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Kinetics of the permanent deactivation of the boron-oxygen complex in crystalline silicon as a function of illumination intensity

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Based on contactless carrier lifetime measurements performed on *p*-type boron-doped Czochralski-grown silicon (Cz-Si) wafers, we examine the rate constant R_{de} of the permanent deactivation process of the boron-oxygen-related defect center as a function of the illumination intensity I at 170°C. While at low illumination intensities, a linear increase of R_{de} on I is measured, at high illumination intensities, R_{de} seems to saturate. We are able to explain the saturation by assuming that R_{de} increases proportionally with the excess carrier concentration Δn and take the fact into account that at sufficiently high illumination intensities, the carrier lifetime decreases with increasing Δn and hence the slope of $\Delta n(I)$ decreases, leading to an apparent saturation. Importantly, on low-lifetime Cz-Si samples no saturation of the deactivation rate constant is observed for the same illumination intensities, proving that the deactivation is stimulated by the presence of excess electrons and not directly by the photons. © 2017 Author(s). All article content, except where otherwise noted, is licensed under a Creative Commons Attribution (CC BY) license (<http://creativecommons.org/licenses/by/4.0/>). [<http://dx.doi.org/10.1063/1.4978266>]

Since the 1970s it is known that the power output of solar cells fabricated on boron-doped Czochralski-grown silicon (Cz-Si) degrades under prolonged illumination at room temperature.¹ This reduction in power output was related to a degradation of the carrier lifetime in the silicon bulk.¹ In the past two decades, this light-induced degradation (LID) effect has been extensively investigated and it was shown that the simultaneous presence of boron and oxygen in the silicon material is a necessary prerequisite for the LID.^{2,3} Hence, defect models were developed which attribute the lifetime degradation to the activation of a boron-oxygen-related defect (BO defect).⁴ Furthermore, in 2006 it was discovered that the lifetime degradation, and hence also the degradation in solar cell efficiency, can be permanently reversed by illumination at elevated temperature,⁵ a process referred to as ‘permanent deactivation’ of the BO defect. While the impact of temperature on the deactivation rate constant R_{de} follows an Arrhenius law,^{6,7} only very limited data has been published concerning the dependence of R_{de} on the illumination intensity during the process of permanent deactivation. Measurements by Herguth et al.⁸ suggested a linear increase up to illumination intensities of 1 sun (100 mW/cm²) on solar cell level.

In this contribution, we analyze the impact of illumination intensity I on R_{de} over a broad intensity range from 0.5 to 3 suns. Our experiments show that the $R_{de}(I)$ dependence does indeed follow a linear dependence at low illumination intensities, whereas at high intensities above ~ 2 suns an apparent saturation in R_{de} is observed. We discuss our experimental findings based on the assumption that R_{de} is proportional to the excess carrier concentration Δn independent on the illumination intensity, which fully explains the observed $R_{de}(I)$ behavior.

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We use *p*-type boron-doped Cz-Si wafers with resistivities of 1.0 Ωcm and 2.2 Ωcm , respectively. All wafers receive a damage etch step and an RCA cleaning⁹ of the surfaces and a subsequent phosphorus diffusion in a quartz-tube furnace using POCl_3 at 850°C, resulting in n^+ -regions on both surfaces with a nominal sheet resistance of 100 Ω/sq . We then split the wafers into two groups of samples: for the samples of group I, the phosphorus silicate glass (PSG) as well as the n^+ -regions are removed. The remaining sample thickness is then about 144 μm for the 1- Ωcm material and 133 μm for the 2.2- Ωcm material. The samples of group II retain the phosphorus-diffused n^+ -regions through the complete subsequent process sequence and the measurements, only the PSG is removed. These samples have a thickness of about 148 and 136 μm , respectively.

