

Impact of Solar Cell Processing **on LeTID in Crystalline Silicon**

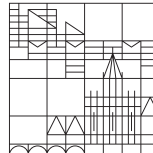
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Introduction

Solar cell modules based on crystalline silicon are known to experience performance degradation in field applications over time [1], particularly in warmer climates [2]. Various mechanisms can contribute to the decline in solar cell efficiency. While some losses are due to chemical degradation or mechanical stress at the module level, others are intrinsic to the solar cell and occur under light exposure at elevated temperatures.

The photovoltaic research community has extensively studied degradation phenomena that affect module reliability. These include potential-induced degradation (PID) [3, 4], several types of light-induced degradation (LID), such as boron-oxygen-related degradation (BO-LID) [5], UV-induced degradation [6–8], encapsulant discoloration [9], and a variety of other degradation mechanisms [10].

One additional degradation mechanism, specific to crystalline silicon absorbers, is known as light- and elevated temperature-induced degradation (LeTID) [11]. The defect is hereby named after the conditions it was first observed under. LeTID is characterized by an initial loss of solar cell efficiency during exposure to light and elevated temperature, followed by a subsequent recovery phase. In field applications, this degradation unfolds over several years of solar cell operation [12].

Research over the past decade has revealed that the extent of LeTID is strongly influenced by solar cell processing conditions [13]. While the solar industry has successfully implemented regeneration steps to mitigate certain light-induced degradation effects, such as BO-LID in boron-doped material [14], no universally effective solution has been found for LeTID, apart from reducing the excess hydrogen concentration in the bulk [15]. Historically, LeTID has been primarily studied in p-type silicon, which was the prevalent base material in commercial solar cells until recent years. Despite extensive research, the mechanisms driving LeTID remain unclear.

Chapter 1 introduces the fundamental properties of excited semiconductors and the concept of effective excess charge carrier lifetime, with emphasis on limiting recombination mechanisms and corresponding measurement techniques. This is followed by an overview of methods to detect LeTID. The chapter concludes with a comprehensive literature review on LeTID and

related phenomena. The conditions under which LeTID occurs, such as treatment settings and material dependencies, are examined. As many studies point to the involvement of hydrogen, an overview of related research is provided. Since the defect structure of LeTID has remained unresolved for more than a decade, several proposed defect models are also discussed.

Chapter 2 discusses the production of monocrystalline silicon, typically grown using the Czochralski (Cz) method, where segregation processes cause the accumulation of dopants and impurities. Subsequently, the processing techniques required to prepare silicon wafers cut from Cz-grown crystals for solar cell production are presented. These include wet-chemical surface treatments, diffusion processes, high-temperature steps, and surface passivation methods. Finally, the evaluation procedures used throughout this work are introduced, forming the basis for the data analysis in the following chapters.

Chapter 3 explores impurity accumulation during Cz-silicon growth with melt recharging (RCz-Si). This process offers a practical solution to economically grow silicon ingots using dopant elements with low segregation coefficients, which quantify the incorporation of atoms into the crystal. The discussion links theoretical models of impurity accumulation during p-type RCz-Si growth with experimentally observed degradation extent.

Chapter 4 extends the study to n-type material, focusing on its stability under different treatments. Based on insights from this qualitative analysis, the influence of dopant species, doping concentration, and impurity profiles in RCz-Si on the extent of degradation is evaluated.

Chapter 5 analyzes the impact of solar cell processing steps after wafer production. Particular emphasis is placed on hydrogenation, examined through variations in firing profiles and passivation schemes. Special attention is given to tunnel oxide passivating contacts (TOPCon) due to their central role in modern silicon solar cells. The chapter concludes with an outlook on the short- and long-term stability of p-type interdigitated back-contact (pIBC) solar cells, thereby completing the investigation.

1 Fundamental Concepts

This chapter establishes the fundamental concepts governing recombination in crystalline silicon, with particular emphasis on point defect-mediated mechanisms such as LeTID. While silicon remains the dominant semiconductor material with extensive research history, specific defect-related recombination pathways require detailed examination for photovoltaic applications.

Section 1.1 outlines the fundamentals for doped semiconductors, providing context for subsequent discussions. Section 1.2 summarizes the key features of different recombination channels arising from photogenerated charge carriers, introducing the effective carrier lifetime as a key metric for material quality assessment.

Section 1.3 mentions various measurement techniques used to detect LeTID, with a focus on injection-dependent lifetime spectroscopy of excess charge carriers via photo-conductance decay (PCD).

Section 1.4 summarizes research on degradation under light exposure at elevated temperatures. The main section discusses advances in understanding the LeTID defect in p-type silicon, followed by an examination of n-type silicon degradation under similar conditions. Finally, an overview of additional mechanisms, including surface-related degradation phenomena, is provided.

1.1 Properties of Doped Semiconductors

The fundamental properties of semiconductors are a widely studied field. This section aims to give a short overview on the most relevant qualities of doped semiconductors. The following introduction on of fundamental concepts is based on [16–18].

Silicon is a semiconductor with an indirect band gap of $E_{\text{gap}} = 1.12 \text{ eV}$ at 300 K [18]. Therefore, photons with energies greater than E_{gap} can be absorbed to create pairs of electrons and holes. Hereby, the electrons are excited above the conduction band edge E_C while a hole remains below the valence band edge E_V . Thus, E_{gap} corresponds to the energy difference $E_C - E_V$. By excitation of a semiconductor, the electron concentration n_0 present in the dark is increased by

an excess carrier concentration or injection Δn . Equally, the dark concentration of holes in the valence band p_0 is increased by the same amount of excess carrier concentration $\Delta p = \Delta n$.

Due to the increase of electrons in the conduction band and holes in the valence band, the system deviates from thermal equilibrium. This means that electron and hole concentrations are no longer determined by a single Fermi level E_F as it is the case without injection. While the Fermi level is located close to the middle of the band gap in the intrinsic case, the level shifts towards to the conduction band or the valence band depending on the type of dopant that is used. As a consequence of the generation of charge carriers, quasi-Fermi levels for electrons in the conduction band (E_{Fn}) and holes in the valence band (E_{Fp}) are introduced to describe carrier distribution during excitation. Integration of the charge carrier distribution in the bands results in the electron and hole concentrations according to

$$n = n_0 + \Delta n = N_C \cdot \exp\left(-\frac{E_C - E_{Fn}}{k_B \cdot T}\right) \quad (1.1)$$

$$p = p_0 + \Delta n = N_V \cdot \exp\left(-\frac{E_{Fp} - E_V}{k_B \cdot T}\right) \quad (1.2)$$

where N_C and N_V are effective densities of states in the conduction and valence bands, respectively. The injection-dependence on the right side of the equation is included by the corresponding quasi-Fermi levels.

The splitting of the quasi-Fermi levels allows the definition of an electrochemical potential. This potential difference corresponds to the open-circuit voltage V_{OC} , expressed as

$$E_{Fn} - E_{Fp} = q \cdot V_{OC} \quad (1.3)$$

with q denoting the elementary charge. For the case of $V_{OC} \rightarrow 0$ the system corresponds to the situation without excitation, where only a single Fermi level exists. The mass action law in thermal equilibrium $n \cdot p = n_i^2$ can be expanded to a more general case using the above equations, so that

$$n \cdot p = N_C N_V \cdot \exp\left(-\frac{E_C - E_V}{k_B \cdot T}\right) \cdot \exp\left(\frac{E_{Fn} - E_{Fp}}{k_B \cdot T}\right) = n_{i,eff}^2 \cdot \exp\left(\frac{q \cdot V_{OC}}{k_B \cdot T}\right) \quad (1.4)$$

This formulation considers the bandgap narrowing due to charge carrier interactions by the use of an effective intrinsic charge carrier density $n_{i,eff}$. The potential difference can be written as

$$V_{OC} = \frac{k_B \cdot T}{q} \cdot \ln\left(\frac{n \cdot p}{n_{i,eff}^2}\right) \quad (1.5)$$

and corresponds to the highest possible voltage a solar cell can generate.

Selective charge carrier separation is required to utilize the generated voltage. This separation is most commonly achieved through either a pn-junction formed by a highly doped emitter region (homo-junction) or through a hetero-junction between semiconductors of opposite polarity to the base material. In both cases, the built-in electric field in the depletion region drives electrons and holes in opposite directions. This necessitates a sufficiently long diffusion length, which strongly depends on charge carrier lifetime (see Section 1.2.3).

The behavior of the electron system can be described by the continuity equation

$$\frac{\partial \Delta n}{\partial t} = G - R - \nabla \cdot \underline{j} \quad (1.6)$$

where G represents the generation rate of electron-hole pairs, R the recombination rate, and j the current density [16]. The charge carrier lifetime is hereby mainly governed by the recombination rate as it will be discussed in the upcoming section. Under steady-state conditions ($\partial \Delta n / \partial t = 0$), the system reaches dynamic equilibrium where the carrier generation rate exactly balances the combined effects of recombination and carrier transport. The various recombination mechanisms that can occur will be examined in the following section.

1.2 Recombination Mechanisms

Recombination can occur from different processes, which can all be independently described from each other. Inversely to the generation process, electrons may relax from the conduction band back into the valence band if there is an empty state or a hole to occupy or recombine with, respectively. With an increased excess carrier concentration the recombination gets more likely. Under the assumption that R is proportional to Δn , the recombination rate can be written as

$$R = -\frac{d\Delta n}{dt} = \frac{\Delta n}{\tau} \quad (1.7)$$

with τ^{-1} being the proportionality factor between recombination rate and injection. The equation can be solved by an exponential decay

$$\Delta n(t) = \Delta n(0) \cdot \exp\left(-\frac{t}{\tau}\right) \quad (1.8)$$

where τ is the time constant which gives the duration until Δn has dropped to a value $1/e$. This quantity is therefore often referred to as excess charge carrier lifetime or in more simplified terms, lifetime. Since proportionality between R and Δn is not always given, the more general injection-dependent lifetime $\tau(\Delta n)$ is used. Under constant illumination, the generation rate

