Light-Induced Boron-Oxygen Recombination Centres in Silicon: Understanding their Formation and Elimination

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Abstract. Lifetime-degrading recombination centres – those that emerge in the presence of excess carriers in boron and oxygen containing silicon - show a peculiar dependence on the concentrations of the relevant impurities, B and O, and on the hole concentration p_0 (net doping) in materials that contain compensating donors (phosphorus or Thermal Donors) or added Ga acceptors. The data indicate involvement of both substitutional (B_s) and interstitial (B_i) boron atoms in the major recombination centres observed in p-Si. A suggested model ascribes degradation to the presence of a $B_i B_s O$ latent defect inherited from the thermal history in a recombination-inactive atomic configuration. In the presence of excess electrons, this latent defect reconfigures into a recombination-active centre. The defect concentration dependence on the material parameters is reduced, in some special cases, to a proportionality to $p_0 [O]^2$ or to $[B] [O]^2$. The essential feature is an involvement of a fast-diffusing species B_i in the defect. This species can be removed to the boron nano-precipitates thus eliminating the defects responsible for the degradation.

Introduction

Light-induced degradation (LID) of the minority carrier lifetime is a long established effect [1-4] that leads to a significant efficiency reduction of solar cells. In sufficiently pure material, the emerging recombination centres responsible for LID are known to be due to simultaneous presence of boron and oxygen impurities [4]. These recombination centres emerge in the presence of excess minority carriers whatever the source of the carriers, illumination or injection through a junction. Numerous experimental data on LID phenomena have been collected, but often these data seem to be controversial. The present paper is aimed to describe the current understanding of the boron-oxygen lifetime-degrading centres based on the most relevant part of the reported data, mostly for p-type Si. LID in boron-containing n-Si will be discussed in a separate section.

Generation of B-O recombination centres in p-Si

There is no way to deduce the actual concentration M of the B-O recombination centres, and the effective concentration R – a contribution into the recombination rate - is used instead. This is defined as an increment in the reciprocal lifetime: $R = 1/\tau(t) - 1/\tau_0$, where τ_0 is the initial lifetime and $\tau(t)$ refers to the current moment t. This quantity is equal to M multiplied by a certain function [5, 6] of the carrier concentration ratio $x = n/p$ (n refers to electrons, p – to holes). To be proportional to M, the effective concentration R should be taken at some specified value of $x = n/p$ or equivalently for a specified injection level n/p_0 where p_0 is the dark hole concentration (under illumination, p is close to $p_0 + n$, and $n/p_0 = x / (1 - x)$). Most reported data refer to a relatively low injection level, normally $n/p_0 = 0.1$.

An extensive work was done on boron-only doped Si [4] (where p_0 is almost identical to the boron concentration [B]). There are also data on p-Si compensated with phosphorus donors [7-10] or Thermal Donors [11] (when $p_0 < [B]$) and on B + Ga co-doped material [12, 13] (when $p_0 > [B]$). Some general features of the generation kinetics of the B-O recombination defects have been established:

- There are two distinct stages in defect production [4]: a fast one with a time scale of roughly a minute and a slow one with a time scale of hours (if the illumination temperature is close to T_{room}). It can be concluded that two kinds of recombination centres are produced, labelled FRC (fast stage centres) and SRC (slow stage centres). In p-Si, the dominant contribution into the lifetime degradation is by SRC (excepting a special case of a very short illumination).

- At sufficiently high illumination power W, the SRC effective concentration follows a simple exponential kinetics with a final saturation. The rate constant is independent of W and proportional to the squared hole concentration p_0^2 - and neither correlated to the boron concentration [B] or to oxygen concentration [O]. The rate constant is an increasing function of T, of a small activation energy [4] close to 0.47 eV. At a very low W, the generation kinetics is retarded and becomes non-linear. In this regime the rate constant is roughly proportional to W [14, 15].

- The saturated SRC concentration, R_{sat}, in boron-only doped samples, was found [4] to be proportional to [B] [O]^2 and independent of the illumination power W. Only at extremely low W [16], is R_{sat} slightly reduced. For instance, R_{sat} at $W = 0.001$ sun is about 0.7 of the value achieved at $W = 1$ sun.

- In compensated samples R_{sat} was reported [8] to be proportional to p_0 rather than to [B]. This finding is supported by measuring R_{sat} along a crystal compensated with phosphorus [9, 10] in which [B] increases only slightly while p_0 progressively decreases along the crystal length (due to a progressively higher phosphorus concentration). R_{sat} decreases following a change in p_0 rather than a change in [B]. Further experimental support is found by compensating boron with Thermal Donors (TD) generated by 450°C anneal [11]: R_{sat} was reduced due to compensation. This important piece of evidence is discussed in more detail below.

- In contrast to these findings, the data on non-compensated material co-doped with two acceptors, B and Ga [12, 13], show that R_{sat} is proportional to [B] and seemingly independent of $p_0 = $ [B] + [Ga].

- The degraded lifetime is recovered by annealing in the dark at around 180°C [4]. Subsequent illumination at T_{room} leads again to the same degradation. This is a reversible phenomena that can be repeated again and again. The rate constant for the dark recovery was found [17] to be inversely proportional to p_0 (and not correlated to [B]).