Subsequently, all samples pass through an RCA cleaning before receiving a 10-nm thick Al_2O_3 layer deposited on both wafer surfaces using plasma-assisted atomic layer deposition (plasma-ALD)¹⁰ plus a 70-nm thick SiN_x capping layer on top (refractive index $n = 2.05$ at $\lambda = 632$ nm) deposited via plasma-enhanced chemical vapor deposition (PECVD). The passivation of the surfaces by an $\text{Al}_2\text{O}_3/\text{SiN}_x$ stack reduces the surface recombination velocity (SRV) well below 10 cm/s.¹¹ Now, all samples undergo a rapid thermal annealing (RTA) step in order to accelerate the permanent deactivation using fast cooling ramps.¹² We perform the RTA step in a commercially available belt firing furnace (DO-FF-8.600-300, Centrotherm). As previously shown,^{12,13} the RTA process has a crucial impact on the kinetics of the permanent deactivation. The highest deactivation rate constant R_{de} after RTA treatment is obtained for a fast belt speed of $v_{\text{belt}}=7.2$ m/min and a set-peak temperature of $\vartheta_{\text{peak}}=850^\circ\text{C}$ to 870°C .¹² However, in order to enable us to determine the deactivation rate constant also at high illumination intensities, we have chosen a slightly slower belt speed of $v_{\text{belt}}=6.0$ m/min in this study that results in slightly lower deactivation rate constants which facilitates the experimental extraction of the deactivation rates. After the RTA treatment, the initially 15.6×15.6 cm^2 wafers are laser-diced into samples of 5×5 cm^2 size.

We examine the deactivation process starting from the state after annealing at 200°C in darkness, leading to a non-permanent deactivation of the BO complex and a corresponding lifetime τ_0 .^{3,14} On the other hand, we denote as τ_{op} the lifetime after complete permanent deactivation. Note that the actual value of τ_{op} depends strongly on the details of the thermal history of the sample and in particular on the previous RTA treatment.¹² We vary the light intensity of the halogen lamp used for the deactivation process between 0.5 and 3 suns by changing the lamp-sample distance. The measurement uncertainty of the light intensity is within 2 %. During deactivation the samples are placed on a hotplate at an effective sample temperature of $(169.5 \pm 3.5)^\circ\text{C}$ for all illumination intensities. We monitor the lifetime $\tau(t)$ during the permanent deactivation process by removing the samples in defined intervals from the hotplate and measuring the lifetime using the photoconductance decay (PCD) technique¹⁵ or the quasi-steady-state photoconductance (QSSPC) method,¹⁶ both at $\sim 31^\circ\text{C}$ (Sinton Instruments Lifetime Tester WCT-120). Unless otherwise stated, we report τ at a fixed injection level of $\Delta n/p_0=0.1$ with Δn being the excess carrier concentration and p_0 being the hole concentration in darkness that equals in our samples the boron doping concentration N_{dop} . From the measured lifetimes we extract the effective defect concentration N_t^* with $N_t^* = 1/\tau(t) - 1/\tau_0$. The rate constant R_{de} of the permanent deactivation process is then determined by fitting the evolution of $N_t^*(t)$ using a single-exponential decay function of the form $N_t^* = A \times \exp(-R_{\text{de}} \times t) + B$.

Figure 1 shows the measured R_{de} values as a function of illumination intensity I during the permanent deactivation treatment performed at 170°C. The rate constant R_{de} is determined in a light intensity range between 0.5 and 3 suns for Cz-Si materials with two different resistivities, 1.0 and 2.2 Ωcm , respectively. We observe an approximately proportional increase of $R_{\text{de}}(I)$ for light intensities between 0.5 to 2 suns for both materials. The rate constant R_{de} of the 1.0 Ωcm -material increases from a value of ~ 37 h^{-1} at 0.5 suns to $(110\text{-}130)$ h^{-1} at 2 suns. However, surprisingly, at illumination intensities above 2 suns we do not observe any significant further increase of the rate constant and R_{de} virtually saturates at (120 ± 20) h^{-1} . On the 2.2- Ωcm material, we measure a comparable saturation value as measured on the 1.0- Ωcm for intensities above 2 suns. Note that the extracted rate constants show a significant scatter, which could be related to background effects of hitherto unknown nature, however, our data unambiguously show a weaker-than-linear dependence of $R_{\text{de}}(I)$ at high intensities (> 2 suns).

