LIGHT-INDUCED DEGRADATION IN CZ SILICON SOLAR CELLS: FUNDAMENTAL UNDERSTANDING AND STRATEGIES FOR ITS AVOIDANCE

Jan Schmidt and Rudolf Hezel

Institut für Solarenergieforschung Hameln/Emmerthal (ISFH)
Am Ohrberg 1, D-31860 Emmerthal, Germany

Abstract: Solar cells manufactured on boron-doped Czochralski-grown silicon (Cz-Si) degrade in performance when exposed to light or minority carriers are injected in the dark until a stable efficiency is reached. This effect, which is now known for almost 30 years, is due to the activation of a specific metastable defect in the Cz-Si material. Although a conclusive explanation of the effect is still to be found, recent investigations have clearly revealed that the Cz-specific defect is correlated with the boron and the oxygen concentration in the material. The first part of this paper reviews the current status of the physical understanding of the effect and gives an overview of the defect models proposed in the literature. In the second part, an overview of different strategies for avoiding or reducing the light-induced degradation in Cz-Si solar cells is presented.

1. INTRODUCTION

Approximately 90% of the present world solar cell production is based on boron-doped crystalline silicon, with Czochralski-grown monocrystalline silicon (Cz-Si) having a market share of about 40% and cast multicrystalline silicon (mc-Si) having a share of approximately 50%. The main problem of solar cells manufactured on Cz-Si is that their initial efficiency degrades under illumination until a stable performance level, well below the initial efficiency, is reached. In the case of high-efficiency laboratory solar cells, like the PERL cell, the efficiency was found to degrade by up to 10% relative, while in commercially manufactured solar cells an efficiency degradation by typically 3-7% (relative) has been reported. Despite the fact that the efficiencies obtained on monocrystalline Cz-Si are initially much higher compared to those attained on the cheaper cast mc-Si materials, efficiencies closely approach after a few hours of illumination. This is due to the fact that mc-Si solar cells are, in most cases, stable under illumination. Since, in general, Cz-Si is more expensive than mc-Si, the future of solar-grade Cz-Si crucially depends on whether it is usable for the mass-production of high-efficiency solar cells or not. Hence, in recent years, a lot of research has been devoted to the light-induced degradation (LID) problem, which is presently the main obstacle for making solar-grade Cz-Si a perfect high-efficiency solar cell material. This paper discusses the present physical understanding of the LID effect and gives an overview of the different approaches for reducing or even completely avoiding it.

2. FUNDAMENTAL UNDERSTANDING

2.1 Discovery of the effect and early models

To our knowledge, the first observation of LID in non-particle-irradiated solar cells fabricated on boron-doped Cz-Si wafers was made by Fischer and Pschunder in 1973. Figure 1 shows the evolution of the power output $P_m$, the short-circuit current $I_{sc}$, and the open-circuit voltage $V_{oc}$ of a Cz-Si solar cell under illumination, as published in the original paper by Fischer and Pschunder. The initial cell parameters were measured directly after cell fabrication and are characterized by an intermediate state, labeled X. After only a short period of light exposure, all three cell parameters degrade until a stable level B is reached. Interestingly, it was found that the cell performance can be completely recovered by a low-temperature annealing treatment at 200°C (state A). By additional photoconductance decay measurements it was shown that the observed effect is due to a bulk carrier lifetime varying between two values, corresponding to two different states, A and B, of the material. State A is associated with a high lifetime and requires low-temperature annealing to be activated, while state B is associated with a
low carrier lifetime and is caused by illumination. Both levels were found to have the tendency to saturate and can reversibly be changed by applying the appropriate treatment.\textsuperscript{4}

While the study performed by Fischer and Pschunder was more of phenomenological nature, in the following years, several attempts were made to develop a defect model which explains the observed lifetime instabilities in boron-doped Cz-Si solar cells. Weizer et al.\textsuperscript{5} proposed a model where the effect was attributed to a complex of a lattice defect and a silver atom or a cluster of atoms. Graff and Pieper\textsuperscript{6} proposed a vacancy-gold complex as the lifetime-limiting recombination center in the material. However, none of these models was capable of explaining the complete degradation/recovery cycle observed in boron-doped Cz silicon. Corbett et al.\textsuperscript{7} noted that the lifetime variations in Cz silicon are probably not due to a direct creation of the metastable defect by photons and suggested that the lifetime degradation might be due to the dissociation of donor-acceptor defect pairs caused by excess carriers via a recombination-enhanced mechanism. A recombination-enhanced defect reaction (REDR) was believed to be the responsible physical mechanism for the defect formation, as it explains the experimental observation that the degradation of the carrier lifetime occurs not only under light exposure, but also in the dark if a forward bias voltage is applied.\textsuperscript{5,8,9}