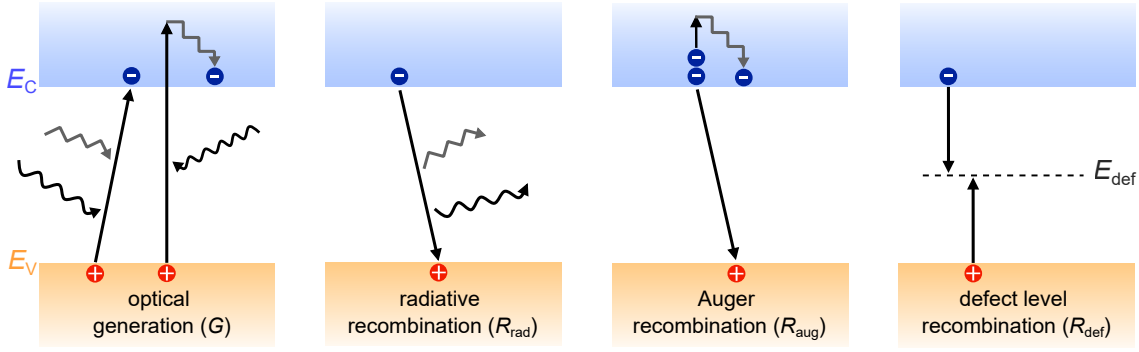


Figure 1.1: Illustration of possible charge carrier transitions (straight black arrows) between the conduction (c) and valence bands (E_v) in a semiconductor with an indirect bandgap. Shown from left to right are charge carrier generation, radiative recombination, electron-Auger recombination, and the recombination via point defects. Gray wavy arrows denote phonons, while black wavy arrows indicate photons. Inspired by [19].

balances the recombination and $d\Delta n/dt = 0$ so that

$$G = R = \frac{\Delta n}{\tau} \quad (1.9)$$

The generation and recombination mechanisms are shown in Figure 1.1. These mechanisms are namely the optical generation by incident photons, the radiative recombination, the Auger recombination and the recombination via defect levels in the band gap. Generally, both charge carriers will always occupy their lowest state which is the minimum of the conduction band for electrons and the maximum of the valence band for holes, respectively. If electrons are excited to higher states, relaxation will occur by the emission of phonons.

1.2.1 Bulk-Related Degradation

Intrinsic Recombination

The radiative and Auger recombination can be summed up as intrinsic recombination because they are unavoidable, even in intrinsic pure silicon. For the radiative recombination, also known as band-to-band recombination, an electron in the conduction band recombines with a hole in the valence band, emitting a photon. This process is the inverse of photo-generation and is described by the recombination rate R_{rad} . For the transition over the indirect band gap, a phonon is necessary to conserve momentum. Since exactly one electron and one hole are involved, the recombination rate is proportional to the density of electrons in the conduction

band n and holes in the valence band p so that

$$R_{\text{rad}} = B_{\text{rad}} \cdot n \cdot p = B_{\text{rad}} \cdot (n_0 + \Delta n) \cdot (p_0 + \Delta p) \quad (1.10)$$

Hereby, B_{rad} is the temperature-dependent radiative recombination coefficient which can be determined experimentally through photoluminescence measurements [20]. At 300 K, a value of $4.71 \cdot 10^{-15} \text{ cm}^3 \text{ s}^{-1}$ could be obtained [20]. This coefficient is orders of magnitudes lower, as it is the case for direct semiconductors due to the requirement of an additional phonon. This recombination mechanism is therefore relatively unlikely, except at higher injection levels. Additionally, B_{rad} is injection-dependent as a consequence of the Coulomb interaction between electron and hole [21].

The other intrinsic recombination mechanism is the Auger recombination. During this non-radiative process either an electron or a hole transfers its energy to another electron or hole, respectively. If a hole (electron) is available in the valence band (conduction band), recombination may occur. In this process, momentum is also exchanged with the second charge carrier, enabling the transition. This process involves three particles and is described by the recombination rate

$$R_{\text{Aug}} = C_{\text{eeh}} \cdot n^2 \cdot p + C_{\text{ehh}} \cdot n \cdot p^2 \quad (1.11)$$

where $C_{\text{eeh}} = 3.41 \cdot 10^{-31} \text{ cm}^6 \text{ s}^{-1}$ and $C_{\text{ehh}} = 1.17 \cdot 10^{-31} \text{ cm}^6 \text{ s}^{-1}$ are the Auger recombination coefficients at 300 K [22]. The eeh (ehh) process dominates in n-type (p-type) silicon [23]. These coefficients are determined experimentally and are revised whenever improvements in preparation methods yield higher material quality [24, 25]. Auger recombination becomes relevant at high excess carrier concentrations or in highly doped silicon because of its quadratic dependence on carrier concentrations. The most recent parametrization by Niewelt et al. [26] additionally accounts for photon recycling. In this case, photons emitted during radiative recombination can generate new electron-hole pairs, provided they remain within the sample.

Recombination via Point Defects

Crystal lattice defects, whether impurities or structural imperfections, introduce energy states within the bandgap that act as additional recombination centers. The recombination rate through these defects is quantitatively described by Shockley-Read-Hall (SRH) theory, which relates the recombination rate R_{srh} to the defect concentration N_{def} . The SRH recombination rate is given by

$$R_{\text{srh}} = \frac{n \cdot p - n_{\text{i,eff}}^2}{\tau_n \cdot (p + p_1) + \tau_p \cdot (n + n_1)} \quad (1.12)$$

where $n_{i,\text{eff}}$ is the effective intrinsic carrier concentration, and τ_n and τ_p are the electron and hole capture time constants, respectively [27, 28]. This recombination process occurs through sequential electron and hole capture events at defect sites, with the overall rate scaling linearly with defect concentration. The capture time constants themselves are determined by fundamental defect properties, expressed as

$$\tau_n = \frac{1}{\sigma_n \cdot v_{\text{th},n} \cdot N_{\text{def}}} \quad \text{and} \quad \tau_p = \frac{1}{\sigma_p \cdot v_{\text{th},p} \cdot N_{\text{def}}} \quad (1.13)$$

Here, σ_n and σ_p represent the capture-cross sections for electrons and holes, while $v_{\text{th},n}$ and $v_{\text{th},p}$ correspond to their respective thermal velocities. The charge carrier densities at the defect level E_{def} can be expressed as

$$n_1 = N_C \cdot \exp\left(-\frac{E_C - E_{\text{def}}}{k_B \cdot T}\right) \quad \text{and} \quad p_1 = N_V \cdot \exp\left(-\frac{E_{\text{def}} - E_V}{k_B \cdot T}\right) \quad (1.14)$$

The defect's impact on charge carrier lifetime depends critically on its position within the band gap. Deep-level defects near mid-gap are particularly detrimental, especially under low-injection conditions, as they create efficient recombination centers. Remarkably, even trace impurity concentrations as low as 10^{10} cm^{-3} can significantly degrade device performance [29, 30]. To minimize this recombination mechanism, it is essential to maintain low defect concentrations which requires high-purity silicon and clean room manufacturing conditions.

The corresponding lifetime can be calculated with

$$\tau_{\text{srh}} = \frac{\Delta n}{R_{\text{srh}}} = \frac{\tau_n \cdot (p + p_1) + \tau_p \cdot (n + n_1)}{n_0 + p_0 + \Delta n} \quad (1.15)$$

For p-type silicon with $n_0 \ll p_0$, Δn and $p_0 \ll n_0$, Δn for n-type, the SRH lifetime can be expressed as

$$\tau_{\text{srh},n} = \frac{\tau_n \cdot (\Delta n + p_1) + \tau_p \cdot (n_0 + \Delta n + n_1)}{n_0 + \Delta n} \quad (1.16)$$

$$\tau_{\text{srh},p} = \frac{\tau_n \cdot (p_0 + \Delta n + p_1) + \tau_p \cdot (\Delta n + n_1)}{p_0 + \Delta n} \quad (1.17)$$

For a deep-level defect (e.g. LeTID [31]) with $n_1 \ll \Delta n$ and $p_1 \ll p_0 + \Delta n$, the above lifetime can be further simplified to

$$\tau_{\text{srh},p,\text{deep}} = \tau_n \cdot \left(1 + \frac{\tau_p}{\tau_n} \cdot \frac{\Delta n}{\Delta n + p_0}\right) \quad (1.18)$$

$$\tau_{\text{srh},n,\text{deep}} = \tau_p \cdot \left(1 + \frac{\tau_n}{\tau_p} \cdot \frac{\Delta n}{\Delta n + n_0}\right) \quad (1.19)$$

From this equation the symmetry factor $\tau_p/\tau_n = \sigma_n/\sigma_p \cdot v_{th,n}/v_{th,p}$ can be derived. This factor is a defect specific parameter which can be used to distinguish between different defects. Importantly, this factor enables defect differentiation without requiring precise knowledge of either the defect concentration N_{def} or the absolute capture cross-section values. This simplified form proves particularly useful for identifying defect signatures in lifetime spectroscopy measurements which will be discussed in Section 1.3.1. The reduced parameter dependence makes it valuable for comparative defect analysis, especially when absolute defect concentrations are unknown. For a comprehensive analysis of the equation's behavior and applications, see [32].

1.2.2 Recombination at the Surface

Surface recombination represents an additional loss mechanism beyond bulk recombination, occurring when charge carriers reach the crystal surface. The surface recombination rate R_{srf} follows similar principles as the recombination via point defects. At the surface, accumulating impurities and dangling bonds can lead to a high density of defects, creating a quasi-continuum of defect states within the bandgap. This process can be expressed equivalently to Equation (1.7) as

$$R_{srf} = S \cdot \Delta n_{srf} \quad (1.20)$$

by the use of a surface recombination velocity S and the injection present at the surface. This formulation presents experimental challenges because Δn_{srf} depends on the surface charge distribution which either repels or attracts electrons and is difficult to obtain experimentally. Furthermore, S is not an intrinsic material property but varies with injection level and surface treatment. To facilitate practical analysis, it is often more useful to define an effective recombination rate for the surface $R_{srf,eff}$ to express the recombination current as

$$j_{rec} = q \cdot S_{eff} \cdot \Delta n = q \cdot R_{srf,eff} \quad (1.21)$$

The effective surface recombination velocity S_{eff} remains injection-dependent and is only directly comparable between samples with identical surface band bending. A more robust metric for evaluating surface passivation quality is the surface-related saturation current density j_0 , which characterizes the recombination strength. This quantity relates to the recombination current through

$$j_{rec} = j_0 \cdot \left(\frac{p \cdot n - n_{i,eff}^2}{n_{i,eff}^2} \right) \quad (1.22)$$

where j_0 remains independent of Δn as long as the condition $n \ll p$ or $n \gg p$ is fulfilled [33]. This applies to surfaces with sufficient charge to establish stable band bending. The connection

between j_0 and effective recombination velocity is given by

$$j_0 = \frac{q \cdot n_{i,\text{eff}}^2 \cdot S_{\text{eff}} \cdot \Delta n}{p \cdot n} = \frac{q \cdot n_{i,\text{eff}}^2 \cdot S_{\text{eff}}}{N_{\text{dop}} + \Delta n} \quad (1.23)$$

The corresponding surface lifetime τ_{srf} incorporates both surface recombination and bulk diffusion effects:

$$\tau_{\text{srf}} \approx \frac{w}{2S_{\text{eff}}} + \frac{w^2}{D \cdot \pi^2} = \frac{q \cdot w \cdot n_{i,\text{eff}}^2}{2 \cdot (N_{\text{dop}} + \Delta n)} \cdot \frac{1}{j_0} + \frac{w^2}{D \cdot \pi^2} \quad (1.24)$$

Here, w represents the sample thickness and D the ambipolar diffusion constant, which lies between the electron and hole diffusivities. This constant is appropriate because, during lifetime measurements, both electrons and holes are generated near the surface and subsequently redistribute toward the rear side [32]. The second term in Equation (1.24) accounts for the time required for carriers to diffuse to both surfaces, though this contribution is often neglected in practice [34]. Surface passivation strategies will be examined in Section 2.2.3, while the experimental determination of j_0 will be discussed in Section 2.3.2.