The nature of B-O recombination centres

Based on the proportionality of R_{sat} to [B][O]^2 in boron-only doped material, the initially suggested model [4, 18] for SRC formation was an electron-enhanced diffusion of oxygen interstitial dimers O_2 to the substitutional boron atoms B_s; the SRC centres have been thus identified with B_sO_2 defects. A symbol of oxygen is used without a subscript since the oxygen atoms involved are always in the same (interstitial) state. The O_2 species are frozen-in from high T in a concentration [19] proportional to [O]^2. This model is however not consistent with the data:

- The boron concentration [B] is typically around 10^{16} cm^{-3} while the dimeric concentration [O_2] is much lower, around 3×10^{14} cm^{-3}. Hence all [O_2] will be trapped by B_s, and the saturated defect concentration [B_sO_2] will be identical to the initial concentration of [O_2] – and independent of [B].

- The rate constant for SRC formation by trapping of mobile O_2 by boron would include a proportionality to the concentration of traps, that is to the boron concentration [B]. However, as was already mentioned, in compensated p-Si ($p_0 < $ [B]) the rate constant is proportional to p_0^2 and independent of [B].

- The dimeric concentration [O_2] is known [20] to be reduced dramatically by annealing at $T = 350$°C; this is caused by O_2 trapping by monomeric oxygen, into O_3 trimers, while the production rate of new dimers by O + O pairing is negligible at this low T. However the samples subjected to a prolong annealing at 350 or 300°C show the same degradation [21] as the initial (not-annealed) samples. Therefore the free (not bound) dimers do not participate in formation of SRC.

Considering these facts it can be concluded that formation of SRC is not related to any long-range diffusion but rather based on the presence of some latent (recombination-inactive) defects that have been formed in the course of the wafer thermal history and are present before illumination in a

concentration proportional to $[B][O]^2$, in boron-only doped p-Si. In the presence of excess electrons, these centres reconstruct (reconfigure) into another atomic configuration that is recombination-active. This reconstructed centres are manifested as SRC; the initial latent centres will be denoted LCS. One possible reason for electron-induced reconstruction [22] is that the LCS defects are initially in +1 charge state; for n/p exceeding some small threshold value, they are totally recharged into a neutral state. The ground state (the energy minimum) for +1 defect is reached for LCS configuration, but the minimum for a neutral defect is reached for SRC configuration (this situation is known as a defect bistability). In other words, the defect will convert into LCS configuration in the dark (in +1 charge state) but into SRC in the presence of excess electrons. This feature gives a straightforward explanation for the reversible degradation/recovery mentioned above. The observed proportionality of the rate constant for the LCS $\rightarrow$ SRC reconfiguration to p_0^2 indicates that two holes should be temporarily captured to facilitate this process. At low light power W, only a small fraction of LCS is recharged into a neutral state – the state that is ready for reconfiguration. This accounts for a retardation of degradation [14-16] below some threshold value of W. The proportionality of the backward reaction SRC $\rightarrow$ LCS ((lifetime recovery in the dark) to $1/p_0$ [17] indicates that, for the reaction to occur, the SRC should be temporarily recharged by emitting one hole, from +1 to neutral state.

Similar reasons may hold even if the LCS is not +1 charged but neutral or even negative [5]; then recharging will occur for a transient configuration intermediate between LCS and SRC.

What is the chemical composition of the LCS/SRC defect ? The simplest possibility is that it is a B_sO_2 defect frozen-in from some high temperature where it existed in equilibrium with boron atoms and oxygen dimers constituting a small fraction of $[O_2]$. In that case the LCS concentration will have a proper dependence on the boron and oxygen concentrations, $[B][O]^2$. This attribution, however, contradicts the proportionality of R_{sat} to p_0 - rather than to $[B]$ - in compensated p-Si.

Another model for LCS [22] relates this defect to interstitial boron atoms B_i rather than to the substitutional ones, B_s. The B_i species may be produced by self-interstitials ($B_s + I \rightarrow B_i$) while the self-interstitials may be produced by emission from growing oxygen precipitates. It is assumed in this model that most of B_i are precipitated, and the remaining dissolved B_i atoms are in equilibrium with these small (nano-size) precipitates. The B_i atom is known [23] to have +1 charge in p-Si, and dissolution of one B_i atom from a neutral nano-precipitate is accompanied by consumption of one hole. Then the B_i concentration (solubility) is proportional to the hole concentration. This concentration is of an intrinsic value at higher T. Below some temperature (roughly, 350^oC for the net doping of 10^{16} cm^{-3}), the hole concentration becomes equal to the net doping, p_0. If the exchange between B_i and the nano-precipitates is frozen-in at a temperature within the extrinsic temperature range - below 350^oC - then $[B_i]$ will be proportional to p_0. The B_i atoms, at the freezing-in temperature, co-exist in equilibrium with various complexes, in particular with B_iO_2 defects – assumed to dominate over B_i. The frozen-in B_iO_2 defects will then have a concentration proportional to $p_0[O]^2$.

This attribution for LCS/SRC cannot however explain why in B + Ga co-doped material the SRC concentration depends on $[B]$ and not on p_0. Another objection is that a reduction in $[O_2]$ by above-mentioned prolonged annealing at 350^oC [21] does not lead to a proportional reduction in the LCS concentration.