One of the probably best studied donor-acceptor complexes in crystalline silicon is the iron-boron pair. This defect pair dissociates under illumination and interstitial iron is formed.\textsuperscript{10} Interstitial iron is, under low-injection conditions, a more effective recombination center than the iron-boron pair, and hence leads to a strong degradation in the carrier lifetime. Reiss et al.\textsuperscript{11} investigated solar cells fabricated on boron-doped Cz silicon wafers with comparatively high iron contamination levels and hence very low bulk lifetimes ($\sim 4 \mu $s). They observed a pronounced degradation in cell performance during illumination, during the application of a forward bias voltage in the dark, and during thermal treatment above $\sim 250^\circ$C. In order to recover the cell efficiency, the cell had to be stored in the dark at temperatures below 100\(^\circ\)C. The authors clearly showed that this behavior can undoubtedly be explained by iron-boron pairs.

The annealing behavior of the material investigated by Reiss et al.\textsuperscript{11} is very different to the one reported by Fischer and Pschunder\textsuperscript{4} who measured a complete lifetime recovery during annealing at temperatures above about 200\(^\circ\)C and no lifetime recovery when storing the cells at room temperature in the dark. The latter researchers investigated Cz silicon with negligible iron content. Hence, it is very likely that the fundamental LID effect reported in Ref. 4 was screened in the solar cells of Reiss et al. by the superimposed iron-related effect. At this point it should be noted that several inconsistencies in the literature are due to the fact that often no clear distinction between both effects is made. The present paper only deals with the fundamental LID observed even in highest-purity electronic-grade boron-doped Cz-Si with virtually no metal contamination.
2.2 Structure of the metastable defect and mechanism of defect transformation

While all former attempts to clarify the LID of the carrier lifetime in Cz-Si were based on the formation of metal-containing defect complexes, it was not until 1997 that a complete defect reaction model was proposed by Schmidt et al.¹² that did not involve any metallic impurities. This was also the first model capable of explaining the lifetime degradation under illumination (or, alternatively, minority-carrier injection in the dark) as well as the lifetime recovery during annealing at temperatures above ~200°C. The most important feature of this model is the formation of a defect pair composed of one interstitial boron and one interstitial oxygen atom (BiOi) during illumination of the Cz silicon. The qualitative correlation of the magnitude of degradation with the boron and the oxygen concentration in the material was demonstrated by means of carrier lifetime measurements performed before and after LID on Cz wafers with different boron and oxygen concentrations.¹² Furthermore, photoconductance decay measurements on gallium-doped p-type Cz silicon and on phosphorus-doped n-type Cz material did not show any lifetime degradation.¹² Based on these results, several methods for reducing the lifetime degradation in Cz silicon solar cells were proposed, which will be discussed in Section 3. According to recent theoretical considerations of Ohshita et al.,¹³ the BiOi pair could only exist in a stable configuration if a substitutional silicon atom is sited between the boron and the oxygen atom.

