

**HOW TO PROPERLY ASSESS
BORON-OXYGEN RELATED DEGRADATION IN CRYSTALLINE SILICON**

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ABSTRACT: Boron-Oxygen related light induced degradation (BO-LID) may seriously limit the efficiency of silicon solar cells. It is therefore essential to assess its impact correctly. Within this contribution it is shown by means of simulations how temperature and doping level as well as injection level influence the degradation behavior and on which time scale degradation occurs. It is furthermore shown how regeneration may influence BO-LID results leading to spoiled interpretations. A suggestion for appropriate degradation conditions is given.

Keywords: Degradation, BO-LID, Simulation

1 INTRODUCTION

The efficiency potential of silicon solar cells depends among other things on the lifetime of excess charge carriers in the base of the cell. It is known for quite a while that this lifetime is subject to light induced degradation in boron-doped silicon contaminated with oxygen [1-4] leading to noticeably reduced lifetimes [5]. As typical single silicon crystals grown by Czochralski's (Cz) method contain more oxygen than typical multicrystalline (mc) ingots, this effect mainly affects Cz-Si but is detectable in mc-Si as well.

Even though the general impact of the BO-LID effect is widely known, there seems to exist confusion on the duration required for complete degradation under certain degradation conditions. Furthermore, if degradation is done at elevated temperatures, be it intentionally or not, e.g. in order to accelerate the process, it may happen that the sample not only degrades, but also begins to regenerate as well.

Within this contribution, it will be shown, based on theoretical calculations, under which combination of light intensity, temperature and duration degradation should be performed and what happens, if these entities are varied.

2 THE THEORY BEHIND BO-LID (IN PARTS)

To the current state of knowledge, the BO related defect may appear in at least three different defect states: the recombination inactive but instable annealed state A,

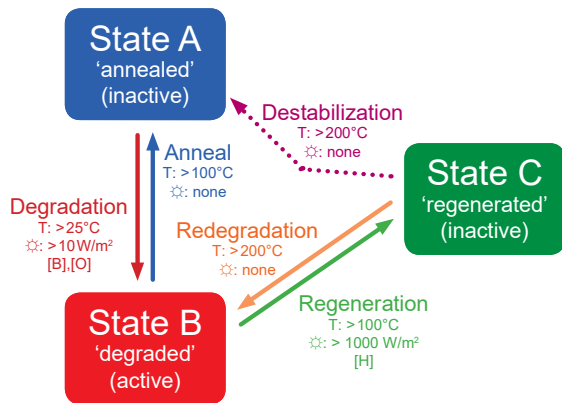


Figure 1: Sketch of the 3-state model of the defect responsible for BO-LID including experimental conditions for which the different reaction paths are active (after [2,3]).

the recombination active metastable degraded state B, and the recombination inactive stable regenerated state C [6,7] which is hardly distinguishable from the annealed state A. The different defect states may convert into each other via reaction paths, e.g. from A to B via the degradation reaction $A \rightarrow B$. The mathematical approach presented in [7] is used within the CASSANDRA framework [8] in the following to describe and simulate the defect pool.

2.1 Reaction rates

All reactions seem to be describable by an Arrhenius-type temperature dependence (thermally activated) following the formula

$$\kappa_{ij}(T, p_0, \Delta n) = \kappa_{ij}^*(p_0, \Delta n) \cdot \exp\left(-\frac{E_{ij}}{k_B T}\right) \quad (1)$$

with κ_{ij}^* being the specific pre-exponential factor and E_{ij} the specific activation energy of the respective reactions between state i and j ($i, j = A, B, C$).

To the current state of knowledge, the anneal reaction rate κ_{BA} is believed to only depend on temperature with activation energy $E_{BA} = 1.32 \text{ eV}$ and trial frequency $\kappa_{BA}^* = 7.4 \times 10^{12} \text{ s}^{-1}$ [4] determining the reaction rate.

The degradation reaction rate κ_{AB} (of the slow forming defect) features more complex dependencies. On the one hand it is believed to follow an Arrhenius-type behavior with activation energy between 0.46 and 0.48 eV [4].