A modified model – to be consistent with the above-listed experimental data - should clearly involve both B_i and B_s species, and should not necessary involve O_2 dimers.

A plausible version of such a model will be now outlined. The central assumption is that the LCS defects are formed due to two different frozen-in defects. One is B_sO; this defect is frozen-in from a relatively high T (like 600^oC, as estimated below), and has a concentration proportional to $[B][O]$. The other frozen-in defect is B_iO, with a concentration proportional to $p_0[O]$ – if it is frozen-in from a relatively low T (below 350^oC). In this model, the oxygen is involved only in its monomeric form O, not as O_2 dimers. The formation of LCS occurs at still lower T, by redistribution of B_i from the initially dominant traps O to the B_s and B_sO traps that are less numerous but have a larger binding

energy. In other words, the initial B_iO defects are gradually replaced, upon lowering T, by B_iB_s and B_iB_sO defects. This can be described as a "pumping" of B_i atoms from O traps to B_s and B_sO traps, through the isolated mobile B_i atoms that exist in equilibrium with B_iO. The next point of the model is that, after B_i redistribution, the dominant state is B_iB_s; its concentration is identical to the initial (frozen-in) concentration of B_iO and thus proportional to $p_0[O]$. The concentration ratio of the minor B_iB_sO centres and the major B_iB_s centres is proportional to the concentration ratio of the B_sO and B_s traps – which is in turn proportional to [O]. Hence

$$[B_iB_sO] = a\,p_0[O]^2\,. \tag{1}$$

This has a proper dependence on p_0 and [O] reported for boron-only doped and compensated samples. Therefore the LCS (future SRC) defect is identified as B_iB_sO. In spite of involvement of only one oxygen atom, this defect has a frozen-in concentration proportional to $[O]^2$. This is due to the two source defects, B_sO and B_iO: each one adds a proportionality to [O].

In B + Ga co-doped material, the B_i atoms can be passed from initial O traps to two major competing traps, B_s and Ga_s. The binding energy of B_i to these two acceptors may be almost the same, especially if this energy is mostly due to a coulombic attraction of a single-positive B_i to a single-negative acceptor. In this case the concentration ratio of B_iB_s and B_iGa_s will be equal to the concentration ratio of the two acceptor traps, [B]/[Ga]. The B_iB_s defect will then have a reduced concentration – compared to the material without Ga - by a fraction of B_iB_s defects among B_iB_s + B_iGa_s which is equal to [B]/([B] + [Ga]). The concentration of B_iB_sO – that are in equilibrium with B_iB_s - is reduced by the same factor:

$$[B_iB_sO] = a\,p_0\,[O]^2\,[B]\,/\,([B] + [Ga])\quad. \tag{2}$$

This is a general expression that is valid (within the present model) for all materials containing both B, Ga and any compensating donors. In the absence of Ga dopant, it is reduced to Eq.(1). In the absence of compensation, when $p_0 = [B] + [Ga]$, it is reduced to

$$[B_iB_sO] = a\,[B]\,[O]^2\,, \tag{3}$$

showing a proportionality to [B], and not to the net doping p_0.

The present modified model – although relatively simple – gives a general explanation for a complicated dependence of R_{sat} (that is, of the frozen-in concentration of LCS = B_iB_sO) on the material parameters [B], [O] and p_0. It also explains why a suppression of O_2 dimers by 350°C anneal has no effect on LID. This is simply because O_2 is not involved at all in the LCS defect.

One general remark should be made at this point. The mobile species that is frozen-in in a concentration proportional to p_0 was assumed to be B_i. However any fast-diffusing interstitial impurity of +1 charge - that exists mostly in a precipitated state - will lead to precisely the same conclusions since a small dissolved component of such an impurity will have a concentration proportional to p_0. Therefore, generally speaking, the symbol B_i in all the expressions should be replaced with a general symbol X_i standing for an unknown interstitial impurity. The attribution of X_i to B_i is preferable only from the point of view of reducing the number of impurities involved in LID to just boron and oxygen.

LID in p-Si compensated with thermal donors

For a further check of the validity of Eq.(1) for compensated material (in the absence of Ga), it is worth considering the effect of compensation of boron-only doped material with Thermal Donors (TD) on LID. An advantage of such an experiment – as compared to compensation with phosphorus- is that the boron concentration [B] has a fixed and precisely known value. The saturated degradation R_{sat} was reported [11] in three reference (not annealed) samples of various resistivity (various [B]), and after annealing these samples at 450°C for 16 and 32 h. It is expected that R_{sat} is somewhat dependent on the cooling rate in a temperature range of defect freezing-in (below 350°C).

The cooling rate is identical for all the annealed samples but it is different for the reference (initial) samples. For this reason only annealed samples are used to plot the dependence of R_{sat} on p_0. If all the samples (including the initial ones) were used, the scatter of points would somewhat increase. The hole concentration p_0 was calculated by the measured resistivity ρ (increased by annealing, due to Thermal Donors), taking into account the effect of double-charged TDs on the hole mobility: the TD contribution into the carrier scattering is 4 times larger than that of single donors of the same concentration. The TD concentration is related to [B] and p_0 by $p_0 = [B] - 2$ [TD]. Using in computations p_0 as an independent variable, first the TD concentration, then the mobility, and finally the resistivity ρ is found; this procedure gives $ρ(p_0)$ and hence a calibration curve $p_0(ρ)$ for any specified [B]. The dependence of R_{sat} on p_0 is shown in Fig.1; an expected proportionality is evident, within a scatter.

