

Degradation of Crystalline Silicon Due to Boron–Oxygen Defects

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Abstract—This paper gives an overview on the current understanding of a technologically relevant defect group in crystalline silicon related to the presence of boron and oxygen. It is commonly addressed as boron–oxygen defects and has been found to affect silicon devices, whose performance depends on minority charge carrier diffusion lengths—such as solar cells. The defects are a common limitation in Czochralski-grown p-type silicon, and their recombination activity develops under charge carrier injection and is, thus, commonly referred to as light-induced degradation. A multitude of studies investigating the effect have been published and introduced various trends and interpretations. This review intends to summarize established trends and provide a consistent nomenclature for the defect transitions in order to simplify discussion.

Index Terms—Boron–oxygen (BO) defects, Czochralski (Cz), Czochralski silicon degradation, light-induced degradation (LID), review, silicon.

I. INTRODUCTION

THE Czochralski (Cz) crystal pulling method offers an established way to create high-quality silicon single crystals. However, dissolution of the quartz crucibles introduces relevant amounts of oxygen to the crystal. Adding boron to the melt allows for a mostly homogeneous p-type doping along the crystal due to the favorable segregation coefficient of boron in silicon. The resulting silicon is widely used in semiconductor industry. One important application is the photovoltaic conversion of solar energy in solar cells. However, the efficiency of solar cells produced on boron-doped Cz silicon suffers from a degradation in the first hours of illumination that is known as light-induced degradation (LID). This effect has been intensively studied over the last decades, creating a multitude of insights to the underlying defects. However, ambiguous results in several studies caused a lot of scientific discussion on the defect composition and formation mechanisms. Several authors have provided recapitulatory works on the topic, focusing on certain aspects of it, e.g., [1]–[4].

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This paper aims to summarize the trends and insights that are established at the time of writing and provide a scientific framework for their discussion. It should be noted that the ascription of being established is derived from subjective but thorough assessments of literature and scientific discussions. This is especially important for a strongly discussed and vivid research field such as LID with a lot of contradictory theories and experiments: LID research has been exemplary because of the necessity to revise and reconsider established interpretations in science.

It would not have been useful to include all studies in the field. Therefore, we did not include studies based on experiments we considered noncoherent. While citing the originally given statements, several studies are reassessed taking current knowledge into account. Sections III and IV focus on the systematic presentation of experimental studies of LID, while Sections V and VI focus on their conjunction and interpretation.

II. PHENOMENOLOGY AND NOMENCLATURE

Early indications that the efficiency of solar cells based on Cz silicon undergoes significant changes under illumination were presented as early as 1973 by Fischer and Pschunder [5]. They observed a degradation of the conversion efficiency of solar cells fabricated on 1- Ω -cm p-type Cz substrates of 3 – 5%_{rel} during a 12-h illumination with light. The degradation was found to be reversible by annealing at 200 °C in the dark and did not occur on cells made on substrates grown by the float-zone (FZ) method or Cz substrates with strongly reduced boron content. Spectral response measurements revealed a decreased red light response with degradation, indicating LID to be a decrease in bulk charge carrier lifetime, which was further confirmed by lifetime measurements.

LID occurs independent of light wavelength (for above bandgap illumination) as shown by Hashigami *et al.* [6] and even during carrier injection in the dark, as demonstrated by Knobloch *et al.* [7] and Glunz *et al.* [8]. This implies that a more precise term for the effect would be carrier-induced degradation (CID), as light only contributes indirectly via carrier generation. However, both terms are ambiguous in the framework of silicon, as multiple further degradation mechanisms have been found, which can be related to illumination or carrier injection. Such effects are found in particle-irradiated silicon (see, e.g. [9]), can be caused by copper precipitation (see, e.g., [1] for a review) or redistribution of iron contaminations (see, e.g., [10]), and have been demonstrated to affect current multicrystalline silicon (see, e.g., [11]). Thus, instead of adapting the term CID, it is more convenient to use a term specific to the degradation effect under discussion. The characteristic degradation has

been shown to occur in boron-doped Cz silicon and in FZ intentionally doped with oxygen, e.g., by Glunz *et al.* [12]. It does not occur if boron is replaced by gallium, as demonstrated, e.g., by Schmidt *et al.* [13]. Therefore, the effect is addressed to as the **boron–oxygen defect lifetime degradation** or short **BO-degradation**. The ascription to “**BO defects**” is motivated by a broad range of scientific findings that will be outlined in Section III-B and does not refer to the actual defect composition.

When the lifetime decay is monitored with sufficiently high temporal resolution, it can be observed to consist of two processes happening on different timescales. They are commonly ascribed to the activation of two electrically different defect centers. For typical p-type resistivity ranges, the degradation proceeds via a fast initial decay (fast-formed recombination center—**FRC**) within a few minutes followed by a slower decay on a timescale of several tens of hours to a few days (slow-formed recombination center—**SRC**) [6], [14], [15]. The observation for most p-type studies has been that the influence of SRC on the device operation of solar cells is stronger than for FRC. In addition, there is only a short timeframe for observation of mostly FRC-limited state. Therefore, most studies of BO-degradation focus on SRC, and the influence of FRC is often neglected. The atomistic nature of BO defects has not yet been determined, and thus, the assumption of two different defect centers is empirical. Lately, Hallam *et al.* disputed the existence of two defects with different recombination activities [16] and suggested the two-stage progression to arise from activation of a single defect from a pre-equilibrium.

Another crucial feature of BO defects is their metastability. Macroscopically speaking, samples prone to BO-degradation have been found to exhibit three fundamentally different states and their mixtures. In the fully **degraded state**, the bulk lifetime is limited by recombination-active BO defects and shows a characteristic injection-dependent charge carrier lifetime, as described by Rein *et al.* [17] (and others, as discussed in Section III-D). This state is stable to illumination at room temperature and usually limits device performance of p-type Cz silicon solar cells [18]. The defect can be transferred to the fully **annealed state** by annealing at elevated temperatures (typically a few minutes around 200 °C) in the dark. Measurements of the charge carrier lifetime in the annealed state are usually limited by recombination channels that are not related to BO-degradation. Therefore, the annealed state is regarded to introduce no or only weak recombination. The annealed state is prone to degradation under charge carrier injection and, therefore, not dominant during device operation. The third defined state can be reached by subjecting suited samples to illumination at elevated temperature, which causes a recovery of the lifetime [19], [20]. The fully **stabilized state** is characterized by elevated carrier lifetimes (compared with the degraded state) that are stable under illumination. This indicates a reduced recombination activity. The state is also denoted as the *regenerated* or *permanently recovered state* related to the lifetime or performance recovery during the process or as the *passivated state* referring to the assumption that present BO defects are electrically passivated during the process. We have chosen to adapt the label *stabilized* to attribute the key features of the defect state, that are stability

to illumination (contrary to the annealed state) and temperature (compared with degraded state—indicated by the concentration decay transition rates R (see Section IV-A) differing by orders of magnitude e.g., in [21]), and the fact that this state does not occur without intentional preparation (thus *stabilized* instead of *stable*). The label *passivated* implies similarity of the underlying transition mechanism to known passivation mechanisms despite the current nescience of the actual mechanism.

The transitions between these three states have been found to be reversible and can be incomplete in dependence of the sample and process conditions [13], [19], [22]. This will be discussed in more detail in Section IV, including a definition of the transition nomenclature in Fig. 1. It should be kept in mind that due to the metastability of all three states, the observation of mixed states in experiments is common. Care should be taken to account for this in the discussion of results.

III. DEFECT PROPERTIES

Many defect formation processes can be regarded in analogy to chemical reactions in the form of equilibrium reactions. The equilibrium of a reaction of multiple components is influenced by their concentrations, the stoichiometry of the resulting complex, the temperature, and can be influenced by charge carrier concentration effects. This section will present an overview of the experimentally demonstrated influences and the resulting conclusions to the defect composition. In Section III-A, the common metrology to study the magnitude of BO-degradation is introduced. Based on the presented approach, the established chemical and electronical influences are discussed in Section III-B, and studies on the influence of thermal treatments are presented in Section III-C. Section III-D introduces empirical prediction models for BO defect limitation, and Section III-E discusses findings concerning the injection-dependent recombination activity.