1.2.3 Effective Excess Charge Carrier Lifetime

The total effective recombination rate R_{eff} can be expressed as the sum of all independent recombination mechanisms:

$$R_{\text{eff}} = \sum_i R_i = R_{\text{rad}} + R_{\text{Aug}} + R_{\text{srh}} + \frac{2}{w} \cdot R_{\text{srf}} \quad (1.25)$$

where radiative and Auger recombination are often combined into a single intrinsic recombination term R_{int} . The factor $2/w$ accounts for surface recombination occurring at both wafer surfaces. The inverse effective excess carrier lifetime can therefore be expressed by the sum

$$\frac{1}{\tau_{\text{eff}}} = \frac{R_{\text{eff}}}{\Delta n} = \frac{1}{\tau_{\text{rad}}} + \frac{1}{\tau_{\text{Aug}}} + \frac{1}{\tau_{\text{srh}}} + \frac{1}{\tau_{\text{srf}}} = \frac{1}{\tau_{\text{bulk}}} + \frac{1}{\tau_{\text{srf}}} \quad (1.26)$$

The effective lifetime can be decomposed into a bulk-related lifetime τ_{bulk} which includes all intrinsic and SRH recombination and the surface-related lifetime τ_{srf} .

Corresponding to the effective lifetime, an effective diffusion length $L_{n/p}$ for electrons and holes can be defined. This parameter describes the average distance a charge carrier can travel before recombination. Using the diffusion constant $D_{n/p}$ of the respective carrier type, the diffusion length is given by

$$L_{n,\text{eff}} = \sqrt{D_n \cdot \tau_{\text{eff}}} \quad \text{and} \quad L_{p,\text{eff}} = \sqrt{D_p \cdot \tau_{\text{eff}}} \quad (1.27)$$

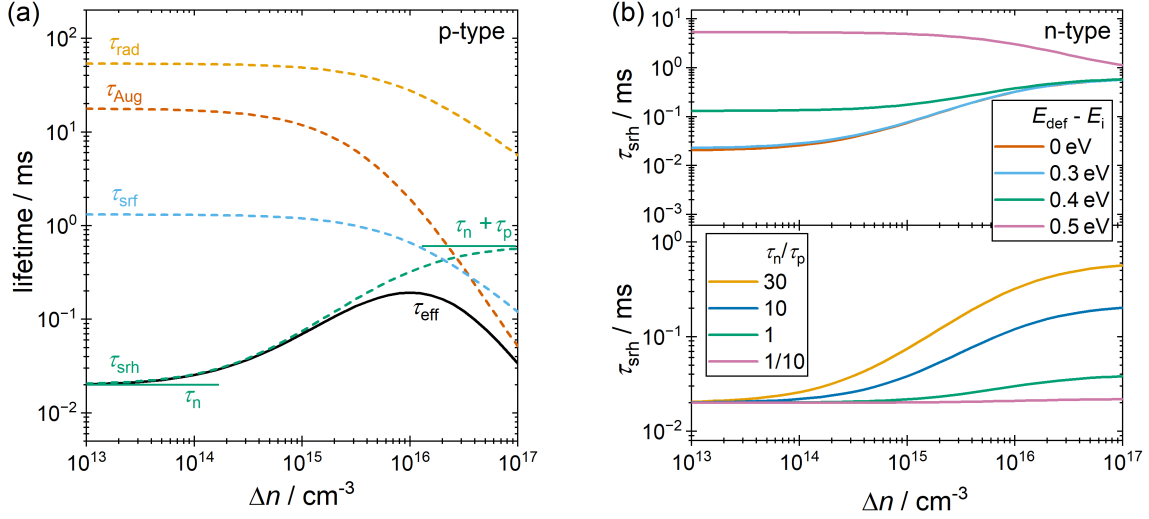


Figure 1.2: (a) Injection-dependent lifetimes for the different recombination mechanisms and the resulting effective lifetime τ_{eff} for a p-type sample with a doping concentration of 10^{16} cm^{-3} , $\tau_n = 20 \mu\text{s}$, $\tau_p = 600 \mu\text{s}$. Data are calculated using the latest Auger recombination parameterization [26] available via [35]. The surface recombination lifetime τ_{srf} is obtained from Equation (1.24) with $j_0 = 10 \text{ fA cm}^{-2}$ and a sample thickness of $150 \mu\text{m}$. Parameters are chosen to represent the most common cases in this work. (b) Injection dependence of the defect-related lifetime τ_{srh} in n-type silicon for different defect energy level $E_{\text{def}} - E_i$ (top) and symmetry factors τ_n / τ_p (bottom). The case $\tau_n / \tau_p = 30$ with $E_{\text{def}} - E_i = 0 \text{ eV}$ can be compared with the p-type scenario in (a), where $\tau_p / \tau_n = 30$. A doping concentration of $1 \cdot 10^{16} \text{ cm}^{-3}$ is assumed.

In Figure 1.2a, all lifetime components are exemplarily calculated for a p-type sample with a doping concentration of $p_0 = 1 \cdot 10^{16} \text{ cm}^{-3}$, using $\tau_n = 20 \mu\text{s}$, $\tau_p = 600 \mu\text{s}$ and $j_0 = 10 \text{ fA cm}^{-2}$. For the intrinsic recombination the most recent parametrization is applied [26]. Bulk-related lifetimes are determined according to [35], while τ_{srf} is calculated using Equation (1.24).

It can be observed that intrinsic recombination mechanisms become relevant only at higher excess charge carrier concentrations, with Auger recombination dominating due to its quadratic dependence on carrier concentration. In this example, the characteristic time constants for electrons and holes are selected to match known parameters for LeTID, using a specific ratio of $\tau_p / \tau_n = 30$ [36–39]. In p-type material, this asymmetry results in a significant reduction of lifetimes in the low-injection regime. A comprehensive discussion on LeTID is provided in Section 1.4.1.

For n-type material, a variation of defect-specific parameters used to calculate the injection-dependent τ_{srh} is shown in Figure 1.2b. In the upper graph, the defect energy level $E_{\text{def}} - E_i$ is varied while assuming a symmetry factor $\tau_n / \tau_p = 1/30$. Hereby, E_i corresponds to the intrinsic Fermi level of the semiconductor. In the lower graph, the symmetry factor is varied

while maintaining a deep-level defect ($E_{\text{def}} - E_i = 0 \text{ eV}$). Although some studies suggest that the evolving defect during carrier injection may exhibit a symmetry factor of $\tau_n/\tau_p \sim 35$ [40], reliable data on the exact defect energy level remain scarce. Overall, the literature lacks consistency, preventing a conclusive identification of the underlying defect. A broader discussion of the observed degradation phenomena in n-type silicon is provided in Section 4.2.

Figure 1.2b further shows that SRH recombination becomes less limiting for shallow-level defects, particularly those located near the conduction band edge, exhibiting an injection dependence similar to that of surface-related recombination. Defects of this nature are especially difficult to characterize accurately without detailed knowledge of the surface passivation quality. Additionally, for symmetry factors less than one, the injection dependence of τ_{srh} is further reduced, making the analysis even more challenging.

From Equation (1.5) it can be seen that the open-circuit voltage of a solar cell with dopant concentration N_{dop} is dependent on the charge carrier lifetime due to Equation (1.7) so that

$$V_{\text{OC}} = \frac{k_B \cdot T}{q} \cdot \ln \left(\frac{\Delta n^2 + \Delta n \cdot (n_0 + p_0) + p_0 \cdot n_0}{n_{i,\text{eff}}^2} \right) \quad (1.28)$$

Additionally, lifetime is also linked to the photo generated current and therefore the maximum current that can be extracted from the device as it is indicated by Equation (1.6). Hence, monitoring of the τ_{eff} allows to make statements on the long-term stability of solar cells.

However, several aspects must be considered. First, testing conditions usually deviate from those found in field applications, since light intensity and temperature are often increased to accelerate degradation. In addition, day-night cycling is typically neglected. Second, it is not always clear whether a test structure that does not exhibit all characteristics of a complete solar cell (often referred to as a lifetime sample) shows the same behavior during long-term stability testing. Thus, the most reliable way to assess the stability of a specific cell design is to measure the lifetime directly on the device itself. Nevertheless, simplified sample structures can be highly useful to gain more fundamental insights into defect dynamics and material properties. In the following section, the techniques used to determine carrier lifetime in both dedicated lifetime samples and complete solar cells are introduced.

1.3 Detecting LeTID

Detecting LeTID in crystalline silicon poses a significant challenge due to the low expected defect concentration ($\sim 10^{12} \text{ cm}^{-3}$) [2, 41]. Here, it is especially problematic that the underlying nature of the defect is not yet fully understood. In this section, methods to evaluate the impact

of LeTID on the effective excess charge carrier lifetime are discussed. Importantly, these techniques do not necessitate complete solar cell structures. Instead, simplified lifetime samples enable the access to certain defect characteristics by lifetime measurements but possibly not all. This streamlined approach reduces experimental complexity while avoiding interference from unrelated degradation effects, such as contact deterioration. Since efficiency losses in solar cells cannot be exclusively linked to LeTID, as other degradation mechanisms may cause similar performance declines, methods to confidently identify LeTID are necessary.

