Modelling lifetime degradation in boron-doped Czochralski silicon

Vladimir V. Voronkov[*,1], **Robert Falster**[1], **and Anna V. Batunina**[2]

[1] MEMC Electronic Materials, via Nazionale 59, 39012 Merano, Italy
[2] Institute of Rare Metals, B. Tolmachevski 5, 109017 Moscow, Russia

[*] Corresponding author: e-mail vvoronkov@memc.it, Phone: +39 0473 333 308, Fax: +39 0473 333 270

Electron lifetime in boron- and oxygen-containing silicon is known to decrease under illumination. The emerging recombination centre was previously thought to be a complex B_sO_2, of a substitutional boron atom and an oxygen dimer. However this attribution has turned out to be inconsistent with recently published data. A new model was proposed, based on a latent single-positive complex B_iO_2 that involves an interstitial boron atom B_i rather than B_s. Excess electrons lead to recharging the latent B_iO_2 centre into the neutral state, with subsequent reconstruction into recombination-active configuration. This model was used to simulate the reported data on production of recombination centres, in a wide range of applied illumination intensity – and found to provide a good reproduction of the data.

1 Introduction The efficiency of solar cells, fabricated from boron-doped Czochralski (CZ) silicon, is known to degrade with time; this effect is caused by production of new recombination centres in the presence of excess electrons [1, 2]. The concentration of the generated centres is characterized by an increment in the reciprocal lifetime, $R = 1/\tau(t) - 1/\tau(0)$ measured at a fixed injection level. The $R(t)$ function saturates after some characteristic time τ_s (not to be confused with the lifetime, τ). In boron-only doped material, the saturated value, R_s, is proportional to the boron concentration N and to a squared concentration of oxygen, C^2 [2]. Based on these data, the recombination centre was identified with a complex B_sO_2 of a boron atom (in the major substitutional state) and an oxygen dimer, O_2. The dimers were assumed [3] to diffuse fast in the presence of excess electrons, and become trapped by boron. However recent data on boron-doped CZ silicon strongly compensated with phosphorus [4] revealed that the actual dependence of R_s is on the hole concentration p rather than on N ($R_s \sim pC^2$). This result – completely inconsistent with the B_sO_2 model – can be easily understood within an alternative model [5] based on generation of interstitial boron B_i in the course of crystal cooling, by self-interstitials emitted by growing oxide precipitates. The majority of B_i is thought to form small clusters, and the remaining dissolved concentration of B_i (the solubility) is a function of temperature. Since B_i is a single-positive species, the solubility is proportional to p; below some temperature (typically at $T < 350\,^\circ$C) the material is no longer intrinsic, and p is controlled by the acceptor and donor dopants. The concentration of frozen-in B_iO_2 complex is proportional to p and to the concentration of oxygen dimers, and thus matches the pC^2 dependence found for the degrading recombination centres. The frozen-in B_iO_2 centre is of a low recombination activity, and it can be called a latent centre (abbreviated to LC). In the presence of excess electrons, the LC captures an electron, and becomes neutral. In the neutral state, it reconstructs into a different configuration (abbreviated to SRC) which is recombination-active, and accounts for the degradation.

A possible involvement of B_i in degradation was also proposed earlier [6], without specifying the origin of B_i. The B_i species were assumed to exist initially as complexes with carbon that dissociate in the presence of excess electrons, and subsequently get trapped by oxygen, into recombination-active B_iO defects. This version of B_i-based degradation is however inconsistent with the established square dependence of degradation on C.

The generation rate of SRC is proportional to the concentration of the LC that exists in the neutral charge state. Hence it should be an increasing function of the excess electron concentration, n, that saturates at sufficiently large n. Within this simple concept, the $R(t)$ function can

be simulated for any specified illumination intensity. Experimentally, $R(t)$ was traced in a wide range of illumination power [7], and the main purpose of the present work is to see if our model can reproduce the data.

Another point of the present paper is to clarify an important issue of the charge state of oxygen dimers. In the previous model [3] – of electron-enhanced migration of O_2 – the dimers were assumed to exist in a double-positive state, and to migrate by alternating capture of electrons and holes. On the contrary, our model assumes that the dimers are neutral defects – implying that the ground charge state of B_iO_2 is +1 (a combination of a single-positive B_i and a neutral O_2). By Hall effect measurements of very pure CZ material, it is definitely concluded that O_2 is basically a neutral defect; if double-positive dimers exist at all, their fraction is low (less than 1%). This part of the present work is put into an Appendix.