A. Effective Defect Concentrations

The characteristic lifetime degradation described by Fischer and Pschunder [5] has been studied thoroughly by many groups due to the high relevance of p-type Cz silicon for the photovoltaic industry. It has been consistently found to appear only in silicon that contains relevant amounts of both boron and interstitial oxygen and is, thus, related to defects emerging from interaction of these species. The defect concentration has not yet been associated with a direct and unambiguous feature in any chemical or physical measurement other than its recombination activity. Despite the usually good suitability of deep-level transient spectroscopy (DLTS) for detection of defects in silicon, BO defects do not give rise to strong signals, and many groups were unable to extract specific signatures. Recently, Mchedlidze and Weber [23] detected a signal related to the BO defect by applying the method to samples prepared from an affected solar cell instead of lifetime samples. They suggested unintentional defect hydrogenation in the probed volume during sample preparation to be a possible reason for many failed attempts to study the defect with DLTS before. This first direct detection of a signal related to BO defects is promising but requires time-consuming

sample preparation and has yet to be developed to a quantitative evaluation.

In order to study the defect, many studies have tried to relate the degradation on different materials to material properties and process influences, e.g., [2], [4], [6], [8], [12], [13], [15], [17], [24]–[56]. Due to the absence of a more direct concentration measurement technique for BO defects, the observed lifetime degradation was studied and compared. The common approach to assess the BO-degradation is the comparison of charge carrier lifetimes in the annealed state τ_{ann} and the degraded state τ_{deg} of a sample. This approach is based on the linear relation between recombination rate via defects and their concentration following from Shockley–Read–Hall (SRH) statistics [57], [58], i.e., $R_{\text{defect}} \sim N_{\text{defect}}$. However, due to the dependence of recombination rate on the charge carrier concentrations $R_{\text{defect}} = f_{\text{SRH}}(n, p)$, it is crucial for this approach to take the injection conditions into account [59]. In p-type silicon, recombination via BO defects is dominated by a donor level deep in the bandgap, as discussed in Section III-E. Therefore, the injection dependence $f_{\text{SRH,BO}}$ of room temperature lifetime is similar for a range of doping concentrations, when normalized with respect to the doping concentration to $f_{\text{SRH,BO,rel}}(X)$. Therefore, many studies assumed an identical normalized injection dependence for different doping concentrations and compared recombination at a constant ratio of injected electrons to doping concentration of $\Delta n = 0.1 \times p_0$. This corresponds to a fixed ratio of electrons to holes $X = n/p \approx 1/11$ and the assumption $f_{\text{SRH,BO,rel}}(X) \neq f(p_0)$.

The additional recombination due to active BO defects can be calculated from the effective lifetime measured in degraded state (resembling $1/R_{\text{total}}$) and in annealed state (resembling $1/R_{\text{other}}$) according to

$$N_{\text{BO}} \sim R_{\text{BO}}(X) = R_{\text{total}}(X) - R_{\text{other}}(X) \quad (1)$$

$$N_{\text{BO}} \sim \frac{1}{\tau_{\text{BO}}(X)} = \frac{1}{\tau_{\text{deg}}(X)} - \frac{1}{\tau_{\text{ann}}(X)}. \quad (2)$$

A detailed discussion on the necessity to evaluate lifetimes at a defined constant injection density can be found in [59] or [60]. Due to the unknown charge carrier capture cross sections of the BO defects, it is not possible to resolve the proportionality indicated in (1). The resulting quantity, therefore, is in the unit of an inverse lifetime, and the values are regarded as **effective defect concentrations**, which are usually denoted as N_{BO}^* . This quantity does not by itself take the possible occurrence of two defect centers FRC and SRC into account and represents a superposition $N_{\text{BO}}^* = N_{\text{FRC}}^* + N_{\text{SRC}}^*$.

This approach has served as a convention for BO defect studies and allows an easy assessment of N_{BO}^* with, e.g., the common measurement technique of photoconductance decay. However, it must be noted that it is—strictly speaking—not physically correct. It has been shown that FRC and SRC introduce pronounced—and different—injection-dependent recombination [4]. More recent studies have shown the recombination activity of FRC and SRC to each be caused by two energetic levels in the silicon bandgap [61], [62]. The potential parallel formation of FRC and SRC means that the injection dependence

of the lifetime due to BO defects $f_{\text{SRH,BO}}$ is not constant but a superposition of multiple recombination channels, limiting the general validity of the approach presented above when studying temporal lifetime evolution.

Furthermore, the complex dependence of the recombination activity of two-level SRH defects (as introduced in [63]) weakens the assumption of the deep donor level of SRC dominating recombination activity, as discussed in [62]. The comparison of samples with different net doping is then affected by significant changes of the injection dependence $f_{\text{SRH,BO,rel}}(X)$ with net doping. The injection dependence should thus be taken into account for a more physically meaningful determination of defect concentrations N_{BO}^* , N_{FRC}^* , and N_{SRC}^* . This was done to derive N_{FRC}^* and N_{SRC}^* from the temporal evolution of the lifetime at a fixed injection level by Schön *et al.* [48].

A sensible method to determine N_{BO}^* is to fit complete injection-dependent lifetime curves of τ_{BO} instead of reducing the information to a single injection level. This provides qualitative information on whether the observed degradation agrees with BO defect activation and includes correction for effects of $f_{\text{SRH,BO,rel}}(X)$. If two different BO defects FRC and SRC are assumed, their recombination activity superposes, and evaluation of injection-dependent lifetime curves can yield both N_{FRC}^* and N_{SRC}^* .

B. Established Chemical and Electronical Influences

1) *Influence of Oxygen:* Since the oxygen content is an obvious difference between the affected Cz and nonaffected FZ silicon, many studies have investigated the influence of the oxygen content on the magnitude of BO-degradation [4], [12], [24], [28], [34], [45], [60], [64], [65]. It is widely accepted that significant amounts of oxygen are introduced into the crystals during Cz crystal pulling due to the interaction of the silicon melt and the quartz crucible. Most oxygen is incorporated in the form of single interstitial oxygen atoms. Larger agglomerates, e.g., oxygen dimers, interstitial clusters (i.e., thermal donors), and Si_xO_y precipitates have been found to coexist with interstitial oxygen [66], and oxygen likely also pairs with other crystal defects to minimize lattice strains. Depending on the thermal history during and after crystal growth, these larger agglomerates usually exist in frozen-in equilibrium with the interstitial oxygen, e.g., [67].

A common way to study the oxygen content in conventional Cz silicon crystals is by means of Fourier-transformed infrared (FTIR) spectroscopy. A characteristic peak at 1107 cm^{-1} originating from a vibration of the Si–O–Si bond can be evaluated according to DIN 50438-1 or ASTM F 121-80 to derive absolute concentrations of interstitial oxygen $[\text{O}_i]$.

Experiments on a range of different Cz materials with similar [B] but varying $[\text{O}_i]$ conducted by Glunz *et al.* [12] established a strong dependence of N_{BO}^* on $[\text{O}_i]$. $[\text{O}_i]$ was found to be an important measure of the BO defect response of a given material. This explains the absence of BO-degradation in conventional FZ silicon and its very small impact on multicrystalline silicon (see, e.g., [68]) and Cz silicon with strongly reduced oxygen content (*magnetic Czochralski or MCz*) [28]. Systematic

studies by Rein *et al.* [65], as well as Schmidt and Bothe [4], [14], [24], [45], [46], [68], [69], found a quadratic dependence of N_{BO}^* on $[\text{O}_i]$. This dependence was found to be valid for both N_{FRC}^* and N_{SRC}^* [4]. Forster *et al.* [25] suggested to utilize this well-established dependence on the oxygen content and normalize values of N_{BO}^* by $[\text{O}_i]^2$ in order to increase comparability of defect concentration data. This allows comparison of data gathered on various materials with different oxygen contents and eases the discussion of trends. However, it must be taken into account that the two measurement standards mentioned above use different calibration factors and, therefore, result in different absolute numbers of $[\text{O}_i]$. Therefore, it is crucial to mention the applied standard for FTIR measurements when reporting BO-degradation.

