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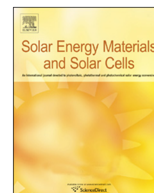

# Impact of hydrogen on the permanent deactivation of the boron-oxygen-related recombination center in crystalline silicon

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ABSTRACT

In a series of lifetime experiments, we examine the impact of hydrogen on the permanent deactivation of the boron-oxygen (BO)-related defect center in Czochralski-grown boron-doped silicon. In the first experiment, the hydrogen concentration in the external source is varied by the deposition of dielectric layers containing various hydrogen concentrations (aluminum oxide and silicon nitride layers) before applying a fast-firing step at high temperature ( > 800 °C). In the second experiment, the sample cooling rate after high-temperature treatment is varied without hydrogen-rich dielectric layer being present and the surface passivation based on aluminum oxide is applied at low temperature afterwards. In both experiments, it is observed that the sample cooling after the high-temperature treatment has the major impact on the dynamics of BO deactivation process and fast cooling rates enable a fast deactivation. No direct impact of the hydrogen content in the dielectric layers being present during the fast-firing step on the dynamics of the BO deactivation is observed. However, the highest lifetimes in excess of 1 ms are only achievable when a hydrogenation step is performed, which we interpret in terms of a hydrogen passivation of background defects of hitherto unknown nature. In a third experiment, we apply an organic passivation layer by spin-coating, which is dried at low temperature (130 °C). We find in this experiment that even without any hydrogen intentionally introduced into the silicon bulk, an effective deactivation of the BO center can be observed, clearly supporting that no hydrogen is required to enable the BO deactivation.

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## 1. Introduction

In boron-doped Czochralski-grown silicon (Cz-Si), the carrier lifetime is limited by a recombination center which is related to a defect complex containing boron and oxygen [1,2]. This BO-related defect reveals its recombination-active properties under illumination at room temperature, leading to a degrading lifetime upon illumination over several hours. This effect is often referred to as light-induced degradation (LID), although the excess electron concentration is actually causing the degradation rather than photons [3]. On the other hand, an annealing step in darkness, e.g. at 200 °C for 10 min, fully recovers the initial lifetime. However, the recovered lifetime, obtained by annealing in darkness, is not stable upon renewed illumination but degrades again towards the degraded lifetime value. The switching between these two states is completely reversible [1]. In 2006, however, Herguth et al. [4] found a loophole to this problem. They showed that the lifetime in boron-doped Cz-Si can be permanently regenerated under illumination or, more precisely, within the presence of excess electrons, at elevated temperature.

In the past, several research groups [5–9] have attributed this permanent regeneration of the lifetime to the presence of hydrogen within the silicon bulk, which was conjectured to be able to passivate the BO defect directly through a hydrogenation of the BO defect. In contrast, Voronkov and Falster [10] proposed a defect model which explained the observed regeneration of the lifetime without any hydrogen being involved. In addition to the fact that the mentioned defect models still contain many speculative elements, it turned out that the distinction between the direct impact of hydrogen in the BO deactivation process or the impact of the high-temperature firing step itself is extremely difficult, as typically hydrogenation is performed during firing. Hence, in this contribution we try to separate the effects of hydrogen and the thermal treatment in order to build the foundations for the development of a new and refined unified defect model.

Three different series of experiments are presented in this contribution, which approach the question from different

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directions. In the first experiment, different passivation schemes via the deposition of dielectric layers which feature very different hydrogen concentrations are applied to the Cz-Si wafers. The impact of the various hydrogen contents after high-temperature firing of the Cz-Si samples on the lifetime is then examined. In the second experiment, the cooling of the lifetime samples after a high-temperature treatment is varied without any hydrogen-rich dielectric layer being present. The surface passivation is carried out after the sample cooling, so that an equally small amount of hydrogen is incorporated into each sample. In the final experiment, a low-temperature passivation (the maximum temperature applied is 130 °C) based on depositing the polymer PEDOT:PSS is applied, which further reduces the in-diffusion of hydrogen from the passivation layer into the silicon bulk. In all experiments, we observe a pronounced permanent recovery of the lifetime upon illumination of our lifetime samples at elevated temperature, demonstrating that the presence of hydrogen in the silicon bulk is not a necessary prerequisite for the BO deactivation.

## 2. Experimental details

We use wafers from three different boron-doped Cz-grown silicon ingots. The wafers feature base resistivities of $(1.0 \pm 0.03)\,\Omega$ cm, $(1.6 \pm 0.1)\,\Omega$ cm, and $(2.5 \pm 0.1)\,\Omega$ cm determined via four-point-probe measurements and have a final thickness after processing of $(165 \pm 10)\,\mu$m.

Lifetime measurements within this contribution are performed using the Sinton lifetime tester WCT-120. If not mentioned otherwise, the lifetimes are extracted at a fixed injection level of $\Delta n/p_0 = 0.1$, with $\Delta n$ being the excess electron concentration and $p_0$ the dark value of the hole concentration, which is in our case identical to the boron concentration, as only non-compensated Cz-Si is used.

