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Recombination Activity and Impact of the Boron–Oxygen-Related Defect in Compensated N-Type Silicon

F. E. Rougieux, M. Forster, D. Macdonald, A. Cuevas, B. Lim, and J. Schmidt

***Abstract*—In this paper, we present experimental data regarding the recombination activity and concentration of the boron–oxygen complex in compensated n-type silicon, doped with phosphorus and boron, when subjected to illumination. Unlike the data of Bothe *et al.* in n-type silicon compensated with thermal donors, our results suggest the dominant defect level in our doping range to be a shallow level (E_C–E_T = 0.15 eV), with a capture cross-section ratio σ_n/σ_p of around 0.006, suggesting a negatively charged center. We also confirm previous results showing an increasing defect density with bias light intensity. Due to the strong lifetime reduction observed, we suggest that this material might not be suited to make high-efficiency n-type solar cells, unless practical strategies to reduce the defect concentration can be developed.**

***Index Terms*—Compensated, light-induced degradation, n-type, silicon.**

I. Introduction

Boron–oxygen (BO)-related light-induced degradation (LID) has been shown to significantly reduce the efficiency of p-type solar cells. The defect responsible for the degradation has been extensively studied in boron-doped p-type silicon [1]–[4]. In boron–phosphorus-compensated p-type silicon, the defect density was found to depend on the net doping (n_0 = [B]–[P]) rather than the boron concentration [5]–[7]. This proved to be extremely useful for the use of solar-grade feedstock for solar cells. Indeed, using a feedstock with a high boron concentration, one can obtain BO defect densities similar to pure uncompensated p-type silicon by compensating with phosphorus.

N-type silicon, containing only phosphorus, is not subject to BO LID; moreover, n-type silicon has greater immunity to most metallic impurities and, as such, is well suited to make solar cells. On the other hand, n-type solar cells made out of solar-grade or compensated feedstocks have recently been shown to degrade due to the presence of boron (formation of BO defect) [7]–[11].

Rougieux *et al.* [11] suggested that the defect density is independent of the net doping, but rather depends on the excess carrier density during illumination. In a recent study, Schutz-Kuchly *et al.* [10] have showed the defect to have a smaller impact on cell efficiency in compensated n-type than in compensated p-type silicon. However, the starting lifetime of their material was relatively low (low excess carrier density during illumination) potentially leading to low defect density. In order to assess the suitability of compensated n-type silicon for both standard and high-efficiency solar cells, we generated the BO defect with two different illumination intensities, simulating two different excess carrier densities during illumination.

The recombination activity of the slow forming defect in p-type silicon can be modeled by a deep (E_C–E_T = 0.41 eV, capture cross-section ratio σ_n/σ_p = 10) and a shallow level (E_C–E_T = 0.15 eV, $\sigma_n/\sigma_p \ll 1$) [2]. Bothe *et al.* [2] showed that the Shockley–Read–Hall (SRH) lifetime of B-doped silicon compensated with thermal donors could be modeled with exactly the same SRH parameters. However, these results do not allow us to state with certainty that the recombination active defect in boron–phosphorus-compensated n-type silicon will also be the same as in p-type silicon.

In this study, we investigate the recombination activity of the BO defect in compensated n-type silicon doped with phosphorus and boron and attempt to fit the injection dependence of the resulting carrier lifetime with the SRH model. We confirm that a single defect dominates the entire time dependence of the degradation, unlike in p-type silicon, in which a fast- and slow-forming defect occur. In addition, we discuss the potential of this material as a substrate for efficient solar cells, especially the effect of the carrier generation rate on the defect density and expected open-circuit voltage V_{OC}.

II. Experimental Methods

The samples used in this study were from a single compensated Cz–Si ingot doped with both boron and phosphorus. For more details on these samples, see [11]. Only samples from the n-type part ($n_0 = 5.7 \times 10^{15}$–4.0×10^{16} cm^{-3}) of the ingot were used in this study. The compensation ratio $R_C = (N_D + N_A)/(N_D - N_A)$ was found to vary between 5.6 and 19.1. This

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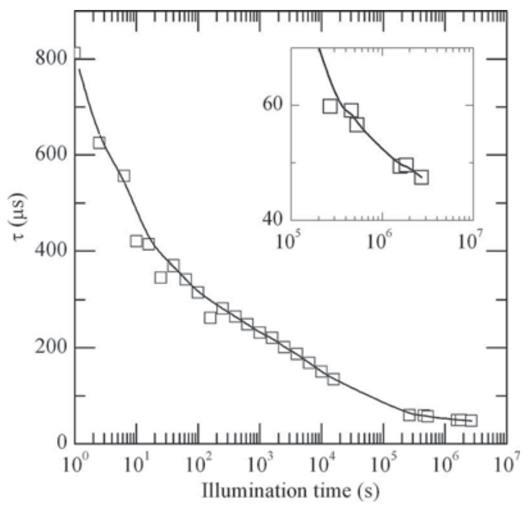

Fig. 1. Evolution of the effective lifetime during BO generation in compensated n-type silicon ($n_0 = 1.9 \times 10^{15}$ cm^{-3}, $G = 60$ mW.cm^{-2}, $T = 60\,^\circ$C). The line is a guide to the eye.