In earlier investigations from Bothe [6] and others the trial frequency was found to depend quadratically on the boron content and not to react to illumination intensities above $\sim 1/100$ suns [9]. However, later investigations with compensated material revealed that it only correlates with the boron content as the hole concentration equaled the boron content, but hole concentration is the actual driving force. Hence, as Kim et al. [10] pointed out, degradation does indeed depend on light intensity, but it becomes only observable if the generated excess carrier density becomes high compared to the doping level.

Therefore, the question is, under which circumstances excess hole concentration matters. Under the assumption of excess electron carrier lifetime being that high that diffusion length is bigger than cell thickness, excess carrier concentration may be estimated according to the equation

$$n \cdot p = (n_0 + \Delta n) \cdot (p_0 + \Delta p) = n_i^2 \cdot \exp\left(\frac{qV}{k_B T}\right) \quad (2)$$

with p_0 and $n_0 = n_i^2/p_0$ being the carrier concentrations in dark thermal equilibrium, Δn and Δp the excess carrier density or injection level (neutrality demands for $\Delta n = \Delta p$), n_i the intrinsic carrier concentration, V the voltage and $q/k_B T$ the thermal equivalent voltage. The degrading cell's voltage is typically left floating, meaning $V = V_{oc}$, however the equation remains valid for any voltage. Here the situation becomes complicated, because V_{oc} depends not only on degradation conditions (intensity and temperature) and doping level p_0 but also on other parameters like emitter saturation current and rear surface recombination velocity.

Table I shows an exemplary comparison of a 1 and 3 Ωcm (high performance PERC-type) solar cell applying strong and weak illumination. As can be seen, strong illumination should have a strong influence especially on weakly doped material. However, as will be discussed later on, applying weak illumination around 0.1 suns yields no significant acceleration especially taking into account that BO-LID (and its dynamic) is most relevant on higher doped material such as 1 Ωcm anyway.

Table I: Comparison of different resistivity base material applying strong and weak illumination

ρ [Ωcm]	1		3	
p_0 [10^{15}cm^{-3}]	15		4.7	
ϕ [suns]	1	$1/10$	1	$1/10$
V_{oc} [mV]	670	611	665	606
Δp [10^{15}cm^{-3}]	1.3	0.14	2.4	0.34
p/p_0	+9%	+1%	+50%	+7%
$\kappa_{AB}(p)/\kappa_{AB}(p_0)$	+18%	+2%	+130%	+15%

2.2 Temporal dynamics in the 2-state model

Only taking the annealed state and the degraded state of the defect in Fig. 1 into account and ignoring the presence of the fast forming defect (or stage) or in other words assuming that only the slow forming defect (or stage [11]) is relevant in the long run, the defect kinetic may be described by a system of coupled differential rate equations as described in [7].

$$\frac{d}{dt} \begin{pmatrix} N_A \\ N_B \end{pmatrix} = \begin{pmatrix} -\kappa_{AB} & +\kappa_{BA} \\ +\kappa_{AB} & -\kappa_{BA} \end{pmatrix} \begin{pmatrix} N_A \\ N_B \end{pmatrix} \quad (3)$$

Here (N_A, N_B) with $N_A + N_B = 1$ represents the normalized defect density or occupation of the individual defect states in the defect pool. $(\kappa_{AB}, \kappa_{BA})$ are the reaction rates converting the defect states into each other. If the reaction rates are treated as constants, the system has the following solution for the degraded state N_B

$$N_B(t) = \frac{\kappa_{AB}}{\kappa_{AB} + \kappa_{BA}} \cdot \left[1 - \left(N_{A0} - \frac{\kappa_{BA}}{\kappa_{AB}} N_{B0} \right) \cdot e^{-\lambda t} \right] \quad (4)$$

with (N_{A0}, N_{B0}) being the occupation at $t = 0$. The system evolves towards equilibrium (degradation is nothing else than a relaxation of a non-equilibrated system) in an exponentially saturating way with the effective rate constant $\lambda = \kappa_{AB} + \kappa_{BA}$. The rates are shown in Fig. 2 for 1 Ωcm and 3 Ωcm under the assumption of $p = p_0$, meaning low intensity illumination. As can be seen, κ_{AB} exceeds κ_{BA} by far below 100°C and thus κ_{BA} does not contribute significantly to the effective rate constant λ . Note that stronger illumination will enhance κ_{AB} (3 Ωcm) more than κ_{AB} (1 Ωcm) narrowing the gap between red and green.

