# Light-Induced-Degradation effects in boron–phosphorus compensated *n*-type Czochralski silicon

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This letter focuses on the evolution under illumination of the carrier lifetime in *n*-type boron–phosphorus compensated Czochralski silicon. Our results show a Light-Induced-Degradation (LID) of the carrier lifetime which we prove to be related to additional boron. The activation energy of the annihilation mechanism for this boron-related defect was found to be 1.7 eV, in agreement with values concerning the annihilation of the $BO_{i2}$ complex responsible for the LID of boron-doped *p*-type silicon. This strongly suggests that $BO_{i2}$ are also responsible for the degradation of *n*-type boron–phosphorus compensated silicon unlike what was expected from previous studies on compensated *p*-type silicon. © *2010 American Institute of Physics*. [doi:10.1063/1.3334724]

The Photovoltaic (PV) industry is moving toward readily available and low-cost Si purified via the metallurgical route ($SoG_M$-Si). This yields a compensated material, in which boron (B) and phosphorus (P) concentrations (respectively, [B] and [P]) are significant. Due to this high [B], *p*-type $SoG_M$-Si solar cells are sensitive to Light-Induced-Degradation (LID) effects.[1] LID is due to the formation under illumination of recombination-active complexes associating a B atom and an oxygen (O) dimer ($O_{i2}$) which reduce the carrier lifetime ($\tau$).[2,3] In compensated Czochralski (Cz) Si the concentration of $BO_{i2}$ complexes was found to depend on the net doping ([B]–[P]) (i.e., the concentration of uncompensated B) rather than the total [B].[4] One possible explanation could be related to the existence of BP pairs.[4–6] Whatever the origins of these effects of the dopant compensation on the LID, compensated *n*-Si with high O and B contents should not be sensitive to LID effects since all the B is compensated.[7] Notice that a recent interest has grown around *n*-type $SoG_M$-Si for other reasons, including a weaker sensitivity to most of the metallic impurities compared to *p*-Si.[8]

The objective of this study is to determine if the previous predictions concerning the absence of LID in B–P compensated *n*-Si[7] are valid, via the crystallization of intentionally compensated *n*-type Cz-Si ingots and the study of $\tau$ under illumination.

A *n*-type Cz ingot was grown from an electronic grade Si (EG-Si) feedstock in which P and B were added. This ingot was then cut in 4 in. wafers. For reproducibility purposes, we used adjacent wafers for which [B] and [P] remained unchanged. [B] and [P] were determined by Glow Discharge Mass Spectroscopy. They were respectively equal to $1.6 \times 10^{17}$ and $2.1 \times 10^{17}$ $cm^{-3}$. The resistivity ($\rho$), determined by four point-probes measurement, was equal to 0.25 $\Omega$ cm. $\tau$ of the compensated wafers were compared with reference uncompensated P-doped EG Cz-Si wafers, respectively, having $[P]=1.2 \times 10^{15}$ and $2 \times 10^{17}$ $cm^{-3}$.

For all wafers, the saw damages were removed by chemical polishing. Electrical passivation of the surfaces was achieved with plasma-enhanced-chemical-vapor-deposited hydrogenated Si Nitride (SiN:H) layers. We then followed the evolution of the effective $\tau$ ($\tau_{eff}$) under illumination using the microwave-photoconductance-decay ($\mu$W-PCD) technique. In our study the laser pulses used by the $\mu$W-PCD technique also act as the light source required for the illumination. Thus, $\tau_{eff}$ reported in this study was measured at the center of the illuminated area. The intensity of each laser pulse was greater than 1650 $W/cm^2$, corresponding to a moderately high injection level. After complete degradation, i.e., when $\tau_{eff}$ reached stable values, a $\tau_{eff}$ mapping of the wafer was then achieved. The study of the annihilation mechanism was done at Temperatures ($T$) between 200 and 250 °C. The annealing was followed by a fast cooling, before each $\tau_{eff}$ mapping of the wafer.

