Electronic properties of light-induced recombination centers in boron-doped Czochralski silicon

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In order to study the electronic properties of the recombination centers responsible for the light-induced carrier lifetime degradation commonly observed in high-purity boron-doped Czochralski (Cz) silicon, injection-level dependent carrier lifetime measurements are performed on a large number of boron-doped *p*-type Cz silicon wafers of various resistivities (1–31 Ω cm) prior to and after light degradation. The measurement technique used is the contactless quasi-steady-state photoconductance method, allowing carrier lifetime measurements over a very broad injection range between 10^{12} and 10^{17} cm^{-3}. To eliminate all recombination channels not related to the degradation effect, the difference of the inverse lifetimes measured after and before light degradation is evaluated. A detailed analysis of the injection level dependence of the carrier lifetime change using the Shockley–Read–Hall theory shows that the fundamental recombination center created during illumination has an energy level between $E_v+0.35$ and $E_c-0.45$ eV and an electron/hole capture time constant ratio between 0.1 and 0.2. This deep-level center is observed in all samples and is attributed to a new type of boron–oxygen complex. Besides this fundamental defect, in some samples an additional shallow-level recombination center at 0.15 eV below E_c or above E_v is found to be activated during light exposure. This second center dominates the light-degraded carrier lifetime only under high-injection conditions and is hence only of minor importance for low-injection operated devices. © *1999 American Institute of Physics.* [S0021-8979(99)02618-3]

I. INTRODUCTION

Carrier lifetime instabilities in boron-doped Czochralski (Cz) grown silicon have been extensively investigated in the past and several distinct phenomena have been reported. One of the effects most frequently investigated is the degradation of the carrier lifetime as a consequence of illumination with ''white'' light, minority-carrier injection in the dark, or annealing. The effect has been explained in terms of the dissociation of iron–boron pairs and is, therefore, linked to the degree of iron contamination in the material.[1–3] It can also be observed in iron-contaminated boron-doped float-zone (FZ) silicon and is not restricted to Cz silicon.[1]

A more fundamental light-induced carrier lifetime degradation has been observed in metal–impurity free boron-doped Cz silicon.[4] Similar to the iron–boron dissociation, this degradation effect also occurs in the dark when minority carriers are injected (e.g., by a forward-biased *pn* junction), leading to the important conclusion that the degradation is caused by excess charge carriers and not directly by photons.[5,6] However, in contrast to the iron-correlated lifetime degradation, which also occurs during annealing above ~100 °C,[1–3] the latter degradation effect is fully reversible by annealing above 200 °C,[4–7] i.e., the degraded lifetime recovers during low-temperature annealing, making it relatively easy to distinguish between both effects. Since most of today's high-purity Cz-grown silicon crystals are virtually free of any metal impurities, a fundamental understanding of the carrier lifetime variations in this material becomes more and more important, in particular with regard to devices such as solar cells and bipolar transistors, where the carrier recombination lifetime is the most influential physical parameter.

Although the light-induced lifetime degradation in metal–impurity free boron-doped Cz silicon had already been discovered more than two decades ago,[4] a conclusive explanation of the effect is still to be found. Schmidt *et al.*[8] recently proposed a defect reaction model capable of explaining the lifetime degradation under illumination (or, alternatively, minority-carrier injection) as well as the recovery during low-temperature annealing. In this model, a lifetime-reducing recombination center made up of one interstitial boron and one interstitial oxygen atom is created under illumination (large concentrations of oxygen are practically unavoidable in Cz silicon due to the partial dissolution of the silica crucible during the growth process). Interestingly, the experiments showed that gallium-doped and phosphorus-doped Cz silicon as well as oxygen-free FZ silicon samples did not present any lifetime degradation effect, which is thus exclusively linked to the simultaneous presence of boron and oxygen in the material.[8]

More recently, Glunz *et al.*[9] have also found a strong correlation between the light-induced lifetime degradation in Cz silicon and the boron as well as the oxygen concentrations. However, whereas they found an approximately linear increase of the lifetime degradation with boron doping concentration, a strongly superlinear increase with interstitial oxygen concentration was observed (approximately to the power of five). These results give rise to the suspicion that

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the recombination center responsible for the light-induced carrier lifetime degradation in Cz silicon is probably associated with a defect compound more complex than the simple boron–oxygen pair.