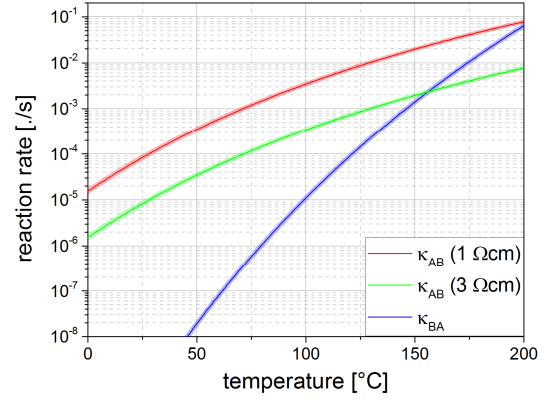


Figure 2: Reaction rates of anneal κ_{BA} and degradation κ_{AB} for 1 Ωcm and 3 Ωcm under the assumption $p = p_0$ (low intensity) including uncertainty (colored area).

3. BO-LID IN THE 2-STATE MODEL

3.1 Long-term equilibrium versus temperature

Long-term occupation of states is given by the pre-factor in Eq. 3 and depends on the reaction rates. Again under the assumption of $p = p_0$, meaning low intensity illumination, the occupation of states for 1 and 3 Ωcm is shown in Fig. 3. The temperature at which κ_{AB} equals κ_{BA} corresponds to the crossover of the occupation of degraded and annealed state. In general, the degraded state is the favored state up to a certain ‘threshold’ temperature setting an upper temperature limit within a degradation treatment. Threshold temperature depends on the extent of BO-LID that should still be achievable in the treatment. E.g., temperature cannot exceed $\sim 107^\circ\text{C}$ if at least 95% degradation in 3 Ωcm material is desired.

However, two effects were ignored in the above calculations: (a) $p = p_0 + \Delta p$ exceeds p_0 and thus $\kappa_{AB}(p)$ exceeds $\kappa_{AB}(p_0)$ especially for high resistivity material and higher illumination intensity. In consequence, the degraded state remains favored even at higher temperatures and the upper limit of applied temperature increases. (b) The assumption of constant reaction rates does not hold if voltage drops during the degradation treatment. For low resistivity material, where Δp is even under 1 sun illumination almost negligible to p_0 , the degradation rate κ_{AB} is almost constant. For high resistivity material, where Δp is comparable to p_0 , the degradation rate κ_{AB} varies noticeably as Δp drops with voltage. For long term equilibrium, the degraded voltage is relevant.

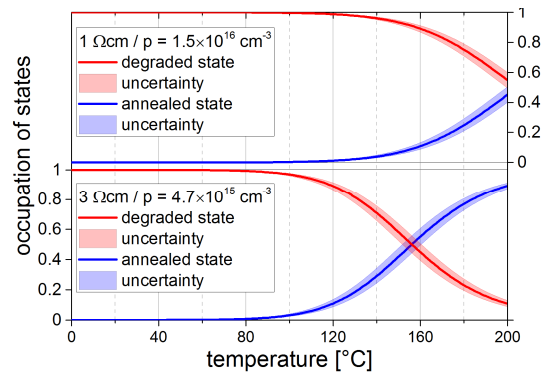


Figure 3: Long-term equilibrium occupation of states resulting from the reaction rates shown in Fig. 2 including uncertainty.