2) *Uncompensated p-Type Silicon:* Most Cz grown p-type single crystals intended for use in photovoltaic application are grown from silicon feedstock doped with boron. Due to its favorable segregation coefficient close to unity, boron-doped crystals feature a small resistivity variation along the crystal length and diameter, and usually, no further dopants are added. It has been demonstrated that Cz silicon doped with different acceptors like gallium does not suffer from BO-degradation [13], [28], [60], [70]. Recombination active defects consisting of aluminum and oxygen are known but have not been demonstrated to be affected by illumination, e.g., [71]. Despite occurrence of LID in Cz silicon doped with indium instead of boron [72] and similarities with BO-degradation [73], it is widely accepted that the characteristic degradation is related to boron.

A multitude of studies conducted by different authors on a broad variety of boron-doped silicon crystals have agreed on a direct correlation of BO-degradation and the boron content, e.g., [4], [12], [13], [17], [24], [28], [34], [45], [60], [65], [68], [69]. If the influence of the oxygen content was taken into account as suggested above or the sample set was limited to a narrow range of oxygen concentrations, this correlation was found to be linear, i.e., $N_{\text{BO}}^* \propto [\text{B}]$ in material doped with boron only. This is a strong indication of a direct involvement of boron atoms in the formation or the composition of the defect.

Bothe and Schmidt [4] demonstrated that this relation holds for both the fast and the slow degradation component with an analysis of the lifetime limitation after the fast stage of defect formation. They observed the fast decay component to be responsible for about 10% of the recombination induced by BO-degradation throughout their sample set. Thus, negligence of FRC formation in the N_{BO}^* approach introduced in Section III-A causes a slight overestimation of N_{SRC}^* but appears not to imply false trends. However, the finding of a $[\text{B}]$ dependence of N_{FRC}^* was not reproduced in a study by Nørland [3] despite application of a similar approach.

3) *Compensated Silicon Containing Boron:*

a) *Compensated p-type silicon:* The absence of BO-degradation on complete absence of boron in a sample is a strong indication of an involvement of boron atoms in the underlying defects. However, the linear relation between N_{BO}^* and $[\text{B}]$ is not necessarily maintained in compensated p-type silicon—i.e., silicon containing further dopant species—as indicated by early experiments of Krühler *et al.* [74] and later

demonstrated by Kopecek *et al.* [30]. Compensated silicon is usually codoped with phosphorus or other dopants either intentionally added in order to modify the material resistivity or being residues in solar-grade silicon feedstock. Studies on p-type silicon codoped with boron and phosphorus found a proportionality of N_{BO}^* to the p-type net doping concentration $p_0 = [\text{Acc}] - [\text{Don}] = [\text{B}^-] - [\text{P}^+]$ instead of the absolute boron content $[\text{B}]$ [2], [33], [37], [75], [76]. Studies conducted on silicon codoped with gallium—i.e., an additional acceptor species and thus $p_0 = [\text{B}^-] + [\text{Ga}^-] - [\text{P}^+]$ —were inconsistent with these results and found indications of the $[\text{B}]$ dependence known from uncompensated p-type silicon [25], [26], [70]. Forster *et al.* suggested the observed dependence on p_0 to be a false consideration of the influence of decreasing $[\text{O}_i]$ along the studied crystals [26], which is a possible but unlikely explanation for the found trend. Further studies on a broad range of samples from different crystals could help solve this disagreement—or reveal a more complex underlying mechanism than plain linearity.

It should be noted that the results on uncompensated boron-doped silicon mentioned above are consistent with both trends, as p_0 equals $[\text{B}]$ there. Despite being contradictory for certain cases of dopant concentration combination, the discussed trends on compensated p-type allow conclusions on the defect composition. The studies indicate that boron atoms are involved in the formation of BO defects, but their concentration itself is not necessarily a limiting factor, unless it is significantly smaller than p_0 . One explanation is that the total concentration of BO defects N_{BO} is significantly smaller than $[\text{B}]$ and mostly determined by p_0 . A dominant influence of the net doping concentration indicates involvement of a species in the formation of the defect whose concentration is related to the Fermi level position, as discussed in Section V.

b) *Compensated n-type silicon:* While BO-degradation does not occur on conventional Cz n-type silicon, it was demonstrated to occur in compensated n-type Cz silicon by Schutz-Kuchly *et al.* [49] and thermal donor compensated high- $[\text{O}_i]$ FZ silicon by Bothe *et al.* [69]. Contrary to the implication of a vanishing N_{BO}^* due to the dependence on the p-type net doping concentration p_0 , BO-degradation was found to be significant [33], [43], [44], [48], [61], [75], [77]. The defect formation is slowed down and depends on the illumination conditions, as discussed in Section III-B3. Furthermore, it has been demonstrated in [61] and [62] that the recombination activity and, thus, injection-dependent lifetime of BO defects are different in n-type silicon compared with p-type. These fundamental differences to p-type silicon caused ambiguous results in degradation studies performed on compensated n-type silicon, complicating their interpretation. These effects were taken into account only in [48] and [61] for the determination of effective defect concentrations. Despite strong scatter and the limited number of investigated crystals, the results rule out a linear dependence of N_{FRC}^* or N_{SRC}^* on the n-type net doping concentration $n_0 = [\text{Don}] - [\text{Acc}]$. While boron is obviously necessary for BO defect occurrence in n-type silicon, a direct dependence on $[\text{B}]$ appears unlikely (but cannot be ruled out) from the given data, if validity of the $[\text{O}_i]^2$ -normalization is assumed. It can be

concluded that the concentration of BO defects in compensated n-type appears to be determined by a still unknown quantity. For the three crystals studied to date, the effective defect concentrations scatter in a narrow range, which indicates that the quantity is either an intrinsic quantity or related to the comparable growth conditions of the crystals.

4) *Influence of Other Impurities:* The strong correlation of BO-degradation with the presence of boron and oxygen is a clear indication that the defect formation includes these species. However, the defect composition is still under debate, and the involvement of further crystal defects cannot be excluded. The influences of several typical crystal defects and contaminations have been investigated.

Carbon is a common contamination in Cz silicon, and substitutional carbon C_s is known to interact and form complexes with oxygen [78]. A specific study by Rein *et al.* on a sample set with similar $[O_i]$ and $[B]$, but a variation of $[C_s]$ between 5×10^{16} and $5 \times 10^{17} \text{ cm}^{-3}$ indicated a weak mitigating influence of $[C_s]$ on N_{BO}^* [60], [65], which was also found by Walter *et al.* [52]. While a direct involvement in the defect can be excluded due to the small effect, carbon appears to interact or bind with interstitial oxygen atoms or other defect precursors and thereby reduce the total N_{BO} . Similar interactions have been hypothesized for the electronically similar germanium by Yu *et al.*, who found decreased BO-degradation on the addition of germanium [54], [55]. A connection between BO-degradation and contamination with copper has been discussed, e.g., [79]. However, studies have found that despite similarities, the copper-induced LID is not directly related to BO-degradation and *vice versa* [1], [80].

The occurrence of intrinsic defects—namely silicon self-interstitials Si_i and/or lattice vacancies V_{Si} —cannot be circumvented in commercial crystal growth. Their involvement in the defect was hypothesized by Rein *et al.* to be a reasonable source of scatter in the N_{BO}^* data [65]. Their possible involvement in BO-degradation has thus been studied by multiple authors. Rein *et al.* studied the influence of specific heat treatments known to modify the silicon lattice vacancy concentration $[V_{Si}]$ on N_{BO}^* [60], [65]. The results excluded a direct involvement of vacancies in the defect composition and indicated a possible small indirect influence via interaction of vacancies and boron atoms. The influence of interstitial silicon atoms was investigated by Macdonald *et al.* via the ion implantation of silicon atoms [35]. Despite introducing large amounts of Si_i , they did not detect relevant changes in N_{BO}^* . Therefore, a direct involvement of Si_i in the defect is ruled out, and the involvement of species sensitive to $[Si_i]$ —e.g., interstitial boron B_i —is deemed to be unlikely. The involvement of Si_i and V_{Si} was further disqualified by Walter *et al.*, who demonstrated that the transition from vacancy-rich to interstitial-rich silicon in a wafer did not affect N_{BO}^* [52]. While the studies of Rein and Macdonald studied cases of high concentrations, the study of Walter *et al.* demonstrates common concentrations in Cz silicon and thus conclusively excludes strong influences of intrinsic point defects.