More data on LID dependence on p_0 and [B]

Recently an extended data set on LID in various materials co-doped with B, Ga and P was presented [13]. The authors concluded that R_{sat} correlates with [B] rather than with p_0. A more attentive look at these data shows however that this conclusion is not justified, considering a very strong scatter of the points. We now re-plot these data using the reported R_{sat} values [13] normalized by [B] [O]^2 combination. It is more convenient to use a reciprocal variable $Y = [B] [O]^2 /$
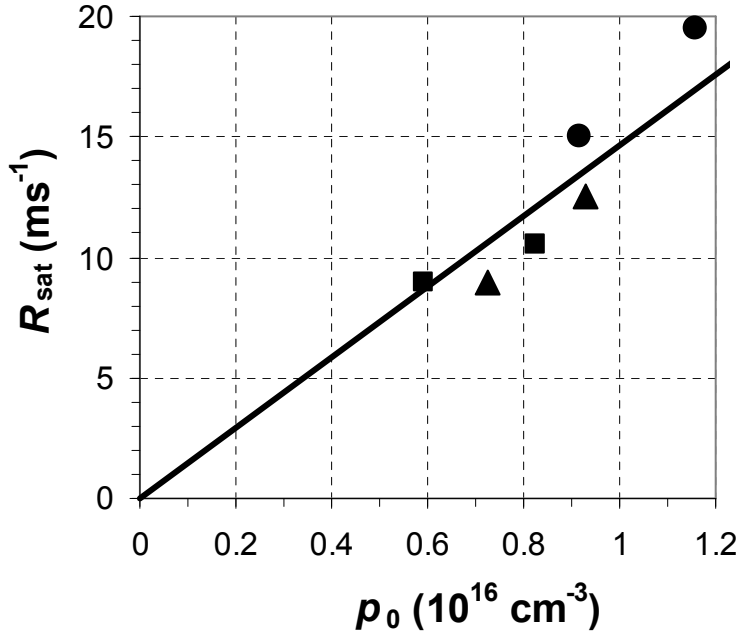

Fig.1 Saturated effective concentration R_{sat} of SRC in boron-doped Si compensated with Thermal Donors (after ref. [11]). Symbols (circles, triangle and squares) correspond to three kinds of starting material.
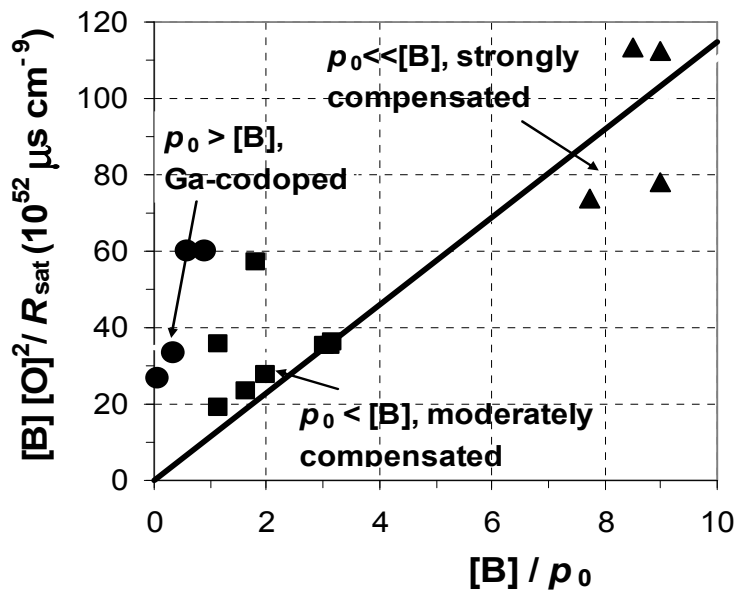

Fig.2 Re-plotted data on the saturated effective concentration R_{sat} of SRC in Si samples co-doped with B, P and Ga (after ref. [13]).

R_{sat} plotted against $X = [B] / p_0$. By Eq.(1) and (3), Y should be independent of X for B+Ga non-compensated samples ($X < 1$) but proportional to X for compensated samples without Ga ($X > 1$). The samples that contain all the three dopants in comparable concentrations, would not strictly follow this rule, which adds somewhat to a scatter. The data re-plotted in such a manner (Fig.2) indicate indeed – in spite of a very strong scatter – the expected two ranges: that of a smaller X where the points should lie on a plateau, and of a larger X where they should lie on a line drawn through the coordinate system zero point.

The frozen-in concentration of B_sO

The B_sO defect is an important component of LCS; its concentration evolves, during crystal (or wafer) cooling by an equation

$$d[B_sO]/dt = 4 \pi r D ([O][B] - K[B_sO]) \quad , \tag{4}$$

where D is the oxygen diffusivity, r is the capture radius (of a conventional value 0.5 nm) and K is the equilibrium dissociation constant of the B_sO defect expressed through the binding energy E

$$K = q \exp(-E/kT) \quad . \tag{5}$$

The prefactor q in this expression is on the order of the lattice site density (5×10^{22} cm^{-3}). At higher T, the dissociation rate constant $4 \pi r D K$ is large, and an equilibrium ratio between the reacting species is maintained: $[O][B]/[B_sO] = K$. At lower T, the rates of both forward (association) and backward (dissociation) reaction becomes negligible.