In this article, the electronic properties of the recombination centers created during illumination with ''white'' light in boron-doped Cz silicon are investigated. While previous work mainly focused on lifetime measurements at a single carrier injection level (usually in the very low injection range), the present study explores a broad carrier injection range between 10^{12} and 5×10^{16} cm^{-3} in conjunction with the use of various Cz silicon wafers with boron doping concentrations ranging from 4.3×10^{14} to 1.4×10^{16} cm^{-3}. The injection level dependence of the lifetime degradation is theoretically analyzed using the Shockley–Read–Hall (SRH) recombination model.[10,11] Given the broad range of dopant densities and carrier injection levels covered in the experiments, the fitting of the SRH model to the measurements allows for a very narrow restriction of the energy levels of the recombination centers and their corresponding electron/hole capture time constant ratios. From this data, conclusions on the nature of the light-induced centers can be made.

II. EXPERIMENTAL DETAILS

The samples investigated in this study are 260–560 μm thick (100)-oriented high-purity Cz silicon wafers obtained from various manufacturers. All wafers are boron doped with resistivities between 1 and 31 Ω cm. In order to minimize the surface recombination, both surfaces of each wafer were coated with silicon nitride films deposited in a remote plasma-enhanced chemical vapor deposition system at 375 °C. This low-temperature surface passivation scheme has proved to result in very low surface recombination velocities below 10 cm/s.[12,13] Prior to the silicon nitride deposition, the wafers were damage etched and received a standard RCA cleaning.

Several Cz wafers were checked for metal impurities by applying a special phosphorus diffusion treatment, which has proved to be a highly effective technique to getter metallic impurities in silicon.[14,15] The phosphorus gettering treatment neither changed the lifetime degradation nor the recovery behavior of the wafers appreciably, indicating that the samples are virtually free from metallic impurities. The interstitial oxygen concentration of all Cz wafers was found to be very similar, ranging from 5.5 to 7.8×10^{17} cm^{-3}, as determined by means of Fourier transform infrared spectroscopy.[16]

The effective carrier recombination lifetime of the Cz silicon wafers was measured by means of the contactless quasi-steady-state photoconductance (QSSPC) method,[17,18] using a WCT-100 system from Sinton Consulting with improved sensitivity. In this system, the sample is inductively coupled to a calibrated rf circuit whose output voltage is directly correlated to the conductance of the sample. During each measurement, the sample is exposed to a slowly decaying illumination intensity (decay time constant ~2 ms), generated by means of an ordinary photo flash lamp (Quantum Turbo T2). Since the light intensity of the flash varies only over about one decade, different combinations of gray filters are used to enlarge the accessible injection range to about 4 decades. The time-dependent output signal of the rf circuit is recorded with an oscilloscope (Tektronix TDS 310) and converted into the photoconductance. Using an appropriate mobility model[19] and assuming a spatially uniform injection profile throughout the wafer, the excess carrier concentration Δn is calculated from the photoconductance signal. Simultaneously, the light intensity is measured with a calibrated silicon concentrator solar cell and the signal is recorded on the second channel of the oscilloscope. From the latter measurement, the generation rate G is calculated. The effective carrier lifetime is then determined by the expression $\tau_{\text{eff}}=\Delta n/(G-d\Delta n/dt)$.[20] In comparison with the traditional photoconductance decay technique, the QSSPC method is capable of measuring carrier lifetimes in a much wider injection range. A detailed comparison of both techniques can be found in the literature.[21] The QSSPC system was also used for the accurate determination of the base resistivity of the investigated Cz wafers.

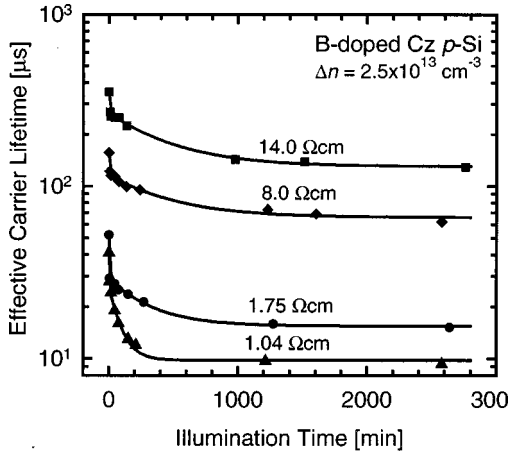

FIG. 1. Measured effective carrier lifetime as a function of the illumination time (halogen lamp, intensity 100 mW/cm^2, 25 °C) of several boron-doped Cz silicon wafers at a fixed injection level of 2.5×10^{13} cm^{-3}.