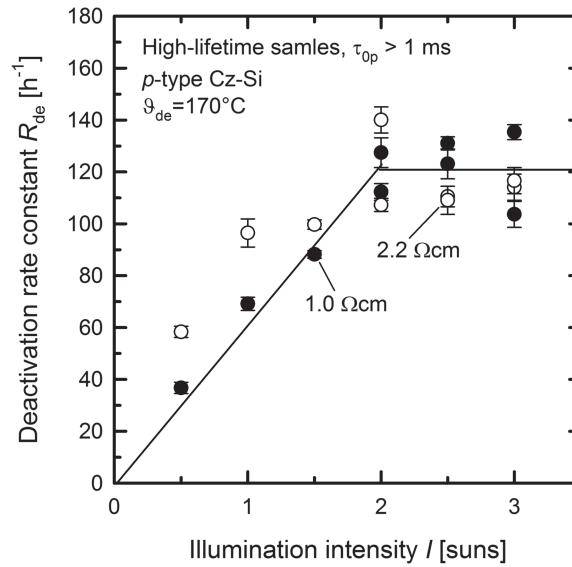


FIG. 1. Deactivation rate constant R_{de} measured as a function of illumination intensity I for boron-doped Cz-Si wafers permanently deactivated at 170°C (symbols). The samples provide high lifetimes of $\tau_{0p} > 1$ ms after deactivation. The black line is a guide to the eyes. All samples shown in this graph are of group I, i.e. the n^+ -regions were removed.

Figure 2 shows the rate constants R_{de} depending on the light intensity of samples with significantly lower lifetime after deactivation ($\tau_{0p} < 350 \mu\text{s}$) compared to the ones shown in Fig. 1 ($\tau_{0p} > 1$ ms). The applied illumination intensity ranges between 1 to 2.5 suns for the 2.2- Ωcm material or between 1 to 3 suns in case of the 1- Ωcm material. Filled circles show the measurements on the 1- Ωcm material, open circles on the 2.2- Ωcm material. The error bars give the uncertainty of the mono-exponential fit to $N_t^*(t)$. The deactivation rate constant R_{de} increases from $(42.5 \pm 2.5) \text{h}^{-1}$ at 1 sun to $(140.8 \pm 9.4) \text{h}^{-1}$ at 3 suns in case of 1- Ωcm samples. The deactivation rate constants of the 2.2- Ωcm samples is comparable with $(38.5 \pm 6.8) \text{h}^{-1}$ at 1 sun to $(104.0 \pm 3.2) \text{h}^{-1}$ at 2.5 suns. Contrary to the dependence

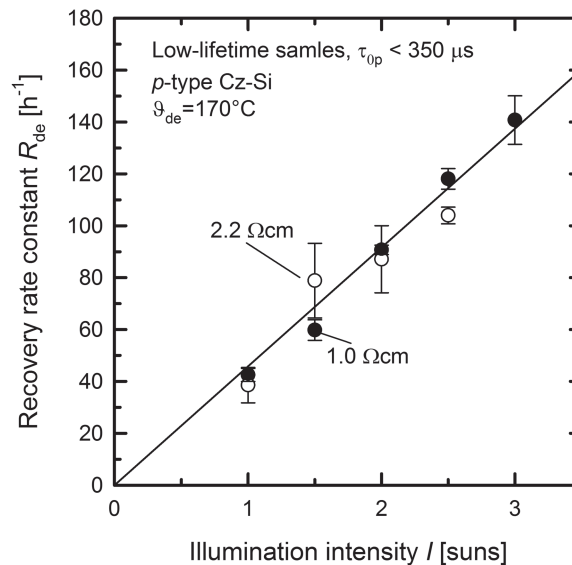


FIG. 2. Deactivation rate constant R_{de} measured as a function of illumination intensity I for boron-doped Cz-Si wafers permanently deactivated at 170°C (symbols). The samples provide low lifetime of $\tau_{0p} < 350 \mu\text{s}$ after deactivation due to background defects of unknown nature. The black line is a linear fit of the data points of the 1.0 Ωcm material. All samples shown in this graph are of group I, i.e. the n^+ -regions were removed.

shown in Fig. 1, we find a linear increase of R_{de} with the increasing light intensity I during deactivation over the entire measured intensity range. Importantly, we do not observe any saturation of R_{de} up to an illumination intensity of 3 suns. The black line represents a linear fit of $R_{\text{de}}(I)$. The experimental results shown in Figs. 1 and 2, the observed saturation of the rate constant as well as the absence of any saturation in low-lifetime samples, clearly support the assumption of an electronically stimulated deactivation process, where the photons are not directly involved.