## 3. Experiment #1: impact of dielectric passivation layers with varying hydrogen content

### 3.1. Sample preparation

Sample processing starts with the removal of the surface damage using a solution of potassium hydroxide (KOH) followed by an RCA cleaning sequence. Afterwards, a phosphorus diffusion is performed at 850 °C for 1:10 h, which results in $n^+$ layers with a sheet resistance of $(100 \pm 10)\,\Omega/\square$. After the removal of the phosphosilicate glass (PSG) in hydrofluoric acid (HF), the phosphorus-doped regions are removed from both wafer surfaces, again using KOH. In the following, two different surface passivation schemes are applied which feature very different hydrogen concentrations. Within the first sample group, 20 nm $Al_2O_3$ are deposited on both wafer surfaces via plasma-assisted atomic layer deposition (plasma-ALD) in a FlexAL tool (Oxford Instruments). In the second group, a 10 nm $Al_2O_3$ layer, also deposited via plasma-ALD, is covered by a 70 nm thick $SiN_x$ ($n = 2.05$) layer deposited via plasma-enhanced chemical vapor deposition (PECVD) using a Roth & Rau SiNA system. Please note that the hydrogen content of the $Al_2O_3$ and the $SiN_x$ layers differ by about one order of magnitude between 12 and 20 at%[11] for the $SiN_x$ layer and between 1 and 2 at%[12] for the $Al_2O_3$ layer. After the deposition of the dielectric layers, all samples underwent a fast firing step in a conventional belt-firing furnace (Centrotherm DO-FF-8.600-300) with a set peak temperature of $\vartheta_{Peak} = 850$ °C and various belt speeds between 1.2 m/min and 7.2 m/min. The temperature profiles are measured on identical samples, processed in parallel, using a DATAPAQ Insight Oven Tracker.

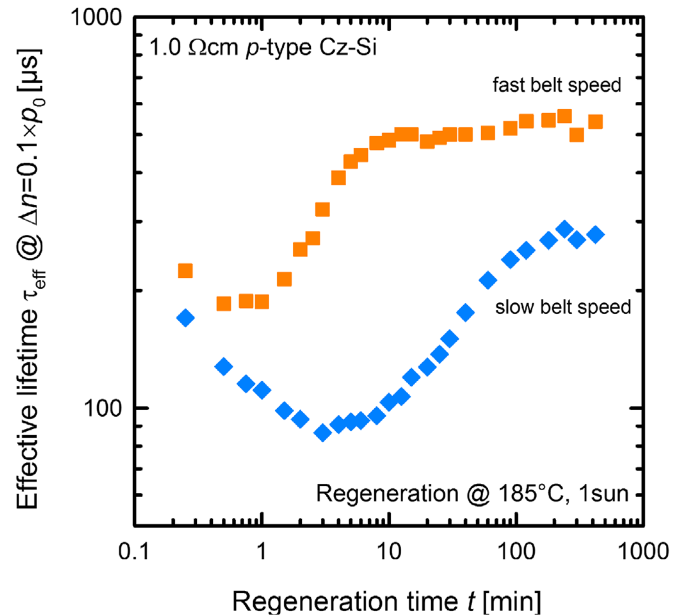


**Fig. 1.** Regeneration of the effective lifetime $\tau_{eff}$ plotted versus the regeneration time $t$ at 185 °C and 100 mW/cm$^2$ (1 sun) light intensity. A fast belt speed (7.2 m/min, orange squares) leads to a fast regeneration of the lifetime, while for a slow belt speed (1.2 m/min, blue diamonds) a longer regeneration time is needed. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Afterwards, the lifetime measurements are performed and the permanent deactivation of the BO center is performed at a temperature of 185 °C and at various light intensities ranging between 3 mW/cm$^2$ and 100 mW/cm$^2$. As illumination source a halogen lamp is chosen. Directly before the permanent deactivation was performed, all samples were annealed at 200 °C for 10 min in darkness.

### 3.2. Results and discussion

In Fig. 1, the regeneration curves of two lifetime samples passivated with single $Al_2O_3$ layers and fired at 850 °C set peak temperature with two different belt speeds are displayed. The orange squares correspond to samples fired at a belt speed of 7.2 m/min, while the blue diamonds correspond to a sample fired at a belt speed of only 1.2 m/min. Comparing the saturated lifetimes of the sample treated with the fastest belt speed with the results we obtained recently on various Cz-Si materials with a fired hydrogen-rich dielectric $SiN_x$ layer [13], we find that the saturated lifetime with $Al_2O_3$ layer is significantly lower compared to that with $SiN_x$, which were larger than 1 ms. This suggests that the hydrogen-rich layer during the firing is indeed required in order to obtain the very high lifetimes ($>1$ ms) we published in [13]. However, we observe the same dynamics for the regeneration process, independent of the hydrogen content in the dielectric passivation layer. As can be seen in Fig. 1, for the fast belt speed, the lifetime clearly regenerates much faster compared to the sample treated with the slow belt speed. In order to evaluate these different regeneration behaviors quantitatively, we extract the recovery rate constants $R_{de}$.

To determine the recovery rate constants, the measured effective lifetime $\tau_{eff}$ is transformed into an effective defect concentration $N_t^*$ using to the equation

$$N_t^* = \frac{1}{\tau_{eff}(t)} - \frac{1}{\tau_0}. \quad (1)$$

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