

# Boron–oxygen-related degradation in multicrystalline silicon wafers

Rune Sondenå, Institute for Energy Technology, Kjeller, Norway

## ABSTRACT

Extended crystal defects, such as grain boundaries and dislocations, have long been considered the main factors limiting the performance of multicrystalline (mc-Si) silicon solar cells. However, because the detrimental effects of these crystal defects are reduced as a result of improvements in the solidification process as well as in the feedstock and crucible quality, the degradation caused by boron–oxygen complexes is expected to be of increasing importance. Light-induced degradation (LID) occurs in both p- and n-type crystalline silicon solar cells that contain both boron and oxygen. Because of the fundamental differences in the solidification processes, mc-Si silicon contains less oxygen than Czochralski silicon; nevertheless, the oxygen content in mc-Si silicon is still sufficient to cause degradation, although to a lesser extent than in the case of Czochralski silicon. Whereas B–O-related degradation of 0.5 to 1% abs. can be found in Czochralski cells, the degradation in conventional mc-Si cells is limited to around 0.1 to 0.2% abs.

## Introduction

The function of a crystalline silicon solar cell is to generate electricity when exposed to light; it therefore seems like a paradox that the same solar cell degrades under illumination. Cell degradation is caused by recombination-active impurity complexes in the bulk silicon that are activated by illumination or charge-carrier injection. As a result, the electron–hole recombination will increase and thus reduce the minority-carrier lifetime in the material: this effect is called *light-induced degradation (LID)*. Several defects are known to affect the performance of a crystalline silicon solar cell upon illumination – these are iron–boron pairs, copper pairs and boron–oxygen complexes. The iron–boron pairs differ in the sense that, depending on the injection level, they may have a positive or a negative effect on the minority-carrier lifetime [1]. The behaviour of copper pairs is reported to be remarkably similar to that of boron–oxygen defects [2]. In mc-Si solar cells additional degradation, not necessarily attributed to the above-mentioned defect mechanisms, has recently been reported [3].

**“Cell degradation is caused by recombination-active impurity complexes in the bulk silicon that are activated by illumination or charge-carrier injection.”**

The work reported on in this paper focuses on the LID caused by boron–

oxygen complexes, hereafter referred to as *B–O-related degradation*. The contribution from copper is assumed to be negligible.

## B–O-related degradation

Monocrystalline p-type silicon wafers containing both boron and oxygen generally exhibit a considerable reduction in minority-carrier lifetime, and therefore in solar cell performance, with prolonged carrier injection. Within a day or two of illumination, the lifetime in Czochralski silicon (Cz-Si) is typically reduced to about 10% of the initial lifetime [4]. The reduction in the minority-carrier lifetime may lead to a reduction in efficiency of 0.5% to 1% abs. in a conventional solar cell. This degradation has been attributed to  $\text{BO}_2$  complexes because of the dependence of the defect concentration on the concentrations of boron and oxygen in the material [5,6]. Charge carriers activate latent  $\text{BO}_2$  complexes, dramatically increasing their recombination activity, thus reducing the minority-carrier lifetime in the material [7].

Experiments on compensated silicon containing phosphorus as well as boron demonstrate a dependency on the net doping  $p_0$  rather than on the total boron concentration [8,9]. Two decay processes describe the degradation kinetics: one fast during the first few seconds of illumination, and one slow on a timescale of hours and days. The fast recombination has been attributed to  $\text{B}_s\text{O}_{2i}$  complexes and the slow one to  $\text{B}_i\text{O}_{2i}$  complexes [8]. As the concentration of the defect is believed to be very low (about  $10^{11}\text{cm}^{-3}$ ), no trace of the defect itself has been found

experimentally, for example by the use of transmission electron microscopy or deep-level transient spectroscopy [7]. The defect can only be studied indirectly by its effect on the electrical properties of wafers and cells.

B–O-related degradation can be completely reversed by heat treatment above  $200^\circ\text{C}$  in the dark; however, renewed degradation occurs upon illumination. In 2006 a regeneration process was presented by Herguth et al. [10]. Simultaneous illumination and heating at intermediate temperatures ( $<200^\circ\text{C}$ ) transforms B–O complexes from recombination-active states into metastable inactive states, called *regenerated states*; these states are characterized by high lifetimes and by defects that are stable under solar cell operating conditions [11]. Complete regeneration and the stability thereof have not yet been demonstrated on multicrystalline wafers.