The evolution under illumination of $\tau_{eff}$ is reported for all wafers in Fig. 1. For both uncompensated wafers, $\tau_{eff}$ remains perfectively stable, around 10 $\mu$s for the wafer P-doped to $2 \times 10^{17}$ $cm^{-3}$ and 380 $\mu$s for the wafer P-doped to $1.2 \times 10^{15}$ $cm^{-3}$. This result is twofold: it shows that the electrical passivation of the surfaces is stable under illumination and that in absence of B atoms, $\tau_{eff}$ is not affected by illumination. The behavior is completely different for the compensated wafer. $\tau_{eff}$ decreases from 55 to 12 $\mu$s and then reaches a stable value in few hours. It is particularly interesting to focus on the initial $\tau$ of the highly P-doped wafers.

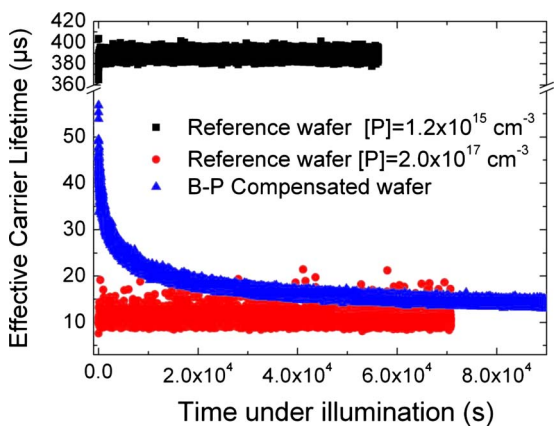


FIG. 1. (Color online) Evolution of the effective carrier lifetime, throughout repeated $\mu$W-PCD measurements, for the reference and compensated wafers.

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These wafers have similar [P], however the initial $\tau$ for the reference and the compensated wafers are respectively equal to 10 and 57 $\mu$s. Thanks to the addition of B in the feedstocks, the initial $\tau$ has been multiplied by 5.7. This result is in very good agreement with recent studies concerning the positive effect of compensation on $\tau$.[9] This effect is explained by compensation-induced reductions of the recombination strength of shallow energy levels as well as the Auger and radiative recombination rates.

All materials have a comparable interstitial oxygen ($O_i$) content ($[O_i]$) of about $1\times10^{18}$ cm$^{-3}$ determined by Fourier-transform infrared (FTIR) spectroscopy. This result shows that a LID of $\tau_{eff}$ occurs on compensated $n$-type Si which is clearly related to the addition of B. This suggests that $BO_{i2}$ could be involved in the LID observed in compensated $n$-Si.

One way to check this hypothesis is to determine the activation energy ($E_{ann}$) of the annihilation mechanism of the presumed defect, and to compare it with $E_{ann}$ values from the literature. In B-doped uncompensated Si, $BO_{i2}$ are known to be unstable at $T$ above 200 °C.[3] At such $T$, it is possible to follow the annihilation kinetics by monitoring $\tau_{eff}$ versus the annealing time ($t$). Then, the normalized concentration ($N^*$) of the illumination-induced defects can be extracted from:[10]

$$N^*(t,T) = \frac{1}{\tau_{eff}(t)} - \frac{1}{\tau_{eff\infty}}, \quad (1)$$

where $\tau_{eff\infty}$ is the value of $\tau_{eff}$ at $t\rightarrow\infty$, i.e., when all the metastable defects are suppressed. For practical purposes, we determined $\tau_{eff\infty}$ by computing the average value of $\tau_{eff}$ at the periphery of the illuminated area, where no metastable defects are present. This way, possible changes in the surface passivation due to annealing do not influence the calculation of $N^*(t)$. In uncompensated B-doped Si, $N^*(t)$ follows an exponential decay during the annihilation process,

