

# Latent complexes of interstitial boron and oxygen dimers as a reason for degradation of silicon-based solar cells

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(Received 22 December 2009; accepted 14 January 2010; published online 4 March 2010)

Reduction in electron lifetime induced by excess electrons is a key effect in degradation of solar cells based on boron-doped and oxygen-containing silicon. Although boron related, degradation is controlled by the concentration of holes and not by the boron concentration. This recent finding is the basis for a new degradation model in which the degradation starts from a latent complex  $B_iO_2$  of an interstitial boron atom and an oxygen dimer. Electron-induced reconstruction of this defect results in a production of recombination centers. This model provides a detailed explanation of the basic features of the degradation, and of subsequent recovery by annealing in the dark. © 2010 American Institute of Physics. [doi:10.1063/1.3309869]

## I. INTRODUCTION

The efficiency of solar cells fabricated from Czochralski (CZ) boron-doped silicon degrades when excess electrons are created by either illumination or injection.<sup>1,2</sup> The effect is caused by a strong reduction in the electron lifetime that occurs<sup>2</sup> in two sequential stages: (1) a fast but moderate reduction and (2) a slow but strong reduction. A measure for the introduced recombination-active centers is an increment in the reciprocal lifetime,  $R(t) = 1/\tau(t) - 1/\tau(0)$ . A representative  $R(t)$  function is shown in Fig. 1 by the thick curve. This is a schematic plot but the two characteristic saturation times  $\tau_f$  and  $\tau_s$  correspond to the actual values<sup>2</sup> observed for degradation at 100 °C. The recombination centers produced during the fast stage will be abbreviated as FRC while those produced during the slow stage abbreviated as SRC. The basic features of the degradation inferred from a review paper<sup>2</sup> are as follows:

- (1) The saturated value of  $R$  both for the fast stage ( $R_f$ ) and for the slow stage ( $R_s$ ) is proportional to the product of the boron concentration  $N$  and the squared oxygen concentration,  $C^2$ . Both  $R_f$  and  $R_s$  seem to be independent of temperature.
- (2) The saturation times  $\tau_f$  and  $\tau_s$  (not to be confused with the carrier lifetime  $\tau$ ) are both proportional to  $1/N^2$  and independent of  $C$ . The temperature dependence of the rate constants  $1/\tau_f$  and  $1/\tau_s$  is characterized by the activation energy  $E_f = 0.23$  eV and  $E_s = 0.475$  eV.
- (3) By annealing in the dark, the lifetime is recovered to its initially high value as shown by the thin curves in Fig. 1. The degradation was traced in a temperature range from 20 to 140 °C, and the recovery in a range of higher  $T$ , from 110 to 200 °C. These two ranges overlap; this means that the degradation is followed by a recovery even if the sample is kept in the dark at the same temperature that was used for the degradation.
- (4) After the slow stage, the recovery is simple exponential, with a characteristic time  $\tau_s^*$  (the thin curve 1 in Fig. 1).

If the recovery is traced after only the fast stage of degradation (the thin curve 2), it proceeds in two steps with two characteristic times  $\tau_f^*$  and  $\tau_f'$ , and  $\tau_f'$  coincides with  $\tau_s^*$ . The explanation for the second step is very simple. At the end of the fast stage there are mainly FRC, but also a small amount of already produced SRC. The FRC are annealed out very quickly with a decay time  $\tau_f^*$ . After that the SRC that remain are annealed out with their own (much longer) decay time  $\tau_s^*$ . The activation energies for the rate constants  $1/\tau_f^*$  and  $1/\tau_s^*$  are  $E_f^* = 0.32$  eV and  $E_s^* = 1.32$  eV. The dependence of these rates on  $N$  and  $C$  was not yet inspected.

The outlined concentration dependence of the parameters was obtained for samples doped only with boron when it is not possible to distinguish between the effect of the boron concentration  $N$  and the hole concentration  $p$ . Recent data<sup>3</sup> on p-type material codoped with boron and phosphorus (with both concentrations close to  $5 \times 10^{16}$  cm<sup>-3</sup>) show that the actual dependence of  $R_s$  and  $\tau_s$  is on  $p$  rather than on  $N$ , the saturation amplitude  $R_s$  is proportional to  $p$  and the rate constant  $1/\tau_s$  to  $p^2$ . It was argued<sup>3</sup> that the compensating P donors may be completely paired with B acceptors such that the concentration  $N$  of isolated B atoms is still equal to  $p$ . But this assumption cannot be correct.

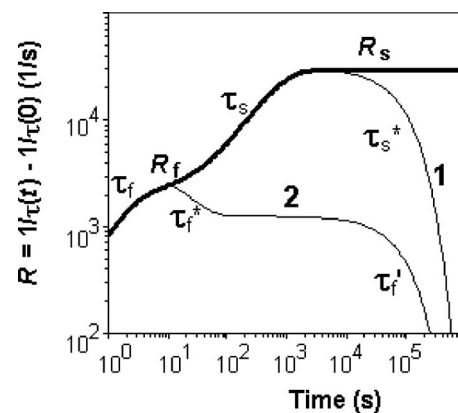


FIG. 1. A plot illustrating the lifetime degradation (thick curve) and subsequent recovery (thin curves 1 and 2).

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First, in material codoped with B and P to a much higher concentration ( $5 \times 10^{19} \text{ cm}^{-3}$ ) local vibration mode (LVM) spectra<sup>4</sup> show abundant lines of isolated B and P, and only weak satellite lines due to BP.

Second, the hole concentration  $p$  can be deduced from the reported resistivity  $\rho$  and compared to the independently measured value of  $p$  (by a light reflection technique). The conversion of  $\rho$  to  $p$  depends on the state of B and P in an essential way:

- (1) If the defect population is B+BP, the conversion is straightforward, by the American Society for Testing and Materials (ASTM)  $p(\rho)$  calibration curve since the neutral BP pairs have a negligible effect on the hole mobility.
- (2) If the defect population is B+P, the hole mobility is close to that of material doped only with boron but to a concentration equal to  $N^* = [\text{B}] + [\text{P}]$  since the effect of charged scatterers on the hole mobility is hardly dependent on the sign of the charge. The sum  $[\text{B}] + [\text{P}]$  was determined by mass-spectroscopy,<sup>3</sup> and the ASTM curve  $p(N^*)$  gives the hole mobility,  $1/[qN^*p(N^*)]$ , where  $q$  is the elementary charge. This mobility is used for the  $\rho$  to  $p$  conversion.