Despite the usage of purified silicon feedstock and high-quality quartz crucibles, the contamination of Cz crystals with an unknown yet important species cannot be excluded. The ab-

sence of absolute concentration information of BO defects prohibits the definition of a concentration limit for a species that would exclude it from direct contribution to the defect formation. However, experiments on intentionally oxygen-doped FZ silicon presented by Glunz *et al.* [12] resulted in BO-degradation of comparable magnitude despite the presumably much lower level of contaminants. This was confirmed in further studies, e.g., [60], [69]. While this still cannot completely exclude impurities or crystal defects to be crucial for defect formation, it is regarded as being unlikely.

C. Influence of Thermal Treatments

While low-temperature anneals in the dark at around 200 °C are known to result in the fully reversible transition to the annealed defect state (e.g., in [13]), early findings by Knobloch *et al.* indicated that high-temperature treatments and solar cell processing affect N_{BO}^* [81]. Studies by Glunz *et al.* and Bothe *et al.* confirmed that typical oxidation and phosphorus diffusion processes at high temperatures can decrease N_{BO}^* on uncompensated samples by significant factors, and that this effect is related rather to the temperature treatment than the process itself [12], [29], [69]. Neither the gas ambient nor the temperature variation between a $POCl_3$ diffusion step and an oxidation were found to influence the effectiveness of the process. A strong influence of the cooldown rate was found, meaning that fast cooldown provides more efficient N_{BO}^* reduction [29], [69], [82]. This indicates that the cooldown during crystal growth can influence the magnitude of BO-degradation, if no additional high-temperature treatment is performed. Application of a high-temperature step, thus, improves reproducibility of results, as it reduces influences from often unknown crystal growth conditions. This is likely to be related to the similar cooldown after the processes and, thus, a decreased dependence on material supplier and position in the crystal related to thermal history during crystal growth.

Annealing at 450 °C for multiple hours was found by Bothe *et al.* to give rise to reduction of N_{BO}^* as well [69]. The possible decrease was found to be similar to the effect of high-temperature treatments, but no beneficial effect of a combination of both effects was found. A study by Voronkov *et al.* found that long annealing treatments of 120 h at 350 °C or eight weeks at 300 °C affected N_{BO}^* only slightly [50]. Conclusions from this experiment are discussed in Section V.

Note that the results concerning temperature treatments were demonstrated on uncompensated material, and their generalization is, thus, speculative.

D. Prediction of Boron–Oxygen Defect Limitation

Combination of the trends and influences discussed in the previous sections allows for predictions of the N_{BO}^* —and thus the lifetime limitation due to BO defects—for a given material. Due to the complex influence of thermal history during crystal growth, these predictions are more reliable for material after a high-temperature process, e.g., a $POCl_3$ diffusion step, as discussed in Section III-C.

As discussed above, the lifetime limitation due to BO defects in the fully degraded state in conventional B-doped silicon is related to the concentration of interstitial oxygen $[O_i]$ and the con-

centration [B] of substitutional boron. This lifetime limitation can be estimated with the parameterization of Bothe *et al.* [68], who derived it to be

$$\tau_{\text{BO}(\Delta n = 0.1p_0)} = 7.675 \cdot 10^{45} \cdot [B_s]^{-0.824} \cdot [O_i]^{-1.748} [\mu\text{s}] \quad (3)$$

for $[B_s]$, and $[O_i]$, both given in cm^{-3} .

This parameterization refers to material in the as-delivered state and should thus be multiplied by a factor of 2–3 when considering material after a high-temperature step (e.g., the POCl_3 diffusion in a solar cell manufacturing process), as discussed in Section III-C. The parameterization was recently extended by Niewelt *et al.* taking the results on compensated silicon and new insights to the recombination activity (see Section III-E) into account [83].

The recombination due to BO defects in the degraded state can be a crucial limitation for the conversion efficiencies of solar cells. Application of the permanent BO defect deactivation process discussed in Section IV-D can mitigate this limitation by transferring defects to stabilized state. The remaining limitation of solar cell efficiency was assessed in the framework of other limitations due to, e.g., metal contaminations in [18]. In a recent contribution, Walter *et al.* study the limitation for state-of-the-art cell concepts and deactivation processes and predict conversion efficiencies above 22% [51]. They also provide a parameterization of the lifetime limitation after the stabilization process, reading

$$\tau_{(\Delta n = 0.1p_0)} = \left(\frac{1}{5500} + \frac{p_0^2}{5 \cdot 10^{35}} \right)^{-1} [\mu\text{s}], \quad (4)$$

for p_0 given in cm^{-3} .

E. Injection-Dependent Recombination

The injection-dependent recombination at defects is related to their electronical structure. Therefore, studies of the recombination in dependence of charge carrier densities can improve the physical understanding of BO defects. Furthermore, it is crucial for device operation and optimization that recombination via BO defects is different for different cell concepts or working conditions.

The injection-dependent lifetime of p-type silicon in the fully degraded state was studied and characterized by means of SRH statistics by Schmidt and Cuevas [47] as well as Rein *et al.* [60], [84]. Rein found good agreement with carrier lifetimes measured on a multitude of materials when assuming a deep donor level 0.41 eV below the conduction band edge. Later studies by Bothe *et al.* assumed existence of FRC and SRC and found both defects to introduce deep donor levels (see, e.g., [4]).

In more recent studies, an advanced approach to SRH statistics (see [63]) was utilized to derive further insights to BO defects. Utilizing the activation of BO defects in compensated n-type, both FRC and SRC have been identified to be two-level defects [61], [62]. Such defects are characterized with a set of two energetic positions E_{defect} in the bandgap and four charge carrier capture coefficients $\alpha_{\text{defect,level,carrier}}$. Studies on compensated n-type silicon by Voronkov *et al.*

have related the recombination activity of FRC with an acceptor level at $E_{\text{a,FRC}} = E_v + (0.28 \pm 0.03)$ eV and a donor level at $E_{\text{d,FRC}} = E_c - (0.36..0.43)$ eV [61], [85]. Similar levels have been identified for SRC by Niewelt *et al.*, who found $E_{\text{a,SRC}} = E_v + (0.26 \pm 0.02)$ eV and $E_{\text{d,SRC}} = E_c - (0.41 \pm 0.02)$ eV [62].

The capture coefficients are assessable only in relative relation via lifetime studies. The relations are $\alpha_{\text{FRC,d,e}}/\alpha_{\text{FRC,d,h}} = 65$, $\alpha_{\text{FRC,a,h}}/\alpha_{\text{FRC,a,e}} = 86$, and $\alpha_{\text{FRC,d,h}}/\alpha_{\text{FRC,a,e}} = 7.4$ for FRC [61] and $\alpha_{\text{SRC,d,e}}/\alpha_{\text{SRC,d,h}} = 9.5$, $\alpha_{\text{SRC,a,e}}/\alpha_{\text{SRC,a,h}} \geq 215$, and $\alpha_{\text{SRC,d,e}}/\alpha_{\text{SRC,a,h}} = 0.55$ for SRC [62].

In a recent study, Niewelt *et al.* used a specialized approach on samples featuring a wide range of net doping concentrations to derive a new parameterization of FRC recombination activity [86]. The parameterization reads $E_{\text{a,FRC}} = E_v + (0.31 \pm 0.02)$ eV, $E_{\text{d,FRC}} = E_c - (0.34 \pm 0.02)$ eV, $\alpha_{\text{FRC,d,e}}/\alpha_{\text{FRC,d,h}} = 18.1$, $\alpha_{\text{FRC,a,h}}/\alpha_{\text{FRC,a,e}} = 85.7$, and $\alpha_{\text{FRC,d,e}}/\alpha_{\text{FRC,a,h}} = 1.2$. Due to the advanced approach and implementation of both doping types, we regard this parameterization to be more reliable than the one from [61]. However, it implies necessity of a reconsideration of SRC recombination due to the application of the parameterization from [61] in [62].