1.3.1 Injection-Dependent Lifetime Spectroscopy

PCD method

One of the easiest and most common ways to investigate defects in silicon is the injection-dependent lifetime spectroscopy (IDLS). Hereby, the injection-dependent effective excess carrier lifetime is calculated for a wide range of Δn from a photo-conductance decay. Because of the different dependencies of $\tau_{\text{eff}}(\Delta n)$ on the recombination mechanisms (see Section 1.2), defect specific parameters like the energy level in the band gap or the symmetry factor can be determined. For the measurement, charge carriers are generated using an intense flash lamp emitting mostly IR light. The generation rate G is determined from the photon flux Φ of the flash, measured by a calibrated reference cell and corrected for the sample's surface reflectivity r and thickness w ,

$$G = \frac{\Phi(1 - r)}{w} \quad (1.29)$$

This assumption holds only if all incident light that is not reflected is fully absorbed by the sample. The generated excess carrier lifetime can then be detected as a result of a photo-conductivity

$$\sigma = q \cdot (p \cdot \mu_p + n \cdot \mu_n) \quad (1.30)$$

by the use of an eddy current sensor beneath the sample, where μ_p is the mobility of holes and μ_n the electron mobility, respectively. From this, the excess carrier concentration Δn and its temporal partial derivative $\partial \Delta n / \partial t$ can be determined, allowing the calculation of τ_{eff} using the continuity equation

$$\frac{\partial \Delta n}{\partial t} = G - R = G - \frac{\Delta n}{\tau_{\text{eff}}} \implies \tau_{\text{eff}}(\Delta n) = \frac{\Delta n}{G - \frac{\partial \Delta n}{\partial t}} \quad (1.31)$$

The transport term can be neglected under the assumption that carrier generation and recombination are homogeneous throughout the sample. When the effective lifetime is significantly longer than the flash decay time, the generation rate G becomes negligible after the flash. In

this case, the effective lifetime can be calculated in the transient mode as

$$\tau_{\text{eff}}(\Delta n) = -\frac{\Delta n}{\frac{\partial \Delta n}{\partial t}} \quad (1.32)$$

Conversely, if the carrier lifetime is much shorter than the flash decay time, the system reaches a quasi-steady-state where the carrier concentration remains nearly constant. The effective lifetime is then given by

$$\tau_{\text{eff}}(\Delta n) = \frac{\Delta n}{G}. \quad (1.33)$$

In general, when neither of these extreme cases apply, the complete form of the continuity equation is used to ensure accurate lifetime determination across a wide injection range (generalized mode). Additional discussions can be found in [42, 43].

The IDLS approach enables extraction of defect-specific parameters, such as the defect energy level and symmetry factor, based on the SRH recombination model. These properties can be identified by analyzing the injection-dependent lifetime $\tau_{\text{eff}}(\Delta n)$ over a broad range of excess carrier concentrations. However, a limitation lies in the differentiation of various defects that may occur simultaneously. In some cases, it can also be difficult to distinguish between defects located in the bulk of the sample and those at the surface. It can therefore be helpful to evaluate only the changes in lifetime as defects evolve under certain conditions, as discussed in Section 2.3.1.

All measurements in this work were carried out using a *WCT-120* at 30 °C from *Sinton Instruments*. Typically, the measurement of τ_{eff} covers an injection of two orders of magnitude between $\sim 10^{14} \text{ cm}^{-3}$ and $2 \cdot 10^{16} \text{ cm}^{-3}$. By the use of Equation (1.28) it is possible to predict the maximal possible open-circuit voltage without the need of contacts. The corresponding quantity can be extracted for a generation corresponding to 1 sun by the implied open-circuit voltage iV_{OC} .

Suns- V_{OC} Approach

For metallized samples such as solar cells the conductance of the Si base material can not be measured anymore as a consequence of the significantly higher conductivity of the metallization. A possible approach to determine an injection-dependent lifetime is the application of variable illumination intensity while maintaining open-circuit conditions. The corresponding approach is often labeled as Suns- V_{OC} [42, 44]. Similar to the PCD method, the generation rate must be determined using a reference cell, while the open-circuit voltage is monitored during the decay phase of a flash. Unlike inductive techniques, this measurement requires direct contacting of both polarities of the sample. Solving the quadratic expression in Equation (1.28) for Δn

in the case of p-type material ($n_0 \ll p_0$), and assuming a negligible injection dependence of $p_0 \cdot n_0 = n_{i,\text{eff}}^2$, yields

$$\Delta n = -\frac{p_0}{2} + \sqrt{\frac{p_0^2}{4} + n_{i,\text{eff}}^2 \cdot \left[\exp\left(\frac{q \cdot V_{\text{OC}}}{k_B \cdot T}\right) - 1 \right]} \quad (1.34)$$

Hereby, only the positive root has a physical meaning [44]. Since $n_{i,\text{eff}}$ is both dependent on the temperature and the dopant concentration a precise knowledge of both is necessary for accurate calculation of Δn [45]. By the knowledge of Δn , the lifetime can now be calculated by the use of Equation (1.33) as long as the decaying lifetime is short in comparison to the decay of the flash (steady state). Similar to the PCD approach, these measurements can also be performed in transient mode or using the generalized approach.

In this work the Suns- V_{OC} method is applied using a flasher device from *H.A.L.M.*, operated with the decay of a $\sim 1000 \text{ W m}^{-2}$ xenon flash. The corresponding generation rate is calculated as

$$G = \frac{P_{\text{opt}}}{1000 \text{ W m}^{-2}} \cdot \frac{q \cdot j_{\text{ph}}}{w} \quad (1.35)$$

under the assumption that illumination at 1000 W m^{-2} yields a photocurrent density j_{ph} that is uniformly distributed across the sample thickness w . To ensure measurement stability, all solar cell measurements are conducted on a water-cooled chuck at 25°C .

1.3.2 Photoluminescence Imaging

In this work, photoluminescence imaging (PLI) is used to assess wafer homogeneity before any stability tests are performed. Samples exhibiting insufficient homogeneity are disqualified from lifetime measurements. Since the PCD method averages the carrier lifetime over the area above the measurement coil, inhomogeneities can lead to artifacts in the excess carrier lifetime that may otherwise be misinterpreted [46].

PLI is a non-contact optical technique used to analyze carrier recombination and defect distributions in silicon wafers and solar cells [47]. The method relies on illuminating the sample with above-bandgap light (typically a laser or LED at 808 nm or similar) which generates electron-hole pairs. A fraction of these carriers recombine radiatively, emitting near-infrared photons that are captured by a high-sensitivity Si-CCD camera. The resulting luminescence intensity provides a spatially resolved map of recombination activity, with darker regions indicating higher non-radiative recombination due to defects, impurities, or structural imperfections.

A key application of PLI is the detection of performance-limiting defects in silicon, including LeTID, LID, metal impurities, grain boundaries, and dislocations. Under low-injection conditions

recombination is dominated by defect-related mechanisms rather than intrinsic recombination or surface effects. PL intensity then correlates closely with minority carrier lifetime [48]. This enables rapid, contactless mapping of lifetime variations across entire wafers, making it particularly valuable for solar cell characterization, where it can identify shunts, cracks, and material inhomogeneities. Quantitative analysis requires enhanced measurement tools e.g. using time resolved methods like it is presented in [49, 50].

1.4 Degradation During Illumination at Elevated Temperatures

Effective lifetime in silicon can be reduced by various degradation mechanisms. This section provides an overview of the literature on degradation during illumination at elevated temperatures. Section 1.4.1 discusses the LeTID defect, first observed in p-type material, covering the impact of material properties, observed kinetics, the role of hydrogen, and several proposed defect models. In Section 1.4.2, an overview of degradation in n-type material under similar treatment conditions is presented. Finally, surface-related degradation, often observed during LeTID studies, is briefly addressed in Section 1.4.3.

1.4.1 LeTID in p-Type Si

The phenomenon now known as LeTID was first discovered by Ramspeck *et al.* [51] in multicrystalline silicon (mc-Si) PERC solar cells that exhibited degradation behavior distinct from either boron-oxygen light-induced degradation (BO-LID) [5, 52, 53] or formation of iron-acceptor pairs [54, 55] (see Section 2.3.3). Initially observed only in mc-Si materials, this was largely because the effect was masked by LID in Cz-Si on account of the material's higher oxygen content [56]. Subsequent research identified an additional defect in boron-doped Cz-Si PERC cells [57, 58] that was later recognized as LeTID [31, 59]. The term LeTID was initially named after the corresponding treatment conditions it could be observed [11]. However, further studies revealed the phenomenon could also be triggered under dark annealing conditions [31, 60, 61] or forward bias current injection [62]. These findings established that while light serves as a trigger, charge carriers are the fundamental driving force behind the degradation, leading to the alternative designation as carrier-induced degradation (CID) [63].

Laboratory studies have documented relative efficiency losses ranging from 3–4 %_{rel} [64, 65] up to 10–12 %_{rel} [11, 57, 66] due to LeTID effects. Field studies across different climates reveal significant variations in degradation rates: 2.5 %_{rel} relative loss in Germany [12], 7 %_{rel} in

Cyprus [37], and 10 %_{rel} in Singapore [67]. Of particular concern are projections from Kersten *et al.* [12] suggesting that Mediterranean climates could experience 15 years of continuous degradation which would substantially impact the assumed 30-year module lifetime.

A characteristic feature of LeTID is the formation of a lifetime limiting defect which subsequently disappears, showing complete regeneration [11]. The defect system shares similarities with BO-LID and can be described by a model involving three relevant defect states, with an optional additional reservoir state as proposed by Fung *et al.* [68]. The three states can hereby be attributed to a recombination-inactive state *A* serving as the defect precursor. During defect formation, the recombination active state *B* is then formed which deactivates eventually to transition into the again recombination-inactive state *C*. Often state *A* is referred to as annealed state, state *B* as degraded and *C* as regenerated state [69].

Since LeTID is not a completely new phenomenon, several reviews regarding this topic are already present in literature. A comprehensive overview over efficiency losses in solar cells due to LeTID is given by Chen *et al.* [70], whereas Ning *et al.* [71] reviews the overall research progress on LeTID. A review on the impact of hydrogen on LeTID is given by Hammann *et al.* [72]. Nevertheless, the different aspects will be discussed here to contextualize the investigations throughout this work and give an overview of the research progress regarding LeTID to the reader.

Materials

The LeTID phenomenon was initially observed in multicrystalline silicon (mc-Si) materials, but subsequent studies have confirmed its occurrence across various silicon material types. Comprehensive investigations have demonstrated LeTID effects in both Czochralski-grown silicon (Cz-Si) [31, 59] and float-zone silicon (FZ-Si) [37, 69, 73, 74]. The degradation appears in B-doped [11, 69], as well as gallium-doped (Ga-doped) materials [39, 51, 75, 76], occurring during various treatment conditions [61, 75, 77, 78]. This broad material manifestation suggests a fundamental degradation mechanism that appears largely independent of both dopant species and bulk material properties. However, critical questions remain regarding whether these observations represent identical defects or merely related defect families that emerge under similar conditions. Significant variation in the timescales for defect formation across different material types and a wide distribution of symmetry factors (τ_p/τ_n) ranging between 20–36 have been observed [37–39].

