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## Light-induced lifetime degradation in boron-doped Czochralski silicon: are oxygen dimers involved?

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### Abstract

Light-induced electron lifetime degradation in boron-doped Czochralski silicon was studied before and after a prolonged annealing at 350°C (up to 120 h) and 300°C (up to 8 weeks). Such a heat treatment is known to reduce significantly – by a factor of 3 or more - the concentration of oxygen dimers. The lifetime degradation observed in these samples was not however remarkably reduced; on the contrary, it was sometimes slightly increased. This result shows unambiguously that oxygen dimers - present in the material before illumination - do not participate in formation of the lifetime-degrading centres. This conclusion is in line with some other features of the degradation. The known proportionality of the centre density to the squared oxygen concentration and to the boron concentration can originate from  $B_5O_2$  defects already present before illumination – in a concentration which depends on thermal history and, in particular, may slightly increase during above-mentioned prolonged annealing.

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### 1. Introduction

In silicon containing boron and oxygen, the excess carriers (introduced by illumination or by injection through a junction) promote generation of new and efficient recombination centres [1-3]. The resulting severe degradation of the carrier lifetime is an important effect that limits solar cell efficiency. A fundamental feature is that in boron-only doped Czochralski Si, the saturated concentration  $N_s$  of these recombination centres [3] is proportional to the boron concentration  $N_B$  and to the squared oxygen concentration,  $C^2$ . In an early proposed model [3, 4], the recombination centres responsible for the lifetime degradation were thought to be  $B_5O_2$  – produced due to a carrier-enhanced diffusion of oxygen dimers ( $O_2$ ) to the substitutional boron atoms ( $B_s$ ). However, if this were the case, the saturated concentration  $N_s$  would be identical to the starting concentration of  $O_2$  dimers - and not dependent on  $N_B$ .

This is because the estimated concentration of  $O_2$  (about  $3 \times 10^{14} \text{ cm}^{-3}$  [5, 6]) is much less than the concentration of boron atoms (about  $10^{16} \text{ cm}^{-3}$ ) which act as traps for  $O_2$ . Another strong piece of evidence against this model is that the rate constant for the degradation – if treated as trapping of  $O_2$  by  $B_s$  - would be proportional to the trap concentration,  $N_B$ . In reality, it was found [7] that in material doped with both boron and phosphorus, the rate constant depends only on the hole concentration. This can be understood if the degradation is caused by a carrier-induced reconfiguration of some already present latent defects of a low recombination activity into another, recombination-active state [6]. The latent defects have a concentration proportional to  $N_B C^2$ . In particular, the  $B_s O_2$  complexes - formed in the course of cooling of crystals or wafers – will have a proper dependence on  $N_B$  and  $C$ . In other words, the recombination centres (emerged from the latent centres) do contain oxygen dimers but these dimers have been already incorporated into these centres long ago while the free dimers present during illumination are not involved at all in the degradation process.

In the present work we obtain a further – and more direct - piece of evidence against involvement of free (not yet complexed) oxygen dimers in the degradation process. It is known [8] that a prolonged annealing at  $350^\circ\text{C}$  leads to a significant reduction in the  $O_2$  concentration monitored by the IR vibrational band at  $1012 \text{ cm}^{-1}$ . The reason for this is that the  $O_2$  defects are mobile at this temperature, and they are trapped by (practically immobile) monomeric oxygen thus producing trimers  $O_3$ . The emerging trimers can be monitored by a band at  $1005 \text{ cm}^{-1}$ . Even stronger suppression of  $O_2$  is expected after a still more prolonged anneal at lower temperature such as  $300^\circ\text{C}$  when the equilibrium ratio of  $O_3$  to  $O_2$  is larger. It is thus highly informative to study the lifetime degradation in such a material – in which the concentration of free dimers have been reduced significantly – to check if the degradation (the saturated concentration  $N_s$ ) is affected.