It turns out that the values of  $p$  calculated within the second assumption coincide with the optical values for  $p$  while those calculated within the first assumption deviate significantly.

It is thus concluded that the BP pairing is negligible, and the concentration  $N$  (of isolated boron acceptors) is identical to the total boron concentration  $[\text{B}]$  while the hole concentration,  $p = [\text{B}] - [\text{P}]$ , is much smaller. A proportionality of  $R_s$  to  $p$  means that the saturated degradation does not correlate with the concentration  $N$  of the isolated boron atoms. On the other hand, the boron impurity is definitely a key player since no degradation is found<sup>1,2</sup> in CZ silicon doped with Ga instead of B. The goal of this paper is to provide a model accounting for these and for many other features. First, a widely adopted attribution of the SRC to the  $\text{B}_s\text{O}_2$  complex (of a substitutional boron atom  $\text{B}_s$  and an oxygen dimer  $\text{O}_2$ ) is discussed and shown to be dramatically inconsistent with the available data.

## II. MODELS BASED ON $\text{B}_s\text{O}_2$

A degradation model discussed recently<sup>5-7</sup> assumes that the major degrading center SRC is formed in the course of illumination through the trapping of oxygen dimers by boron. The dimers are thought to diffuse fast in a double-positive state by recombination-enhanced jumps, and to form a  $(\text{B}_s\text{O}_2)^+$  recombination center.

As demonstrated in the Appendix, dimers are frozen-in, in the course of crystal or sample cooling, from a relatively high temperature (above 440 °C) when the material is still intrinsic. The frozen-in dimeric concentration  $C_2$  is proportional to  $C^2$  and independent of  $N$ . The concentration  $C_2$  is only slightly sensitive to the cooling rate, a representative value is  $3 \times 10^{14} \text{ cm}^{-3}$ . Oxygen dimers are a predominantly neutral species. Indeed, there are CZ silicon crystals that are

only lightly doped with boron ( $N < 10^{13} \text{ cm}^{-3}$ ), and in such crystals the concentration of compensating donors is smaller than  $N$  and, therefore, much lower than  $C_2$ . Hence only a very small fraction of  $\text{O}_2$  can be present in a double-positive state.

The degradation model based on trapping of  $\text{O}_2$  by  $\text{B}_s$  can have various versions: the exchange between the two states of  $\text{O}_2$  can be assumed either fast or negligible, and the dimers can be assumed to be trapped almost completely or only partially due to a fast backward dissociation of  $\text{B}_s\text{O}_2$ . However, in any version the  $\text{B}_s$  species is directly involved in the production of degrading defects and hence the saturated degradation  $R_s$  and the rate constant  $1/\tau_s$  cannot be both independent of  $N$ .

For instance, in a recent version<sup>7</sup> any exchange of double-positive  $\text{O}_2$  with neutral dimers was disregarded and the former species was assumed to be completely trapped by  $\text{B}_s$ . The rate constant corresponds to the trapping reaction, and it is proportional to the trap concentration  $N$  (and in addition to the hole concentration  $p$  through the enhanced dimeric diffusivity<sup>7</sup>). No explanation was given for the concentration dependence of the amplitude  $R_s$ . Clearly, it is not possible to obtain the required law  $R_s \sim pC^2$  within this model.

If one assumes that only a small fraction of the dimers is trapped, then the saturation time  $\tau_s$  is equal to the dissociation time of  $\text{B}_s\text{O}_2$  while the saturated concentration is proportional to the product of the concentrations of the two reacting species and thus proportional to  $N$  and not to  $p$ .

An alternative possibility is that the boron–oxygen center is already present before illumination as a latent complex  $(\text{B}_s\text{O}_2)^-$  of a boron atom and a neutral dimer. The degradation may proceed by a reconstruction of some latent defect<sup>8</sup> [in the present case of  $(\text{B}_s\text{O}_2)^-$ ] into a recombination-active configuration  $(\text{B}_s\text{O}_2)^+$ . However, the grown-in concentration of  $(\text{B}_s\text{O}_2)^-$  is proportional to  $NC^2$ , and not at all to  $pC^2$ .

In conclusion, the SRC cannot be identified with a  $\text{B}_s\text{O}_2$  complex, and we must search for quite a different attribution for the degrading centers.

## III. MODEL BASED ON $\text{B}_i\text{O}_2$

The suggested scenario is as follows. In the course of crystal cooling, oxygen precipitates are nucleated<sup>9</sup> in a temperature range estimated to be around 700 °C. The growing oxide particles emit self-interstitials, and some fraction of boron is kicked-out into the interstitial state  $\text{B}_i$ . A similar kick-out occurs when self-interstitials are produced by irradiation.<sup>4,10,11</sup> The notation  $\text{B}_i$  refers to a boron atom inserted into the perfect lattice, irrespective of the resulting ground-state location of this atom. At some lower  $T$  most of  $\text{B}_i$  precipitate into  $\text{B}_i$ -clusters. The clustering is a problem to be addressed separately to specify the cluster density  $N_{\text{cl}}$  (by a preliminary estimate, on the order of  $10^{10} \text{ cm}^{-3}$ ) and size (roughly estimated to be around  $10^4$   $\text{B}_i$  atoms). These numbers are given just to show what is meant by “ $\text{B}_i$ -clusters” in the present model. The concentration of still dissolved  $\text{B}_i$  atoms corresponds to the equilibrium with the clusters, this concentration (the solubility, denoted  $N_{i\text{e}}$ ) depends only on  $T$