2 Production of degrading centres at a specified light intensity The immediate source of the degrading centres (SRC) is the neutral state LC^0 of the LC, and thus the most essential point of the model is recharging of LC from the initial +1 state into 0 state, in the presence of excess electrons. If the donor level of LC is around the midgap, the thermal emission of carriers is negligible, and the concentration ratio C_L^0/C_L^+ of the two charge states of LC is controlled simply by the balance of electron and hole capture – and thus by the injection level $X = n/p$ [5]:

$$\frac{C_L^0}{C_L^+} = \frac{\alpha_{nL}n}{\alpha_{pL}p} = \frac{X}{X_L}, \tag{1}$$

where α_{nL} is a capture coefficient of electrons by the +1 state, and α_{pL} is the capture coefficient of holes by 0 state (each coefficient is a product of a cross-section and a thermal velocity). The characteristic injection level for recharging, X_L, is equal to α_{pL}/α_{nL}; it is likely to be very small since the electron capture (by +1 state) is expected to be much faster then the hole capture (by 0 state). The concentration C_S of degrading centres (SRC) evolves in proportion to C_L^0, which is equal to the total concentration C_L of LC multiplied by the fraction of neutral state, $X/(X + X_L)$:

$$\frac{dC_S}{dt} = \frac{C_L X/(X + X_L)}{\tau_s}, \tag{2}$$

The total concentration of B_iO_2, $C_T = C_L + C_S$, remains constant in the course of reconstruction. The characteristic time τ_s refers to conversion from LC^0 to SRC. At high injection level ($X \gg X_L$) the conversion from LC into SRC is exponential, and the apparent conversion time is equal to τ_s. At low injection level ($X < X_L$) the conversion rate is reduced, and the conversion kinetics is no longer simple exponential, since the injection level X depends on the concentration C_S of already produced recombination centres.

The SRC contribution into the reciprocal electron lifetime is known [2] to depend on X, due to recharging of SRC

$$R = \frac{\alpha_{nS}C_S}{1 + Q_S X}, \tag{3}$$

where $Q_S = \alpha_{nS}/\alpha_{pS}$ is the capture ratio of electrons and holes for the SRC recombination level. A similar expression holds for the contribution of the background recombination centres (referred to by a subscript B). The whole balance equation for production and loss of electron–hole pairs is thus

$$I = n\left[\frac{\alpha_{nB}C_B}{(1 + Q_B X)} + \frac{\alpha_{nS}C_S}{(1 + Q_S X)}\right], \tag{4}$$

The capture ratio Q_S was reported to be 10 while Q_B is about 40, judging by Fig. 4 of Ref. [2]. The light intensity I is the number of electron–hole pairs produced by unit time per unit volume of an illuminated sample. The reported quantity [7] is not I but the power density P of the light adsorbed in a sample. The carriers are produced close to the surface at a rate P/E, where E is the average energy spent for creation of one electron–hole pair (close to the gap width, 1.2 eV). Then the carriers are spread almost uniformly through the depth since the diffusion length is normally larger than the sample thickness w (about 300 μm) while the sample surface was passivated to suppress the surface recombination. Hence I is equal to $(P/E)/w$. With P expressed in mW/cm², and I in cm⁻³s⁻¹, the scaling coefficient I/P is close to 1.7×10^{17}. This value is approximate, and it should be tuned to achieve the best fit of the data by the computed curves.

An injection level $X(t)$, in the course of degradation, is calculated by Eq. (4), for a specified light intensity I and for a current concentration $C_S(t)$ of SRC. This value of X is used in the kinetic Eq. (2) to trace further evolution of C_S. Experimentally [7], the degradation process was occasionally interrupted to measure the lifetime at a fixed injection level (chosen to be $X = X_R = 0.1$). Accordingly, the simulated function $R(t)$ is computed by Eq. (3) with $X = X_R$.