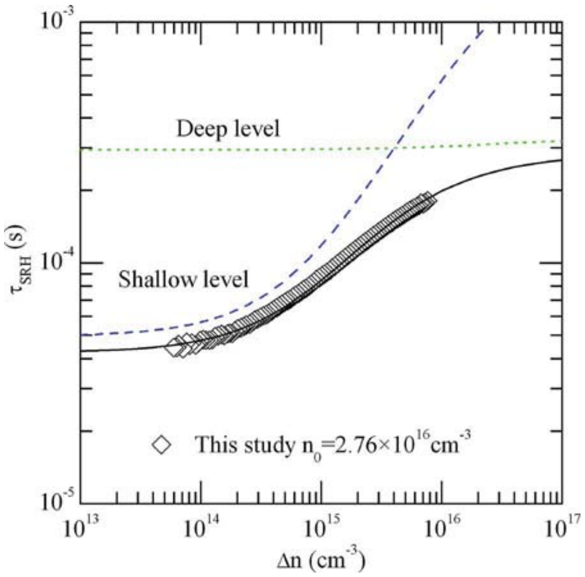

Fig. 2. Measured injection level dependence of the SRH lifetime for a compensated n-type silicon sample ($n_0 = 2.76 \times 10^{16}$ cm^{-3}). The lines are fits using the SRH equation. The dotted line represents the effect of the deep level, while the dashed line represents the effect of the shallow level. The solid line represents their combined impact.

compensation ratio is somewhat higher than usually obtained in p-type silicon from the upgraded metallurgical grade route. All samples were gettered to remove any metallic impurities that could affect the lifetime. The BO defect has been shown previously to deactivate very slowly in compensated n-type Si [7]. To ensure full deactivation, the samples were annealed at 200 °C for 100 h. The samples were then degraded under various light intensities.

Effective lifetime measurements were performed using the quasi-steady-state photoconductance technique (QSSPC) [13]. The measured lifetime after full deactivation is referred to as τ_{annealed}, while the degraded lifetime is τ_{degraded}. The lifetime measured was extracted at a fixed injection level equal to 10% of the net doping n_0. The effective defect concentration was then determined as $N_t^* = 1/\tau_{\mathrm{degraded}} - 1/\tau_{\mathrm{annealed}}$. QSSPC measurements are sensitive to the mobility sum, and mobility reductions have been observed before in compensated silicon [14]. Therefore, we used the sum of acceptor and donor concentrations in a well-known mobility model (see [15] and [16]) to obtain reasonable values of the lifetime [14].

III. Results and Discussion

A. Light-Induced Degradation in Compensated N-Type Silicon

Fig. 1 shows the evolution of the effective lifetime during BO generation in compensated n-type silicon ($n_0 = 1.9 \times 10^{15}$ cm^{-3}). At similar net doping, the BO generation process is slower than in p-type silicon. Even after a month of illumination, the lifetime reduction is still ongoing. Contrary to p-type silicon, in compensated n-type silicon, the degradation proceeds in one slow lifetime decay as observed earlier [7], [9], [11]

B. Recombination Activity of the BO Defect in Compensated N-Type Silicon

Schmidt and Cuevas showed that the recombination of the BO defect in p-type silicon could be modeled by the combination of a deep defect (E_C–E_T = 0.45 eV) and a shallow defect (E_C–E_T = 0.15 eV) [3]. Later, Rein and Glunz determined precisely the energy level of the deep defect to be E_C–E_T = 0.41 eV [1].

Bothe *et al.* [2] showed that the SRH lifetime of B-doped silicon compensated with thermal donors could be modeled with a mid-gap energy level (E_C–E_T = 0.5 eV) with a capture cross-section ratio of $\sigma_n/\sigma_p = 10$ [2]. The same parameters were used for the p-type and n-type samples.