In 1998, Glunz et al.¹⁴ confirmed the strong correlation between the LID in Cz-Si and the boron as well as the oxygen concentration by means of lifetime measurements on a very large number of boron-doped Cz-samples. Whereas they found an approximately linear increase of the lifetime degradation with boron doping concentration, a strongly superlinear increase with interstitial oxygen concentration, approximately to the power of five, was observed. It is important to note that, in the study of Glunz et al.,¹⁴ surface recombination of the Cz-Si wafers was suppressed by a high-temperature oxidation step at 1050°C and a subsequent deposition of corona charges on top of the thermally grown silicon dioxide layer, while in the upper study of Schmidt et al.¹² silicon nitride films deposited at low temperature (375°C) were used for surface passivation. The results of Glunz et al.¹⁴ gave rise to the suspicion that the Cz-specific recombination center is probably associated with a defect complex different from the BiOi pair. Besides, it is questionable if any interstitial boron exists in non-particle-irradiated silicon at all. These considerations were supported by measurements of Schmidt and Cuevas¹⁵ using injection-dependent lifetime spectroscopy (IDLS). They showed that the energy level of the light-induced recombination center is relatively close to the middle of the silicon band gap and hence it is very different from that of the BiOi pair (Fig. 2). On the basis of these results, they proposed a new structure consisting of one substitutional boron B, and several oxygen atoms. Rein et al.¹⁶ determined the energy level of the metastable Cz-specific defect in its passive state (Fig. 2) by means of temperature-dependent lifetime spectroscopy (TDLS) and combined their own TDLS measurements with the IDLS measurements published in Ref. 15 to obtain a narrower range for the energy level of the active state.

![Figure 2: Energy levels of the metastable Cz-defect in its active and passive state, as determined by means of lifetime spectroscopy.¹⁵,¹⁶ For comparison, the energy level of the BiOi pair is shown.](image-url)
Bourgoin et al.\textsuperscript{17} proposed a possible atomic configuration of the boron-oxygen complex where the B\textsubscript{s} atom is surrounded by three O\textsubscript{i} atoms (Fig. 3). They also suggested a new degradation mechanism where electron trapping induces a Jahn-Teller distortion, shifting one of the energy levels of the defect to the middle of the silicon band gap. However, an experimental verification of the proposed mechanism was not performed.

Rein et al.\textsuperscript{16} investigated the defect generation as a function of doping concentration and found that it shows a quadratic increase with doping level, excluding the previously proposed REDR mechanism. Moreover it was shown, in good agreement with results of Hashigami et al.,\textsuperscript{18} that the defect generation rate is virtually independent of the light intensity. These somewhat surprising results led to the hypothesis that the mechanism of defect transformation might be a simple charging process. More recently, it was discovered that the defect generation is a thermally activated process with a relatively low barrier energy of $E_{\text{gen}} = 0.4$ eV.\textsuperscript{19} This finding points towards a diffusion-limited defect formation process, where the minority-carrier injection plays merely an indirect role.

The defect annihilation process has been shown to be thermally activated as well\textsuperscript{16,19} Isothermal annealing experiments were performed by different groups using different experimental approaches and revealed barrier energies of $E_{\text{ann}} = 1.3$ eV\textsuperscript{16} and $E_{\text{ann}} = 1.8$ eV\textsuperscript{19} respectively, which are both well above the barrier energy of the defect generation process of $E_{\text{gen}} = 0.4$ eV. It was also shown that the defect annihilation rate decreases approximately linearly with the doping concentration $N_{\text{dop}}$, while $E_{\text{ann}}$ seems to be independent of $N_{\text{dop}}$.\textsuperscript{19}

Most recently, the impact of boron and oxygen on the light-induced metastable defect concentration in Cz-Si was re-examined\textsuperscript{19} using the quasi-steady-state photoconductance method, enabling the accurate measurement of carrier lifetimes at defined injection levels. Figure 4 shows the measured normalized defect concentration $N_t^{*}$ as a function of the substitutional boron concentration $[B_s]$ (from Ref. 19).

$$[O_i] = (7.5 \pm 0.5) \times 10^{17} \text{ cm}^{-3}$$

$$N_t^{*} \sim [B_s]$$

Figure 4: Measured normalized defect concentration $N_t^{*}$ as a function of the substitutional boron concentration [B\textsubscript{s}] (from Ref. 19).

$$[B_s] = (0.8-1.2) \times 10^{16} \text{ cm}^{-3}$$

$$N_t^{*} \sim [O_i]^{1.8}$$

Figure 5: Measured normalized defect concentration $N_t^{*}$ as a function of the interstitial oxygen concentration [O\textsubscript{i}] (from Ref. 19).
studies, a linear increase of $N^*_t$ with increasing [B$_s$] was found. Figure 5 shows the measured $N^*_t$ values as a function of the interstitial oxygen concentration [O$_i$]. The boron concentration, as determined from resistivity measurements, was chosen to be approximately the same for all samples [B$_s$]=(0.8-1.2)$\times$10$^{16}$ cm$^{-3}$. The most striking result of Fig. 5 is the fact that $N^*_t$ shows an approximately quadratic increase with [O$_i$], which is a much weaker dependence compared to that found by Glunz et al. This discrepancy might be due to the fact that in Ref. 14 a high-temperature oxidation, which could lead to a change of the bulk properties, was performed to passivate the surfaces, whereas in Ref. 19 low-temperature silicon nitride films were used for surface passivation.