Typically Cz-Si contains interstitial oxygen  $\text{O}_i$  in the range  $5 \times 10^{17}$  to  $2 \times 10^{18}\text{cm}^{-3}$ . In the case of mc-Si, the  $\text{O}_i$  content is about one order of magnitude lower [12–15];  $\text{O}_i$  concentrations of  $2 \times 10^{17}\text{cm}^{-3}$  and lower can be expected in current mc-Si wafers. Despite the lower oxygen levels in mc-Si, it is still sufficient to cause some degradation of both the minority-carrier lifetime and the solar cell conversion efficiency. Lifetime decays of 25% [12] and up to 50% [16,17] of the initial lifetime have been reported.

In cells with approximately 15% efficiency, a degradation of 0.1% abs. has been attributed to B–O defects [18]. Cells with efficiencies of 16% show a degradation of about 0.15% abs. [19], while up to 0.2% abs. degradation has been reported for

cells with 17% efficiency [20]. Recent results from Hanwa Q-cells are largely in agreement, showing a B–O-related degradation of less than 1% relative [3]. These results also report a considerably higher LID in wafers from the bottom third of high-performance multicrystalline blocks, not related to B–O defects. In an advanced cell structure, namely an mc-Si PERC cell with an efficiency of 18.4%, even higher degradation is found; however, additional performance-limiting effects are suspected in this type of cell [21]. Additionally, in mc-Si that contains more oxygen, higher B–O-related degradation has been found [22].

Studies in which the B–O-related degradation is found to be less severe have also been published [14,23]. For cells with conversion efficiencies below 15%, where other defects limit cell performance, degradation is difficult to measure [18], which may explain the low degradation reported in some studies.

### Determination of B–O defects

A normalized defect concentration  $N_t^*$  is commonly used for determining the B–O defects attributed to the defect density in mc-Si wafers:

$$N_t^* = \frac{1}{\tau_{\text{BO-activated}}} - \frac{1}{\tau_{\text{initial}}} \quad (1)$$

where the minority-carrier lifetimes  $\tau_{\text{initial}}$  and  $\tau_{\text{BO-activated}}$  represent the lifetimes before and after degradation respectively [24]. According to Shockley-Read-Hall (SRH) theory, the B–O-related defect concentration can be related to the measured lifetimes as stated by Equation 1 if the generated defects are the dominating recombination-active defects [25,26].

In the case of mc-Si, however, B–O-related defects cannot be considered the dominating recombination path, because of the considerable spatial variation in lifetime across the wafer. Equation 1 is therefore not directly applicable for quantifying the B–O-related degradation in mc-Si wafers. If the average lifetime across the entire wafer is used, thus interpreting all lifetime-limiting defects as B–O complexes, the defect concentration of B–O complexes will be overestimated, depending on the number of grain boundaries and dislocations in the wafer. Image analysis and evaluation of the high-lifetime areas has therefore been proposed for quantification of the normalized defect concentration of B–O complexes in multicrystalline wafers [17].

### Experimental results

Time-resolved degradation of the minority carrier lifetime in an illuminated multicrystalline wafer is shown in Fig. 1. The wafer is phosphorus-diffusion gettered – in other words, a phosphorus emitter is in-diffused, followed by an etch-back process, and the surfaces are subsequently passivated using hydrogenated amorphous silicon. The lifetime is continuously monitored by an automated quasi-steady-state photoconductance (QSSPC) set-up with

an external bias light source for in situ illumination between measurements [4,27]. A conventional mc-Si wafer from the bottom part of a block is chosen.