Wafer thickness has been shown to influence LeTID characteristics, with thinner wafers exhibiting both reduced degradation extent and faster regeneration kinetics [79–81]. This thickness dependence has been attributed to enhanced hydrogen out-diffusion per unit volume

in thinner substrates, as further supported by studies manipulating hydrogen out-diffusion through controlled cooling ramps during firing processes [82].

Kinetics

The degradation behavior under illumination at elevated temperature exhibits complex kinetics that are fundamentally determined by the resulting charge carrier concentration [63]. This perspective also explains the degradation observed under dark annealing conditions, where thermally generated carriers are sufficient to drive the degradation process [40, 83].

Extensive experimental studies have characterized LeTID across a wide range of conditions. The effect has been observed under illumination intensities from 0.1 sun to 26 suns [68, 84], demonstrating its persistence across diverse irradiance levels. Systematic investigations under varied injection conditions [11, 63] and temperature regimes, with and without additional carrier injection [64, 85–87], revealed a broad spectrum of LeTID kinetics and extents. The degradation rate was shown to scale linearly with injection level [63], whereas the regeneration rate exhibits a more complex and less clearly defined dependence. Both degradation and regeneration processes are thermally activated, with acceleration at elevated temperatures and similar activation energies in the range of 0.6–0.8 eV under constant injection conditions [88]. This similarity suggests that the underlying mechanisms of degradation and regeneration may share a common rate-limiting step.

Further insights into the degradation mechanism were given from studies examining the interplay between dark annealing and light soaking treatments. The work of Luka *et al.* [89] and Sio *et al.* [90] demonstrated that samples degraded through light soaking (at elevated temperatures) could be regenerated during subsequent dark annealing. Conversely, dark-annealed samples degraded when subjected to light soaking. This bidirectional behavior strongly indicates that the degradation process is fundamentally reversible under appropriate conditions. Kwapil *et al.* [91] characterized this reversibility as temporary recovery, noting that the recovery rate shows strong dependence on injection level while appearing to decrease with increasing temperature [92].

The influence of pre-annealing treatments on subsequent LeTID behavior has been extensively investigated, revealing significant modifications depending on the specific thermal history. As documented by multiple studies [2, 68, 89, 93–95], both the duration and temperature of pre-annealing treatments can substantially alter the subsequent degradation kinetics under light soaking, suggesting that the initial defect configuration and hydrogen distribution play crucial roles in determining the degradation pathway.

Hydrogen involvement

The precise defect structure underlying LeTID remains unidentified, though substantial evidence points to the involvement of hydrogen [40, 68, 74, 96, 97], which is typically introduced through hydrogen-rich surface layers. Research indicates that peak firing temperature significantly impacts LeTID extent [13, 31, 66, 67, 98–101], with the firing profile itself being a critical factor [66, 69, 82]. Notably, Eberle *et al.* [100] demonstrated that temperature ramp rates play a decisive role, with subsequent studies confirming that cooling ramp parameters substantially influence LeTID severity [15, 64, 102, 103]. Further discussion on the impact of the cooling ramp in Ga-doped Cz-Si will be given in Section 5.1. LeTID in hydrogen-rich silicon nitride ($\text{SiN}_x\text{:H}$) passivated samples occurs only when processed above 675 °C, with no observable degradation below approximately 650 °C [37, 64, 66]. In addition, the thermal budget before and after firing has been shown to significantly influence LeTID behavior [93, 104]. Recent investigations into Ga-doped materials have revealed strong correlations between LeTID severity and bulk hydrogen concentration [105–107], reinforcing the hypothesis that atomic or molecular hydrogen species act as primary triggers [60, 105]. Hydrogen concentrations are quantified either via infrared spectroscopy (see Section 2.3.5) [107] or by exploiting the GaH pairing mechanism (see Section 2.3.4) [105, 106]. A particularly clear finding is the linear correlation between the initial H_2 concentration and the observed LeTID extent [105, 106].

Alternative approaches to understanding LeTID mechanisms have focused on boron-hydrogen (BH) dynamics during dark annealing conditions (see Section 2.3.4). Hammann *et al.* [108] demonstrated similar kinetics between BH pair dynamics and defect formation during dark anneals, suggesting a potential connection. Complementary work by Schmidt *et al.* [109] examined BH pairs and their relationship to maximum defect extent.

The properties of the surface layers also influence LeTID dynamics [85, 97], a relationship first postulated in [57]. For silicon nitride layers it was found that an increased $\text{SiN}_x\text{:H}$ thickness correlates with enhanced degradation [87, 110], while specific stoichiometric variations also alter the degradation extent [93, 97, 111–113]. Studies examining hydrogen effusion from $\text{SiN}_x\text{:H}$ films have established relationships with maximum defect concentrations [111, 112, 114], though these analyses did not account for potential hydrogen redistribution within the bulk or environmental losses. Similar limitations apply to coated sample studies of hydrogen out-diffusion [110].

In B-doped silicon, aluminum oxide (AlO_x) layers demonstrate effective barrier properties against hydrogen diffusion [110, 115–118], with thicker AlO_x coatings resulting in reduced LeTID severity [117–119]. The effectiveness of the AlO_x as a barrier layer for hydrogen diffusion on Ga-doped material will be discussed in Section 5.2.5. With the rise of the tunnel-oxide

passivating contact technology for solar cells, the influence of (n)poly-Si layers on the hydrogen content after firing is of interest and further investigated in Section 5.2.

The hydrogen reservoir model proposed by Fung *et al.* [68], validated through dark annealing and light soaking cycles, provides important mechanistic insights. Complementary work by Jensen *et al.* [120] revealed that extended hydrogen plasma exposure prior to testing amplifies degradation extent. Kwapil *et al.* [91] proposed a defect model wherein hydrogen dissociation from a metastable precursor (LP) generates recombination-active defects (LD) through the reaction $LP \rightarrow LD + H$.

While LeTID appears universally observable in p-type materials across this wide range of conditions, the field currently lacks a comprehensive atomistic model. Most investigations having focused on boron-doped materials, leaving open questions about potential variations in other material systems.

Defect Models

The understanding of LeTID has evolved through multiple defect models, some of which have been disproven by subsequent research. The involvement of metal impurities in LeTID has been proposed through several mechanisms. Bredemeier *et al.* [121, 122] suggested that mobile metal impurities are activated by a firing step and can form complexes with other species that become recombination-active during treatment at elevated temperatures. The subsequent regeneration is then explained by the diffusion of these mobile impurities to the surface [121]. It has further been proposed that hydrogen from the surface can diffuse into the sample and passivate the defects [122], which could in turn explain the occurrence of subsequent surface degradation. However, contradictory evidence emerged from Varshney *et al.* [81], showing reduced degradation extent in thinner wafers. Chan *et al.* [94] proposed an alternative hypothesis where one hydrogen atom activates the defect while another passivates it. Various studies collectively suggested metallic impurities as potential candidates for a second defect component alongside hydrogen [36, 94, 122, 122, 123].

Deep-level transient spectroscopy (DLTS) analysis identified molybdenum (Mo) and titanium (Ti) as potential matches for $E_{\text{def}}-k$ combinations [124]. The factor k is often used in literature for the symmetry factor τ_p/τ_n or τ_n/τ_p with the issue that it not entirely clear which ratio is meant exactly. Niewelt *et al.* [74], argued that the metal must be fast-diffusing, thus excluding Mo and Ti while favoring a combination of cobalt and hydrogen. There are publications indicating that phosphoryl chloride (POCl_3) diffusion processes (introduced in Section 2.2.2) may reduce impurities and consequently decrease the defect magnitude [125], though follow up experiments at that time did not show consistent results. Additionally, the reduction of

LeTID as a consequence of gettering has only been observed in B-doped mc-Si [109, 125, 126], which could not be reproduced in Ga-doped Cz-Si (see Section 3.2.3) [127].

De Guzman *et al.* [128] developed a defect model using density functional theory, demonstrating that BH_2 complexes remain stable under specific conditions and create an electron donor state 0.24 eV below the conduction band. DLTS confirmed this energy level, with recombination activity supporting the hypothesis that LeTID results from pairing between mobile H_2 and boron dopants. The model explains regeneration through formation of recombination-inactive BH from BH_2 , with recent calculations confirming the relative stability of these species [129]. However, subsequent studies of GaH_2 complexes showed no recombination activity [130]. The degradation in Ga-doped material could then potentially be explained by residual boron content.

Temperature- and injection-dependent lifetime spectroscopy measurements by Vargas *et al.* [124] yielded two possible solutions for $E_{\text{def}}-k$ combinations: $E_{\text{def}} - E_i = -0.32(5)$ eV with $k = 56(23)$ in the lower bandgap half, or alternatively in the upper bandgap half $E_{\text{def}} - E_i = 0.22(5)$ eV with $k = 49(21)$. Analysis following Murphy *et al.* [131] revealed deviations from single-defect assumptions, suggesting better fits with two defects where one dominates. Mchedlidze *et al.* [132] observed electron traps at $E_C - 0.34$ eV in degraded samples, consistent with [124], and identified a second trap state at $E_C - 0.19$ eV that may represent the missing second defect. Estimated defect concentrations ranged between $0.4\text{--}1.6 \cdot 10^{12} \text{ cm}^{-3}$ [36].

Recent investigations point to bulk vacancies [2, 133]. EPR measurements revealed a degradation-correlated signal corresponding to a dangling bond, with deuterium studies confirming hydrogen involvement [2]. Signal broadening suggests hydrogen alone cannot explain the observations, leading to hypotheses about the role of oxygen within extended vacancy agglomerates containing hydrogen. This aligns with findings on hydrogen-oxygen correlations [134], though the exact defect formation and dissolution mechanisms remain unclear.

These current hypotheses suggest that hydrogen does not directly constitute the recombination-active defect but instead interacts with an as-yet-unidentified precursor defect, forming a complex that exhibits strong carrier recombination activity. In Chapter 3 the accumulation of LeTID defects during crystal growth will be further discussed.

1.4.2 Degradation in n-Type Si

Light- and elevated temperature-induced degradation has also been observed in n-type silicon materials [40, 60, 64, 135, 136]. However, studies present conflicting observations regarding degradation behavior under illumination. Some reports indicate no measurable degradation [37], or only observe degradation when an additional boron or phosphorus emitter is

present [40, 60, 137]. Conversely, other investigations have identified bulk defects in n-type silicon exhibiting reaction kinetics similar to those in p-type material [64, 138], suggesting comparable degradation mechanisms may operate in both material types under certain conditions. In a study from Niewelt *et al.* [139], p- and n-type FZ wafers were investigated with n-type wafers showing the lowest lifetime and a similar pattern in PLI initially after firing compared to p-type samples after reaching maximal degradation. This hints a different defect configuration for n-type initially, after firing compared to p-type material which is the hypothesis for the investigation conducted in Section 4.1.