if the material is intrinsic. For a representative boron concentration of  $10^{16} \text{ cm}^{-3}$ , this is true at  $T > 350^\circ \text{C}$ . At lower  $T$ , the hole concentration  $p$  is equal to  $N$  (or, generally speaking, to the difference of acceptor and donor concentrations). Since  $B_i$  is a single-positive defect in p-type silicon,<sup>10</sup> the solubility  $N_{ie}$  is proportional to  $p$ . The mobile  $B_i$  species migrate and form complexes with all possible traps such as  $O_2$ ,  $O$ , and  $B_s$ . The trapped species  $B_iO_2$ ,  $B_iO$ , and  $B_iB_s$  exist in parallel, each in equilibrium with  $B_i$ , and  $[B_i]$  is supported at the solubility value  $N_{ie}$  by exchanging with the clusters. The equilibrium  $B_iO_2$  concentration is expressed by the mass-action law

$$[B_iO_2] = \frac{[B_i][O_2]}{K}, \quad (1)$$

where  $K$  is the dissociation constant equal to  $\rho \exp(-E/kT)$  where  $E$  is the binding energy of  $B_i$  and  $O_2$ , and the prefactor  $\rho$  is roughly equal to the lattice site density. Hence  $[B_iO_2]$  is proportional to  $[B_i] = N_{ie}$  and to  $[O_2] = C_2$ , and thus to  $pC^2$  in a temperature range below  $350^\circ \text{C}$ . Only  $B_iO_2$  has a proper concentration dependence while the other complexes have a different dependence  $[B_iO] \sim pC$ , and  $[B_iB_s] \sim pN$ .

Below some freezing-in temperature  $T_{fr}$  (assumed to be well below  $350^\circ \text{C}$ ) the exchange of the dissolved species with the clusters stops, and the complexes are frozen-in. It is not essential whether the  $B_iO_2$  is stable or not at  $T_{fr}$  (in the usual sense of the word “stable” implying a low degree of dissociation, here  $[B_iO_2] > [B_i]$ ). It is neither essential which kind of complexes is dominant at  $T_{fr}$  (most likely, the dominant one is  $B_iB_s$ ). The only essential point is whether the frozen-in concentration  $[B_iO_2]$  is sufficient to account for the concentration of SRC, which is thought to be extremely low on the order of about  $10^{11} \text{ cm}^{-3}$  since no trace of SRC has been found by deep level transient spectroscopy (DLTS).<sup>2</sup> To get such a concentration by Eq. (1) at a tentative freezing-in temperature  $T_{fr} = 300^\circ \text{C}$  and a tentative solubility  $N_{ie} = 10^{12} \text{ cm}^{-3}$ , the binding energy  $E$  should be about  $0.85 \text{ eV}$ . This is somewhat larger than the first-principle estimate<sup>12</sup> of  $0.6 \text{ eV}$  for the  $B_iO_2$  defect but the difference does not seem too large.

The frozen-in  $B_iO_2$  is considered as a latent center of a low recombination activity, abbreviated as LC. The degradation is caused by a reconstruction of LC into a recombination-active center. The reconstruction rate cannot depend on  $N$  or  $C$  but it can depend on  $p$  if holes participate in the process. Two configurations were found<sup>12</sup> for the single-positive  $B_iO_2$  defect by first-principle calculations, in each of them, the defect has a deep donor level close to midgap. These two forms of  $B_iO_2$  can be identified with LC and SRC. The nature of FRC is not certain since there is no data on the actual concentration dependence of the degradation amplitude  $R_f$  whether on  $N$  or on  $p$ . One possibility is that FRC is another configuration of  $B_iO_2$  in which  $R_f$  is independent of  $N$  (and thus proportional to  $p$ ). On the other hand, FRC may originate from a different grown-in defect such as  $B_sO_2$  in which  $R_f$  would be proportional to  $N$ . If FRC is another configuration of  $B_iO_2$ , the reconstruction sequence could be  $LC \leftrightarrow FRC \leftrightarrow SRC$ . However, according to Ref. 2, the FRC is not an immediate precursor for SRC. Hence, the

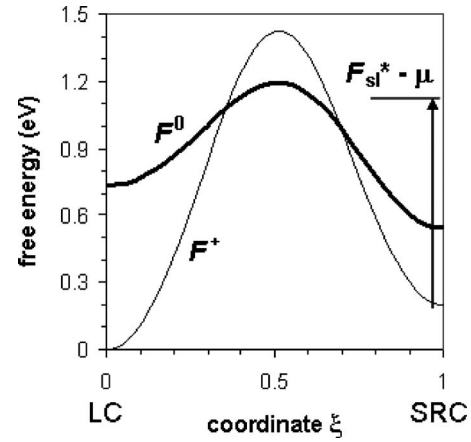


FIG. 2. Schematic dependence of the free energy  $F^0$  (in the neutral charge state) and  $F^+$  (in the single-positive state) on the structural coordinate  $\xi$  that corresponds to the reconstruction path from the LC ( $\xi=0$ ) to the SRC ( $\xi=1$ ). The relative location of the profiles corresponds to the equilibrium case (in the dark).

exchange between the three configurations would proceed rather in a sequence  $FRC \leftrightarrow LC \leftrightarrow SRC$ , in other words, the LC is a common source for both FRC and SRC. Because of the still uncertain nature of FRC, the present paper concentrates on the behavior of the major recombination center, SRC.

#### IV. DEGRADATION KINETICS

The reconstruction path from the latent form LC to the recombination center SRC is described as a variation in a structural coordinate  $\xi$  that changes from 0 (for the LC) to 1 (for SRC). A different but similar path may lead from LC to FRC. In the dark, the free energy  $F(\xi)$  is at a minimum for the latent form. Only in this case the recovery can occur, the SRC reconstructs back into the ground-state LC at  $\xi=0$ .