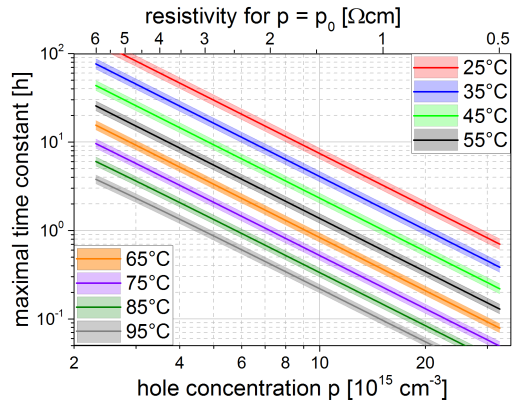


Figure 4: Degradation time constant in dependence of hole concentration p and applied temperature. For low intensity illumination, hole concentration p can be approximated by p_0 and thus resistivity. However, p always exceeds p_0 and thus the time constant t_0 given here is in respect thereof only an upper limit.

3.2 Needed duration for BO-LID

The expectable duration required for complete degradation till equilibrium scales with effective rate constant λ (from Eq. 4) defining a time constant $t_0 = \lambda^{-1}$ which is depicted in Fig. 4. However, it should be noted that interrupting the degradation treatment at t_0 will not result in complete degradation as the exponential function then has only decayed to $e^{-1} \approx 37\%$. Some durations for characteristic completeness are summarized in Table II.

For example, $1.5 \Omega\text{cm}$ ($p_0 \approx 10^{16} \text{ cm}^{-3}$) materials degrade at 25°C with $t_0 \approx 7.3 \text{ h}$ and thus degradation requires $\sim 22 \text{ h}$ ($3 \cdot t_0$) for $N_B(t) = 95\%$ and $\sim 34 \text{ h}$ ($4.6 \cdot t_0$) for $N_B(t) = 99\%$. Increasing temperature to 45°C reduces t_0 to $\sim 2.3 \text{ h}$ thus degradation would take $\sim 7 \text{ h}$ for $N_B(t) = 95\%$ and $\sim 11 \text{ h}$ for $N_B(t) = 99\%$.

Table II: Durations needed for a specific degree of completeness of BO-LID

$N_B(t)$	63%	90%	95%	99%
t/t_0	1.0	2.3	3.0	4.6

4. BO-LID IN THE 3-STATE MODEL

So far, degrading properly was only a matter of keeping $\kappa_{AB} > \kappa_{BA}$ and waiting long enough. And with respect to Fig. 3 and Fig. 4, the duration of BO-LID should be reducible by raising temperature to, e.g., 100°C even for $3 \Omega\text{cm}$ material without compromising the achievable extent of degradation in long-term equilibrium too much.

However, there exists third, ‘regenerated’ defect state (see Fig. 1) which is accessible from the degraded state via the regeneration reaction. The regenerated state is recombination inactive and therefore not directly distinguishable from the annealed state.

Unfortunately, the regenerated state is the preferred defect state under degradation conditions; therefore Fig. 3 is, strictly speaking, only valid for vanishing regeneration reaction rate κ_{BC} . The regeneration rate κ_{BC} does not only depend on temperature [6,7], but also on injection [6,7,12], providing the possibility to intentionally manipulate this reaction. Herguth [6,7] and Wilking [12] have shown that regeneration rate κ_{BC} seems to scale more than linear with injection level thus changing