While high-temperature processes like tabula rasa (TR) (see Section 2.2.2) may show a relation between vacancy concentration and LeTID magnitude [140], contradictory evidence comes from Khan *et al.* [141], who found no connection between defect magnitude and elevated vacancy concentration in electron-irradiated silicon. The impact of high-temperature treatments on the degradation extent is discussed in Section 4.2.3.

1.4.3 Surface-Related Degradation

Sperber *et al.* [38] demonstrated that the surface passivation quality remains constant during both degradation and regeneration phases of LeTID, while increasing in parallel with a following lifetime decay after regeneration of the LeTID defect. Surface-related degradation (SRD) with a following regeneration has been observed, with both injection level and temperature influencing the process [73, 142, 143]. SRD occurs specifically in fired samples containing hydrogen-rich layers [144, 145], supporting the hypothesis that hydrogen plays a crucial role in SRD similar to its involvement in LeTID [143].

The choice of passivation layers significantly influences the degradation behavior, with distinct mechanisms observed between $\text{SiN}_x\text{:H}$ and $\text{AlO}_x/\text{SiN}_x\text{:H}$ stacks [144]. For $\text{SiN}_x\text{:H}$, degradation primarily occurs through loss of chemical passivation, whereas in $\text{AlO}_x/\text{SiN}_x\text{:H}$ stacks, it manifests via changes in field-effect passivation as a consequence of charge modifications in the AlO_x layer. However, Niewelt *et al.* [139] reported an absence of SRD during light soaking for $\text{AlO}_x/\text{SiN}_x\text{:H}$ stacks, with degradation only occurring during dark annealing. While highly doped layers have shown potential for suppressing SRD [142, 146], the practical implications for solar cell and module performance remain uncertain.

The fundamental defect mechanism responsible for SRD remains poorly understood. Multiple LeTID studies indicate that SRD manifests only after the regeneration of LeTID defects, a temporal relationship that will be examined in detail through n-type silicon experiments (Section 4.1).

Historically, SRD received limited attention due to its exceptionally long activation period under

illuminated, elevated-temperature conditions. However, with continuous improvements in module material stability [147], SRD may emerge as an increasingly relevant factor limiting long-term solar cell performance, particularly as other degradation mechanisms are progressively mitigated. Within this work, the role of SRD is only secondary.

2 Sample Preparation and Evaluation Procedures

This chapter outlines the procedures used for sample preparation and the techniques employed to evaluate the experimental data presented in this work. Section 2.1 introduces the Czochralski (Cz) method, which is used to produce doped silicon ingots that are subsequently sliced into thin wafers. These wafers serve as the base material for all investigations in this work. Section 2.2 summarizes the preparation methods for the silicon wafers, while Section 2.3 describes the techniques applied to analyze the obtained data.

Material quality can be improved through wet-chemical treatments that remove surface damage and impurities. After crystal growth, high-temperature processes can further modify the sample properties by enabling diffusion and redistribution of atoms, as discussed in Section 2.2.2. Such treatments allow the formation of highly doped regions near the surface, which can be used to create the pn junction in solar cells. All samples require surface passivation to reduce the recombination at the surface. This is typically achieved by depositing dielectric layers on the silicon substrate as it is described in Section 2.2.3.

A distinction is made between lifetime samples, resistivity samples and solar cells. Lifetime samples remain unmetallized, allowing measurement of the excess carrier lifetime via PCD as introduced in Section 1.3.1. They provide access to changes in defect density and defect-specific information during long-term stability testing as detailed in Section 2.3.2.

Resistivity samples, in contrast, have evaporated aluminum contacts to improve the electrical contact with the silicon substrate, as detailed in Section 2.2.5. These samples are employed to investigate different hydrogen species in the silicon bulk via resistivity measurements. During dark annealing, holes are consumed to form acceptor-hydrogen pairs, which can subsequently dissociate under illuminated annealing, as discussed in Section 2.3.4.

Solar cells require electrical contacting of the wafer, which is typically achieved by screen printing metal pastes onto the dielectric layers. Contact formation is then enabled by a subsequent firing step. The evaluation of the resulting solar cell parameters using current-voltage measurements is described in Section 2.3.6.

2.1 Crystal Growth via Czochralski-Method

The Czochralski (Cz) method [148] is the most widely adopted technique for producing monocrystalline silicon, especially in photovoltaic and semiconductor applications.

Raw SiO_2 , typically in the form of high-purity quartz sand, is first reduced with carbon in an electric arc furnace at temperatures above 1900°C , yielding metallurgical-grade silicon with a purity of $\sim 98\%$ [17]. This material is then reacted with hydrogen chloride to form trichlorosilane, which is subsequently purified by fractional distillation. In the Siemens process [149], the purified trichlorosilane is decomposed on heated silicon rods to produce high-purity polycrystalline silicon (poly-Si).

The Cz process begins with melting poly-Si from the Siemens process in a quartz crucible. Heating is achieved through resistance or induction systems at temperatures exceeding 1420°C . The seed crystal, mounted on a rotating shaft, is dipped into the melt and withdrawn slowly. Opposing rotation of the seed and crucible enhances crystal uniformity and reduces thermal stress. The resulting ingot is a cylindrical single crystal, with its diameter and pulling speed influencing the formation of dislocations and other structural defects [150, 151]. The details of adding dopants to the melt to be incorporated into the crystal are discussed in Section 3.1. Possible candidates for p-type doping are usually group-III elements, especially boron, gallium and indium with the first two being the most common for photovoltaics. For n-type doping, electron donors from group-V are used with the most relevant for this work being phosphorus (P) and antimony (Sb).

The growth sequence includes a necking stage to eliminate dislocations, followed by a gradual shoulder expansion to the target diameter [152]. A steady-state body growth phase maintains this diameter under tightly controlled thermal and kinetic conditions. The process concludes with tail formation, where the crystal is tapered to reduce thermal stress during cooling. The ambient atmosphere is typically argon (Ar) to suppress supersaturation of the melt with oxygen, which may lead to boiling, disturbing the crystal pulling [151]. Since a lot of oxygen is expected to be released from the SiO-crucibles, vacuum conditions may also be employed for purity enhancement. However, it is known that highly volatile elements (e.g. antimony) can evaporate from the melt to Ar ambient [153]. Thus, in this case, the evaporation from the melt can be controlled by adjusting the atmosphere.

Compared to the Cz method, the Float-Zone (FZ) technique [154] yields higher-purity crystals with fewer defects by zone-melting a silicon rod and recrystallizing it with a seed crystal. However, due to its complexity and cost, FZ is mostly used for specialized semiconductor applications.

Despite its advantages, the Cz method faces certain limitations. Oxygen incorporation from the quartz crucible, typically around $1 \cdot 10^{17} - 10^{18} \text{ cm}^{-3}$ (see Chapter 3), can degrade electrical properties. Furthermore, the process is energy-intensive and requires precise control to minimize crystal defects.

Nonetheless, the Cz method is today the industrial standard due to its scalability, controlled doping capability (p- or n-type), and lower production costs compared to alternative methods with similar purity. It enables the manufacture of large-diameter ingots up to 300 mm, making it well-suited for high-volume solar cell production.

Thin slices extracted from the ingot by sawing are referred to as wafers in the following. All wafers are cut from ingots by diamond-wire sawing [155], the current standard for ingot wafering. Further processing is carried out on industrial wafers from different years. To standardize the subsequent processing, all wafers are cut to M2 size with an edge length of 156.75 mm, regardless of their original dimensions. Materials with larger side lengths are therefore trimmed to this size using an IR laser, with the M2 wafer always cut from the center.

2.2 Sample Processing Techniques

The sample preparation typically involves preprocessing by etching and cleaning procedures of the wafer which are presented in Section 2.2.1. Further processing involves high-temperature treatment discussed in Section 2.2.2 and deposition of passivation layers explained in Section 2.2.3. As the final processing step, samples are fired in a belt furnace as it is described in Section 2.2.4. While preprocessing, passivation, and firing are mandatory for all samples to ensure suitable charge-carrier lifetimes, high-temperature treatments are employed only for specific investigations.

2.2.1 Preprocessing and Surface Cleaning

Since all samples exhibit surface saw damage after wafering, a KOH etch at 80 °C is applied to remove at least 8 μm from both wafer sides [156]. The wafers are then cleaned in water with an ozone concentration of 30 ppm and hydrochloric acid (HCl) at 25 °C, which oxidizes the surface [157], followed by a short dip in diluted hydrofluoric acid (HF, ~2 %) to remove the oxide. A second cleaning step uses a 3:1 piranha solution ($\text{H}_2\text{SO}_4:\text{H}_2\text{O}_2$) at 80 °C [158], again followed by an HF dip. After drying, wafers are directly subjected to either high-temperature processing (Section 2.2.2) or passivation layer deposition (Section 2.2.3) without further treatments.

2.2.2 Thermal Processing and Gettering Treatment

As a consequence of the crystal growth process by the Cz-method, various defects can be present in the wafer material. By the usage of high-temperature processing steps it is possible to change the structure of defects or completely remove them from the material. One approach is the *tabula rasa* (TR) [159, 160] which can be performed for thermal donor killing [161]. Thermal donors are electrically active shallow defects below the conduction band [162, 163], typically formed by the aggregation of oxygen atoms [164, 165]. In some cases, TR treatments are applied to wafers prior to other high-temperature processing in solar cell production. The dissipation of oxygen precipitates that have grown due to the slow cooling process of the Cz-ingot growth improves the overall performance [166].

A TR treatment is conducted at a temperature of 1050 °C in a *centrotherm* diffusion furnace under either a nitrogen (N_2) or oxygen (O_2) atmosphere. This high-temperature process serves to modify the defect configuration within the silicon wafers by altering the state and distribution of intrinsic point defects and metallic impurities. During this high-temperature treatment, vacancy-interstitial pairs (frenkel-pairs) may form. In a N_2 atmosphere, the vacancy concentration is more likely to increase in the bulk and is frozen in place during rapid cooling [167]. Since the TR treatment is carried out in a diffusion furnace, the cooling is comparably slow with only a few $K\ min^{-1}$. However, in an oxygen-rich atmosphere, a thick SiO_x layer can form, introducing stress near the Si/ SiO_x interface. In this process, oxygen atoms displace silicon atoms from the lattice, leading to a supersaturation of silicon self-interstitials. These are injected into the bulk and effectively lower the vacancy concentration [168]. The resulting recombination activity in treated samples is dependent on the applied condition such as ambient atmosphere and the duration.