However, when using a single mid-gap level, we cannot fit the injection-dependent SRH lifetime in our samples. On the contrary, we required a deep and a shallow defect to produce a good agreement between SRH measurements and simulations. Fig. 2 shows the measured injection level dependence of the SRH lifetime for a compensated n-type sample ($n_0 = 2.76 \times 10^{16}$ cm^{-3}) after defect activation. The theoretical fit suggests that the recombination activity of the BO defect in compensated n-type silicon is dominated at low injection by a shallow defect (E_C–E_T = 0.15 eV) with a capture cross-section ratio σ_n/σ_p = 0.006. At higher injection, a deep level (E_C–E_T = 0.33-0.87 eV) with a capture cross-section ratio of 10 or higher dominates.

C. Influence of the Position of the Fermi Level on the Activity of the Shallow Level

Although Bothe *et al.* simulated the injection dependence of the SRH lifetime with only one defect, it is conceivable that in their case, the deep defect dominates leading to a very small injection dependence of the SRH lifetime. Indeed their net doping is relatively smaller (6 Ω, 7.6×10^{14} cm^{-3}), meaning that the Fermi level is now further away from the shallow defect.

In order to test this assumption, as well as validate our simulation, we simulated the data of Bothe *et al.* with the same SRH parameters as in our samples (same energy level,

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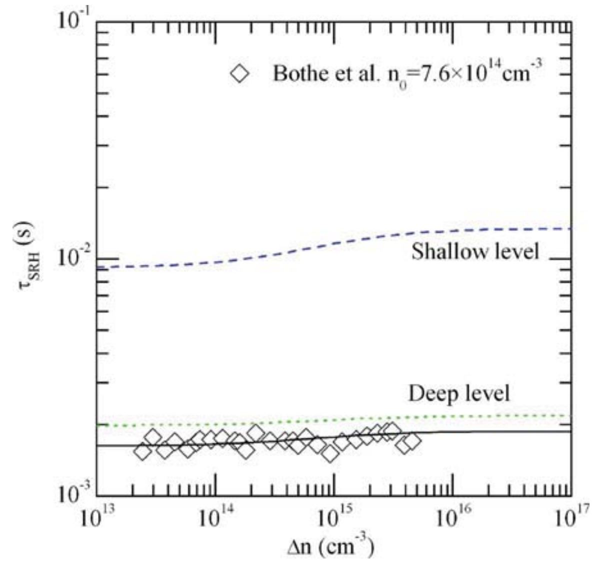

Fig. 3. Injection level dependence of the SRH lifetime from [2]. The lines are fits using the SRH equation. The dotted line represents the effect of the deep level, while the dashed line represents the effect of the shallow level. The solid line represents their combined impact.

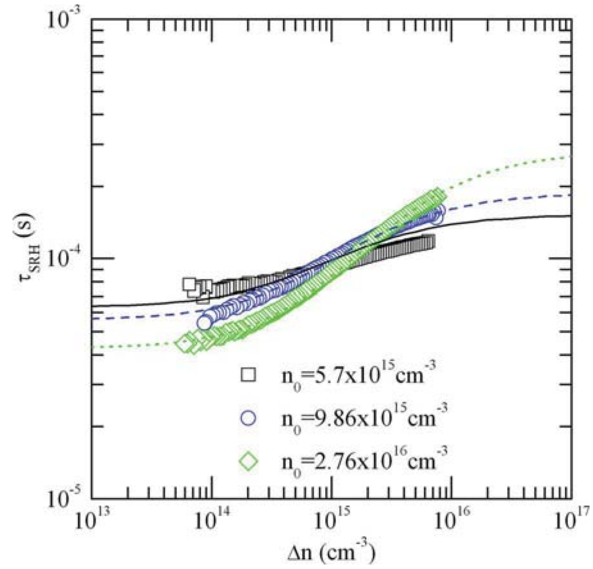

Fig. 4. Measured injection level dependence of the SRH lifetime for three different samples ($n_0 = 5.7 \times 10^{15}$, 9.86×10^{15}, and 2.76×10^{16} cm^{-3}). The lines are fits using the SRH equation with a deep and shallow level.

capture cross-section ratio, and deep/shallow defect concentration ratio). Fig. 3 shows the injection level dependence of the SRH lifetime measured by Bothe *et al.* [2]; the lines are a fit using the SRH equation with a deep and shallow level. The good agreement between simulated and measured data suggests that the deep level dominates across the entire injection range.