Why is the SRC concentration increased in the presence of excess electrons? The key effect is thought to be a recharging of the defect, by capturing electrons, from the initial single-positive charge state to the neutral state. The free energy profiles  $F^+(\xi)$  and  $F^0(\xi)$  for the +1 and neutral states of  $B_iO_2$  are schematically shown in Fig. 2. The free energy  $F^+$  is larger for SRC than for LC. There are two possibilities for the relation between  $F^0(\text{SRC})$  and  $F^0(\text{LC})$ :

- (A) The lowest minimum in  $F^0(\xi)$  still remains at LC but becomes less deep than for the +1 charge state, in this case only a fraction of LC is transformed into SRC.
- (B) The lowest minimum in  $F^0(\xi)$  is at SRC, a situation shown in Fig. 2. In this case, the LC is almost completely transformed into SRC.

In the present work, the second version is adopted. This provides a simple explanation of the  $pC^2$  law found for SRC, due to a complete transformation, the SRC simply inherits this dependence from LC.

The next point to discuss is the degradation time  $\tau_s$ , which is identical to the transition time from LC to SRC. For that, it is first necessary to outline the dependence of the defect concentrations in the different charge states (such as

$N^0$  and  $N^+$ ) on the electron concentration  $n$ . The concentration ratio  $N^0/N^+$  is determined<sup>13,14</sup> by a balance of capturing and emitting electrons and holes

$$N^0/N^+ = \frac{(\alpha_{n1}n + \alpha_{p1}p_1)}{(\alpha_{n1}n_1 + \alpha_{p1}p)}, \quad (2)$$

where  $\alpha_{n1}$  is the capture coefficient of electrons by the positive state and  $\alpha_{p1}$  is the capture coefficient of holes by the neutral state (each coefficient is a product of the thermal velocity and the capture cross-section). The characteristic carrier concentrations  $n_1$  and  $p_1$  in Eq. (2) correspond to a half-filled  $+0$  donor level  $E_1$  in the dark

$$n_1 = N_c \exp\left[-\frac{(E_c - E_1)}{kT}\right], \quad p_1 = N_v \exp\left[-\frac{(E_1 - E_v)}{kT}\right], \quad (3)$$

where  $E_c$  and  $N_c$  are the energy at the bottom of the conduction band and the effective state density in this band,  $E_v$  and  $N_v$  are the energy at the top of the valence band and the effective state density in this band. Equations (2) and (3) will be used for various configurations but the configuration variable  $\xi$  is omitted, to avoid complexity in the notations.

If the donor level  $E_1$  is not too close to either  $E_c$  or  $E_v$ , the emission terms  $\alpha_{p1}p_1$  and  $\alpha_{n1}n_1$  in Eq. (2) can be neglected, and the concentration ratio is proportional to the injection level  $n/p$

$$N^0/N^+ = \left(\frac{\alpha_{n1}}{\alpha_{p1}}\right)\left(\frac{n}{p}\right). \quad (4)$$

The degradation time  $\tau_s$  was found<sup>2,5</sup> to be independent of  $n$  in a range from  $10^{15}$  down to  $10^{13}$  cm<sup>-3</sup> implying that LC remains in the same neutral state within this range of  $n$ . For that, the LC capture ratio  $\alpha_{n1}/\alpha_{p1}$  should be at least  $10^3$ . For SRC, the  $\alpha_{n1}/\alpha_{p1}$  ratio<sup>2,15</sup> is about 10 (while for FRC is about 100). Strictly speaking, it is not clear whether the reported capture ratios refer to the donor levels of SRC and FRC. It cannot be excluded that the operating recombination level is actually the acceptor level  $E_a$  while the donor level  $E_1$  is almost completely filled if the  $\alpha_{n1}/\alpha_{p1}$  ratio for SRC and FRC is as large as for the LC donor level. Yet in the present discussion we accept a conventional identification of the recombination levels as the donor levels of SRC and FRC.

The experimental dependence  $1/\tau_s \sim p^2$  implies that the LC to SRC transition is not just overcoming the barrier in  $F^0(\xi)$  shown in Fig. 2, in this case the rate constant would be independent of  $p$ . A proportionality to  $p^2$  implies that the transition involves a temporary recharging to a double-positive state. In other words, the defect possesses not only a first donor level  $E_1$  but also a second donor level  $E_2$ , for recharging from  $+1$  to  $+2$ . Accordingly, the simple scheme of Fig. 2 should be modified. A most natural modification is to add one more barrier in the path from LC to SRC as shown schematically in Fig. 3, with an intermediate configuration denoted Transient Centre and abbreviated as TC. The essence of this model is that

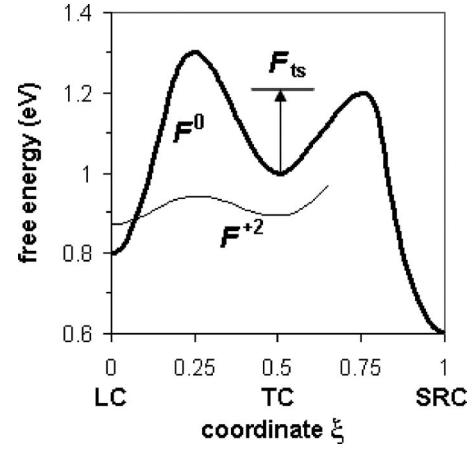


FIG. 3. A model for the transition from LC to SRC through an intermediate configuration TC accounting for the dependence of the rate constant on the hole concentration. The basic charge state is neutral but the exchange between LC and TC occurs in a  $+2$  charge state. A relevant portion of the free energy profile  $F^{+2}(\xi)$  is shown by the thin line.