### Nomenclature

$N_B$	boron concentration
$C$	oxygen concentration
$N_s$	saturated concentration of lifetime-degrading centres
$\tau_0$	electron lifetime before degradation
$\tau_d$	electron lifetime after full degradation
$p_0$	dark value of the hole concentration

## 2. Experimental

The Czochralski-grown boron-doped silicon wafers used in these studies had an oxygen concentration close to  $7 \times 10^{17} \text{ cm}^{-3}$  (using the new ASTM optical calibration coefficient,  $2.45 \times 10^{17} \text{ cm}^{-2}$ ). One group of wafers had a starting resistivity close to 3 Ohm-cm and the other group – close to 10 Ohm-cm. Some wafers were annealed at  $350^\circ\text{C}$  for 30, 60 or 120 h; these durations are sufficient [8] for a significant reduction in the  $O_2$  concentration. Other wafers were annealed at  $300^\circ\text{C}$  for 2, 4 or 8 weeks. The dimeric diffusivity at this temperature is smaller by a factor of 20, taking into account that the activation energy for  $O_2$  diffusion is 1.85 eV [6]. Accordingly, the annealing time was increased by this factor.

Upon annealing, the resistivity was marginally increased due to formation of thermal donors. Each

wafer was then subjected to a surface passivation treatment to suppress surface recombination, and the lifetime was measured by conventional technique of Quasi-Steady-State Photoconductivity, as a function of injected electron concentration  $n$ , in a wide range from  $10^{12}$  to  $10^{16}$   $\text{cm}^{-3}$ . The lifetime measurements were repeated after illumination with 0.1 sun for 60 h (3 Ohm-cm samples) or 1000 h (11 Ohm-cm samples) at room temperature – which is sufficient to reach a saturated lifetime degradation. The pre-degradation lifetime is denoted by  $\tau_0$  while the degraded lifetime – by  $\tau_d$ . The concentration of the degrading centres,  $N_s$ , is proportional to the difference of the reciprocal lifetimes after and before illumination. The absolute value of  $N_s$  cannot be specified, and an effective concentration is used instead - defined as  $N_s = 1/\tau_d - 1/\tau_0$  where both lifetimes,  $\tau_d$  and  $\tau_0$ , are taken at some fixed (reference) injection level  $n/p_0$  where  $p_0$  is the dark value of the hole concentration deduced from the measured resistivity. The reference injection level was adopted to have a conventional value of 0.1.

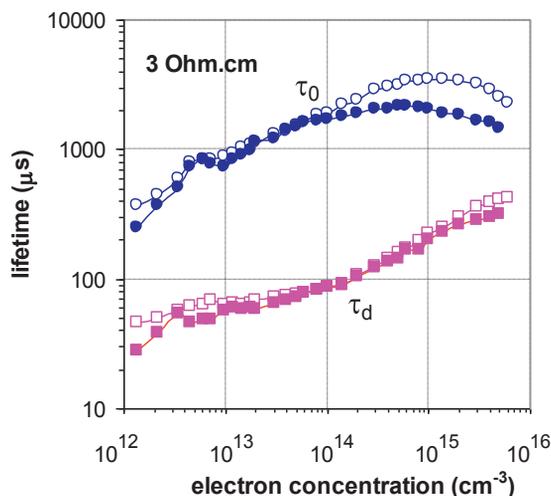


Fig. 1 Steady-state electron lifetime before degradation (circles) and after illumination at 0.1 sun for 60 h at room temperature (squares). Open symbols refer to the non-annealed state and closed symbols – to the sample annealed at 350°C for 60 h.

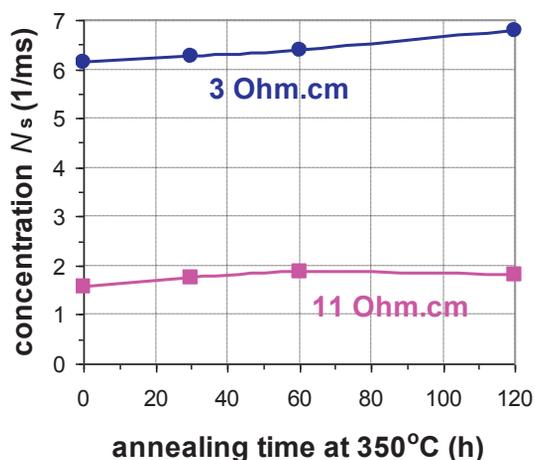


Fig. 2 Effective concentration of lifetime-degrading recombination centres in dependence of the annealing time at 350°C. Circles and squares refer to the samples of two different resistivity, 3 and 11 Ohm-cm, respectively.