The light degradation of the samples was performed on a temperature-controlled stage at 25 °C by means of a dc-powered halogen lamp at a light intensity of 100 mW/cm^2. The relatively short light pulses of the flash lamp did not produce any significant degradation of the lifetime.

III. RESULTS AND DISCUSSION

All Cz silicon wafers investigated in this study showed a pronounced degradation of the effective carrier lifetime under illumination with white light. In Fig. 1, the τ_{eff} values of several samples, measured at a fixed injection level of 2.5×10^{13} cm^{-3}, are plotted versus the duration of the light exposure. In agreement with the behavior reported in the literature, the degradation was found to be fully reversible by a low-temperature anneal above approximately 200 °C. It should be noted that the degradation/recovery cycle was repeatable many times without notable change. In order to exclude the possibility of a changing surface recombination velocity during illumination or annealing, silicon–nitride

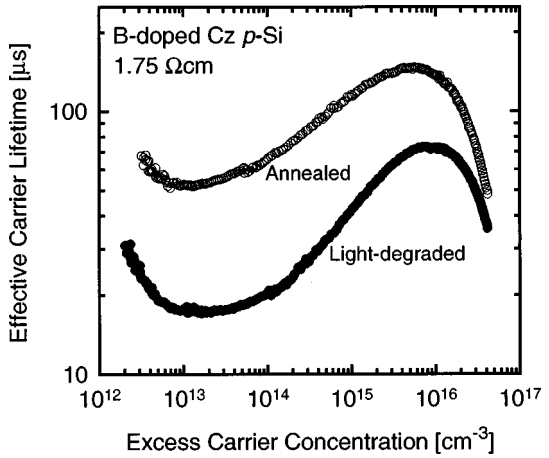

FIG. 2. Measured effective carrier lifetime as a function of the excess carrier concentration of a 1.75 Ω cm boron-doped Cz silicon wafer after annealing at 250 °C for 15 min (open circles) and after light degradation with a halogen lamp (intensity 100 mW/cm^2) at 25 °C for ~40 h (closed circles).

passivated high-purity FZ silicon wafers were illuminated and annealed in parallel with the Cz silicon wafers. The effective carrier lifetime of these reference wafers changed neither during illumination nor during low-temperature annealing. Hence, the observed τ_{eff} variations of the boron-doped Cz silicon wafers are exclusively related to a changing bulk carrier lifetime.

Figures 2 and 3 show the measured effective carrier lifetime as a function of the excess carrier concentration for two Cz silicon wafers representative of the samples investigated in this study. Figure 2 shows the results obtained on a low-resistivity Cz silicon wafer (1.75 Ω cm, commonly used for solar cells), while the data of Fig. 3 were measured on a high-resistivity Cz wafer (14.0 Ω cm, typically used for microelectronic applications). The open circles were measured after annealing the samples for 15 min at 250 °C in nitrogen, whereas the closed circles were measured after illuminating the wafers at a controlled temperature of 25 °C for about 40 h with a halogen lamp (light intensity 100 mW/cm^2), leading to a complete degradation of the carrier lifetime (see Fig. 1).

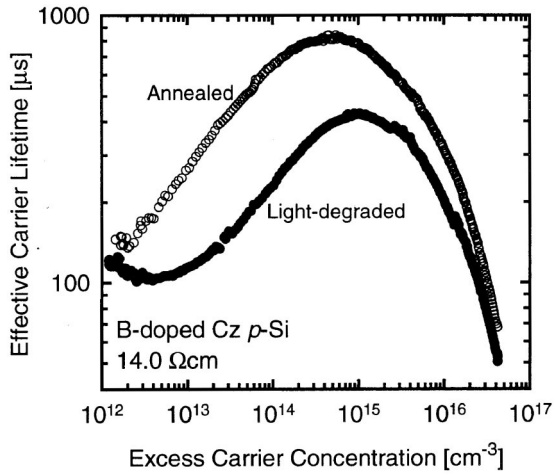

FIG. 3. Measured effective carrier lifetime as a function of the excess carrier concentration of a 14.0 Ω cm boron-doped Cz silicon wafer after annealing at 250 °C for 15 min (open circles) and after light degradation with a halogen lamp (intensity 100 mW/cm^2) at 25 °C for ~40 h (closed circles).