3 Simulation results The lifetime degradation induced by illumination under various specified light powers ($P = 0.5, 1, 5, 10$ and 100 mW/cm²) was traced in Ref. [7] at 60 °C. The material resistivity, 1.5 Ω-cm at room temperature, corresponds to $p = 9.4 \times 10^{15}$ cm⁻³.

The reported value of lifetime before the degradation is $\tau(0) = 75$ μs. By this value, the background recombination coefficient $\alpha_{nB}C_B$ (that enters the Eq. (4)) can be specified as $(1 + Q_B X_R)/\tau(0)$. The precise value depends on the assumed recharging coefficient Q_B. Several tentative values of Q_B (in a range 0–40) were tried, and the simulation results were found to be almost insensitive to the assumed Q_B.

The saturated value of the lifetime at the highest light power ($P = 100$ mW/cm²) is 19 μs, which corresponds to the saturated degradation $R_s = 38$ ms⁻¹. In this case, the
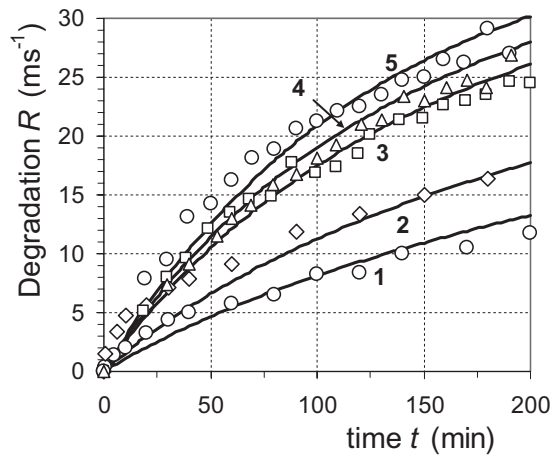
Figure 1 Contribution of the degrading centres into the reciprocal lifetime, $R = 1/\tau(t) - 1/\tau(0)$. The curves 1 to 5 correspond to the light power $P = 0.5, 1, 5, 10$ and $100\,\text{mW/cm}^2$, respectively. The symbols show the measured values [7]; the solid curves are computed by Eqs. (2)–(4) with the best-fit parameters τ_s and X_L.

Figure 2 Computed variation in the injection level under illumination, for the same five values of the light power as those in Fig. 1.

LC to SRC conversion is complete ($C_S = C_T$), and the recombination coefficient $\alpha_{nS}C_T$ is expressed as $R_s (1 + Q_S X_R) = 76\,\text{ms}^{-1}$. The actual concentrations C_S and C_L are convienient to normalize by the total B_iO_2 concentration C_T. After that, the Eqs. (2)–(4), for the normalized concentrations, $Y_S = C_S/C_T$ and $Y_L = C_L/C_T$, contain only two unknown (fitting) parameters: (i) the LC^0 to SRC conversion time τ_s and (ii) the characteristic injection level X_L for recharging LC from +1 to 0 state. In addition, also the scaling intensity ratio I/P should be slightly tuned, to achieve the best fit.

Five experimental curves $R(t)$, for $P = 0.5, 1, 5, 10$ and $100\,\text{mW/cm}^2$, are shown in Fig. 1, together with the best-fit simulated curves.

The best-fit parameters are $\tau_s = 124.5\,\text{min}$ and $X_L = 7.6 \times 10^{-4}$ (which corresponds to $\alpha_{nL}/\alpha_{pL} = 1300$). The tuned scaling ratio I/P is 2×10^{17} – only slightly different from the above-mentioned preliminary estimate of 1.7×10^{17}.

It is also interesting to look at the simulated evolution of the injection level (Fig. 2). The injection level decreases, due to production of SRC, and finally saturates at a value dependent on the light intensity. A range of injection level is quite wide, 2×10^{-4} to 0.3.