The degradation is divided into a fast decay, occurring in the first 30 seconds of illumination, and a slow decay, which takes place during the following 24 to 48 hours. The timescales of both the fast and slow decays correspond quite well with those of Cz-Si wafers containing comparable amounts of boron. In addition, the initial lifetime in the mc-Si wafers can be recovered by

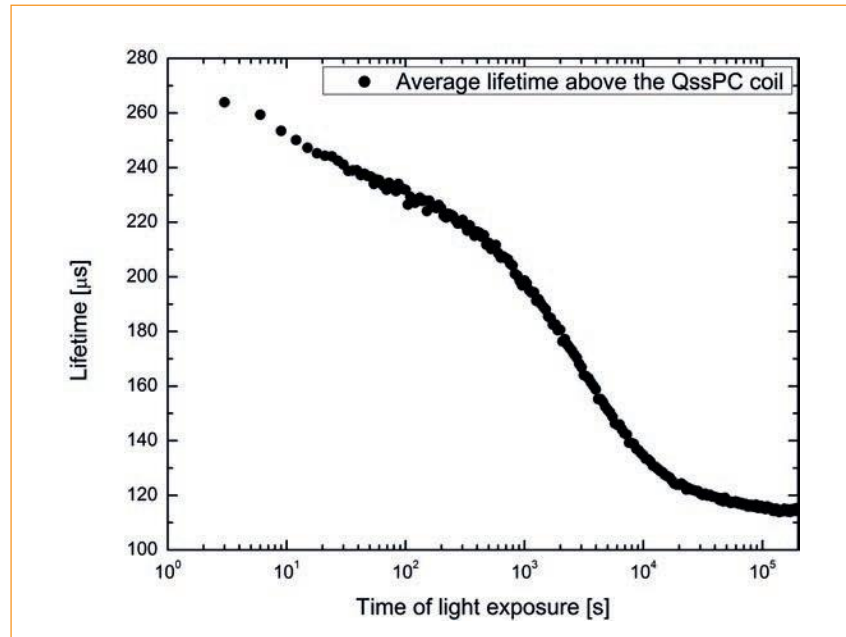


Figure 1. The time-resolved lifetime degradation in an mc-Si solar cell, measured using a customized QSSPC set-up [17]. A phosphorus-gettered wafer from the bottom part of an mc-Si block is shown.

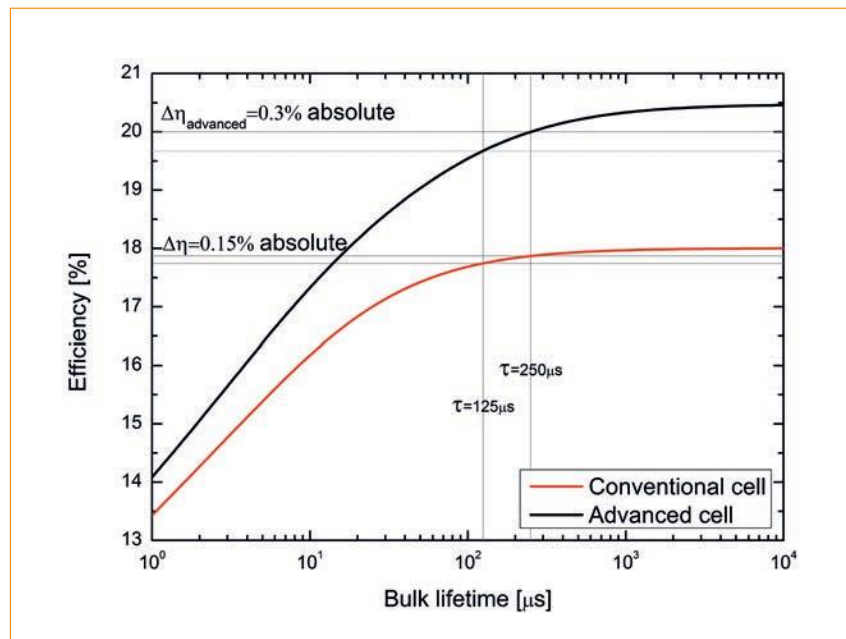


Figure 2. The performance of a solar cell as a function of bulk lifetime. A conventional cell structure is compared with an advanced cell structure having improved surface recombination properties.

subjecting the wafer to a heat treatment for 20 minutes above 200°C. The nature of the recovery mechanism and the timescales of the decay indicate that the degradation mechanism is the same in Cz-Si and mc-Si wafers.