$$N^*(t,T) = N_0^*[\exp(-R_{ann}(T)t)], \quad (2)$$

where $N_0^*$ corresponds to the value of $N^*$ at $t=0$, when all the metastable defects are formed. Thus, by fitting the isothermal experimental $N^*$ data with Eq. (2), the annihilation rate $R_{ann}(T)$ can be determined. Provided that the annihilation mechanism of the defect is thermally activated, $E_{ann}$ can then be obtained from an Arrhenius plot of the variation of $R_{ann}$ with $T$[10] according to the following expression where $\kappa_0$ depends on the physical annihilation mechanism:

$$R_{ann}(T) = \kappa_0 \exp\left(-\frac{E_{ann}}{k_B T}\right). \quad (3)$$

Our purpose was to determine $E_{ann}$ for the defect involved in the LID effects observed in our Si, and to compare it with available results on $p$-Si. We have first locally degraded the compensated wafer until $\tau_{eff}$ reaches a stable minimum value. Starting from this fully degraded state, we then recorded the step-by-step isothermal evolutions of $\tau_{eff}$ for six different $T$ ranging from 200 to 250 °C. Figure 2 depicts $\tau_{eff}$ mappings of the degraded area for various annealing times at 215 °C. The shrinkage of the degraded area reveals that the involved defect is indeed annihilated in this range of $T$.

From the isothermal evolutions of $\tau_{eff}$, $R_{ann}(T)$ were computed using Eqs. (1) and (2). The variation of $R_{ann}$ with $T$ is plotted in Fig. 3. $R_{ann}$ is found to follow an Arrhenius law with an activation energy of 1.7 eV ± 0.2 eV. This is in good agreement with the values of 1.3 and 1.8 eV reported in[3,10,11] concerning the annihilation of $BO_{i2}$ in uncompensated $p$-Si. The value of 1.8 eV reported by Schmidt *et al.*[10] was also derived from room $T$ measurements of $\tau_{eff}$ after successive annealing steps at high $T$. According to the authors, this $T$ cycling is a fundamental drawback of this method and they believe that $E_{ann}$ is rather equal to 1.3 eV. Nevertheless, as we found an $E_{ann}$ very close to their value with a similar protocol, this indicates that the LID effects in our study are related to the formation of $BO_{i2}$. Regarding the dissociation kinetics, our $R_{ann}$ values are around four orders of magnitude below $R_{ann}$ in $p$-Si.[10] As a consequence, $\kappa_0$ is as low as $1.5\times10^{14}$ s$^{-1}$. This could be related to $O_{i2}$ diffusion. As was suggested earlier, once $BO_{i2}$ is dissociated, $O_{i2}$ migrates and escapes the B electric field.[3] The $O_{i2}$ diffusivity being proportional to the hole concentration,[12] the $O_{i2}$ migration and hence the annihilation rate will be much lower in compensated $n$-Si than in $p$-Si.

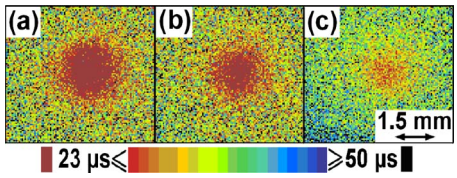


FIG. 2. (Color online) Effective carrier lifetime maps of the illuminated zone after different annealing times at 215 °C (spatial resolution of 62.5 $\mu$m). (a) Initial degradation, (b) 1 h at 215 °C, and (c) 3.5 h at 215 °C.