The kinetic equation (4) is essentially the same as that for formation of O_2 dimers in a cooling sample [22]: the forward reaction is controlled by the monomeric oxygen diffusivity D, while the backward reaction depends on the binding energy of the produced defect, B_sO or O_2. The kinetic equation (4), just as that for O_2 production, can be written in a general form
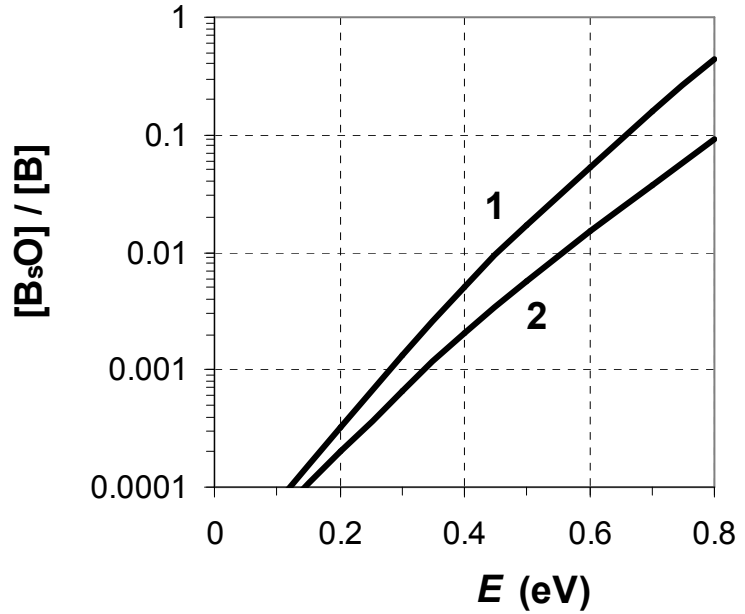

Fig.3 Calculated fraction of boron bound into B_sO during cooling, in dependence of the assumed binding energy E. The curves 1 and 2 correspond to the cooling rate of 0.01 and 10 K/s, respectively.

$$dN/dt = A \exp(-E_A/kT) - B \exp(-E_B/kT) N \quad . \tag{6}$$

Here N is the concentration of produced defects (whether O_2 or B_sO), the activation energy E_A is 2.53 eV (migration energy of monomeric oxygen) while $E_B = E_A + E$. The values of the two prefactors, A and B, are evident by comparing Eqs.(6) and (4).

The freezing-in problem for the Eq. (6) is solved analytically [22]; the frozen-in concentration is

$$N_{frozen} = (A/B) [B kT_f^2/(g E_B)]^\varepsilon \quad , \tag{7}$$

omitting a factor [22] close to 1. In Eq.(7), $g = -dT/dt$ is the cooling rate, and the exponent $\varepsilon = E/E_B$. The temperature T_f is the effective freezing-in temperature defined by equation $kT^2/(g E) = B \exp(-E_B/kT)$. Due to a large value of E_B (larger than 2.53 eV), the freezing-in temperature is only slightly dependent on the cooling rate g or on the binding energy E; a representative value, for $g = 1$ K/s and $E = 0.5$ eV is $T_f = 600^\circ$C.

The frozen-in concentration ratio $N/[B] = [B_sO]/[B]$, calculated by Eq.(7) for $[O] = 7 \times 10^{17}$ cm^{-3}, is shown in Fig.3 in dependence of the assumed binding energy E, and for two cooling rates: 0.01 K/s (representative for crystals) and 10 K/s (representative for quenched wafers). The calculated ratio, should be well smaller than 1, to ensure the required proportionality of N_{frozen} to $[B][O]$. Neither should it be too small: in that case the SRC concentration would be too low to give an appreciable contribution into the recombination rate. A range of E satisfying these limitations is roughly between 0.3 and 0.8 eV.

The sensitivity of N_{frozen} to the cooling rate g is determined, according to Eq.(7), by the parameter $\varepsilon = E / E_B$. For a range of E mentioned above, the exponent ε is 0.1 to 0.25. This small value means that the power-type dependence of N_{frozen} on g is relatively weak. An increase in g by a factor of 1000 leads to a reduction in N_{frozen} only by a factor of 2 to 5, depending on assumed E within the adopted range.

The frozen-in concentration of B_iO can be calculated in a similar way, but now the problem involves, beside the size and density of the nanoprecipitates, several unknown functions of T: the solubility and diffusivity of B_i (or of an X_i species) and the equilibrium dissociation constant of B_iO (or of X_iO). With so many unknown parameters, it is hardly possible to judge of the frozen-in concentration of B_iO in dependence of the cooling rate.