- (1) The direct exchange between LC and TC is hindered by a large barrier in  $F^0(\xi)$  but the exchange still occurs rapidly through the double-positive state with a low barrier. A relevant portion of the  $F^{+2}(\xi)$  profile is shown by the thin line in Fig. 3.
- (2) The ratio  $N^0/N^+$  for LC is given by the Eq. (4), and  $N^+/N^{+2}$  by a similar equation, replacing the subscript 1 with 2. Therefore, the ratio  $N^{+2}/N^0$  relevant for the LC to TC transition is equal to

$$N^{+2}/N^0 = \left(\frac{p}{n}\right)^2 \left(\frac{\alpha_{p1}}{\alpha_{n1}}\right)\left(\frac{\alpha_{p2}}{\alpha_{n2}}\right) \quad \text{for LC.} \quad (5)$$

This ratio is presumably low, in spite of a large  $p/n$  due to large capture ratios,  $\alpha_{n1}/\alpha_{p1}$  and especially  $\alpha_{n2}/\alpha_{p2}$  (in this case an electron is captured by  $+2$  attracting center, and a hole by  $+1$  repulsive center).

- (3) For the TC configuration, the donor levels  $E_1$  and  $E_2$  are assumed to reside relatively close to the conduction band such that  $n_1$  and  $n_2$  are sufficiently large to make the electron emission term  $\alpha_{n1}n_1$  in the denominator of Eq. (2) larger than the hole capture term  $\alpha_{p1}p$  (and  $\alpha_{n2}n_2$  larger than  $\alpha_{p2}p$ ). Then  $N^0/N^+ = n/n_1$  and  $N^+/N^{+2} = n/n_2$  in other words, the level filling is controlled simply by the position of the electron Fermi level with respect to the energy levels  $E_1$  and  $E_2$ . The concentration ratio of interest is

$$\frac{N^0}{N^{+2}} = \frac{n^2}{(n_1 n_2)} \quad \text{for TC.} \quad (6)$$

The positions of the first and the second donor levels ( $E_1$  and  $E_2$ ) for the LC and TC configurations are shown schematically in Fig. 4. A dominance of the  $+1$  state of LC (in the dark) implies that  $E_1$  is above the Fermi level while  $E_2$  is below it. For the TC configuration both energy levels are above the Fermi level.

The transition rate from LC to SRC is controlled by overcoming the free energy barrier  $F_{ts}$  (indicated in Fig. 3)



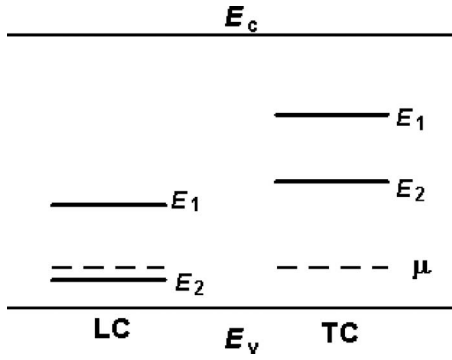


FIG. 4. Tentative location of the first and second donor levels ( $E_1$  and  $E_2$ ) for the LC (the left set) and for the TC (the right set). The Fermi level  $\mu$  (in the dark) is shown by the thin line.

between TC and SRC and thus equals  $N^0(\text{TC})\nu_{\text{ts}}\exp(-F_{\text{ts}}/kT)$  where  $\nu_{\text{ts}}$  is the attempt frequency for this transition (often assumed to be close to  $10^{13} \text{ s}^{-1}$  although it can be somewhat different). The concentration  $N^0(\text{TC})$  is expressed through  $N^0(\text{LC})$  using the Eqs. (5) and (6), the electron concentration  $n$  is excluded from this relation. The flux from LC to SRC is proportional to  $N^0(\text{LC})$ , with  $1/\tau_s$  as the rate constant which is then expressed as

$$\frac{1}{\tau_s} = \left[ \frac{p^2}{(n_1 n_2)} \right] \left( \frac{\alpha_{p1}}{\alpha_{n1}} \right) \left( \frac{\alpha_{p2}}{\alpha_{n2}} \right) \nu_{\text{ts}} \exp\left(-\frac{F_s}{kT}\right), \quad (7)$$

where  $F_s$  includes, apart from the barrier  $F_{\text{ts}}$ , also the free energy difference  $F^{+2}(\text{TC}) - F^{+2}(\text{LC})$  between the double-charged states of TC and LC configurations. The capture ratios in Eq. (7) refer to LC while the characteristic electron concentrations  $n_1$  and  $n_2$  to TC. The time dependence of the SRC concentration is simple exponential,  $N_{\text{SRC}}(t) = N_{\text{lat0}}[1 - \exp(-t/\tau_s)]$ , where  $N_{\text{lat0}}$  is the initial concentration of LC.

The free energy  $F_s$  in Eq. (7) is composed of the energy term  $E_s$  and a vibrational entropy term. The apparent activation energy for the rate constant, taking into account the expression (3) for  $n_1$  and a similar one for  $n_2$ , is  $E_s - (E_c - E_1) - (E_c - E_2) - 3kT$ , a small correction term  $-3kT$  comes from the temperature dependence of the state density  $N_c \sim T^{3/2}$  that enters both  $n_1$  and  $n_2$ . The apparent prefactor in Eq. (7), related to the apparent activation energy, is

$$\nu_s = \left( \frac{p}{N_c} \right)^2 \left( \frac{\alpha_{p1}}{\alpha_{n1}} \right) \left( \frac{\alpha_{p2}}{\alpha_{n2}} \right) \frac{\nu_{\text{ts}}}{e^3}, \quad (8)$$

where  $e=2.72$ , the factor  $1/e^3$  in Eq. (8) comes from the temperature dependence of  $N_c^2$ . In a representative narrow temperature interval, 30 to 100 °C,  $N_c$  is close to  $3 \times 10^{19} \text{ cm}^{-3}$ . The experimental value of  $\nu_s$  is very low,<sup>2</sup> about  $4 \times 10^3 \text{ s}^{-1}$ . This feature is explained by expression (8) that includes several small factors:  $(p/N_c)^2$ ,  $\alpha_{p1}/\alpha_{n1}$ , and  $\alpha_{p2}/\alpha_{n2}$ .