### 3. Results

A representative dependence of the two lifetimes,  $\tau_d$  and  $\tau_0$ , on the injected electron concentration  $n$ , is shown in Fig.1, for 3 Ohm-cm material, both before annealing and after annealing at 350°C for 60 h. Both the pre-degradation lifetime ( $\tau_0$ , circles) and the degraded lifetime ( $\tau_d$ , squares) are only slightly shifted by annealing. This is true also for all the other anneals. Accordingly, the concentration  $N_s$  of the illumination-produced lifetime-degrading recombination centres is only marginally changed by annealing.

This important result is further illustrated in Fig.2 where  $N_s$  is shown in dependence of the annealing time at 350°C. The two curves are for the two different values of the resistivity, 3 and 11 Ohm-cm. The corresponding boron concentrations  $N_B$  (identical to  $p_0$ ) is equal to  $4.6 \times 10^{15}$  and  $1.2 \times 10^{15}$   $\text{cm}^{-3}$ , respectively. Wafers used for annealing at 300°C were cut from a different crystal, of a resistivity close to 3 Ohm-cm. They show somewhat lower values of both lifetimes,  $\tau_0$  and  $\tau_d$  (Fig. 3) but again only a slight shift occurs in the annealed samples. A stronger degradation (a larger  $N_s$ ) is found for this sample (Fig.4). The annealing results in only a slight reduction in  $N_s$ .

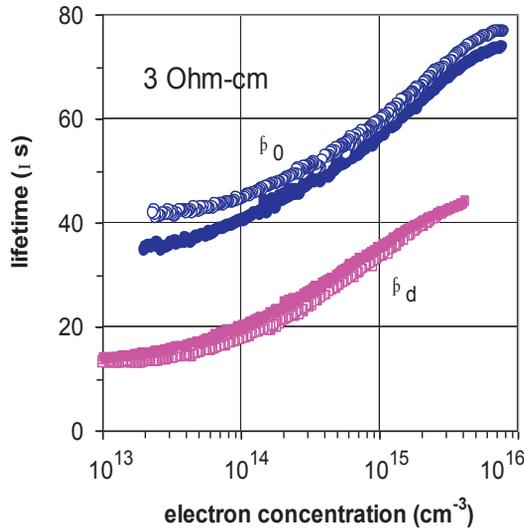


Fig. 3 Steady-state electron lifetime before degradation (blue circles) and after illumination at 0.1 sun for 60 h at room temperature (pink squares). Open symbols refer to the non-annealed state and closed symbols – to the sample annealed at 300°C for 8 weeks.

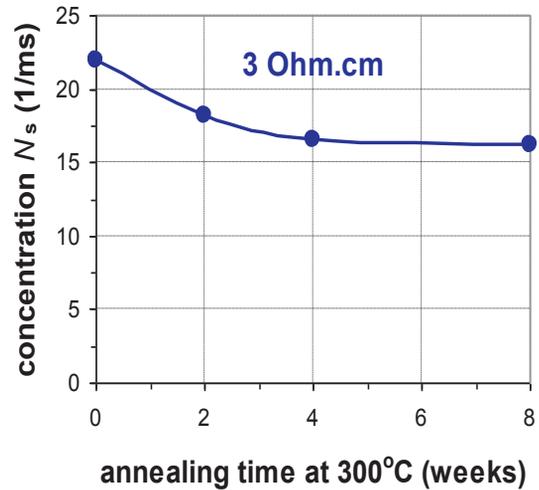


Fig. 4 Effective concentration of lifetime-degrading recombination centres in dependence of the annealing time at 300°C. The material resistivity is 3 Ohm-cm.

#### 4. Discussion

The results of the present work clearly show that the “free” dimers - those present in a sample prior to illumination - do not participate in the lifetime degradation. The concentration of these dimers is known to be reduced essentially by a prolonged annealing at 350°C [8]. It is expected to be reduced still more by a prolonged annealing at 300°C. Were the free dimers responsible for the formation of the lifetime-degrading centres, the degradation in the annealed samples would be strongly diminished. This however does not happen; moreover, there is some (slight) increase in the saturated concentration of the lifetime-degrading centres after 350°C anneal (Fig.2).