The more complex recombination behavior of two-level defects lessens validity of the N_{BO}^* approach outlined in Section III-A. While remaining a reasonable assumption for p-type silicon with $p_0 > 5 \times 10^{15} \text{ cm}^{-3}$, a correction term due to changing injection dependence becomes necessary for lower p-type net doping or compensated n-type silicon. This factor is discussed in [48], [61], [62], and [87].

IV. DEFECT STATE TRANSITIONS

Studying and understanding the progression of BO-degradation allows inference on the reaction mechanism and thus the defect. Therefore, the temporal progression of BO-degradation has been in the focus of research. Since the discovery of the stabilization by Herguth *et al.* [19], [20], a strong additional motivation has been the optimization of the transition to the stabilized state. As shown by Herguth *et al.*, the resulting equilibrium state of BO defects after a stabilization process depends on the ratio of the contributing transition rates [22],¹ rendering their investigation both scientifically and commercially relevant.

In order to avoid ambiguities found in the literature, the diagram in Fig. 1 depicts the transitions discussed in this work.

A. Determination of Transition Rates

The transition of BO defects between the states can be studied in the temporal evolution of cell parameters of affected solar cells or the bulk lifetime of well-passivated silicon samples (i.e., lifetime samples). The measurement of cell parameters during illumination is possible with high precision and temporal resolution but suffers from the unknown injection level of the derived

¹Note that for correct application of the analytical approach outlined in the reference, it is necessary to correct a typing error: The denominator in (5) should read “ $\Omega^2 - \omega^2$ ” instead of “ $\Omega^2 + \omega^2$ ”.

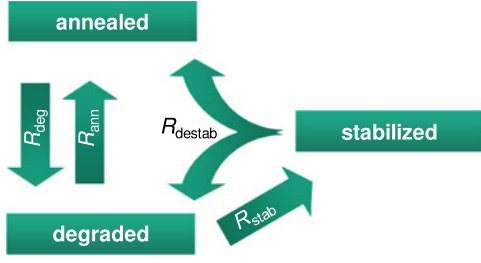


Fig. 1. Definition of the rate factors as discussed in this work. While the state transitions R_{deg} , R_{ann} , and R_{stab} are established based on experiments, there is no unambiguous information yet, regardless of whether R_{destab} leads to the degraded or the annealed state.

quantity. As discussed by Rein *et al.*, evaluation at constant generation rate (and thus unknown injection level) can impair quantitative conclusions from degradation measurements [59]. The injection-dependent recombination at defects can cause an apparent additional component in the temporal progression of a quantity, when it is not determined at a constant injection level.

The same holds true for lifetime measurements conducted with techniques that do not provide defined injection conditions. It should be noted that this applies to the microwave-detected photoconductance decay (MWPCD) method, unless special care is taken to assure lifetime extraction at a constant injection level.

The transition reactions between the BO defect states in p-type silicon can be described well with first-order reaction kinetic models. For the example of the degradation process (i.e., transition from annealed to degraded state), the reaction reads

$$\frac{\partial N_{\text{BO,deg}}(t)}{\partial t} = +R_{\text{deg}}(t) \cdot N_{\text{BO,ann}}(t). \quad (5)$$

For many experiments, the degradation rate coefficient $R_{\text{deg}}(t)$ has been found to be constant over time as indicated by an exponential decay of carrier lifetime (see, e.g., [81]). This allows derivation of

$$N_{\text{BO,deg}}(t) = N_{\text{BO,deg}}(0) + N_{\text{BO,ann}}(0) \times (1 - \exp(-R_{\text{deg}} \cdot t)) \quad (6)$$

and, thereby, an easy way to determine rate constants R_{deg} from fits to experimental concentration data derived according to (2). In this case, a convenient way to start in a defined state for $t = 0$ is starting the measurement after an adequately long annealing step, providing $N_{\text{BO,deg}}(0) = 0$ and $N_{\text{BO,ann}}(0) = N_{\text{BO,total}}$. An example of this approach is depicted in Fig. 2 for the degradation of a typical p-type Cz silicon sample.

Monitoring of the transition at different temperatures allows determination of the activation energy E_A of the process from an Arrhenius approach. Variation of process and sample parameters allows studying the influence of a quantity on the defect state transition.

B. Activation of BO defects

The approach outlined above has been applied to the degradation process by many authors in order to improve the understanding of BO-degradation.

1) *Uncompensated p-Type Silicon*: Glunz *et al.* found a quadratic relation $R_{\text{deg}} \propto [\text{B}]^2$ for conventional boron-doped p-type silicon [27]. The fast initial decay under illumination described by Hashigami *et al.* [6] was demonstrated to exhibit the same quadratic relation by Bothe *et al.* [14], [15]. No influence of $[\text{O}_i]$ on R_{deg} has been found in a multitude of studies (see, e.g., [4] and [42]).

Good agreement of experimental results and fits using the superposition of two exponential decays gave rise to the speculation of two independent reactions and thereby the assumption of the formation of FRC and SRC. Some experiments were found to be in better accordance with double exponential fits [6], [59] and Nærland *et al.* observed improved fit quality for the assumption of second-order reactions [40]. Niewelt *et al.* demonstrated that the fit quality was also improved when the progression was studied in a hole-square-weighted time domain, indicating an influence of the hole concentration under illumination p_{illum} [86]. A recent contribution by Hallam *et al.* suggested this to be due to the formation of only one BO defect type [16]. They suggest that the FRC activation is the fast activation of a defect precursor, while SRC is formed from a species that has to undergo a transition to this precursor state. Assuming very different transition rates to and from this precursor state creates the case of a pre-equilibrium, which would behave very similar to the independent formation of two defects. The rates $R_{\text{deg,FRC}}$ and $R_{\text{deg,SRC}}$ are usually observed to differ by orders of magnitude. Thus, the suggested mechanism is in line with most experimental observations, and the approach introduced in Section IV-A would stay mostly valid (however with another physical origin of $R_{\text{deg,FRC}}$ and $R_{\text{deg,SRC}}$). However, the observation of Bothe *et al.* that they could effectively suppress FRC activation in solar cells during current-induced degradation experiments [14], [24] does not agree with the assumption of a pre-equilibrium. There has yet to be an explanation of the results within the pre-equilibrium assumption or conclusive experimental refutation.

Despite the large implications that nonexponential progression could have, studies applying the approach introduced in Section IV-A provide valuable insights on the reaction mechanism by identifying influencing trends.

The degradation rate has been found to be independent of the illumination spectrum and intensity for common conditions. Hashigami *et al.* demonstrated an independence of R_{deg} from the excitation wavelength (for wavelengths providing electron hole pair generation) and its saturation for intensities above 1 mW/cm² halogen illumination for 0.5 $\Omega\cdot\text{cm}$ material [6]. Below this saturation threshold, R_{deg} was found to increase linearly with the illumination intensity [45]. Further studies on the degradation under low injection conditions by Nærland *et al.* determined a saturation threshold in the range of 10^{11} cm^{-3} excess electrons [39] and detectable degradation for electron concentrations in the range of 10^9 cm^{-3} for 1.6–3.8 $\Omega\cdot\text{cm}$ material [38].

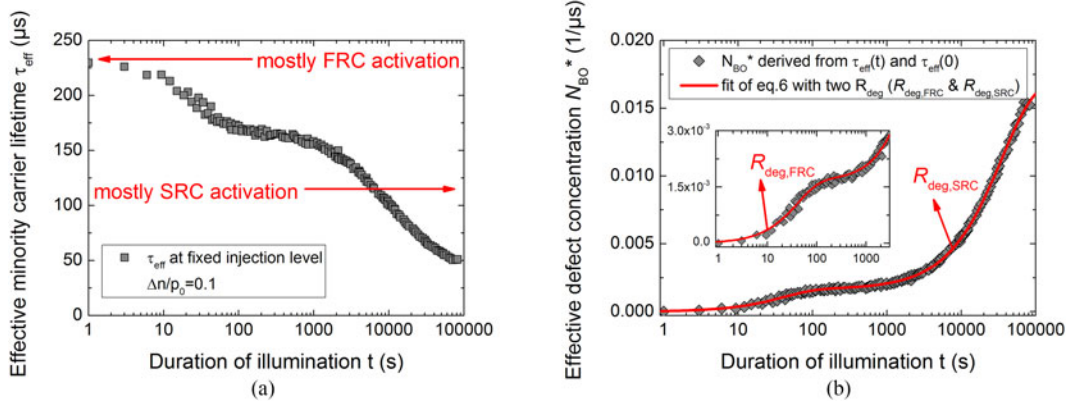


Fig. 2. (a) Example of the lifetime degradation under illumination of a boron-doped p-type Cz silicon sample with $[B] = 6 \times 10^{15} \text{ cm}^{-3}$ and $[O_i] = 8.7 \times 10^{17} \text{ cm}^{-3}$ (Measurement data courtesy of T. U. Nærland). (b) Effective defect concentration N_{BO}^* derived from the lifetime data according to (2) (symbols). The lines represent a fit to the data following the approach outlined in Section IV-A to determine defect activation rates for FRC and SRC formation.