In concluding this section the production of FRC is briefly commented on, under the assumption that FRC is also produced by a reconstruction of LC (but along a different path). The FRC concentration is thought to be a small fraction of  $N_{\text{lat0}}$ . The saturated value  $N_{\text{FRC}}$  corresponds to a balance of a forward transition (with the characteristic time  $\tau_{\text{f}}$ ) and a backward transition (with a much shorter characteristic

time  $\tau_{\text{b}}$ ). The saturation time  $\tau_{\text{f}}$  for FRC is then close to  $\tau_{\text{fl}}$  while the saturated concentration is  $N_{\text{FRC}} \approx N_{\text{lat0}}\tau_{\text{fl}}/\tau_{\text{f}} \ll N_{\text{lat0}}$ . The concentration dependencies are  $N_{\text{FRC}} \sim pC^2$  and  $1/\tau_{\text{f}} \sim p^2$  if both forward and backward transitions are of the same type discussed above for the LC to SRC transition (Fig. 3), in other words, they proceed through an intermediate configuration involving a temporary recharging from the neutral into +2 state. The apparent prefactor  $\nu_{\text{f}}$  for  $1/\tau_{\text{f}}$  is given by an expression similar to Eq. (8), it is as small as  $\nu_s$  which accounts for an extremely low experimental value<sup>2</sup>  $\nu_{\text{f}} = 4 \times 10^2 \text{ s}^{-1}$ .

## V. RECOVERY KINETICS

Recovery corresponds to a return from SRC to LC now in the dominant single-positive charge state. It proceeds by overcoming free energy barriers in this path. Although detailed data on the concentration dependence of the recovery time are absent, a single available example (shown in Fig. 13 of Ref. 2) indicates to  $\tau_s^* \sim N$ , in boron-only doped material. The actual dependence is of course not on  $N$  but on the hole concentration  $p$ . The proportionality of the rate constant  $1/\tau_s^*$  to  $1/p$  implies that passing the saddle point in the path from SRC to LC is accompanied by a recharging from the basic +1 state to the neutral state, as illustrated by the relative positions of the free energy profiles  $F^+(\xi)$  and  $F^0(\xi)$  in Fig. 2,  $F^0 < F^+$  at the saddle point. A reduction in the charge by 1 occurs by emitting a hole or by capturing an electron; thermodynamically, these are equivalent ways since electrons and holes are now in the mutual equilibrium. Hence, the difference  $F^0 - F^+$  includes a term  $-\mu$  where  $\mu$  is the electron chemical potential (the Fermi level) referenced from the top of the valence band

$$\mu = kT \log\left(\frac{N_v}{p}\right). \quad (9)$$

A representative value of  $\mu$ , at room temperature and  $p = 10^{16} \text{ cm}^{-3}$ , is 0.18 eV.

The transition barrier accompanied by a recharging from +1 to 0 has a general form  $F_{\text{sl}}^* - \mu$ . A contribution of the vibrational entropy into  $F_{\text{sl}}^*$  will be transferred into the prefactor, and the barrier height will contain the energy  $E_{\text{sl}}^*$  instead of  $F_{\text{sl}}^*$ . The transition rate constant is expressed in a usual way through the barrier height

$$\frac{1}{\tau_s^*} = \nu_{\text{sl}}^* \exp\left[-\frac{(E_{\text{sl}}^* - \mu)}{kT}\right] = \left(\frac{N_v}{p}\right) \nu_{\text{sl}}^* \exp\left(-\frac{E_{\text{sl}}^*}{kT}\right). \quad (10)$$

The apparent activation energy is  $E_{\text{sl}}^* + 1.5kT$ , it includes a small correction term  $1.5kT$  due to the temperature dependence of  $N_v \sim T^{3/2}$ . The apparent prefactor  $\nu_s^*$  in Eq. (10) corresponding to the apparent activation energy is equal to  $\nu_{\text{sl}}^*(N_v/p)e^{1.5}$ . In a representative narrow temperature interval of 30 to 100 °C,  $N_v \approx 10^{19} \text{ cm}^{-3}$ . The experimental value of the apparent prefactor is  $\nu_s^* = 10^{13} \text{ s}^{-1}$ , which leads to  $\nu_{\text{sl}}^* = 2.2 \times 10^9 \text{ s}^{-1}$ .

The recovery for FRC is now briefly commented on. The loss of FRC is very quick, and the apparent prefactor in the rate constant  $1/\tau_{\text{f}}^*$  is as small ( $10^3 \text{ s}^{-1}$ ) as for the degradation rate constants  $1/\tau_{\text{f}}$  and  $1/\tau_s$ . These features are understood if

the saddle point in the path from FRC to LC is passed in a recharged state, through capturing two holes. If the basic FRC charge state is +1, then the saddle point charge is +3 (the implication is that the FRC center has also the third donor level  $E_3$ ). The free energy difference  $F^{+3}(\xi) - F^+(\xi)$  includes the term  $2\mu$  corresponding to emitting two electrons (or capturing two holes). Note that in the course of degradation the +3 state does not exist due to a fast capture of an electron. The FRC recovery barrier is the difference between  $F^{+3}$  at the saddle point and  $F^+$  at FRC, and it has a general form  $F_{\text{fl}}^* + 2\mu$ . A contribution of the vibrational entropy into  $F_{\text{fl}}^*$  will be again transferred into the prefactor, and the transition rate constant is

$$\frac{1}{\tau_f^*} = \nu_{\text{fl}}^* \exp\left[-\frac{(E_{\text{fl}}^* + 2\mu)}{kT}\right] = \left(\frac{p}{N_v}\right)^2 \nu_{\text{fl}}^* \exp\left(-\frac{E_{\text{fl}}^*}{kT}\right). \quad (11)$$

The apparent activation energy is  $E_{\text{fl}}^* - 3kT$ , including a correction term  $-3kT$  due to the temperature dependence of  $N_v^2$ . The apparent prefactor  $\nu_f^*$  is expressed as  $\nu_{\text{fl}}^*(p/N_v)^2/e^3$ . The experimental value,  $\nu_f^* = 10^3 \text{ s}^{-1}$ , leads to  $\nu_{\text{fl}}^* = 2 \times 10^{10} \text{ s}^{-1}$ . Note that this frequency is of the same order as  $\nu_{\text{sl}}^*$ .