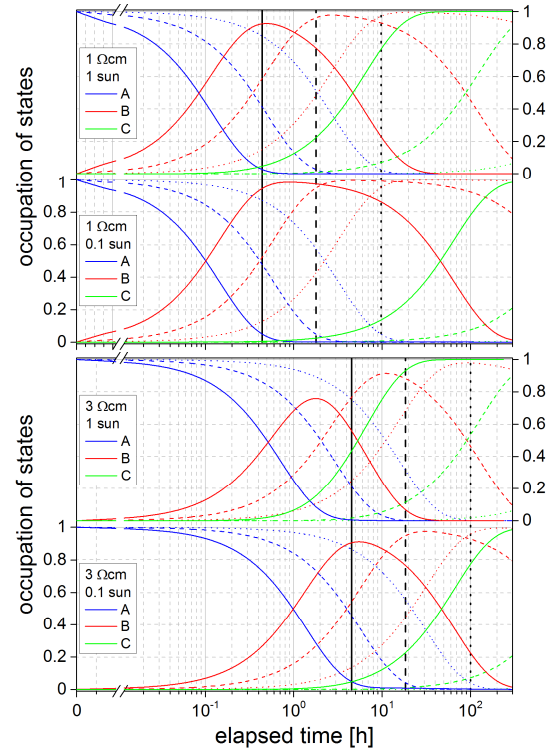


Figure 5: Time resolved evolution of the occupation of states in the defect pool including the regeneration reaction for $1 \Omega\text{cm}$ (top) and $3 \Omega\text{cm}$ (bottom) material. Each graph includes strong (1 sun) and weak (0.1 suns) intensity conditions. Different line styles represent different temperatures: full 85°C , dashed 55°C , dotted 25°C . The black lines mark $3 \cdot t_0$ where 95% completeness would be expected (see Table II).

illumination intensity by a factor of 10 will change the regeneration rate κ_{BC} by at least a factor of 10. In contrast, degradation rate κ_{AB} is for higher doped material (like $1 \Omega\text{cm}$) virtually constant with respect to this strong change in illumination intensity (see Table I) and weakly reacting for lower doped materials.

Fig. 5 depicts the temporal evolution of the defect pool according to the complete mathematical approach in [7] (computed with CASSANDRA [8]) for 1 and $3 \Omega\text{cm}$ material for relatively strong (1 sun) and weak (0.1 suns) illumination conditions as well as for different treatment temperatures (25, 55, 85°C) assuming a rather high regeneration rate κ_{BC} (as found for well hydrogenated lifetime samples and PERC-type cells) and $\kappa_{BC}(1 \text{ sun}) = 10 \cdot \kappa_{BC}(0.1 \text{ suns})$. First thing to note is that the degraded state B (red) starts to fill and the annealed state A (blue) starts to empty in the beginning; the sample degrades. The second thing to note is that the degraded state does not reach unity any more, but features a more or less sharp maximum. In the long run the defect pool’s preference turns to the regenerated state C (green). However, if the degraded state does no longer reach unity after a certain waiting time, interpretation becomes harder. This shall be illustrated in a virtual experiment.

A first experimenter degrades $3 \Omega\text{cm}$ (Fig. 5 bottom) at 25°C and 1 sun (dotted red line) and waits $3 \cdot t_0$ ($3 \cdot 33 \text{ h}$, dotted black vertical line) according to Fig. 4. He then reports 98% of full degradation amplitude.

Another experimenter with the same sample wants to accelerate the degradation, chooses therefore 85°C and 1 sun (full red line) and a waiting time of $3 \cdot t_0$ ($3 \cdot 1.5 \text{ h}$,

full black vertical line) ignoring an injection level enhanced degradation rate κ_{AB} . He reports then only 56% of full degradation amplitude. Even if he would have monitored the temporal evolution, and would report the maximal degradation after 1.8 h, he would only report 76% of full degradation amplitude.

If the second experimenter would have used 0.1 suns illumination instead still waiting $3 \cdot t_0$ (3·1.5 h, full black vertical line), he would have reported 90% of full degradation amplitude – a value at least closer to the result of the first experimenter.

Hence the same material seems to degrade differently strong in the range of 56% to 98% only because the experimenters used different degradation conditions and did not realize (by in-situ monitoring) that a complex dynamic passes off in the background.

5. CONCLUSIONS

Regarding the 2-state model of Boron-Oxygen related light induced degradation (BO-LID), degradation conditions are fairly tolerant to variations of illumination and temperature. BO-LID takes a certain duration mainly depending on applied temperature and doping level, but always results in the long-term in a complete degradation, at least below a threshold temperature, which mainly depends on doping level. Up to this threshold, BO-LID may be sped up by increasing temperature.

However, in reality the 3-state model describes the dynamics better. Unfortunately, not the degraded but the regenerated state is the preferred state and therefore maximum occupation of the degraded state is no longer mandatorily achieved in the long-term. Maximal observable occupation of the degraded state and thus maximal extent of degradation depends on applied temperature and illumination intensity (injection level).

If dynamics are not sufficiently well (in-situ) monitored, the results may severely differ for different experimental conditions. The best results, meaning a degradation as complete as possible, are obtained for low temperature, low intensity degradation conditions. Especially increasing temperature and intensity simultaneously can result in spoiled interpretations.

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