Recent studies by Hamer *et al.* have demonstrated that applying high-intensity laser illumination can increase R_{deg} over the saturation value expected from the $[B]^2$ dependence [88]. This observation agrees well with the suggestion of an influence of p_{illum} instead of $[B]$. However, the high-power input causes a rapid heating of the sample, preventing the determination of precise rate constants.

Both $R_{deg,FRC}$ and $R_{deg,SRC}$ have been found to be thermally activated. Studies concerning the overall lifetime degradation around room temperature found activation energies in the range of 0.37–0.46 eV [8], [15], [45], [46], [89]. Measurements based on capacitance measurements conducted by Crandall indicate a second process with an activation energy of $E_{A,deg,2} = 0.17$ eV to become rate limiting for temperatures above 330 K [89]. More detailed studies by Bothe *et al.* revealed the room temperature value to be a superposition of the activation energies of $E_{A,deg,FRC} = (0.23 \pm 0.02)$ eV [14] and $E_{A,deg,SRC} = (0.475 \pm 0.035)$ eV [4].

2) *Compensated p-Type Silicon:* As discussed in Section III-B, the net doping concentration of compensated silicon usually differs from $[B]$. Careful assessment of experiments on compensated material, therefore, allows discrimination of influences of boron atoms and influences of the electronic environment. Dubois *et al.* demonstrated an LID effect for B-P compensated multicrystalline solar-grade silicon [90] and discussed it in the framework of BO-degradation stating a decreased R_{deg} . Further studies on compensated p-type silicon found a correlation of R_{deg} to p_0^2 [25], [33], [37]. Unlike the total measured BO defect concentration N_{BO}^* , the activation rate constant R_{deg} does not exhibit different trends for $p_0 < [B]$ and $p_0 > [B]$, thus maintaining $R_{deg} \propto p_0^2$ as demonstrated by Forster *et al.* [25].

3) *Compensated n-Type Silicon:* The activation of BO defects in compensated n-type does not exhibit constant degradation rates. The lifetime degradation under illumination does not follow an exponential progression and thus does not allow an easy determination of degradation rate constants R_{deg} . Measurements by Rougieux *et al.* [43], [44] did not indicate a two-stage progression as in p-type, leading to the assumption that only one component is active in n-type silicon [61].

However, experiments featuring long-term illumination by Niewelt *et al.* demonstrated SRC formation in compensated n-type [62].

The degradation was found to proceed faster for increased illumination intensity [31], [44], [48]. Lim *et al.* suggested a dependence of R_{deg} on the hole concentration during illumination p_{illum}^2 [31]. The changing p_{illum} for constant intensity due to lifetime degradation explains the nonconstant $R_{deg}(t)$ and good agreement with experimental data was presented. Studies by Schön *et al.* and Niewelt *et al.* on a wide range of material supported this dependence and extended it to both $R_{deg,FRC}$ and $R_{deg,SRC}$ [48], [86].

a) *Implications for boron–oxygen defects:* The necessity of charge carrier injection via illumination or current for the occurrence of BO-degradation in both doping types indicates that both carrier species are necessary for defect activation. The importance of the net doping in p-type agrees well with the findings on n-type, allowing the conclusion that $R_{deg} \propto p_{illum}^2$ for both doping types and both the fast and the slow degradation component. This is in accordance with the accelerated degradation under high injection conditions observed by Hamer *et al.* [88]. The electron concentration appears to limit R_{deg} only for very small concentrations and, hence, extremely low illumination intensities in p-type silicon.

C. Temporary BO defect Deactivation by Annealing

Monitoring the lifetime recovery during annealing in the dark after preceding degradation provides information on the temporary defect deactivation process.

1) *Annealing of p-Type Silicon:* Similar to the degradation, the temporary deactivation of p-type silicon exhibits rate constants R_{ann} as manifested by exponential progression during experiments. At the typical annealing temperature of 200 °C, the transition to the annealed state saturates within minutes. Rein *et al.* demonstrated the process to occur at temperatures as low as 111 °C with greatly increased timespan and derived a high activation energy of 1.32 eV [59]. This value

was confirmed and associated with SRC by Bothe *et al.*, i.e., $E_{A,ann,SRC} = (1.32 \pm 0.05)$ eV [4]. They found the temporary deactivation of FRC to be a two-step process with two energy barriers $E_{A1,ann,FRC} = (0.32 \pm 0.02)$ eV and $E_{A2,ann,FRC} = (1.36 \pm 0.08)$ eV, respectively.

The annealing rate constant R_{ann} has been found to be inversely proportional to the hole concentration p_0 (resembling [B] in conventional Cz) by Lim *et al.*, meaning that higher net doping concentrations cause slower deactivation, $R_{ann} \propto 1/p_0$ [91].

2) *Annealing of Compensated n-Type Silicon*: The temporary deactivation of BO defects appears to be slower in compensated n-type than in p-type with comparable doping and net doping concentrations. Schutz-Kuchly *et al.* found a high energy barrier of $E_{A,ann,n-type} = (1.7 \pm 0.2)$ eV [49]. Experimental results by Lim *et al.* indicate a decreased transition rate with the n-type net doping $n_0^{-1.85}$ [33]. It should be noted that they applied a stretched exponential equation to account for the nonconstant rate coefficient in n-type. While being an empirical approach without direct physical background, necessity of this approach supports the interpretation that annealing in compensated n-type differs from p-type.

D. Permanent BO Defect Deactivation: Stabilization Process

The transition to higher efficiency solar cell concepts such as PERC (see, e.g., [92]) has increased the relevance of mitigation of BO defect recombination, as these concepts are increasingly sensitive to bulk lifetime. The transition to the stabilized state has been demonstrated by Herguth *et al.* [19], [20] in 2006 to occur for carrier injection—by current or illumination—at elevated temperatures. Since then, a multitude of studies have tried to provide understanding and allow optimization for industrially feasible process conditions [2], [20]–[22], [32], [41], [53], [56], [88], [93]–[108]. Due to the metastability of the three defect states, an optimized R_{stab} is necessary in order to transfer a high fraction of defects to the desired stabilized state [22].

Determination of stabilization rate constants R_{stab} requires more consideration than studies investigating the transition between annealed and degraded state. It should be kept in mind that under the process conditions necessary for stabilization, the studied equilibrium includes all three states, and lifetime measurements usually cannot discriminate annealed and stabilized state.

Various studies have investigated the influences of material properties, sample preparation, and process conditions on the stabilization process. A lot of interdependencies and ambiguous results have caused vivid discussion among the community. This section aims to present established influences and indicate controversial factors.

1) *Process Conditions*: The stabilization process on a given set of identical samples has been demonstrated to be influenced by the process conditions. Multiple studies have been conducted for fixed carrier injection (i.e., constant illumination intensity or injected current), as well as variation of the sample temperature, to determine activation energies of the process. A wide spread of the resulting activation energies has been found in different studies, despite small uncertainty ranges. The activation energy

of the process $E_{A,stab}$ was found to be 0.6 eV [20], [93], 0.7 eV [22], [95], 1.0 eV [94], and even 1.2 eV [22], [96] with all studies claiming uncertainty ranges below 0.1 eV.

This indicates the stabilization transition to be limited by different process steps in the different studies. This hypothesis is supported by the findings of Herguth *et al.* in [22] that indicated different activation energies of the process for low and high temperatures.