LID in boron-containing n-type silicon

Contrary to p-Si, the effective concentration $R(t)$ in n-Si shows a complicated non-exponential dependence on the illumination time [5]. The reason for this is simple: by the data on p-Si, the rate constant is proportional to the squared hole concentration p^2 (and independent of the injected electron concentration n unless n is very low). The same rule should hold for n-Si, where the holes are minority carriers, and thus LID becomes faster at increased light power [5]. For a fixed light power, the hole concentration p depends on the current concentration of the lifetime-degrading centres. Hence p decreases with time upon generation of the lifetime-degrading centres, and the degradation is thus retarded with time. Due to a lower value of p, as compared with the p-Si material, the time scale for production of both FRC and SRC defects is strongly increased in comparison to p-Si. The observed time scale is well consistent [5] with that expected for FRC while the expected time scale for SRC is so large that this kind of degrading centres can not emerge within an illumination time used in the experiments, even if the corresponding latent centres LCS were present. It then follows [5] that the LID phenomenon in boron-containing n-Si is due to FRC and not SRC. The saturated defect concentration R_{sat} shows no correlation with the majority carrier concentration (here, n_0) that increases along the crystal due to an increasing phosphorus concentration (while the boron concentration is increasing only slightly since the boron segregation coefficient is close to 1). In boron-only doped p-Si [4], the value R_{sat} for FRC is proportional to $[B][O]^2$ (the same dependence as for SRC). It can be concluded that this dependence is indeed on $[B]$ and not on the carrier concentration. This means that the latent defect LCF - responsible for FRC production under illumination - is, most likely, just B_sO_2.

Permanent recovery of degraded lifetime

It was discovered [24, 25] that if a sample is illuminated at a slightly elevated temperature (around 180^oC) then the lifetime is first degraded (very fast, following an expected temperature dependence of the degradation rate constant) but then starts a recovery which takes a much longer time. The finally recovered lifetime is not degraded by subsequent illumination at T_{room} - hence the term "permanent recovery". This is in contrast to a recovery observed in the same range of elevated T but in the dark, when the recovered lifetime is degraded again under illumination. It is likely that a normal degradation observed at T_{room} is also followed by a permanent recovery but, in this case, it takes an enormously long time. The elevated temperature is necessary only to accelerate the process.

An important feature of the permanent recovery is that the time scale is strongly scattered [24-27], from some minutes to many hours, in samples with the same $[B]$, $[O]$ and p_0. A plausible reason for the permanent recovery is disappearance of B_i-containing defects (SRC = B_iB_sO and B_iB_s) by losing the fast-diffusing component B_i (generally, X_i) to the nano-precipitates - and not just by reconfiguration into an inactive state like in case of the dark recovery. In other words, in the presence of excess electrons, a small fraction of free B_i species - co-existing with the major trapped states B_iB_sO and B_iB_s – is strongly increased above the solubility. It leads to an irreversible loss of

B_i to the nano-precipitates. The dominant trap for B_i in the dark was assumed to be B_s. The situation may however change under illumination, where the dominant trap may be different: B_sO or even some other defect like B_sO_2. Whatever this dominant trap is, we denote its concentration by N_t, and the concentration of trapped B_i species – by $[B_i]^*$. The relation between the species concentration may be similar to a mass action law although applied to non-equilibrium conditions – due to the presence of excess electrons: $[B_i] N_t/ [B_i]^* = K^*$ where the effective dissociation constant K^* may depend on n. For a diffusion-limited consumption of free B_i species by the precipitates, the resulting reduction in the total concentration of free and trapped B_i is described by the equation:

$$d([B_i]^* + [B_i])/dt = - 4 \pi D_i R_p N_p [B_i] , \tag{8}$$

where D_i is the B_i diffusivity, N_p is the precipitate density and R_p is their average radius. Taking into account a mass action law relating $[B_i]$ and $[B_i]^*$, with $[B_i] \ll [B_i]^*$, the rate constant γ for the permanent recovery is expressed from Eq.(8) as

$$\gamma = 4 \pi D_i R_p N_p K^* / N_t . \tag{9}$$

The nano-precipitate parameters, N_p and R_p, may significantly differ for various samples (depending on the thermal prehistory) which accounts for a wide interval of the observed rate constant γ. This rate constant also correlates with boron and oxygen concentrations, through the trap concentration N_t. It was reported [26, 27] that γ is smaller in samples of a higher [B] and [O] indicating that the major trap for B_i under illumination involves both boron and oxygen impurities. This major trap is probably B_sO or B_sO_2.

This model for the permanent recovery is further supported by the observed reduction in the rate constant in samples annealed at 450°C or at higher T [28]. Such an anneal should lead to Ostwald ripening of nano-precipitates: the smaller precipitates dissolve and disappear while the larger ones grow collecting the B_i species lost by the smaller ones. Accordingly, the density N_p decreases while the average radius R_p increases. The parameter combination of interest, $R_p N_p$ in Eq.(9), decreases. The predicted dependence of $(R_p N_p)^{-3/2}$ on the anneal time t is linear [28] which means, by Eq.(9), that also $\gamma^{-3/2}$ should be a linear function of t. This expected dependence is well obeyed by the measured rate constant for the permanent recovery [28].

This model relates the permanent recovery exclusively to the sample bulk properties - in the first place, the nano-precipitate parameters N_p and R_p. It was recently reported [29] that the permanent recovery depends on the properties of the hydrogen-containing surface layer (deposited with a purpose to diminish the surface recombination). This observation indicates a possible involvement of hydrogen in the permanent recovery. The basic mechanism may be still the same: B_i loss to the nano-precipitates, with a rate constant defined by the same Eq.(9). But the concentration N_t of the available traps may be diminished by the reaction of these traps with hydrogen.