Another approach that can lower the impurity concentration in the silicon bulk is use of a phosphoryl chloride ($POCl_3$) diffusion. At elevated temperatures, the $POCl_3$ reacts with oxygen to form phosphorus pentoxide (P_2O_5) which reacts with the native oxide and forms a phosphosilicate glass (PSG) layer [169]. This PSG layer acts both as a dopant source for phosphorus diffusion and as a gettering sink for metallic impurities [170]. Especially for iron it is well known that a $POCl_3$ diffusion can effectively lower its concentration in the silicon bulk. [171, 172]. Besides the gettering effect, highly doped phosphorus layers at the surface of the semiconductor are thereby forming a pn junction with a p-type substrate.

For impurity gettering, the same diffusion furnace system is used to perform phosphorus diffusion using $POCl_3$ as the dopant source. The gettering process works by relocating recombination-active metallic impurities from the bulk silicon to specific regions where they become electronically inactive and no longer contribute to minority carrier recombination. The

POCl_3 -based gettering process begins with the thermal decomposition of POCl_3 in an oxidizing atmosphere, where liquid POCl_3 is vaporized and transported by a nitrogen carrier gas into the furnace tube.

For all experiments where the resulting emitter is removed prior to further passivation, this process step will be labeled as phosphorus diffusion treatment (PDT). This PDT is carried out at a temperature of $\sim 840^\circ\text{C}$ for ~ 22 min. It is always followed by a PSG removal via diluted HF and KOH etching to remove the created emitter. Afterwards the cleaning procedure described in Section 2.2.1 is applied again.

Throughout Chapter 5 the POCl_3 -diffusion is carried out in another *centrotherm* diffusion furnace using a recipe optimized to form a suitable front floating emitter in a p-type IBC solar cell [173, 174]. Afterwards only the PSG layer is removed and the emitter remains.

2.2.3 Passivation with Dielectric Layers and (n)poly-Si

Various dielectric layers are deposited on silicon surfaces to reduce surface recombination. This surface passivation is achieved through two main mechanisms: chemical passivation and field-effect passivation. In practice, most passivation layers rely on a combination of both.

Chemical passivation reduces recombination by neutralizing silicon surface dangling bonds, which would otherwise act as defect states. Elements such as hydrogen or oxygen are commonly used for this purpose, as they form bonds that introduce only shallow energy levels within the bandgap. As a result, the density of interface states and recombination centers is significantly lowered [175]. The overall effectiveness depends strongly on the chemical compatibility and bonding stability of these bonds with the silicon surface.

Field-effect passivation reduces surface recombination by modifying the charge carrier distribution near the semiconductor interface. This is typically achieved through band bending induced by fixed or mobile charges at the surface, or by charged dopants in an emitter layer. Depending on the type and polarity of the surface charge, the interface can exhibit different regimes. When the surface is in accumulation, minority carriers are pushed away from the interface. Under inversion conditions, minority carriers are drawn toward the surface, yet recombination remains limited because majority carriers are scarce. In the depletion regime, both carrier types are present in comparable densities, which creates the highest recombination losses.

Dielectric layers that are used throughout this work are silicon oxide (SiO_x), aluminum oxide (AlO_x) and hydrogen-rich amorphous silicon nitride ($\text{SiN}_x\text{:H}$). Typically, all SiO_x and $\text{SiN}_x\text{:H}$ layers are positively charged, whereas AlO_x is negatively charged [176]. The SiO_x is used as an

interfacial oxide which is formed during dry thermal oxidation in a *centrotherm* tube furnace, resulting in thicknesses of ~ 1.5 nm.

The AlO_x deposition is performed by two different tools for sample preparation. For TOPCon structures (see Section 5.2), the deposition is performed by a plasma-enhanced chemical vapor deposition (PECVD) tool from *centrotherm*. Hereby, the precursor gases trimethylaluminum (TMA) and O_2 are ionized and dissociated in a plasma which is formed under the right conditions of temperature, pressure, voltage and excitation frequency. The dissociated precursors then react at the wafer surface to form AlO_x . Before each PECVD AlO_x deposition, the wafer is oxidized as previously described. This process results in a layer of approximately 4 nm.

In another experiment (see Section 5.2.5), the role of aluminum oxide as a barrier layer is investigated. The AlO_x thickness is varied using an atomic layer deposition (ALD) system from *Oxford Instruments*, providing precise control over the layer thickness. The ALD process employs alternating exposures of trimethylaluminum (TMA) vapor and oxygen plasma to grow AlO_x through self-limiting surface reactions [177]. Each deposition cycle adds approximately 0.1 nm of material, with the oxygen plasma ensuring complete oxidation of chemisorbed aluminum species to form stoichiometric AlO_x . The cyclic nature of precursor exposure and chamber purging enables precise, layer-by-layer growth of high-quality dielectric films. For the thickness variation experiment in Section 5.2.5, AlO_x is deposited at 300 °C for cycles ranging from 50 to 250. Afterwards a $\text{SiN}_x\text{:H}$ is deposited on top of the AlO_x . The $\text{SiN}_x\text{:H}$ deposition is performed in the same PECVD tool used for AlO_x growth. The process utilizes simultaneous silane (SiH_4) and ammonia (NH_3) gas flows, which undergo plasma dissociation above the wafer surface to form amorphous $\text{SiN}_x\text{:H}$ with a thickness of roughly 75 nm.

Tunnel-oxide passivated contact (TOPCon) architecture are widely used in various solar cell concepts due to their excellent surface passivation and low contact resistance [178]. The investigation in Section 5.2 focuses specifically on the tunnel oxide and thin polycrystalline silicon ((n)poly-Si) components, excluding metallization effects. Fabrication continues after pre-processing with the depositing of n-type amorphous silicon ((n)a-Si:H) via PECVD using silane (SiH_4) and phosphine (PH_3) precursor gases. Plasma-generated radicals adsorb onto the wafer surface, forming the (n)a-Si:H layer. Crystallization of this layer is then achieved either through a POCl_3 -diffusion or by high-temperature annealing at ~ 800 °C. The crystallization temperature and duration can influence the resulting crystallite size [179]. When POCl_3 -diffusion is applied, the sheet resistance of the (n)poly-Si remains largely unchanged at $\sim 320 \Omega \text{ sq}^{-1}$. The resulting (n)poly-Si films have a final thickness of 240 nm. A thin thermal oxide is subsequently grown to optimize interfacial properties before depositing either a single-layer $\text{SiN}_x\text{:H}$ or an $\text{AlO}_x/\text{SiN}_x\text{:H}$ stack for passivation.

2.2.4 Firing in a Belt Furnace

Firing in a belt furnace serves multiple purposes, with the primary goal being the activation and sintering of the metal contacts. Additionally, the firing process activates passivation, typically inducing hydrogenation of the wafer and surface interfaces through the $\text{SiN}_x\text{:H}$ layer.

For all investigated samples, the final processing step is performed in an industrial *c.fire9000* belt furnace (*centrotherm*). Wafers are loaded onto one side of the furnace and transported through it on a moving belt, heated by infrared lamps. The heating zone is divided into six independently controlled areas, allowing precise adjustment of the lamp power in each section. After heating, the wafers pass through a water-cooled zone, where they cool primarily via thermal radiation. Figure 5.1a shows typical temperature profiles with variations in peak firing temperature. The actual wafer temperature is monitored using a thermocouple pressed onto the wafer and covered with a heat shield, which travels behind the wafer through the furnace while recording data.

All samples in this study underwent individual temperature profiles during firing to achieve consistent thermal processing conditions. This method ensured a measured peak firing temperature of $800(10)^\circ\text{C}$ with controlled maximal cooling rates below 100 K s^{-1} , which was critical for maintaining comparable hydrogen concentrations across samples.

The maximal cooling rate is obtained by the derivation of the tracked temperature over time which will be discussed in more detail in Section 5.1. Individual tracking for every sample type is necessary as the optical absorption and heating of the wafer depends on wafer thickness, doping level and optical constants of the surface passivation.

Additionally, sufficient temperature stabilization time of the furnace was maintained prior to each firing process. After single wafer tracking, a continuous firing approach was applied by putting 30 dummy wafers into the furnace with a constant repetition of 10 s followed by the wafers for each experiment in the same repeating scheme. Directly afterwards another 5 dummy wafers are pushed through. This approach was applied to significantly enhance temperature uniformity across the wafer area, as demonstrated in [180]. For the standard firing process in this work a belt speed of 6 m min^{-1} was used. Further analysis of firing temperature variations is presented in Section 5.1.

2.2.5 Resistivity Measurement with Direct Contacts

The bulk hydrogen concentration can be quantified through resistivity measurements. As hydrogen is known to change its charge state under certain conditions (see Section 2.3.4), hence, impacting hole concentration, resistivity measurements can be used to quantify hydrogen. For

all investigations, preparations are performed on samples that were already fired. This section focuses on the preparation methods for the corresponding samples which can be separated in two possible cases.

The first case relies on the standard laser-fired contact (LFC) process using only $\text{SiN}_x\text{:H}$, which is suitable exclusively for samples with at least one emitter-free surface. Electrical contacts are established using two pairs of aluminum pads, each 100 nm thick, deposited via electron-beam evaporation using a tool from *Pfeiffer*. All aluminum pads are applied to the same side of the sample. Laser-fired contacts (LFCs) provide electrical contact to the substrate [181]. In this process, both the aluminum and the silicon underneath the $\text{SiN}_x\text{:H}$ locally melt, creating a highly doped p-type region in the base material.

For the TOPCon structures examined in Section 5.2, an extended processing sequence is required due to the presence of highly doped layers at the wafer surface. Figure 2.1 illustrates the complete fabrication process used to establish contacts to the base material in this case. This extended procedure is necessary to prevent contacting of emitter areas, which could otherwise skew the measured resistivity by allowing charge transport through these layers rather than through the base material.

The procedure begins with localized ablation of the $\text{SiN}_x\text{:H}$ layer using a *microSTRUC* picosecond laser operating at 355 nm [182]. The exposed (n)poly-Si layer is then etched with KOH at 80 °C until the base material is reached. This step requires removal of at least 0.5 μm per side to completely eliminate either the (n)poly-Si layer or an emitter. During etching, the remaining $\text{SiN}_x\text{:H}$ acts as an effective KOH etch barrier [183], enabling precise local exposure of the base material. Following surface preparation, 100 nm aluminum contact pads are deposited via e-beam evaporation. The quality of the base contact is further improved using standard LFCs. All resistivity measurements are performed on dedicated sister samples to avoid interference with photoconductance decay (PCD) characterization for long-term stability assessment.