Qualitatively, the $\tau_{\text{eff}}(\Delta n)$ dependencies of all the Cz wafers investigated in this study are very similar. The most important feature of all $\tau_{\text{eff}}(\Delta n)$ curves is a strong increase of the measured effective carrier lifetime with increasing Δn above an injection level of about 10^{13} cm^{-3}. However, in the case of the 1.75 Ω cm Cz silicon wafer of Fig. 2, the observed increase in carrier lifetime is more pronounced after light degradation than after annealing, while the opposite behavior is observed for the 14.0 Ω cm Cz wafer of Fig. 3. The reason for this difference between low- and high-resistivity material is the influence of the surface recombination on the measured effective lifetime. Since the carrier lifetime of the high-resistivity wafer of Fig. 3 is approximately one order of magnitude larger than the lifetime measured on the low-resistivity wafer of Fig. 2, the surface recombination has a much stronger influence in the case of the 14.0 Ω cm compared to the 1.75 Ω cm Cz silicon wafer. This applies in particular to the annealed wafers. As the applied silicon nitride surface passivation scheme is known to produce a strongly injection-level dependent effective surface recombination velocity,[12,13] it is highly likely that the effective carrier lifetime measured on the annealed 14.0 Ω cm Cz silicon wafer reflects mainly the injection level dependence of the surface passivation quality. In contrast, the $\tau_{\text{eff}}(\Delta n)$ dependencies measured on the 1.75 Ω cm Cz silicon wafer, after annealing as well as after light degradation, are largely determined by the recombination in the bulk of the wafer. Hence, the enhancement of the increase of τ_{eff} with increasing Δn after light exposure observed for the 1.75 Ω cm Cz silicon wafer is predominantly due to the properties of the light-induced recombination centers in the bulk. At high injection levels (above the doping concentration of the wafer), a decrease of the measured lifetime with increasing excess carrier concentration is observed (see Figs. 2 and 3). This decrease is partly due to a shallow-level recombination center in the bulk (discussed below) and partly due to an increasing surface recombination velocity. At very large injection levels, the measured lifetime is dominated by Auger recombination, as indicated by an inversely quadratic decrease of the lifetime with increasing injection level.

At very low injection levels ($\Delta n < 10^{13}$ cm^{-3}), the measured carrier lifetime increases with decreasing excess carrier concentration. This strange behavior has also been observed recently in multicrystalline silicon wafers (although occurring at much higher injection levels),[22] where it was explained in terms of a carrier trapping model developed by Hornbeck and Haynes in 1954.[23] Since the present study concentrates on the investigation of recombination properties, the trapping effect is not further considered here.

From the above discussion it becomes evident how difficult it is to extract only the behavior of the light-induced recombination centers from the measured effective carrier lifetimes. Therefore, in the following instead of considering the measured τ_{eff}, we investigate the injection level dependence of the quantity $(1/\tau_i - 1/\tau_a)^{-1}$, where τ_i is the effective carrier lifetime measured after complete light degradation and τ_a is the effective lifetime measured after low-

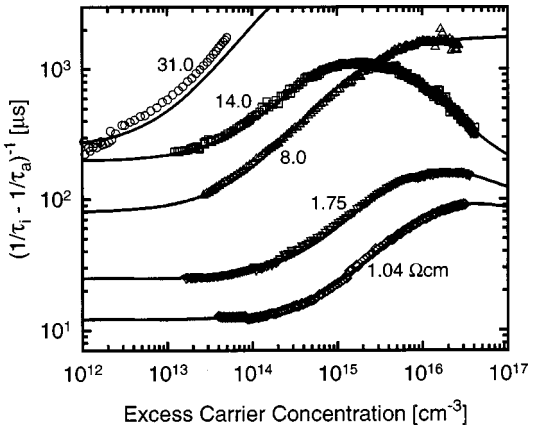

FIG. 4. Measured injection level dependence of the quantity $(1/\tau_i - 1/\tau_a)^{-1}$ for several boron-doped Cz silicon wafers with different resistivity (symbols). τ_i is the effective lifetime measured after complete light degradation and τ_a is the effective lifetime measured after low-temperature annealing. The solid lines are calculated using the SRH equation.

temperature annealing. Assuming that all other defects within the Cz silicon wafers as well as the silicon nitride surface passivation are not affected by the illumination/annealing treatments, the quantity $(1/\tau_i - 1/\tau_a)^{-1}$ should equal the SRH lifetime τ_{SRH} of the light-induced defect centers. This evaluation scheme also eliminates the influence of all intrinsic recombination channels like Auger and radiative recombination.