Capture of electrons and holes by SRC

Lifetime controlled by a single-level recombination centre, in dependence of the excess carrier concentration, is described by the Shockley-Read-Hall (SRH) formula [30, 31]. In case of a deep level, the thermal emission of carriers can be neglected, and only sequential capture of electrons and of holes controls the lifetime. For SRC centre in p-Si:

$$\tau_{src} = (\alpha_n M)^{-1} (1 + Q n/p) , \tag{10}$$

where M is the SRC concentration and $Q = \alpha_n/\alpha_p$ is the ratio of the two capture coefficients, α_n (for electrons, by the initial centre) and α_p (for holes, by the recharged centre). The reported SRC-controlled lifetime well corresponds [4, 16] to the expected linear dependence of τ_{src} on $x = n/p$, and the deduced capture ratio Q is about 14 (a similar linear dependence is found also for FRC, with Q close to 65). Within a previous attribution of SRC to B_iO_2 defect (single-positive in the dark) a large value of Q was natural since the electrons are then captured by attractive +1 charged centre while the holes are captured by neutral (recharged) centre. However, within the modified model of the present paper, the SRC is identified as a reconfigured B_iB_sO defect that, most likely, is neutral in the dark, and has -1 charge for a recharged state (upon capturing an electron).

In this case it is a hole that is captured by an attractive centre, and one would expect a small value for Q. A possible explanation for a large observed Q is discussed below.

The B_iB_sO defect is treated as a bistable one, reconfiguring from LCS into SRC in the presence of excess electrons. The energy barrier for this reconfiguration is relatively large, and the reconfiguration (leading to the lifetime degradation) takes a long time, many hours. Now the SRC itself can exist not in a unique atomic configuration but have different ground-state configurations for the initial (neutral) charge state and for the recharged (single-negative) state. A tentative energy diagram for SRC, suitable for accounting for a large Q, is shown in Fig.4. Upon capturing an electron (a thick downward arrow in Fig.1) the SRC finds itself in an excited state separated from the ground state by a barrier that is assumed to be low. Then the transition from the excited to the ground state is almost instantaneous, and the two states coexist in an equilibrium ratio. The fraction of the excited state, denoted by f and assumed to be $\ll 1$, is about $\exp(-\Delta E /kT)$
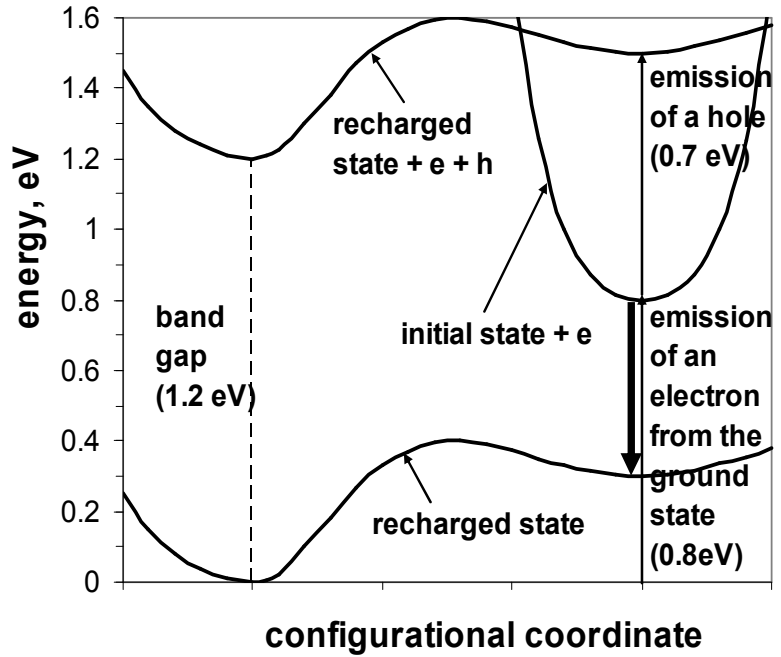

Fig.4 Tentative energy diagram for a bistable recombination centre (SRC). The recharged centre (with one added electron) has two minima: the excited state (the right minimum) and the ground state (the left minimum). The thick downward arrow indicates a capture of an electron by the initial state; the energy level for this transition is 0.5 eV below the conduction band.

where ΔE is the energy difference between the excited and ground states (in an example of Fig.4 this energy is equal to 0.3 eV).

The concentration of the centre in the initial charge state is denoted by m_1, and that in the recharged ground state – by m_2; the concentration in the recharged excited state is $m_2^* = f m_2$. The balance equation for m_1 is precisely the same as in SRH statistics:

$$dm_1/dt = - \alpha_n\, n\, m_1 + \alpha_p^*\, p\, m_2^* = 0 , \qquad (11)$$

where α_p^* is the hole capture coefficient by the excited state. The only difference from the SRH case is that m_2^* is now a small fraction of recharged centres, and it should be expressed through the ground state concentration m_2. The total concentration of the centre in all charge states is $M = m_1 + m_2$. The product $\alpha_p^* m_2^*$ in Eq.(11) is thus expressed as $f \alpha_p^* m_2$, and the recombination statistics for a bistable recombination centre becomes identical to the SRC case, if one uses, instead of the hole capture coefficient α_p, the effective value $f \alpha_p^*$. The Eq.(10) for the lifetime is then still applicable but the capture ratio Q should be treated as the effective value equal to

$$Q = \alpha_n/(f \alpha_p^*) . \qquad (12)$$

The actual ratio of the electron and hole capture coefficients, α_n/α_p^*, may be small due to hole capture by an attractive centre, but the effective capture ratio Q in Eq.(10) – now defined by Eq.(12) - may be still large due to a small fraction f of the recharged excited state.