Based on their experimental lifetime data, a new defect reaction model was developed by Schmidt et al. In this model, fast-diffusing oxygen dimers O$_{2i}$ are captured by substitutional boron B$_s$ to form a B$_s$-O$_{2i}$ complex, acting as highly effective recombination center (Fig. 6). The defect formation process is governed by the diffusion of the oxygen dimer and, hence, is a thermally activated process, in good agreement with the experimental results of Ref. 19. The role of the minority-carrier injection could not be fully revealed. However, it was conjectured that the diffusivity of O$_{2i}$ in silicon might depend on its charge state, which could change under illumination or minority-carrier injection. The defect formation process suggested in Ref. 19 is similar to the thermal donor (TD) formation mechanism proposed by Gösele and Tan, where the O$_{2i}$ molecules are captured by other oxygen atoms or clusters to form the different TDs. In fact, a detailed theoretical and experimental analysis shows that during the first few hours of TD formation, the concentration of the O$_{2i}$ dimer shows a pronounced decrease. As less O$_{2i}$ molecules are available, the model proposed in Ref. 19 predicts a decrease in the B$_s$-O$_{2i}$ concentration and hence a reduced light degradation of the carrier lifetime after TD formation. In order to verify this hypothesis, Bothe et al. have annealed different boron-doped Cz-Si wafers at 450°C for up to 32 h. These conditions are ideal for the formation of TDs. After TD formation they measured a pronounced reduction of the metastable defect concentration by up to a factor of 3, giving an indirect confirmation of the proposed defect reaction model.

3. STRATEGIES FOR SUPPRESSING THE LIGHT-INDUCED DEGRADATION

3.1 Alternative Cz-Si materials

The correlation of the magnitude of degradation with the boron and the oxygen concentration in the Cz material had been proven by means of carrier lifetime measurements on a large number of Cz wafers from different manufacturers. Furthermore, measurements on Ga-doped $p$-type Cz silicon as well as on P-doped $n$-type Cz material had shown no degradation of the carrier lifetime. Based on these experimental results, several methods for reducing the lifetime degradation in Cz silicon solar cells were proposed. The two most promising approaches were: (i) replacement of B with another dopant element, like Ga or P, and (ii) reduction of the oxygen concentration in the Cz material. In a recent international joint research project, organized by Saitoh, a large number of Cz-Si wafers with different dopant elements (B, Ga) and different oxygen concentrations (including conventional and magnetic Cz-Si) were manufactured by Shin-Etsu Handotai (SEH) and supplied to various international institutions (Sharp Co., Hitachi Ltd., FhG-ISE, Georgia Tech, ISFH, UNSW, TUAT) for characterization and solar cell fabrication. Figure 7 shows the typical behavior of the different Cz materials: while the carrier lifetime of conventional B-doped Cz-Si (solar-grade as well as electronic-grade material) degrades under illumination, Ga-doped Cz-Si of similar doping concentration has a stable lifetime on a much higher level, comparable to that of B-doped float-zone (FZ) silicon, even if the interstitial oxygen con-
The high oxygen concentration in silicon ingots grown with a conventional Cz single crystal puller is due to the partial dissolution of the silica crucible during the growth process. The oxygen content can be strongly reduced by damping the melt flows with magnetic fields. This so-called magnetic Cz (MCz) silicon with strongly reduced O\textsubscript{i} concentration shows an almost vanishing light degradation (see Fig. 7) and has bulk lifetimes which are comparable to that of Ga-doped Cz-Si. Also included in Fig. 7 is a P-doped Cz-Si material with high O\textsubscript{i} content, which is also completely stable under illumination. However, since the latter material is an n-type semiconductor and most industrial solar cell processes have been developed for p-type base material, at present the most promising alternative Cz silicon materials seem to be Ga-doped Cz-Si and B-doped MCz-Si.