In a recent theoretical work by Voronkov and Falster,¹⁸ it was assumed as most likely that R_{de} is proportional to the electron concentration Δn during the permanent deactivation of the BO defect. Due to the increased temperature of the deactivation process it was furthermore conjectured that the bulk lifetime is not limited any longer by the BO defect, but by some background defects and the lifetime might hence be constant during the deactivation treatment. The latter assumption was in particular needed to explain the strictly exponential decrease of $N_t^*(t)$ during permanent deactivation,¹⁸ which is generally experimentally observed, also in this study, and is not consistent with the strict proportionality of R_{de} on Δn . To verify in particular the latter assumption experimentally, we have performed in-situ lifetime measurements during the permanent deactivation process using the dynamic infrared lifetime mapping (dynamic-ILM)¹⁷ technique. During the measurement the sample is placed on a hotplate at a set temperature of 140°C and illuminated by an LED array of 950 nm wavelength. Figure 3 shows the measured lifetime evolution $\tau(t)$ during permanent deactivation at 140°C and an illumination intensity corresponding to 0.92 suns, clearly showing that the lifetime is not constant during the set deactivation temperature of 140°C. Nevertheless, we find an exponential decrease of $N_t^*(t)$ at 140°C deactivation temperature. A further development of the BO deactivation theory seems to be necessary to explain this experimental finding. However, our experimental results shown in Figs. 1 and 2 do now clearly prove that the permanent deactivation must be related to the injected carriers during deactivation. We hence chose a pragmatic approach here and replot our measured R_{de} data as a function of the excess carrier concentration Δn . Based on the aforementioned, the question arises which Δn value would be the most meaningful in this plot. In fact, we follow here the pragmatic approach of Wilking et al.¹⁹ and determine an average excess carrier concentration $\Delta n_{\text{av}} = 1/2 \times (\Delta n_{\text{min}} + \Delta n_{\text{de}})$, where Δn_{min} is extracted right before the deactivation starts, i.e. in the minimum lifetime state, and Δn_{de} is measured in the fully deactivated state, where the lifetime and hence Δn is maximal. Note that the excess carrier concentrations were extracted not at the deactivation temperature, but at the temperature of the lifetime measurements, which were performed at $\sim 31^\circ\text{C}$,

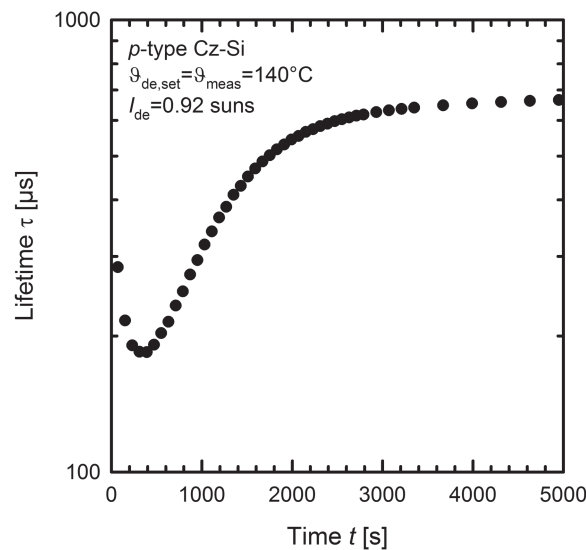


FIG. 3. Lifetime τ of a sample of group I (i.e. n^+ -regions were removed) measured during permanent deactivation at $\vartheta_{\text{de,set}} = 140^\circ\text{C}$. The lifetime measurement was performed using the dynamic infrared lifetime mapping (dynamic-ILM)¹⁷ technique, where the sample was placed on a hotplate and illuminated by an LED array of 950 nm wavelength at an intensity of $I=0.92$ suns. Each measurement took 20 s.

because the Δn values during the deactivation process were not experimentally accessible to us. However, due to the similar lifetime trend at 140°C and 31°C we assume here that the lifetime at the deactivation temperature of 170°C behaves in a similar way, which, however, needs to be confirmed in future experiments.

Figure 4 shows the measured deactivation rate constant R_{de} as a function of Δn_{av} . The data in Fig. 4(a) recorded on 1.0 Ωcm and in Fig. 4(b) on 2.2 Ωcm p -type Cz-Si samples can be fitted using proportionality functions (black solid lines). The deviation from this linear behavior may be due to inaccuracies when determining the lifetime in the minimum during the deactivation process, since we determine the first lifetime data point after 10-20 s of illumination at 170°C and the actual minimum may be reached even faster than within time span.