In Fig. 4, the measured dependencies of $(1/\tau_i - 1/\tau_a)^{-1}$ on Δn of Cz silicon wafers with different boron concentrations are shown. The solid lines represent the theoretically calculated dependencies using the standard SRH equation[10,11]

$$\tau_{\mathrm{SRH}} = \tau_{p0}\frac{(n_0+n_1+\Delta n)}{(n_0+p_0+\Delta n)} + \tau_{n0}\frac{(p_0+p_1+\Delta n)}{(n_0+p_0+\Delta n)}, \tag{1}$$

where τ_{n0}, τ_{p0} are the capture time constants and n_0, p_0 are the thermal equilibrium concentrations of electrons and holes, respectively. Trapping is assumed to be negligible, i.e., the excess carrier concentrations of electrons and holes are equal $(\Delta n = \Delta p)$. The quantities n_1 and p_1 are given by the expressions

$$\begin{aligned} n_1 &= N_c \exp[-(E_c - E_t)/kT], \\ p_1 &= N_v \exp[-(E_t - E_v)/kT], \end{aligned} \tag{2}$$

where E_t is the energy level of the recombination center, E_c and E_v are the energetic positions of the conduction and valence band edge, and N_c and N_v are the effective state densities in the conduction and valence band.

The increase of the quantity $(1/\tau_i - 1/\tau_a)^{-1}$ with increasing Δn at low excess carrier concentrations observed for all Cz silicon wafers independent of their resistivity can be modeled assuming a recombination center with a deep energy level. For the calculations shown as solid lines in Fig. 4, the defect energy level was fixed at midgap (the range of possible energy levels is discussed further below) and the characteristic ratio τ_{n0}/τ_{p0} of the center was varied to obtain the best possible fit. The optimum τ_{n0}/τ_{p0} ratio was found to lie in a very narrow range between 0.1 and 0.2. Only in the case of the 31.0 Ω cm Cz wafer a higher τ_{n0}/τ_{p0} value of 0.4 had to be used. This deviation might be due to the relatively large error of the data points obtained on the 31.0 Ω cm wafer, because the maximum light-induced change in the effective carrier lifetime of this sample was only 32%. Nevertheless, the measurement on the 31.0 Ω cm wafer gives very important information, since it strongly restricts the range of possible energy levels. The detailed analysis shows that the calculated injection-level dependent SRH lifetimes (solid lines in Fig. 4) are invariant against variations of the defect energy level between $E_v + 0.35$ eV and $E_c - 0.45$ eV. Hence, it can be concluded from our measurements that this is the energy range in which the fundamental recombination center responsible for the light-induced carrier lifetime degradation in boron-doped Cz silicon can be found. It is important to note that even if the capture time constant ratio τ_{n0}/τ_{p0} is strongly modified, it is *not* possible to simultaneously obtain good fits to all measurement curves with a defect energy level above or below this energy range.

The most important result of this analysis is that the restriction of the energy level *excludes* the boron–oxygen pair as a possible candidate for the light-induced defect center, since the energy level associated with the boron–oxygen pair is known to lie in the range between $E_c - 0.27$ eV and $E_c - 0.26$ eV, as determined from deep-level transient spectroscopy (DLTS) measurements on electron-irradiated Cz silicon.[24–26] It should be noted that, in contrast to the situation on the high-resistivity wafers, in the case of the Cz silicon wafers with resistivity <2 Ω cm it is also possible to model the injection level dependence of the measured $(1/\tau_i - 1/\tau_a)^{-1}$ by the energy level of the boron–oxygen pair.[27] However, due to the large doping concentration of these wafers, the same injection-level dependent SRH lifetime is obtained for a very broad range of possible energy levels. Hence, the results obtained on low-resistivity Cz wafers alone would not result in a sufficient restriction of the energy level to exclude the boron–oxygen pair.

In order to successfully model the *complete* injection-level dependence of $(1/\tau_i - 1/\tau_a)^{-1}$, for some samples it was necessary to introduce a second recombination center with a shallow energy level. The shallow energy level produces a decreasing SRH lifetime at the upper end of the measured injection range, a behavior which was indeed observed in several samples (see Fig. 4). An excellent agreement between experiment and theory was obtained for an energy level of $E_c - 0.15$ eV in combination with a τ_{n0}/τ_{p0} value $\leqslant 1$ or, alternatively, for an energy level of $E_v + 0.15$ eV and $\tau_{n0}/\tau_{p0} \geqslant 1$.