There have been experimental indications of an increased R_{stab} with increased illumination intensity in several studies, e.g., [93], [109]. However, a recent study by Hamer *et al.* applying intense laser illumination refutes an increased R_{stab} for higher illumination intensity and relates the faster saturation of the process to the increased R_{deg} [97]. The stabilization appears to be a transition from degraded to stabilized state, as indicated by the finding of Hamer *et al.* that a given short process was more efficient when starting with fully degraded samples [97]. Therefore, a shift of the equilibrium between degraded and annealed state favoring degraded state during a stabilization process could increase the absolute transition rate (which is dependent on the absolute concentration of defects in degraded state) without changing R_{stab} itself. In the framework of a three state equilibrium (as discussed in [22]), both assumptions (increased R_{deg} or R_{stab}) could reasonably explain that the resulting equilibrium state is reached faster and the stabilized fraction is higher for increased illumination intensity or current injection.

While early publications reported stabilization processes with durations until saturation of multiple hours (see, e.g., [20]), more recent studies have demonstrated industrially feasible process durations of a few seconds to minutes under high illumination at temperatures above 200 °C (see, e.g., [88], [98], and [99]).

2) *Material Properties*: Stabilization treatments under similar conditions have been found to give rise to different R_{stab} when performed on samples from different materials. Studies focusing on the influence of certain sample parameters like [B], $[O_i]$, or p_0 have reported various influences of these quantities. However, in contrast with the degradation or the annealing processes, no clear linear or quadratic dependencies have been found, and few trends were independently confirmed.

Lim *et al.* reported a dependence in the oxygen concentration of $R_{stab} \sim [O_i]^{-1.54+/-0.2}$ for a sample set of uncompensated boron-doped material [105]. The influences of [B] and p_0 were studied in multiple studies on conventional and compensated silicon [2], [21], [32], [53]. The studies agreed on a general trend that an increase of [B] decreases R_{stab} and Lim reported $R_{stab} \sim [B]^{-1.67+/-0.52}$ [2] and found indications of an influence of [B] on $E_{A,stab}$. No clear evidence of a direct dependence on p_0 was found (see, e.g., [21] and [53]).

Only few studies have applied the stabilization process to compensated n-type [2], [21], [41], [56]. The lifetime recovery was found to be very slow, and upon subsequent illumination, a degradation was observed. This effect has been interpreted as the instability of the stabilized state in n-type [2]. Niewelt *et al.* demonstrated it to likely arise from an only partial defect stabilization for the applied process parameters instead [41]. In the framework of a three-state equilibrium, the occurrence

of low stabilization rates R_{stab} (which are reasonable for the studies in [2] and [41]) can create a situation where a fraction of defects remains in the nonstabilized states. This was further confirmed by Wilking *et al.*, who demonstrated illumination stable lifetimes after an optimized stabilization process believed to provide high R_{stab} [21]. The different transition kinetics for the degradation and annealing process in n-type silicon have prevented assessment of R_{stab} in n-type material so far.

3) *Sample Preparation:* The variation in stabilization results on similar samples from different groups indicates that the details of sample preparation have a strong influence on the stabilization process.

Multiple studies have found the surface passivation of lifetime samples and solar cells to influence the stabilization process (see, e.g., [100]–[103]), while others refuted a direct influence [105], [108]. The influence of the surface passivation has mainly been attributed to its potential to act as a source for hydrogen indiffusion to the silicon bulk, which has been demonstrated to be beneficial for the stabilization process, e.g., in [101] and [104]. While the role of hydrogen for the stabilization process is still under debate, it is consensus that its presence supports a fast stabilization process and high final bulk lifetimes, e.g., [108].

The thermal budget and history of investigated samples has a crucial influence on the stabilization process. Application of a phosphorus diffusion step at high temperatures provides an increase of R_{stab} compared with as-grown silicon [95]. On the other hand, prolonged annealing procedures in the range of 300–500 °C have been shown to significantly decrease R_{stab} [94], [105], [106]. Annealing in this temperature regime is common for the deposition or activation of dielectric passivation layers or the intentional formation of thermal donors. This implies the different thermal budgets of passivation schemes to be a possible explanation for the observed influences of the applied passivation scheme on stabilization. The validity of studies on identically processed samples should be unaffected by this influence, but quantitative comparison of different studies could be distorted.

Studies focusing on the optimization of the stabilization process in terms of quick processes and high resulting bulk lifetimes have found significant influence of fast and short high-temperature steps. In solar cell fabrication, such processes are common for the formation of metal contacts and are typically addressed to as firing steps. An optimized firing process can cause the difference between a hardly traceable and an efficient stabilization (see, e.g., [95] and [101]). Studies by Wilking *et al.* and Walter *et al.* have demonstrated highest improvement of the stabilization process (in terms of achieved R_{stab} for given stabilization process conditions) for firing steps with high peak temperature and belt speed, corresponding to fast temperature ramps [98], [99], [107].

4) *Summary:* Many experimental observations and drawn conclusions concerning the stabilization process are controversial, and some reported trends do not align. The influence of process conditions and sample parameters appears to be strongly related to the precise conditions during sample preparation. However, several general trends appear to be consistent in the overview of the presented studies. Sample conditions or

processes decreasing N_{BO}^* —such as a low [B] or $[\text{O}_i]$ and phosphorus diffusion steps—result in increased R_{stab} when compared with respective reference samples. In conjunction with the observed increase of R_{stab} for processes with high charge carrier injection, this suggests that actually an improved injection density Δn_{illum} due to weakened BO defect limitation is beneficial for R_{stab} . This also harmonizes with the beneficial effect of processes that introduce hydrogen into the bulk, which could passivate recombination channels—maybe even partially or temporally including BO defects.

A recent contribution by Wilking *et al.* suggested an empirical normalization approach based on an effective injection density [109]. This approach was shown to be successful in normalizing R_{stab} determined for different sample types and process conditions. It appears promising to improve the understanding of the effect of process steps and sample conditions.

E. Reactivation of BO defects at Elevated Temperatures

After a stabilization process, a fraction or all of the BO defects are present in the stabilized state. This state is then mostly stable to illumination at low temperatures and exhibits low or vanishing recombination activity [110]. However, this defect state is still a metastable configuration and a transition to the degraded or to the annealed state has been found at elevated temperatures. The transition has been labeled *redegradation*, *destabilization*, and *depassivation* by different authors, based on different assumptions of the underlying process. We adapt the label *destabilization* with rate R_{destab} , as it is coherent with the point of view that it dissolves the most stable defect state. Experimental discrimination of a transition to degraded or annealed state is difficult, as $R_{\text{ann}} \gg R_{\text{destab}}$ (see, e.g., [21]), and therefore no relevant fraction occupies the degraded state either way. In order to suppress the counteracting stabilization reaction, studies of R_{destab} are usually performed by annealing in the dark. Subsequent illumination and thus transition of all reactivated defects into degraded states then allows determination of the reactivated BO defect fraction. A study by Walter *et al.* demonstrated a slight bulk lifetime instability during illumination at room temperature [110]. A slow and weak degradation was also observed for continuous illumination at elevated temperatures by Herguth *et al.* [111] and Wilking *et al.* [94]. It is not yet clear whether this effect resembles the reaction found for annealing in the dark, which is labeled destabilization in this work. Results by Wilking *et al.* indicate it to be partially related to surface passivation deterioration.

The activation energy of the destabilization process has been determined by Herguth *et al.* to be $E_{\text{A,destab}} = 1.0$ eV on solar cells [19], [20], [22]. Experiments on lifetime samples by Wilking *et al.* resulted in a higher activation energy of $E_{\text{A,destab}} = (1.25 \pm 0.05)$ eV [94], which is quite similar to the annealing reaction.

Multiple studies have addressed the relevance of the destabilization process for the long-term stability of solar cells. Studies by Fertig *et al.* demonstrated the resilience of the stabilized state to the conditions during module integration [112] and module

certification tests [113]. Considerations of Wilking *et al.* based on the aforementioned destabilization rates debilitated concerns of instability for typical solar cell lifecycle durations [94]. A recent study by Hallam *et al.* based on actual module temperature data assured destabilization to be an insignificant issue as soon as even slight occurrence of the stabilization transition during in-field application was assumed [114].