The computed curves in Fig. 1 reproduce the experimental data quite well, with an exception of short time interval. In this interval, some other kind of degrading centres, beside SRC, is known to be produced [2]: these are so called fast-stage centres (abbreviated to FRC). The nature of these minor centres is not yet definite; it is possible that FRC is another structural form of B_iO_2 (different from SRC). In this case, the latent centres LC could reconstruct into both SRC and FRC by two independent paths but with different time scales. The FRC can be taken into account by adding an extra term into Eqs. (3) and (4): $\alpha_{nF}C_F/(1 + Q_F X)$. The
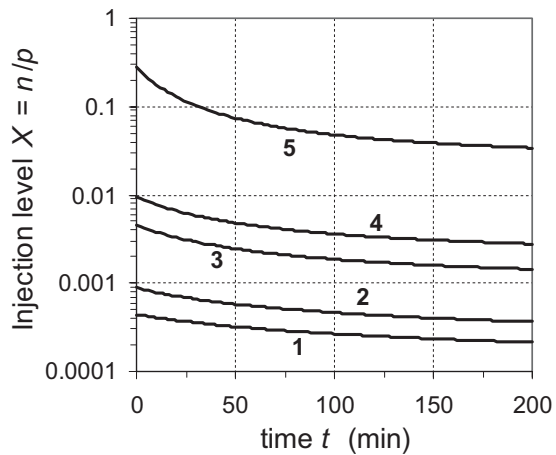
recharging coefficient Q_F was reported to be about 100 [2]. With this modification, several new fitting parameters are added: the transition times from LC to FRC and back, and the capture coefficient ratio α_{nF}/α_{nS}. The effect of FRC is a separate problem to be described elsewhere; at present, it suffices to mention that the fit quality in Fig. 1 is essentially improved: the curves go close to the experimental points also at short times. The best-fit values of τ_s and X_L are however hardly changed within this advanced treatment.

4 Summary A degradation model – used to simulate the degradation kinetics at an arbitrary illumination intensity – is based on recharging of latent B_iO_2 centres (LC) by excess electrons, from the basic +1 charge state into 0 state, with subsequent reconstruction of LC^0 into recombination-active centres (SRC). The model provides a simple and successful fit to the reported degradation data in a wide range of intensity. At a sufficiently high intensity, when the LC recharging is complete, the degradation kinetics is linear (exponential) – and insensitive to the intensity. At low intensity it is necessarily nonlinear, since the LC to SRC conversion then depends on the injection level – which is in turn dependent on the amount of already produced SRC. Even a simple version of the model – taking into account only the major recombination centres (SRC) and neglecting minor centres (FRC, that are relevant for a short-duration stage) – provides a good fit to the experimental data. The fit quality can be further improved by taking FRC into account.

Strictly speaking, the present quantitative description of degradation, in dependence of an applied light intensity, is quite general and not actually limited to a particular mechanism of producing degradation centres. Indeed, the only relevant notion used in simulations was the dependence of the SRC production rate on the injection level X through a factor $X/(X + X_L)$ – which, in the present model, means a fraction of LC^0 among all the LC species. The same factor may appear in a variety of models, including even the rejected model of dimeric migration towards the B_s traps,

Phys. Status Solidi A **208**, No. 3 (2011)

579

where the dimeric diffusivity may depend on X through the same factor. The reason for rejecting this model is not related to the observed effect of the illumination intensity on the degradation kinetics but to the arguments [5] discussed previously.

Appendix: The charge state of O$_2$ The B$_i$O$_2$ LC is treated as single-positive species – composed of a single-positive B$_i$ and neutral O$_2$. The charge state of oxygen dimers is thus a crucial issue. Dimers were thought to exist, at least partially, in $+2$ charge state [3]. If so, they would act as compensating defects, along with phosphorus, in boron-doped p-type silicon. The frozen-in concentration of O$_2$ was found [5] to be close to 3.5×10^{14} cm^{-3}, at a representative oxygen concentration of 7×10^{17} cm^{-3}. If an appreciable fraction of O$_2$ were in $+2$ state, their contribution into boron compensation would be significant in lightly doped material. To clarify this point, several samples – cut from CZ crystals not intentionally doped, and of an oxygen content close to 7×10^{17} cm^{-3} – were inspected. Upon killing the grown-in thermal donors (by 900 °C, 5 min pre-anneal), the samples were of p-type which itself shows that the total concentration of compensating donors is low – smaller than a low concentration of boron. For more definite conclusions, the Hall effect was measured, down to the liquid Helium temperature, to determine separate concentrations of boron and compensating donors. The measured Hall coefficient is equal to $r/(ep)$, where e is the elementary charge and r is a so-called Hall-factor, on the order of 1. In pure p-type Si, the function $r(T)$ is known [8]: it is at maximum (close to 1.15) at 50 K, and remarkably decreases towards both lower and higher T. An example of resulting temperature dependence $p(T)$ is shown in Fig. 3 by open circles.