With the observed proportional dependence of the deactivation rate constant R_{de} on the excess carrier concentration averaged from the lifetime minimum during the deactivation process and from the permanently recovered state, the apparent saturation behavior observed in Fig. 1 can now be understood as follows: At relatively low illumination intensities, during the deactivation process, the excess carrier concentration Δn increases in proportion with the illumination intensity I . However, at higher intensities, the lifetime starts to decrease with increasing injection level, e.g. by recombination via a shallow Shockley-Read-Hall center or Auger recombination, and in this injection range, Δn increases only marginally with increasing illumination intensity. Hence, assuming that R_{de} increases proportionally with Δn_{av} would explain the apparent saturation behavior observed in Fig. 1. Note that our latter conclusion also holds if we plot R_{de} as a function of Δn_{min} or as a function of Δn_{de} , showing that despite the fact that we cannot explain the exponential decay of $N_t^*(t)$ during the permanent deactivation process at this point in time, we are nevertheless able to conclude that $R_{de} \sim \Delta n$ seems to be a generally valid law of the BO deactivation process.

In this letter, we have shown that the deactivation rate constant R_{de} depends linearly on the excess carrier concentration Δn during the deactivation of the BO-related defect center. As a consequence, R_{de} increases linearly with the illumination intensity at low intensities, but shows an apparent saturation at high illumination intensities, when Δn becomes a weaker-than-linear function of the illumination intensity. This results in an apparent saturation of R_{de} when plotted versus the illumination intensity which we varied between 0.5 and 3 suns in this study. On our investigated 1.0 and 2.2 Ωcm high-lifetime Cz-Si samples, we have observed the apparent saturation for intensities above ~ 2 suns resulting at a maximum R_{de} of $120 \pm 20 \text{ h}^{-1}$. Note, that the actual lifetime of the sample under investigation determines the intensity above which R_{de} saturates and that in low-lifetime samples, much

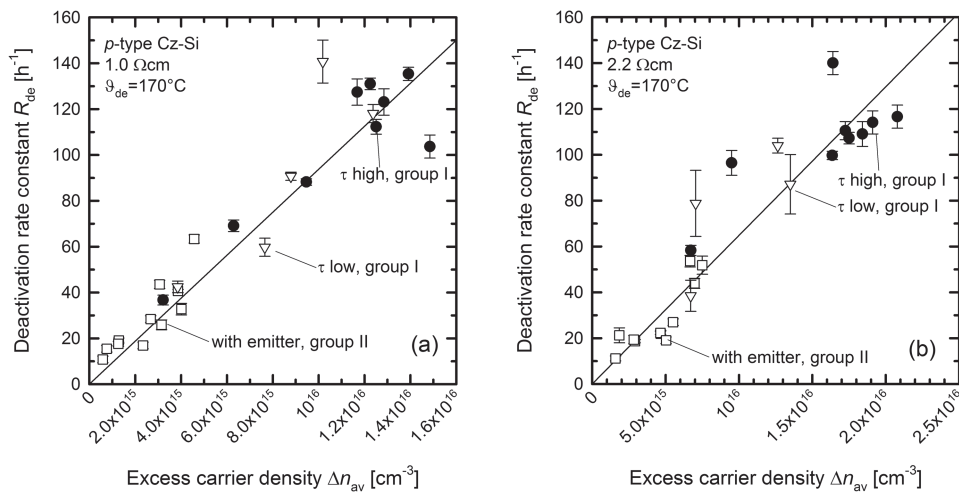


FIG. 4. Deactivation rate constant R_{de} as a function of excess carrier concentration Δn_{av} for (a) 1.0 Ωcm and (b) 2.2 Ωcm p -type Cz-Si samples. Cz-Si samples of group I (i.e. n^+ -regions were removed) with high lifetimes (>1 ms) are shown as filled circles, low-lifetime ($<350 \mu\text{s}$) samples, also of group I, as open triangles. Open squares show data measured on Cz-Si samples with n^+ -regions still present (group II) and hence reduced lifetimes. Error bars show the uncertainty according to the exponential fit. The black line is a proportional fit of all data points.

higher intensities are required to reach the saturation in R_{de} compared to high-lifetime samples. The latter is a direct consequence of the $R_{de} \sim \Delta n$ dependence and also clearly shows that the deactivation is an electronically stimulated process where photons are not directly involved.

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