**“The degradation is divided into a fast decay, occurring in the first 30 seconds of illumination, and a slow decay, which takes place during the following 24 to 48 hours.”**

Fig. 1 shows, however, that the fast decay is less pronounced in mc-Si wafers than in Cz-Si ones. The total degradation is also less severe for mc-Si wafers, with a degraded lifetime of about 50% of the initial value for this wafer; this may be a result of the reduced oxygen content in mc-Si, but it may also indicate that other defects contribute to carrier recombination, reducing the initial lifetime in the mc-Si wafer. As the wafer shown is from the bottom part of the multi-block, it is reasonable to assume that the oxygen levels are in the upper end of the range. Less oxygen, and thus less B–O-related

degradation, can be expected towards the middle and top parts of the block.

A rule of thumb is that the performance of a conventional cell is significantly reduced when the diffusion length is less than three times the thickness of the device [28]; for 180µm wafers this occurs at a lifetime of approximately 100µs. For purposes of illustration, the performance of a solar cell is modelled using PC1D [29,30]. If a conventional cell structure is assumed, the efficiencies for different bulk lifetimes are as presented in Fig. 2. A reduction in the lifetime from 250µs to 125µs corresponds to a reduced efficiency of 0.15% abs., which is in good agreement with experimental results. The PC1D model does not, however, include other lifetime-limiting defects, such as grain boundaries and dislocation clusters. When considering an advanced cell, for example one with improved surface recombination properties, the efficiency loss due to B–O degradation is estimated to increase to 0.3% abs. PC1D model parameters are given in Table 1.

Lifetime images of the wafers after the initial heat treatment  $\tau_{\text{initial}}$  and after degradation  $\tau_{\text{BO-activated}}$  are obtained using band-to-band photoluminescence (PL) imaging [31]: lifetime maps before and after degradation are shown in Fig. 3(a) and (b) respectively. The mean lifetime in the entire wafer is reduced

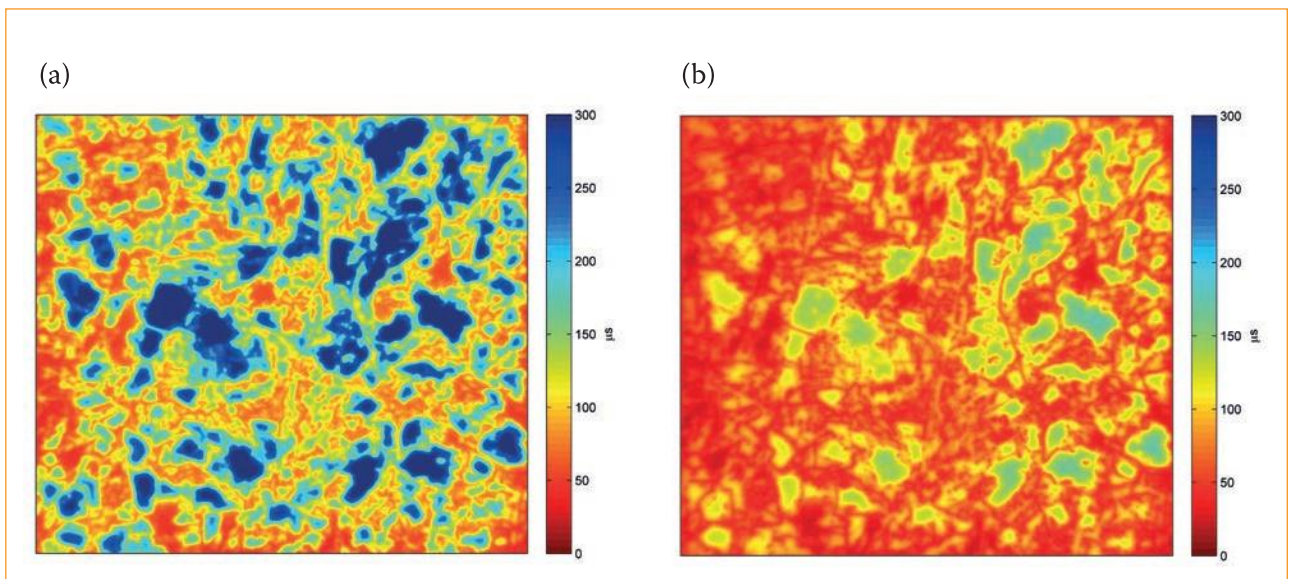
from 150µs to 75µs during 48 hours of illumination; this average reduction across the whole wafer is smaller than the decay indicated in Fig. 1. While the values in Fig. 1 represent the area directly above the QSSPC coil, the average values across an entire wafer are also reduced by the extended crystal defects, i.e. grain boundaries and dislocation clusters. The impact of B–O-related defects in mc-Si is reduced when other defects contribute to limiting the lifetime.

