-Si assuming that FRC is a B_sO_2 defect involving a substitutional boron atom B_s .

In conclusion, the nature of the major lifetime-degrading centre is different in two kinds of boron-containing material: B_iO_2 (SRC) in p-Si but B_sO_2 (FRC) in compensated n-Si.

A proposed re-configuration model from the latent configuration of B_sO_2 into the recombination-active one (FRC) provides a generalized expression for the rate constant in dependence of the carrier concentrations.

¹H. Fischer and W. Pschunder, in *Proceedings of the 10th IEEE Photovoltaic Specialists Conference* (IEEE, New York, 1973), p. 404.

²S. W. Glunz, S. Rein, J. Y. Lee, and W. Warta, *J. Appl. Phys.* **90**, 2397 (2001).

³K. Bothe and J. Schmidt, *J. Appl. Phys.* **99**, 013701 (2006).

⁴J. Schmidt and K. Bothe, *Phys. Rev. B* **69**, 024107 (2004).

⁵D. Macdonald, F. Rougieux, A. Cuevas, B. Lim, J. Schmidt, M. Di Sabatino, and L. J. Geerligs, *J. Appl. Phys.* **105**, 093704 (2009).

⁶B. Lim, F. Rougieux, D. Macdonald, K. Bothe, and J. Schmidt, *J. Appl. Phys.* **108**, 103722 (2010).

⁷J. Geilker, W. Kwapil, and S. Rein, *J. Appl. Phys.* **109**, 053718 (2011).

⁸V. V. Voronkov and R. Falster, *J. Appl. Phys.* **107**, 053509 (2010).

⁹T. Schulz-Kuchly, J. Veirman, S. Dubois, and D. R. Heslinga, *Appl. Phys. Lett.* **96**, 093505 (2010).

¹⁰J. Veirman, S. Dubois, N. Enjalbert, J. P. Garandet, D. R. Heslinga, and M. Lemit, *Solid State Electron.* **54**, 671 (2010).

¹¹W. Shockley and W. T. Read, *Phys. Rev.* **87**, 835 (1952).

¹²R. N. Hall, *Phys. Rev.* **87**, 387 (1952).

¹³J. S. Blackmore, *Semiconductor Statistics* (Pergamon, New York, 1962).

¹⁴R. D. Harris, J. L. Newton, and G. D. Watkins, *Phys. Rev. B* **36**, 1094 (1987).

¹⁵V. V. Voronkov, R. Falster, and A. V. Batunina, *Phys. Stat. Solidi A* **208**, 576 (2011).

¹⁶V. V. Voronkov, R. Falster, J. Schmidt, K. Bothe, and A. V. Batunina, *ECS Trans.* **33**, 103 (2010).