High-efficiency solar cell processes were applied to the alternative Cz materials at different institutes and stable efficiencies well above 20% were obtained on Ga-doped Cz-Si, B-doped MCz material, and...
P-doped $n$-type Cz-Si (Fig. 8). For comparison, cell results obtained on B-doped FZ-Si and B-doped Cz-Si are also included in Fig. 8. Solar cell efficiencies above 20% can only be achieved with the new Cz materials, while the stable efficiency of cells fabricated on conventional 1-$\Omega$cm B-doped Cz-Si is always well below 20%. Note that the degree of complexity of the three cell processes compared in Fig. 8 is very different, with the PERT process being by far the most complex manufacturing process, whereas the OECO process, on the other hand, is completely avoiding any photolithography and alignment steps. The latter process is currently transferred to industrial pilot production.

The segregation coefficient of gallium in silicon is two orders of magnitude lower compared to that of boron in silicon. Hence, Ga-doped Cz-Si crystals exhibit a considerably higher variation in resistivity along their growth axis compared to B-doped crystals. Metz et al. have investigated the usability of a complete 6" Ga-doped Cz-Si crystal in their high-efficiency OECO solar cell process. The resistivity of the crystal varied from 1.3 $\Omega$cm at the top to 0.4 $\Omega$cm in the tail region. Figure 9 shows the measured OECO solar cell efficiencies as a function of the base resistivity. Peak efficiencies of up to 21% were obtained on 0.4-$\Omega$cm material and, more important, in the broad resistivity range between 0.25 and 1.34 $\Omega$cm, cell efficiencies were found to reach more than 97% of the peak value, demonstrating that the inherent resistivity variations in Ga-doped Cz-Si crystals are well within the range tolerable for the manufacturing of high-efficiency solar cells.

### 3.2 Process optimization

Several approaches aiming at reducing the concentration of the Cz-specific metastable defect in B-doped Cz-Si during the solar cell manufacturing process have been investigated. In particular, certain high-temperature steps, optimized for Cz-Si, were found to be capable of significantly reducing the magnitude of degradation. In a recent comprehensive study, the high-temperature (~1050°C) thermal oxidation process required for the growth of masking oxides and passivation layers was studied in detail. It was found that the concentration of the Cz-specific metastable defect can be reduced by up to a factor of 4 if the ramping conditions are chosen properly. However, the absolute values of the stable lifetimes of conventional B-doped Cz-Si materials were still found to be on a relatively low level between about 20 and 45 $\mu$s after the optimized oxidation step, which is well below the lifetimes measured on Ga-doped Cz-Si and MCz materials. In a more recent study, a phosphorus emitter diffusion step at ~850°C with optimized ramping conditions was also found to have a beneficial effect on the LID, leading to a maximum reduction in the light-induced defect concentration by a factor of 3.5. This effect was attributed to the temperature profile only and was shown to be not due to a gettering of impurities. A permanent improvement of the carrier lifetime in Cz-Si is not only possible using conventional quartz-tube furnaces. A short annealing step of a few seconds at temperatures around 800°C in a belt furnace was found to halve the light-induced defect concentration. Similar results were also obtained using rapid thermal processing.

### 3.3 Other approaches

An alternative method to reduce the harmful effects of lifetime degradation on cell efficiency is to modify the cell design. By simply reducing the thickness of their solar cells to 100 $\mu$m, Münzer et al.
obtained a reduced degradation and an improved stable efficiency. However, this approach requires a very efficient rear surface passivation of the solar cell. Other solar cell structures, like the Emitter-Wrap-Through (EWT) cell, have also the potential to reduce the light degradation considerably.

On the basis of the novel defect reaction model proposed in Ref. 19, it was suggested that carbon-rich B-doped Cz-Si may exhibit a reduced lifetime degradation, because the formation of carbon-oxygen complexes could be a competitive process to the formation of the lifetime-limiting boron-oxygen complex. However, an experimental verification of this promising new way of reducing the metastable defect concentration in B-doped Cz-Si has not been published up to now.

Acknowledgements

The support by the State of Niedersachsen and the German Bundesministerium für Bildung und Forschung (BMBF) is gratefully acknowledged. The ISFH is a member of the German Forschungsverbund Sonnenenergie.

References