The spatially distributed normalized defect concentration, calculated by means of Equation 1, is shown in Fig. 4. Grain boundaries, dislocations and dislocation clusters are easily adorned with impurity atoms, resulting in electrically active recombination centres. Grain boundaries and dislocation-rich areas are therefore represented as low-lifetime areas in the PL images in Fig. 3. Areas with low initial lifetimes show high defect concentrations, despite having a lower relative reduction in the lifetime. It is clear that crystal defects are also interpreted as B–O defects and erroneously included when calculating the B–O defect concentration  $N_t^*$ . The main assumption for calculating the defect concentration and attributing it to the B–O complex was that the relevant defect was the dominating defect mechanism. B–O degradation

Device	Resistivity [ $\Omega\text{-cm}$ ]	Thickness [ $\mu\text{m}$ ]	Emitter [ $\Omega/\text{sq.}$ ]	Front SRV* [ $\text{cm/s}$ ]	Rear SRV* [ $\text{cm/s}$ ]
Conventional	1.1	180	60	$10^5$	350
Advanced	1.1	150	100	2000	10

\*SRV = surface recombination velocity.

**Table 1. Device model parameters for a p-type substrate with an n-type front emitter.**



**Figure 3. PL images showing the lifetimes in the wafer before (a) and after (b) illumination for 48 hours.**

may contribute to reducing the lifetime in these areas, but it certainly cannot be considered the dominating recombination path. Using Equation 1 to calculate  $N_t^*$  in mc-Si wafers will therefore result in an overestimation of the B–O defect concentration.

The average defect concentration will include both B–O-related and other recombination centres when an entire mc-Si wafer is considered. The spatial variation in the lifetime in multicrystalline wafers makes it difficult to compare wafers from

different blocks, and even wafers from different heights in the same block. Since the area fraction of the wafer covered with extended crystal defects may vary, the magnitude of the overestimation of the B–O defect concentration may also vary.

To compare B–O-related degradation in multicrystalline wafers, an approach using image segmentation has been proposed [17]. Image segmentation by means of the Otsu algorithm separates the lifetime images into two distinct parts: high- and low-lifetime areas. Normalized defect concentrations are calculated in high-lifetime areas only, as shown in Fig. 5. If it is assumed that the B–O defect is the dominating recombination path in the high-lifetime areas, the defect concentration in this segment will yield a more representative estimate of B–O defects. The resulting value can then be used for comparing different mc-Si wafers. Table 2 shows the B–O defect concentrations calculated using the arithmetic mean across the entire wafer, and the calculation based on the high-lifetime segment only.

“Normalized defect concentration for the high-lifetime areas may be used for quantification of the B–O-related degradation in mc-Si wafers.”

## Conclusions

Multicrystalline silicon wafers typically contain less oxygen than Cz-Si wafers. The amounts are, however, sufficient to generate B–O-related degradation under illumination in mc-Si wafers as well. A degradation in performance of mc-Si solar cells of up to 0.2% abs. because of B–O defect complexes has been reported. Lifetime measurements combined with PCID measurements confirm that the effect may be in this range in conventional solar cells. The degradation is limited in conventional cell structures, but the impact of the degradation is expected to increase when introducing more-advanced cell concepts, such as rear-side passivation.