Figures 5 and 6 show the data points (open circles) measured on the 1.75 Ω cm and the 14.0 Ω cm Cz silicon wafer, respectively, together with the calculated injection-level dependent SRH lifetimes for the shallow and the deep-level center (dashed lines) as well as the total SRH lifetime (solid lines). The latter quantity was simply determined by calculating the reciprocal of the sum of the inverse deep-level and shallow-level SRH lifetimes. However, the shallow-level center was not found in all samples. The solid line in Fig. 4 corresponding to the 8.0 Ω cm Cz silicon wafer is calculated

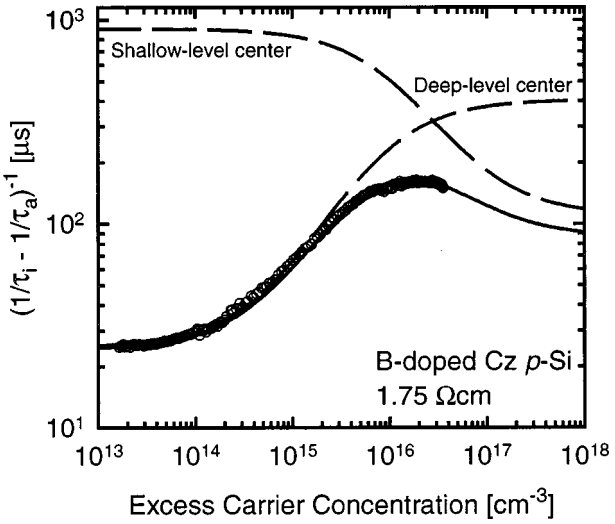

FIG. 5. Injection level dependence of $(1/\tau_i - 1/\tau_a)^{-1}$ for the 1.75 Ω cm boron-doped Cz silicon wafer of Fig. 2 (open circles). The dashed lines show the calculated injection-level dependent SRH lifetime of the assumed shallow and the deep-level recombination center, respectively. The solid line shows the total SRH lifetime.

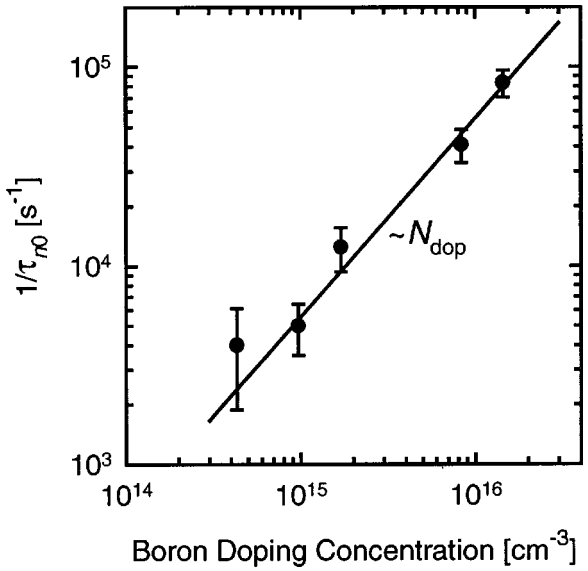

FIG. 7. Inverse capture time constant for electrons $1/\tau_{n0}$ of the light-induced deep-level recombination center as a function of the boron doping concentration N_{dop}. The quantity $1/\tau_{n0}$ increases proportionally with N_{dop}, as indicated by the solid line.

for the deep-level center only. As can be seen from Fig. 4, it perfectly fits the measurement and no additional recombination center is required to adequately model the observed dependence. From these results it can be concluded that only the deep-level center is a really fundamental light-induced recombination center in boron-doped Cz silicon.