To further confirm the influence of the Fermi level on the activity of the shallow level, we modeled samples with different net doping. Fig. 4 shows the measured injection level dependence of the SRH lifetime for three different samples ($n_0 = 5.7 \times 10^{15}$, 9.86×10^{15}, and 2.76×10^{16} cm^{-3}). We used the same SRH parameters as previously. Note that the ratio of deep to shallow levels was kept the same in each case. As the doping changes, the shape of the injection dependent SRH lifetime curve changes, which is characteristic of a shallow defect. The simultaneous good fit obtained for different samples gives added credibility to the dominance of the shallow defect described earlier in compensated n-type silicon. Note that the slight error in the fit with the lower net doping could be due to an error in the doping measurement. Indeed, only a small overestimation of the net doping can lead to a significant change in the shape of the curve.

TABLE I
SRH FITTING PARAMETERS

Type	Defect	Level	Energy E_C-E_T (eV)	σ_n/σ_p
p-type	Slow forming	Deep	0.41[1]	9.3[1]
		Shallow	0.15 or 0.97[3]	>>1 or <<1[3]
	Fast forming	Deep	0.35 - 0.85[12]	100[8, 10-12]
n-type	One defect	Deep	0.33 – 0.87[a]	>10[a]
		Shallow	0.15[a]	0.06[a]

[a]This study.

D. Correlation Between Energy Level and Capture Cross-Section Ratio in P-Type and N-Type Silicon

Table I shows the fitting parameters used in our SRH simulation and the one used in p-type silicon for the fast and slow forming defect. It is interesting to note that using a capture cross-section ratio of 10 (characteristic of the slow forming defect) or of 100 (fast forming defect in p-type silicon) for the deep-defect does not change the result significantly. Thus, the SRH simulation alone does not allow us to determine whether the BO defect in p-type silicon (slow or fast) is similar to the BO defect in compensated n-type silicon or not.

E. Single Level of the BO Defect in Compensated N-Type Silicon

As seen previously, the degradation in compensated n-type silicon was not found to conform to a fast initial decay followed by a slow decay, but rather to a single slow decay [7], [11]. Fig. 5 shows the SRH lifetime after three lengths of time under illumination. Again, we used the exact same SRH parameters as earlier. As the BO defect is generated, the whole SRH lifetime curve is translated downward. If a fast- and slow-forming defect (with different energy levels) were to form in these samples, one would expect the shape of the injection-dependent SRH lifetime to change with time. However, the fact the shape of the curve does not alter confirms previous data that only a single defect (with a deep and a shallow level) forms in compensated n-type silicon [11].

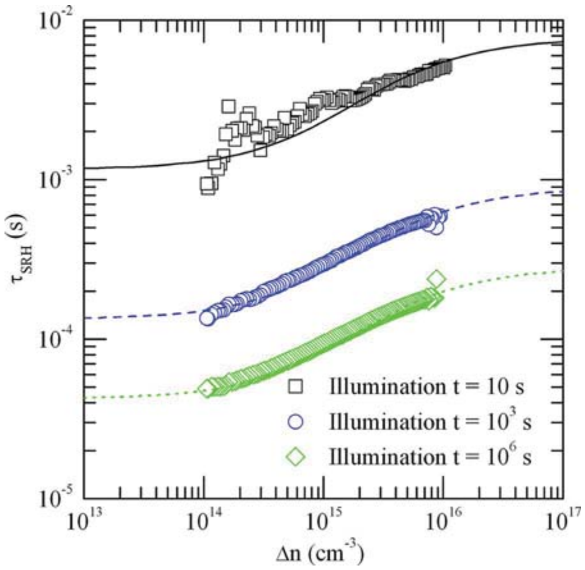

Fig. 5. Measured injection level dependence of the SRH lifetime after three length of time under illumination. The lines are fits using the SRH equation with a deep and shallow level.

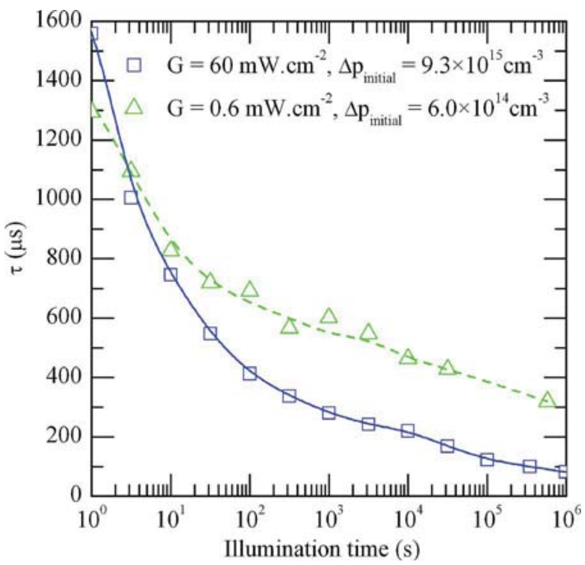

Fig. 6. Evolution of the effective lifetime during BO generation in compensated n-type silicon for two different carrier generation rates ($G = 60\,\mathrm{mW.cm^{-1}}$, $T = 60\,^\circ\mathrm{C}$ and $G = 0.6\,\mathrm{mW.cm^{-1}}$, $T = 30\,^\circ\mathrm{C}$). The lines are guides to the eye.