The early proposed formation mechanism of the degrading centres, by enhanced diffusion of O<sub>2</sub> dimers in the presence of excess carriers, and their trapping by boron, is thus ruled out.

This conclusion further supports an alternative general explanation [6] – that the material already contains some recombination-inactive (latent) defects, and that the excess carriers (here, electrons) induce a reconstruction of these latent centres into a recombination-active atomic configuration.

The latent defects are definitely some complexes involving boron and oxygen, but their chemical composition is a subtle matter to be yet solved. In a simple version, one may assume that the latent defects are B<sub>s</sub>O<sub>2</sub> complexes inherited from the cooling process of a crystal or – if the wafers have been then annealed at high *T* - from the cooling process of wafers. In a range of sufficiently high *T*, the B<sub>s</sub>O<sub>2</sub> complexes are in equilibrium with the source defects, B<sub>s</sub> and O<sub>2</sub>, and exist in a concentration that is equal to [B<sub>s</sub>] [O<sub>2</sub>] / *K*. The equilibrium mass-action law constant *K* is proportional to exp(-*E*/*kT*) where *E* is the binding energy of the two source defects into a complex. The dimers are in turn in equilibrium with

monomeric oxygen, and the concentration  $[O_2]$  is proportional to  $C^2$ . The concentration of  $B_sO_2$  defects is thus proportional to  $N_B C^2$ , and increases upon lowering  $T$  following a reduction in  $K(T)$ . Below some freezing-in temperature  $T_f$ , the pairing reaction becomes too slow to contribute into further accumulation of the complexes. The frozen-in concentration of  $B_sO_2$  will be close to the equilibrium value at  $T_f$ , and thus proportional to  $N_B C^2$ .

This simple identification however cannot be true for the major recombination centres that represent a Slow Stage in the kinetic curve of centre production [3] and accordingly labelled SRC. In B-doped material compensated with phosphorus, the saturated SRC concentration (almost identical to  $N_s$ ) was reported [7] to be proportional to the hole concentration  $p_0$  rather than to  $N_B$  (although the data are scattered). This indicates [6] an involvement of an interstitial boron atom  $B_i$  in the latent centre which then reconstructs into SRC. This latent centre is denoted LCS. The  $B_i$  atoms are initially produced by self-interstitials emitted by oxide precipitates; later they mostly aggregate into nano-precipitates (NPs). The remaining dissolved concentration - in equilibrium with the NPs - is proportional to the hole concentration since a  $B_i$  atom has a single-positive charge. The hole concentration has an intrinsic value at higher  $T$  but below some characteristic temperature (roughly 350°C) it is identical to the net doping concentration,  $p_0$ . Therefore, a frozen-in LCS defect, if it contains  $B_i$ , will have a concentration also proportional to  $p_0$ . This concept does not exclude a possibility that the previously discussed  $B_sO_2$  defect is contained, as a core, in the LCS defect which can be then identified, for instance, as  $B_iB_sO_2$  [9]. This identification will be discussed in more detail elsewhere. It is mentioned here with the purpose to account for a slight increase in  $N_s$  due to a prolonged annealing at 350°C which implies an increase in the LCS concentration (an opposite trend found after 300°C anneal is not yet understood; we should note that there are no direct IR evidence for a reduction in  $[O_2]$  by this anneal). During annealing at 350°C, most of initial  $O_2$  dimers will be trapped by the major point defects – oxygen atoms, but some minor fraction of  $O_2$  will be trapped also by  $B_s$  thus increasing the concentration of  $B_sO_2$ . Very roughly, this fraction is equal to the concentration ratio of the two traps,  $B_s$  and O, and thus expected to be about 1%. If the initial  $O_2$  concentration is assumed to have a representative value of  $3 \times 10^{14} \text{ cm}^{-3}$  then the concentration of added  $B_sO_2$  defects is on the order of  $3 \times 10^{12} \text{ cm}^{-3}$ . This is manifested as an increment of  $N_s$  in Fig.2, roughly by 20%. Then the absolute value of  $N_s$  can be estimated, by the order of magnitude, as  $10^{13} \text{ cm}^{-3}$ . This is the first – although very rough – estimate of the absolute concentration of the LCS / SRC defects.

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