The degradation curve in mc-Si, including both a fast and a slow decay, shows similarities to the degradation observed in p-type Cz-Si wafers. Because of the similarities in the decay rates as well as in the recovery mechanisms, the LID observed in the mc-Si wafers is attributed to B–O

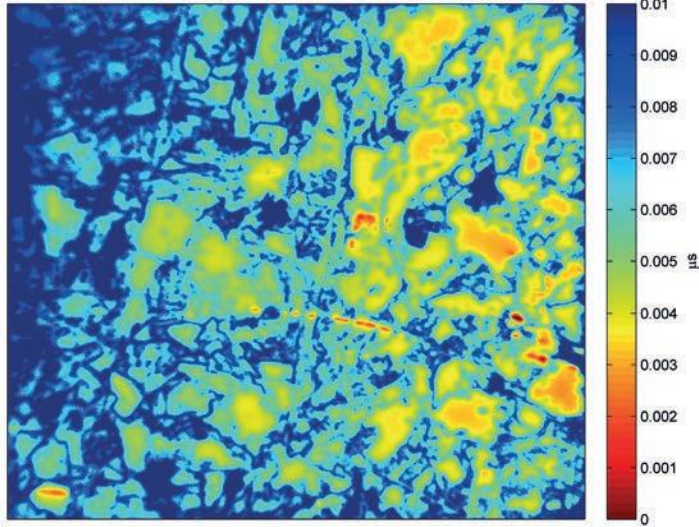


Figure 4. The spatial distribution of  $N_t^*$ , calculated using the PL images before and after degradation. High defect concentrations are obtained in areas with low initial lifetimes.

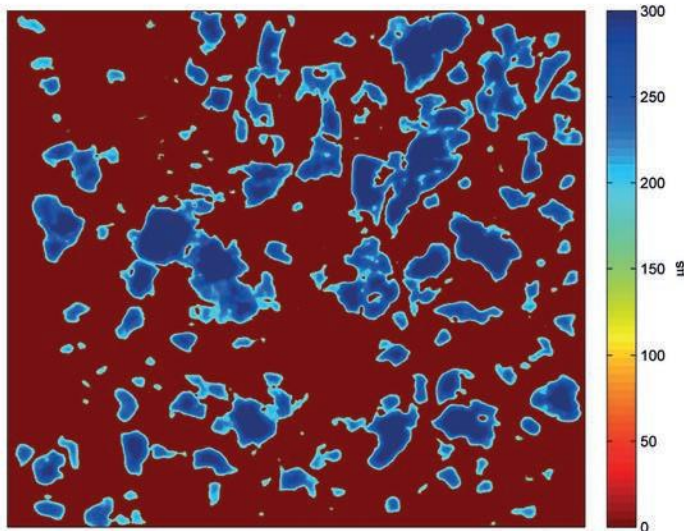


Figure 5. Image segmentation is performed in order to evaluate only the high-lifetime areas. A threshold value is found using the Otsu algorithm.

Area	$\tau_{\text{initial}}$ [ $\mu\text{s}$ ]	$\tau_{\text{BO-activated}}$ [ $\mu\text{s}$ ]	$N_t^*$ [ $\mu\text{s}^{-1}$ ]
Arithmetic mean – wafer	150	75	$6.7 \times 10^{-3}$
High-lifetime segment	246	112	$4.9 \times 10^{-3}$

Table 2. Normalized defect concentrations  $N_t^*$ .

complexes. It is reasonable to assume that mc-Si cells will respond to the same regeneration process as in the case of Cz-Si cells, but a methodology for such a regeneration process has yet to be demonstrated for mc-Si cells.

Conventional approaches to the quantification of B–O-related degradation in monocrystalline silicon are not easily applied to mc-Si, because of the non-uniform nature of the lifetime distribution. In the calculation of the B–O defect concentration, only one dominating recombination mechanism is assumed, which is unlikely to be the case in mc-Si wafers. When image segmentation is used, high-lifetime areas can be evaluated separately; in these areas the assumption that one recombination path dominates is more likely to be applicable. Thus, the normalized defect concentration for the high-lifetime areas may be used for quantification of the B–O-related degradation in mc-Si wafers.

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## About the Author



**Rune Sondenå** is a research scientist in the department of solar energy at the Institute for Energy Technology (IFE) in Norway. He holds an M.Sc. in physics from the Norwegian University of Science and Technology and a Ph.D. in chemistry from the University of Oslo. Rune has worked in the field of silicon-based PV for seven years; his research interests include defects in silicon, wet-chemical processes and thin-film deposition.

## Enquiries

Institute for Energy Technology  
PO Box 40  
N-2027 Kjeller  
Norway

Tel: +47 92029610  
Email: Rune.Sondenå@ife.no  
Website: www.ife.no