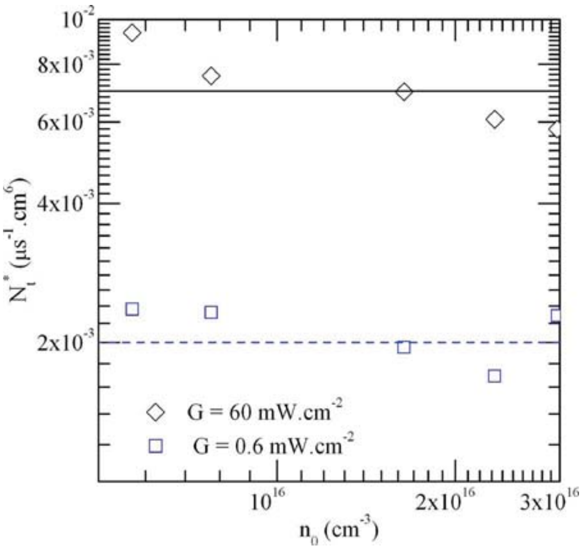

Fig. 7. Defect density in compensated n-type silicon for two different generation rates ($G = 60\,\mathrm{mW.cm^{-1}}$, $T = 60\,^\circ\mathrm{C}$ and $G = 0.6\,\mathrm{mW.cm^{-1}}$, $T = 30\,^\circ\mathrm{C}$). The lines are guides to the eye.

F. Effective Impact of the Light Intensity on the BO Defect Density

It has been suggested previously that the BO defect density depends on the excess carrier density during illumination [11]. Multicrystalline solar cells and monocrystalline solar cells operating at different excess carrier densities can thus be expected to have different defect densities.

In order to determine the extent of the difference in terms of lifetime, defect density, and implied V_{OC}, we measured the light-induced degradation using two different generation rates ($G = 60\,\mathrm{mW.cm^{-1}}$ and $G = 0.6\,\mathrm{mW.cm^{-1}}$).

Fig. 6 shows the evolution of the effective lifetime during BO defect generation in compensated n-type silicon for these two different carrier generation rates. As observed earlier [11], the lower light intensity creates a lower defect density. In terms of expected device voltage V_{OC}, the drop in lifetime implies a final V_{OC} of $V_{\mathrm{OC}} = 599$ mV ($\Delta V_{\mathrm{OC}} = 89.5$ mV) at high generation ($G = 60\,\mathrm{mW.cm^{-1}}$, after 3.1×10^5 s) and $V_{\mathrm{OC}} = 629$ mV ($\Delta V_{\mathrm{OC}} = 38.6$ mV) at low generation ($G = 0.6\,\mathrm{mW.cm^{-1}}$, after 6.0×10^5 s). The implied V_{OC} reduction is very significant when the samples are injected with a lot of carriers ($\Delta p = 9.3 \times 10^{15}\,\mathrm{cm^{-3}}$). However, when injecting the material with less carriers ($\Delta p = 6.0 \times 10^{14}\,\mathrm{cm^{-3}}$), the V_{OC} reduction is less pronounced. Therefore, it should still be possible to make reasonably efficient solar cells with this material. However, the expected defect density and V_{OC} degradation is likely to depend on the initial bulk lifetime and cell design.

Fig. 7 shows the defect density in compensated n-type silicon as a function of the net doping for two different generation rates. The defect density more than triples with the increase in carrier generation rate but is not strongly dependent on the net doping. This confirms previous study that reducing the net doping in the starting material is not an effective way to reduce the defect concentration, unlike in compensated p-type silicon [11].

IV. Conclusion

In summary, our results suggest that recombination via the BO defect at low injection is dominated by a shallow defect ($E_C - E_T = 0.15$ eV) with a capture cross-section ratio $\sigma_n/\sigma_p = 0.006$. At high injection, the lifetime is limited by a deep defect similar to the ones in p-type silicon (E_C–E_T = 0.33–0.87 eV). We showed that the effective defect density more than tripled when the carrier generation rate is increased by a factor of 100. This translates into a twofold increase of the implied V_{OC} reduction, leading to a final V_{OC} of 599 mV (high light intensity) instead of

629 mV (low light intensity). The strong implied V_{OC} reduction may limit the applicability of this material to high-efficiency solar cells.

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