This result shows that a fraction of B atoms is able to bond with $O_{i2}$ to form $BO_{i2}$ in B–P compensated $n$-Si. Now, is this fraction very small, as suggested from recent studies,[4] or close to unity? To answer this question, we compared our $\tau_{eff}$ limited by the $BO_{i2}$ only ($\tau_{BO}$) with the value ($\tau_{th\_p}$) given by the following empirical expression,[13] extracted from data in uncompensated B-doped Si obtained at an injection level ($\Delta n$) equal to $\Delta n = 0.1\times p_0$, $p_0$ being the equilibrium hole concentration,

$$\tau_{th\_p}(\mu s) = 7.675\times10^{45}[B]^{-0.824}\times[O_i]^{-1.748}. \quad (4)$$

If for a given [B], the concentration of $BO_{i2}$ formed under illumination is the same in both $p$- and $n$-Si, we can estimate from Eq. (4) the corresponding value at high $\Delta n$ in $n$-Si ($\tau_{th\_n}$). However this is not straightforward since the dependence of $\tau_{BO}$ on $\Delta n$ is completely different in $n$- and $p$-Si. To take this behavior into account, in parallel with the different $\Delta n$ for which $\tau_{th\_p}$ and $\tau_{th\_n}$ are computed, $\tau_{th\_p}$ extracted from Eq. (4) has to be multiplied by a factor ($\alpha$) which can

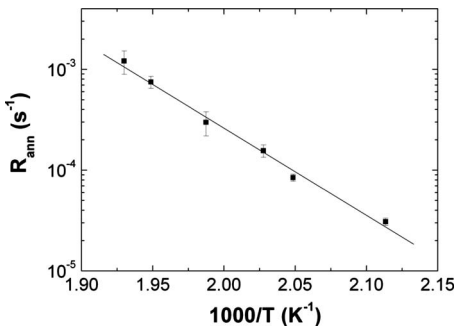


FIG. 3. Arrhenius plot of the defect annihilation rate. The solid line represents a single exponential fit to the experimental data.

be computed from the Shockley-Read-Hall statistics,[14] with the recombination parameters of $BO_{i2}$.[15] The result of this computation is $\alpha=5.5$. Inserting our [B] and $[O_i]$ values in Eq. (4) and multiplying the result by $\alpha$ yielded $\tau_{th\_n}=5.4$ $\mu$s. As previously mentioned, $\tau_{eff}$ corresponding to the fully degraded state of the compensated wafer was equal to 12 $\mu$s. Because no defect other than $BO_{i2}$ is suspected to reduce $\tau$ in our sample, $\tau_{BO}$ can be estimated to be around 12 $\mu$s. Our $\tau_{BO}$ and $\tau_{th\_n}$ values, despite the uncertainties regarding the measured $[O_i]$ and [B], are of the same order of magnitude. This result means first that for the studied compensation level, Eq. (4) multiplied by $\alpha$, can reasonably be transposed to B–P compensated *n*-Si. In addition, the fact that our measured $\tau_{BO}$ is in good agreement with $\tau_{th\_n}$ (which considers that all the B is available for pairing up with $O_{i2}$) shows that a significant fraction of the total [B] is able to bond with $O_{i2}$. Notice that we obtained similar conclusions by changing [B] in Eq. (4) by the net doping content ($|[B]-[P]|$) since $\tau_{BO}$ in *p*-Si was found to depend on this parameter.[4–6]

Previous studies on compensated *p*-Si evidenced that the LID effects were reduced for a given [B], when increasing the compensation level (i.e., when increasing [P]).[4–6] This behavior has been linked to the possible existence of BP pairs, as observed by FTIR analyses on compensated Si.[16] Our work, by showing that $BO_{i2}$ is efficiently formed in compensated *n*-Si, appears as a contradiction with these previous studies, since in this Si, the pairing of B with P should leave no B available for $BO_{i2}$ formation. Therefore it suggests that BP pairs, if they do exist, are present in a minor amount (to our opinion the existence of $BPO_{i2}$ complexes is unlikely since they would probably have different recombination activity and annihilation kinetics compared to $BO_{i2}$). This supports the recent study conducted by Macdonald *et al.*[7] based on measurements of the hole mobilities and the characteristic crossover point caused by interstitial iron in compensated Si, and the work of Lim *et al.*[17] on the deactivation of the BO centers. Thus, our contribution brings further evidence that the BP pairs cannot be responsible for the reduced LID in compensated Si. The physical causes behind this behavior remain unresolved.