V. DEFECT MODEL

The multitude of experimental studies has given rise to a series of theoretical models of the defect composition and configuration. Such models can provide an understanding of the occurring defect transitions and predict or explain reactions to sample conditions and process steps. This section is not intended to provide a full historic renarration but rather mentions relevant development steps. The focus is on the interpretation and discussion of the aforementioned established trends. The interpretations were derived from comparative literature study for this work and scientific discussion.

A. Defect Composition

The correlation of the BO-degradation to boron doping and the oxygen content makes defects composed of boron and oxygen atoms obvious candidates for its origin. Early suggestions by Schmidt *et al.* referring to the known B_iO_i defect were not consistent with DLTS results on its electronic structure [13], [47]. Schmidt and Cuevas suggested the involvement of multiple interstitial oxygen atoms, which was later specified by Schmidt and Bothe to interstitial oxygen dimers based on the found relation to $[O_i]^2$ [45], [47]. They suggested an oxygen dimer diffusing at room temperature and binding with substitutional boron to form a B_sO_{2i} defect. This suggestion was supported by theoretical considerations (see, e.g., [42], [115], and [116]). However, no experimental proof of oxygen dimer diffusion at room temperature was found, refuting this model [50], [117].

Without room temperature diffusion of a species, the reasonable assumption is existence of a latent defect formed at elevated temperatures and activated during illumination. The influence of the net doping concentration in compensated p-type silicon gave rise to the assumption of interstitial boron atoms to be involved in the complex, resulting in the suggestion of a B_iO_{2i} defect by Voronkov *et al.* [118]. This approach allows modeling for the occurrence of BO-degradation on compensated n-type silicon [36]. However, the degradation of n-type was inconsistent with the model [36], [48] and theoretical assessments [120]. Voronkov *et al.* extended their model to provide explanations for n-type degradation by suggesting FRC to be B_sO_{2i} [61]. The controversial influence of substitutional boron and the net doping concentration was suggested to indicate the latent defect to be $B_sB_iO_i$ resulting from the interaction of B_iO_i and B_sO_i [121].

In a recent model, Voronkov and Falster suggest both FRC and SRC to be B_sO_2 defects activated from latent defect centers of the same composition but an electronically different configuration [87]. They suggest that the defect is formed

in a temperature range between 500 and 600 °C, that is, at temperatures at which the material behaves intrinsic. A formation through the binding of diffusing oxygen dimers to stationary boron atoms is assumed, and the concentration N_{BO} is suggested to be determined by the equilibrium frozen in during crystal cooldown. This approach is in line with the results of Forster *et al.* [26] and provides agreement with many of the studies presented in this contribution.

However, it does not agree with results from [33], [48], and [76] that indicate a correlation to the net doping in compensated p-type and the indication from [48] that no dependence on $[B]$ was found for n-type silicon. These results could indicate an interaction with a precursor species at lower temperatures, where the concentration of this species is related to p for p-type but constant for n-type silicon. The observed beneficial influences of treatments at high temperatures discussed in Section III-C harmonize with the assumption of an equilibrium with defect components frozen in during cooling. However, they are not a direct experimental proof of a reaction mechanism and could agree with other models as well.

B. Defect State Transitions

Many contributions have suggested mechanisms of the defect transitions in the frameworks of the defect models under discussion at that time. Experiments under various conditions contradicted the early assumptions of a defect formation upon illumination and favor the activation of latent defect centers.

This activation corresponds to the transition from annealed to degraded state and has been conclusively shown to depend strongly on the hole concentration in both p- and n-type silicon. It does not occur in p-type samples without carrier injection; therefore, electrons are necessary for the process, but apparently not in the rate limiting step. The finding of an increased R_{deg} upon intense illumination by Hamer *et al.* [88] and the findings of Niewelt *et al.* [86] clearly point to a dependence on p_{illum}^2 that is usually not observable due to the small difference of p_0 and p_{illum} in p-type. This proportionality $R_{deg} \sim p_{illum}^2$ and the findings of Nærland *et al.* indicate that the rate-limiting step involves the capture of two holes. The observed R_{deg} of fast and slow decay are very different and, thus, do not allow discrimination between the activation of two independent defects or a transition via a pre-equilibrium.

The transition of the defect to the annealed state during annealing in the dark indicates that the annealed state is energetically favorable under these conditions. The transition proceeds via a large energy barrier as indicated by the activation energy of more than 1 eV, and the influence of the net doping concentration indicates that the rate-limiting step involves the emission of a charge carrier. The influence of the net doping concentration is inverse for both doping types, and the difference of the determined activation energies resembles the difference of the two energetic levels determined for SRC in [62]. This indicates the transition from annealed to degraded state to require recharging to the neutral state.

In the case of carrier injection at elevated temperature, the annealing transition is competed by the stabilization transition. The overview given in Section IV-D indicates that multiple—not yet unambiguously identified—factors influence the stabilization rate and, thus, the position of the resulting equilibrium. Despite being well performed and coherent in themselves, several studies presented experimental results disagreeing to other studies. This caused vivid discussions concerning the influence of certain parameters on the stabilization reaction in literature and scientific discourse. While some general conclusions on the underlying mechanism can be drawn from the digest given in this work, resolution of contradictions will require thorough reassessment or revision of the respective studies. The authors assume an assessment of stabilization rates with respect to the injection level or Fermi level position during the stabilization process to be a promising approach for this.

In a recent contribution, Voronkov and Falster have suggested a mechanism for the stabilization transition based on the assumption that SRC reconstructs to a non-recombination-active configuration at elevated temperature under illumination before the actual transition to the stabilized state [85]. This approach provides an explanation for the otherwise unsolved mystery of the constant R_{stab} , despite the observed lifetime recovery and dependence on injection intensity. Assuming this vanishing SRC limitation, Voronkov and Falster are able to explain observed trends and provide quantitative agreement to experiments with reasonable assumptions.

VI. CONCLUSION

The phenomenon of LID is a decrease of bulk charge carrier lifetime caused by the recombination activity of BO defects. The recombination activity of these defects is determined by metastable equilibria of three macroscopically observable states that are addressed to as *annealed*, *degraded*, and *stabilized state*. It is assumed that two defects labeled FRC and SRC are activated. Both are believed to introduce two energy levels into the silicon bandgap that contribute to their recombination activity.

BO-degradation can be clearly attributed to defects related to the simultaneous presence of both boron and oxygen in the silicon crystal. While the presence of other impurities and crystal defects might affect the defect concentration, no further mandatory component of the defect has been identified. Results on compensated material indicate an influence of the Fermi level position. The effects of various heat treatments on the BO-degradation imply that a fast cooldown during crystal growth or after high temperature steps decreases either the defect concentration itself or affects a necessary component of later formed defects. Either way, the impact of BO-degradation can be reduced by optimized thermal treatment.

Due to few traces in DLTS measurements, BO defect concentrations are usually calculated from the lifetime change between annealed and degraded state. Most studies evaluate lifetimes at $\Delta n = 0.1 \times p_0$, which gives a good estimation for the effective defect concentrations. A physically more meaningful evaluation of defect concentrations requires application of advanced

lifetime characterization and has recently been demonstrated to be crucial for studies on compensated n-type.

The recombination due to BO defects is detrimental, but the limitation is well predictable, provided a high-temperature step is performed.

Activation of BO defects has been found to be related to the injection of minority charge carriers in both p- and n-type silicon. While therefore both charge carrier types appear to be required for the defect activation, its rate is dominated by a quadratic dependence on the hole concentration.

The thermally activated temporary BO defect deactivation rate by annealing in the dark was found to decrease with increased net doping in both p- and n-type. This indicates that the defect transition from degraded to annealed state involves a recharging of the defect.

The stabilization of BO defects in a state of low recombination activity through the injection of charge carriers at elevated temperatures appears to be influenced by various factors of the sample preparation and the stabilization process. The process has been developed to be feasible for industrial application despite unknown details of the reaction mechanism. Application of high illumination intensities (e.g., provided by laser irradiation) and optimized sample preparation allow for process durations of a few seconds. While the stabilized state can be transformed back to a recombination active state by annealing in the dark, the low transition rate is usually overcompensated by stabilization under illumination, e.g., during solar cell operation. A stabilized solar cell is, therefore, believed to be resilient to BO-degradation during in-field operation.

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