The boron concentration N_a and the effective compensating concentration N_d (composed of the contributions of single and double donors) are found by fitting a conventional theoretical dependence $p(T, N_a, N_d)$ [9] to the experimental points. For that, the position of the boron acceptor level should be specified. With a conventional level position at 45.7 meV above the top of the valence band, the deduced compensation degree N_d/N_a is low (about 0.3) but the best-fit curve does not follow precisely the experimental points. An essentially improved fit (shown by the solid line in Fig. 3) is achieved assuming a more shallow energy level, 42 meV. The compensation degree is then larger: $N_d/N_a = 0.9$; to some extent, this may be caused by not completely killed grown-in thermal donors. Even if this, relatively high compensation, is adopted, the total donor concentration is still quite low: $N_d = 7 \times 10^{12}$ cm^{-3}. The boron concentration is accordingly $N_a = 7.7 \times 10^{12}$ cm^{-3}.
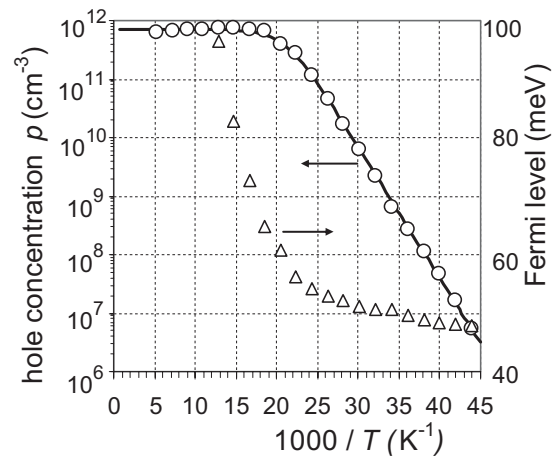

Figure 3 Hole concentration deduced from the temperature dependence of the Hall effect, of a p-type sample of non-doped CZ-Si (open circles). The solid curve is the theoretical hole concentration with the best-fit values for the concentrations of boron and of compensating donors (assuming the acceptor level of boron to be at 42 meV above the top of the valence band). The triangles show the position of the Fermi level (the right axis).

The highest possible estimate for the concentration of double-positive oxygen dimers is a half of N_d – which is about 3.5×10^{12} cm^{-3}. This is only 1% of the total O$_2$ concentration. In conclusion, if double-positive state of O$_2$ exists at all, it constitutes only a very small fraction of all the dimers; a vast majority of O$_2$ is in the neutral state.

References

[1] S. W. Glunz, S. Rein, J. Y. Lee, and W. Warta, J. Appl. Phys. **90**, 2397 (2001).
[2] K. Bothe and J. Schmidt, J. Appl. Phys. **99**, 013701 (2006).
[3] D. W. Palmer, K. Bothe, and J. Schmidt, Phys. Rev. B **76**, 035210 (2007).
[4] D. Macdonald, F. Rougieux, A. Cuevas, B. Lim, J. Schmidt, M. Di Sabatino, and L. J. Geerligs, J. Appl. Phys. **105**, 093704 (2009).
[5] V. V. Voronkov and R. Falster, J. Appl. Phys. **107**, 053509 (2010).
[6] J. Schmidt, A. G. Aberle, and R. Hezel, in: Proceedings of the 26th Photo-voltaic Specialist Conference (IEEE, New York, 1997), p. 13.
[7] J. Schmidt and K. Bothe, Phys. Rev. B **69**, 024107 (2004).
[8] V. V. Voronkov, G. I. Voronkova, A. V. Batunina, and R. Falster, in: High Purity Silicon Vol. X, edited by B. O. Kolbesen, C. L. Claeys, L. Fabri, M. Sarsani, O. Giubertoni, and G. Pepponi (ECS Trans., ALTECH, Pennington, NJ, 2009), p. 25.
[9] J. S. Blackmore, Semiconductor Statistics (Pergamon, NewYork, 1962).