As compensated *n*-Si is a promising material for the future of PV, the quantification of the LID at the cell level has to be undertaken. However, one can remain optimistic because even if $BO_{i2}$ can be formed under illumination in compensated *n*-Si, their effect on the cell's efficiency at a given [B] should be less pronounced than in *p*-Si. Indeed the capture cross section ratio ($\sigma_n/\sigma_p$) of $BO_{i2}$ being equal to 9.3,[15] these complexes are more virulent in terms of carrier recombination in *p*- than in *n*-Si.

As a conclusion, we showed that B–P compensated *n*-Si is sensitive to the LID effects related to the formation of $BO_{i2}$. The main result is that, unlike what was expected from several studies, if BP pairs exist in compensated Si, they should be present in a minor amount and their involvement in the reduced LID in B–P compensated *p*-Si may appear questionable.

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[1] S. Dubois, N. Enjalbert, and J. P. Garandet, Appl. Phys. Lett. **93**, 103510 (2008).
[2] J. Schmidt, A. G. Aberle, and R. Hezel, *Proceedings of the 26th IEEE Photovoltaic Specialists Conference*, Anaheim (IEEE, New York, 1991), p. 13.
[3] J. Schmidt and K. Bothe, Phys. Rev. B **69**, 024107 (2004).
[4] D. Macdonald, F. Rougieux, A. Cuevas, B. Lim, J. Schmidt, M. Di Sabatino, and L. J. Geerligs, J. Appl. Phys. **105**, 093704 (2009).
[5] W. Krühler, C. Moser, F. W. Schulze, and H. Aulich, in *Proceedings of the Eighth European Photovoltaic Solar Energy Conference*, Florence, Italy (Kluwer Academic, Dordrecht, The Netherlands, 1988), p. 1181.
[6] R. Kopecek, J. Arumughan, K. Peter, E. A. Good, J. Libal, M. Acciarri, and S. Binetti, *Proceedings of the 23rd European Photovoltaic Solar Energy Conference*, Valencia, Spain (WIP-Renewable Energies, Munich, Germany, 2008), p. 1855.
[7] D. Macdonald, A. Liu, F. Rougieux, A. Cuevas, B. Lim, J. Schmidt, M. Di Sabatino, and L. J. Geerligs, *Proceedings of the 24th European Photovoltaic Solar Energy Conference*, Hamburg, Germany (WIP, Munich, 2009), p. 877.
[8] S. Martinuzzi, I. Périchaud, C. Trassy, and J. Degoulange, Prog. Photovoltaics **17**, 297 (2009).
[9] S. Dubois, N. Enjalbert, and J. P. Garandet, Appl. Phys. Lett. **93**, 032114 (2008).
[10] J. Schmidt, K. Bothe, and R. Hezel, *Proceedings of the 29th IEEE Photovoltaic Specialists Conference*, New Orleans, LA (IEEE, New York, 2002), p. 178.
[11] S. Rein, T. Rehrl, W. Warta, S. W. Glunz, and G. Willeke, *Proceedings of the 17th European Photovoltaic Solar Energy Conference*, Munich, Germany (WIP, Munich, 2001), p. 1555.
[12] D. W. Palmer, K. Bothe, and J. Schmidt, Phys. Rev. B **76**, 035210 (2007).
[13] K. Bothe, R. Sinton, and J. Schmidt, Prog. Photovoltaics **13**, 287 (2005).
[14] W. Shockley and W. T. Read, Phys. Rev. **87**, 835 (1952).
[15] S. Rein and S. W. Glunz, Appl. Phys. Lett. **82**, 1054 (2003).
[16] V. Tsvetov, W. Allred, and W. G. Spitzer, Appl. Phys. Lett. **10**, 326 (1967).
[17] B. Lim, A. Liu, D. Macdonald, K. Bothe, and J. Schmidt, Appl. Phys. Lett. **95**, 232109 (2009).