## VI. RECOVERY UNDER PROLONGED ILLUMINATION

It was recently discovered<sup>16–18</sup> that if illumination (or electron injection) is performed at a temperature above 100 °C, the lifetime is first degraded (to the same degree as at lower  $T$  but much faster) but later slowly recovered to the initial high value. The recovered high lifetime is persistent under subsequent illumination at lower  $T$ . This phenomenon can be accounted by the present model in a most straightforward way. The mechanism of recovery in the presence of the excess electrons is, most likely, a slow dissociation of the  $\text{B}_i\text{O}_2$  defects (in the SRC form). The released  $\text{B}_i$  are either consumed by the  $\text{B}_i$ -clusters or trapped into  $\text{B}_i\text{O}$  or  $\text{B}_i\text{B}_s$ . The time scale for the observed recovery varies in a wide range,<sup>16–18</sup> which suggests that the recovery is controlled by sinking the released  $\text{B}_i$  to the  $\text{B}_i$ -clusters rather than by dissociation itself or by trapping the released  $\text{B}_i$  by O or  $\text{B}_s$ . In the end of the recovery process, there is no more  $\text{B}_i\text{O}_2$  and thus no degradation by illumination at any other  $T$ .

However, if a sample recovered in this way is annealed in the dark, the  $\text{B}_i\text{O}_2$  species will be rebuilt, by supplying  $\text{B}_i$  from the  $\text{B}_i$ -clusters. After such annealing, the material keeps a high value of the lifetime but becomes degradable again. The recreation of latent defects was indeed observed<sup>17</sup> by annealing in the dark in a range 170–200 °C.

Now it is possible to draw a general chart illustrating the basic reactions involved in degradation, recovery by dissociation of SRC, and recreation of latent  $\text{B}_i\text{O}_2$  (Fig. 5). The first reaction (reconstruction of latent  $\text{B}_i\text{O}_2$  into SRC) accounts for the degradation. The two subsequent reactions, dissociation of SRC and then sinking the released  $\text{B}_i$  to the clusters, account for a recovery under prolonged illumination. The two last reactions in the chain recreate the latent defect  $\text{B}_i\text{O}_2$  in the dark, by supplying  $\text{B}_i$  atoms from the clusters with subsequent trapping of  $\text{B}_i$  into the latent form of  $\text{B}_i\text{O}_2$ .

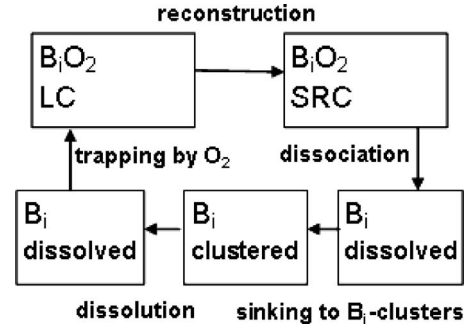


FIG. 5. A flow chart for degradation, subsequent recovery upon prolonged illumination, and final recreation of the latent defects in the dark.

## VII. SUMMARY

The lifetime-degrading recombination center produced in the presence of excess electrons in boron-doped and oxygen-containing silicon was previously attributed to the  $(\text{B}_s\text{O}_2)^+$  complex of a substitutional boron atom and an oxygen dimer. However, the experimental data on degradation in dependence of the concentrations of boron  $N$ , of oxygen  $C$ , and of holes  $p$ , are inconsistent with this attribution. The key parameter that controls the degradation has turned out to be  $p$  rather than  $N$ .

The basic features of the degradation (and of subsequent recovery by annealing in the dark) can be accounted for in detail within the new model presented here. Within this scenario the degradation proceeds starting from a latent complex  $(\text{B}_i\text{O}_2)^+$  that involves an interstitial boron atom  $\text{B}_i$  rather than  $\text{B}_s$ . In the presence of excess electrons this latent complex LC recharges into the neutral state and reconstructs into the major recombination center SRC. In the dark, in the single-positive charge state the latent  $\text{B}_i\text{O}_2$  configuration is of the lowest energy, and the SRC reconstructs back into LC.

The degradation includes also a fast stage resulting in a moderate reduction in the electron lifetime. The nature of the related recombination center FRC is not yet clear but it is possible that FRC is just another configuration of the same  $\text{B}_i\text{O}_2$  defect, produced by reconstruction of LC through a different path independent of that leading to SRC.

The  $\text{B}_i$  atoms responsible for the  $\text{B}_i\text{O}_2$  defects are produced by self-interstitials emitted by oxygen precipitates. Hence, oxygen plays a twofold role in the degradation through producing the dimers (by pairing reaction of oxygen monomers) and through producing self-interstitials (by the oxygen precipitation). In other words, oxygen is responsible for both constituents of the latent defect,  $\text{O}_2$  and  $\text{B}_i$ .

Since everything starts with self-interstitials, the degradation of space solar cells may proceed by the same mechanism. The only difference is in the source of self-interstitials in space, they are produced by irradiation. A plausible reaction sequence, in this case, is kicking out boron atoms into  $\text{B}_i$  state with subsequent trapping of  $\text{B}_i$  by  $\text{O}_2$ . The latter reaction, when it occurs at low  $T$ , may produce not only the latent form of  $\text{B}_i\text{O}_2$  but directly the recombination-active form SRC.

It can be further expected that introducing self-interstitials from the sample surface (which, in principle, can result from many treatments such as nonpenetrating radia-

tion, implantation, and exposure to a chemically-active ambient, or even probably just illumination with photons of sufficiently high energy) will lead, in all the cases, to the same universal consequence, the self-interstitials penetrate deep into the bulk where they produce first  $B_i$  and then  $B_iO_2$  the universal lifetime-degrading center.

## ACKNOWLEDGEMENTS

The authors would like to thank Karsten Bothe and Jan Schmidt of the Institut für Solarenergieforschung Hameln/Emmerthal for many helpful discussions and patient answers to our questions.