In addition to the energy level, the SRH model also gives information on the capture time constant for electrons τ_{n0}, i.e., the minority-carrier lifetime, of the fundamental deep-level center. As shown in Fig. 7, the values of τ_{n0} for the different samples are strongly dependent on the respective boron doping concentration N_{dop}. According to the SRH theory, the quantity $1/\tau_{n0}$ equals the product $v_{\mathrm{th}}\sigma_n N_t$, where v_{th} is the thermal velocity of electrons, σ_n is the electron capture cross section, and N_t is the concentration of the recombination center. Hence, $1/\tau_{n0}$ is directly proportional to the concentration of the light-induced defect centers. The solid line in Fig. 7 shows that $1/\tau_{n0}$, and hence the concentration of the recombination centers, increases proportionally with N_{dop}. This finding suggests that one boron atom is involved in the defect complex responsible for the light degradation in boron-doped Cz silicon. Although it should be kept in mind that the experiments by Glunz *et al.*[9] do not allow for a determination of the capture time constant, their finding that there is a linear correlation between the boron concentration and the magnitude of the lifetime degradation supports our conclusion. In addition, they also found that the inverse SRH lifetime of the light-induced centers increases with the interstitial oxygen concentration by a power law of order five. Taking this finding into account, our results allow us to tentatively identify the deep-level center as a new boron–oxygen complex, probably of the type BO_n with $n \approx 5$. However, it should be remarked that our results do not exclude the participation of other point defects usually present in Cz-grown silicon, like silicon self interstitials or vacancies.

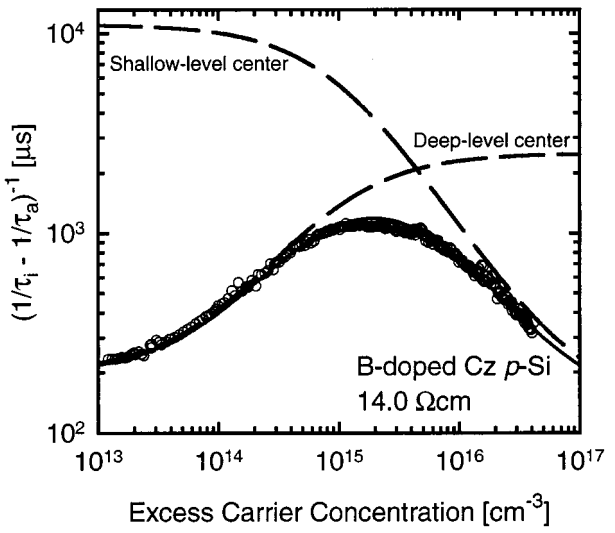

FIG. 6. Injection level dependence of $(1/\tau_i - 1/\tau_a)^{-1}$ for the 14.0 Ω cm boron-doped Cz silicon wafer of Fig. 3 (open circles). The dashed lines show the calculated injection-level dependent SRH lifetime of the assumed shallow and the deep-level recombination center, respectively. The solid line shows the total SRH lifetime.

The nature of the light-induced shallow-energy center observed in some of the investigated Cz silicon wafers can only be speculated on. The energy level of $E_c - 0.15$ eV could, for example, be associated with a thermal donor (TD) level. Two different TD levels have been identified by means of DLTS measurements on Cz silicon with high oxygen concentration ($>10^{17}$ cm^{-3}).[28] One of these levels was found at $E_c - 0.07$ eV, the other at $E_c - 0.15$ eV.[28] A recently reported bistability of these defects[29] might be able to explain the observed behavior.

IV. CONCLUSIONS

Our analysis of injection-level dependent carrier lifetime measurements has shed some light on the nature of the recombination centers created during illumination of boron-doped Cz silicon. We have found two different kinds of light-induced defect centers. One of them is a shallow-level center at 0.15 eV below E_c or above E_v. This center was, however, found only in some samples and it contributes to the total SRH lifetime only at injection levels much larger than the dopant density.

The recombination center mainly responsible for the lifetime degradation has an energy level located close to the middle of the silicon band gap, with our experiments indicating that it lies in the energy range between $E_v+0.35$ and $E_c-0.45$ eV. This excludes the formerly proposed boron–oxygen pair as a possible candidate for the light-induced defect center. We have also studied the capture time constant for electrons associated with the recombination center and found that its inverse increases proportionally with boron concentration, implying that the light-induced deep-level center contains one boron atom. Our results indicate, therefore, the formation of a new boron–oxygen complex of the type BO_n with preliminary evidence from other investigators that $n \approx 5$, that is, that five oxygen atoms might be involved in the complex. However, it cannot be ruled out that other defect species, like silicon self interstitials or vacancies, are constituents of the defect complex. Further theoretical as well as experimental investigations have to be performed in order to reveal the detailed structure and the formation kinetics of the new BO_n complex.

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