An assumed bistability of SRC also accounts for an old mystery: why the lifetime-degrading SRC centres were never detected by DLTS [32]. The SRC defects exist either in the initial charge state or in the recharged ground state. For the initial charge state, the defect can emit a hole but this will not

be detected by DLTS if the emission energy is larger than a half of the gap (in Fig.4, this emission energy - indicated by a thin upward arrow - is 0.7 eV). For a recharged state, the defect can emit an electron, but for that it should first go to the excited configuration. The total emission energy is indicated in Fig.4 by a thin upward arrow. The sum of the two emission energies, for emitting an electron and emitting a hole, is equal to the band-gap plus the excitation energy ΔE (in the present example, this sum is 1.5 eV). Due to the excitation involved in the hole emission, each emission energy can be larger than a half-gap which prevents detection of the centre by DLTS, in either of the two charge states. An emission signal could be probably detected only if the temperature range used in DLTS is well above T_{room}.

Summary

The basic experimental facts on the light-induced lifetime degradation – related to the simultaneous presence of boron and oxygen impurities - can be understood within a model that can be outlined as follows:

- Already before illumination, there are some boron-oxygen latent (recombination-inactive) defects inherited from the sample thermal history, with a concentration that depends on the impurity concentrations (and, slightly, on the cooling rate). More strictly, there are at least two such latent defects responsible for production of fast-stage recombination centres (FRC) and slow-stage recombination centres (SRC).
- In the presence of excess carriers these latent defects reconstruct into recombination-active atomic configuration which is manifested as a lifetime degradation.
- A plausible chemical composition of the defect responsible for SRC, the major lifetime-degrading centres in p-Si is B_iB_sO – involving both an interstitial (B_i) and substitutional (B_s) boron atoms and an interstitial oxygen atom O.
- This latent defect is produced in the course of crystal (or wafer) cooling. First the B_sO defects are formed at a relatively high T like 600°C; their frozen-in concentration is proportional to the concentration product of the constituents, [B] [O].
- The interstitial boron atoms B_i are produced by a kicking-out reaction of boron with self-interstitials (emitted by oxide precipitates). These mobile species form numerous tiny precipitates (nano-precipitates). The remaining dissolved B_i atoms exist in equilibrium with the nano-precipitates, and have a concentration (solubility) proportional to the hole concentration, due to +1 charge of B_i. The same behaviour will be exhibited by any interstitial impurity of +1 charge, and the symbol B_i should be, generally speaking, replaced by X_i – standing for this impurity.
- The B_i species form B_iO defects, that exist in equilibrium with B_i and O and have a concentration proportional to [B_i] [O]. If these defects are frozen-in from a relatively low T (below 350°C, when the material has extrinsic conductivity) then the frozen-in concentration of B_iO is proportional to p_0 [O] where p_0 is the hole concentration controlled by the net doping.
- At still lower T (not yet specified) the B_i atoms, initially trapped by O, are passed to less numerous but more efficient traps B_s and B_sO. In other words, the B_i-containing defects will be mostly B_iB_s and B_iB_sO, of the total concentration identical to that of the previously formed B_iO defects. In this new community, B_iB_s is the dominant defect while a fraction of B_iB_sO is small and proportional to [B_sO]/[B_s] and thus to [O]. Accordingly, the frozen-in concentration of B_iB_sO is proportional to p_0 $[O]^2$. It has a proper (experimentally-proven) square dependence on the oxygen concentration although the defect involves only one oxygen atom (not a dimer as was thought in the past). It also shows a proportionality to the net doping p_0 rather than to [B] – again in accordance with the data for compensated p-Si.
- A special case is realized in non-compensated p-Si co-doped with B and Ga. In this case the B_i atoms are distributed between two major traps, B_s and Ga_s. The B_iB_s concentration is then reduced by a factor [B] / ([B]+[Ga]) = [B] / p_0. The frozen-in concentration of B_iB_sO – proportional to that of B_iB_s - is reduced by the same factor and becomes proportional to [B] $[O]^2$.

- The degradation kinetics, being essentially a carrier-affected reconfiguration of the latent defects – is dependent only on the carrier concentrations and independent of the impurity concentrations. In many cases the kinetics is linear but sometimes it can be non-linear, when the relevant carrier concentration changes with time, due to a time-dependent concentration of the recombination centres.

- At elevated T, and in the presence of excess carriers, the B_i species are released from the traps in a concentration far exceeding the solubility. It results in an irreversible loss of B_i to the nano-precipitates and accordingly to disappearance of all B_i-containing defects including B_iB_sO. This is a plausible reason for a so called permanent recovery of a degraded lifetime achieved by illumination at elevated T.

- In boron-containing n-Si the degradation of the hole lifetime is due to production of FRC – the same recombination centres as those found in the early stage of illumination in p-Si. The chemical composition of the latent defects for FRC is likely to be B_sO_2, not involving any fast-diffusing species.

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