## APPENDIX: FROZEN-IN CONCENTRATION OF OXYGEN DIMERS

Oxygen dimers, in a concentration  $C_2$ , are produced through pairing of oxygen monomers

$$\frac{dC_2}{dt} = 4\pi rD(C^2 - K_2C_2), \quad (A1)$$

where  $D$  and  $C$  are the diffusivity and concentration of the monomeric oxygen,  $r$  is the capture radius for the pairing reaction, and  $K_2$  is the dissociation constant of dimers

$$K_2 = \rho_2 \exp\left(-\frac{E_b}{kT}\right). \quad (A2)$$

The binding energy of two O into  $O_2$  was estimated<sup>19</sup> to be  $E_b=0.3$  eV by the temperature dependence of the steady-state value of  $C_2$  measured optically. A more careful fit of this dependence<sup>20</sup> (taking into account that the steady-state value of  $C_2$  somewhat deviates from the equilibrium concentration,  $C_{2e}=C^2/K_2$ , at  $T \leq 450$  °C) gives a slightly larger energy,  $E_b=0.4$  eV. The prefactor in Eq. (A2) was determined using the absolute value of the equilibrium concentration  $C_{2e}$  at 425 °C, deduced from the transient time for the thermal donor generation rate<sup>20</sup> (this time is limited mostly by accumulation of dimers upto the steady-state concentration). The deduced prefactor is  $\rho_2=7.1 \times 10^{23}$  cm<sup>-3</sup> as expected, not much different from the lattice site density.

The Eq. (A1) can be rewritten in a general form as a combination of two Arrhenius-type terms

$$\frac{dC_2}{dt} = A \exp\left(-\frac{E_A}{kT}\right) - B \exp\left(-\frac{E_B}{kT}\right) C_2. \quad (A3)$$

The activation energy  $E_A$  is identical to the migration energy<sup>21</sup> of monomeric oxygen, 2.53 eV. The activation energy  $E_B$  is equal to  $E_A+E_b$ . The prefactors  $A$  and  $B$  are defined by comparison with the source Eq. (A1)

$$A = 4\pi r\{D\}C^2, \quad B = 4\pi r\{D\}\rho_2, \quad (A4)$$

where  $\{D\}=0.13$  cm<sup>2</sup>/s is the prefactor in  $D(T)$ .

At higher  $T$ , the equilibrium between  $O_2$  and O is maintained, and  $C_2=C_{2e}$ , this concentration is gradually increasing upon lowering  $T$ . Below some “freezing-in temperature”  $T_q$  the concentration  $C_2$  is no longer increased. This happens when the equilibration time,  $\tau_e=1/(4\pi rDK_2)$  by Eq. (A1), becomes longer than the characteristic time  $\tau_b$  for an essen-

tial increase in  $C_{2e}$ . An essential increase occurs within a temperature interval  $\Delta T$  that corresponds to an increment in  $E_b/kT$  by 1, hence  $\tau_b=kT^2/(E_bg)$  where  $g=-dT/dt$  is the cooling rate. The freezing-in temperature  $T_q$  is found from the equation  $\tau_e=\tau_b$ . Due to a very steep temperature dependence of  $D$ , the dependence of  $T_q$  on  $g$  is relatively weak, by increasing  $g$  within a wide representative range, from 0.01 to 100 K/s,  $T_q$  is increased from 445 to 605 °C.

The frozen-in value of  $C_2$  is found by solving Eq. (A3) in the vicinity of  $T_q$ . The relevant temperature interval is narrow, and a variable  $u=1/kT$  can be treated as a linear function of  $t$ , with  $du/dt=g/(kT_q^2)$ . The Eq. (A3) then takes a form

$$\frac{dC_2}{du} = A^* \exp(-E_A u) - B^* \exp(-E_B u) C_2, \quad (A5)$$

where  $A^*=AkT_q^2/g$  and  $B^*=BkT_q^2/g$ .

The linear Eq. (A5), with two simple exponential terms, is solved analytically to give the frozen-in value of  $C_2$

$$C_2 = \left(\frac{A}{B}\right) \left[\frac{BkT_q^2}{(gE_B)}\right]^\varepsilon \Gamma(1-\varepsilon), \quad (A6)$$

where  $\varepsilon=1-E_A/E_B=E_b/(E_A+E_b)$  and  $\Gamma$  is the gamma-function. The energy parameter  $\varepsilon$  is close to 0.137, it is small since the binding energy  $E_b$  is far lower than the monomer migration energy  $E_A$ . The value of  $\Gamma(1-\varepsilon)$  is then only slightly larger than 1.

By Eq. (A6) the frozen-in concentration  $C_2$  is proportional to  $C^2$  through the coefficient  $A$ , the dependence on the cooling rate is  $\sim 1/g^\varepsilon$  very weak, due to small  $\varepsilon$ . By increasing  $g$  from 0.01 to 100 K/s,  $C_2$  is reduced from  $3.5 \times 10^{14}$  down to  $1 \times 10^{14}$  cm<sup>-3</sup>, for a representative oxygen concentration  $C=7 \times 10^{17}$  cm<sup>-3</sup>. In the process of crystal growth the cooling rate, at  $T$  close to  $T_q$ , is usually within a narrower range 0.01–0.1 K/s, and then  $C_2=(2.6-3.5) \times 10^{14}$  cm<sup>-3</sup>. A dependence of  $C_2$  on the somewhat indefinite capture radius  $r$  is also extremely weak ( $\sim r^\varepsilon$ ), therefore, any reasonable value of  $r$  (0.3 or 0.5 nm) can be adopted in calculations.

Using a tentative calibration for the  $O_2$  related LVM line (at 1012 cm<sup>-1</sup>) the grown-in value of  $C_2$  was previously estimated<sup>22</sup> to be about  $8 \times 10^{14}$  cm<sup>-3</sup>. Apparently, the adopted calibration coefficient for the 1012 cm<sup>-1</sup> line was overestimated, it should be reduced by a factor of 2.5 or so.

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