While contactless resistivity measurements using eddy-current sensors (such as with the *WCT-120* system) are theoretically possible, contacted measurements demonstrated superior reliabil-

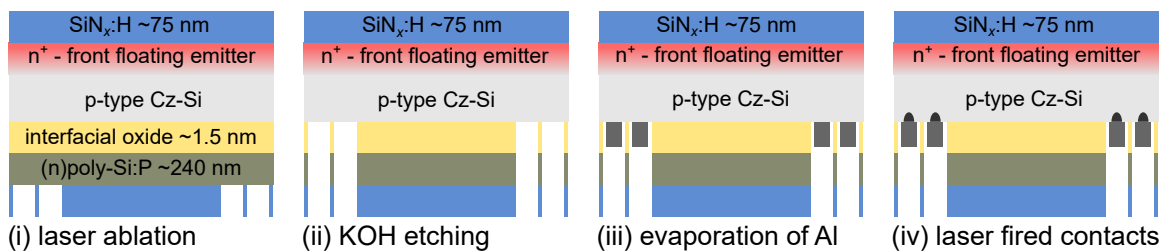


Figure 2.1: Process for establish contacts to p-type Cz-Si beneath the TOPCon layers, exemplarily shown for G3. The steps include (i) laser ablation, (ii) KOH etching, (iii) aluminum evaporation and (iv) contact formation by laser firing. Adapted from [184].

ity. This approach proved particularly advantageous when combined with precise temperature stabilization, a critical requirement for obtaining accurate and reproducible results [185]. The direct-contact approach eliminates potential artifacts associated with non-invasive techniques while providing better control over measurement conditions.

2.3 Evaluation Procedures

In this section the evaluation of effective excess carrier lifetime (see Section 1.2.3) is explained in the context of long-term stability studies. Additionally, the calculation of hydrogen species due to acceptor-hydrogen pair formation and dissociation is discussed. A short summary on all procedures is given and the properties of LeTID specific defect parameters are discussed.

2.3.1 Lifetime-Equivalent Defect Density and LeTID Testing

Long-term stability testing is performed using a temperature-controlled hotplate maintained at 130(1) °C. This temperature is chosen to accelerate the LeTID defect kinetics. Under these conditions, samples are illuminated with a photon-flux equivalent to 1.0(1) sun [186]. This accelerated testing induces the characteristic LeTID signature in p-type material: an initial lifetime reduction followed by subsequent regeneration. Lifetime evolution is monitored by periodic interruptions to obtain PCD measurements at 30 °C. For selected experiments, the illumination source is changed from a constant photo-generation (iso-generation) to an adjustable laser source with a wavelength of 805 nm. In combination with lifetime measurements at 130 °C, using a *WCT-120T*. This allows precise control of the excess carrier density during LeTID testing, enabling iso-injection testing where the carrier concentration remains constant throughout the experiment [88].

While labeled generically as "LeTID testing" for both n- and p-type samples, this terminology reflects the phenomenological similarity of degradation kinetics under light and elevated temperature exposure, not necessarily identical defect physics in different dopant types. The emphasis remains on the observed degradation-regeneration behavior rather than specific defect identification.

For n-type material, an additional light soaking by illumination with 2.0(2) suns at 20.0(1) °C on a water-cooled stage using halogen lamps is conducted. For p-type material, samples are illuminated at ~1 sun to dissociate iron-acceptor pairs prior to LeTID testing. The sample is hereby cooled by the use of a nitrogen stream. This underlying effect of iron-acceptor dissociation will be discussed in more detail in Section 2.3.3. This procedure is not necessary for n-type samples because the iron only forms stable pairs with acceptor atoms.

As mentioned in Section 1.2, various recombination mechanisms are present at the same time and only the effective lifetime can be experimentally accessed. Intrinsic recombination is specific to the properties of a sample and is not expected to change during LeTID testing. It is therefore useful to introduce a lifetime equivalent defect density [187]

$$\Delta N_{\text{leq}} := \frac{1}{\tau_{\text{eff}}(t)} - \frac{1}{\tau_{\text{eff}}(t_0)} \quad (2.1)$$

with time t being the accumulated time under illumination at elevated temperature. As the name of this quantity suggests, it is not a defect density in the true sense but rather a measure of change in active defect species. Inserting of Equation (1.26) and assuming the surface does not change throughout the treatment, this results in

$$\Delta N_{\text{leq}} = \frac{1}{\tau_{\text{def}}(t)} - \frac{1}{\tau_{\text{def}}(t_0)} = \frac{1}{\Delta \tau_{\text{srh}}} = \frac{\Delta N_{\text{def}}}{f_{\text{def}}} \quad (2.2)$$

The factor f_{def} includes all the SRH parameters and injection-dependency, whereas the change in defect density is given by $\Delta N_{\text{def}} = N_{\text{def}}(t) - N_{\text{def}}(t_0)$. Throughout this work, the reference point t_0 corresponds to the initial lifetime at $t = 0$ s, unless stated otherwise.

Most of the time, the defect parameters are not fully known, making the defect density an inaccessible quantity. The lifetime equivalent defect density serves as a powerful tool to compare defect densities in different samples without knowledge about the defect. Since ΔN_{leq} is injection-dependent just like τ_{eff} , a statement on Δn at which evaluation is performed must be made. For most part of this work, lifetimes and calculated ΔN_{leq} are extracted at $\Delta n = 0.1 \cdot p_0$ for p-type and $\Delta n = n_0$ for n-type.

The reason being for choosing this injection level for p-type is a consequence of the upward S-shape of τ_{srh} (see Figure 1.2a) which has its inflection point in logarithmic injection scaling at $\Delta n = p_0$. Comparison of differently doped samples at a fixed injection independent of p_0 would not be a fair comparison regarding τ_n or N_{def} . A fixed fraction of doping, however, yields a constant multiplier irrespective of doping [32]. Because of the injection-dependence of a deep-level defect such as LeTID, 0.1 is used as a multiplier with higher sensitivity for lifetime reduction (increase of ΔN_{leq}) in lower injection regimes. For n-type silicon, however, injection-dependence is not that pronounced and usually lower doping concentrations are present, making it difficult to measure data at low injections for varying doping concentrations via PCD.

2.3.2 Surface-Related Saturation Current-Density and Difference Analysis

The content of this section is partly based on the publication [188]. The surface-related saturation current density j_0 offers the possibility to quantify the surface recombination without being injection-dependent itself as it is discussed in Section 1.2.2. The most common way to determine j_0 is by PCD measurements (see Section 1.3.1). In the original approach from Kane and Swanson [189], the slope of the inverse effective lifetime is determined after correction by intrinsic recombination. The inverse injection-dependent corrected lifetime $1/\tau_{\text{cor}}(\Delta n)$ can be calculated from Equation (1.26) and Equation (1.24) so that

$$\frac{1}{\tau_{\text{cor}}} := \frac{1}{\tau_{\text{eff}}} - \frac{1}{\tau_{\text{intr}}} = \frac{1}{\tau_{\text{def}}} + \frac{2 \cdot (N_{\text{dop}} + \Delta n)}{q \cdot w \cdot n_{\text{i,eff}}^2} \cdot j_0 \quad (2.3)$$

Here, N_{dop} accounts for the dopant concentration of the material used. Now, derivation of corrected inverse lifetime can be expressed as

$$\frac{d}{d\Delta n} \frac{1}{\tau_{\text{cor}}} = \frac{2}{q \cdot w \cdot n_{\text{i,eff}}^2} \cdot j_0 + \frac{d}{d\Delta n} \frac{1}{\tau_{\text{srh}}} \quad (2.4)$$

with the first term corresponding to the slope of the linear expression Equation (2.3). Later, a more precise method was introduced by Kimmerle *et al.* [190] where the diffusion of charge carriers to the sample surface and the injection-dependence of $n_{\text{i,eff}}$ is accounted for

$$j_0 = \frac{q \cdot w}{2} \cdot \frac{d}{d\Delta n} \left(\frac{n_{\text{i,eff}}^2}{\tau_{\text{srf}} - \frac{w}{D \cdot \pi^2}} \right) \quad (2.5)$$

However, the slope-based approach is only valid under the assumption that the injection-dependence of the bulk does not contribute to the slope of $1/\tau_{\text{cor}}$. As discussed in [188], the presence of deep level defects may result in an underestimation of j_0 , in particular for high doping concentrations. This means for samples with relatively high doping concentrations and deep-level defects, the j_0 determined by this approach may result in the overestimation of surface passivation quality.

For studies with changing defects over time, the approach with the difference in lifetimes (see Equation (2.1)) can be extended to include a change in surface-related saturation current density so that

$$\Delta N_{\text{leq}} = \frac{\Delta N_{\text{def}}}{f_{\text{def}}} + \frac{\Delta j_0}{f_{\text{srf}}} \quad (2.6)$$

The injection dependence is still present in the factors that are given by

$$\frac{1}{f_{\text{def}}} = \frac{\sigma_n \cdot v_{\text{th},n}}{\left(1 + \frac{\tau_p}{\tau_n} \cdot \frac{\Delta n}{p_0 + \Delta n}\right)} \quad \text{and} \quad \frac{1}{f_{\text{srf}}} = \frac{2 \cdot (p_0 + \Delta n)}{q \cdot w \cdot n_{\text{i,eff}}^2} \quad (2.7)$$

for a single deep-level defect in p-type material. Throughout this work, the evaluation of surface passivation quality is performed for a temperature of 300 K. Furthermore, the evaluated j_0 or Δj_0 is always given for a single side with the assumption of symmetrical passivation quality on both sides of the wafer. For some samples with asymmetrical layer stacks (see Section 5.2), Δj_0 is used as a mean for both surface sides.

In Figure 2.2a, the measured effective lifetime and lifetime equivalent defect density (see Equation (2.1)) is exemplarily shown for two injection levels corresponding to $0.1 \cdot p_0$ and p_0 over the duration of $\sim 10^4$ h at 130 °C and 1 sun during long-term stability testing. The effect of an emerging deep-level defect in the bulk and surface defects show opposite injection-dependence. This can already be seen by comparing the two injection levels during the course of LeTID testing. During the first phase (< 5 h) a decrease (increase) in τ_{eff} (ΔN_{leq}), followed by an increase (decrease) can be observed in Figure 2.2a. A second phase follows for > 5 h of treatment time where the same behavior occurs. Taking a closer look at the injection-dependence, it can be seen that ΔN_{leq} increased significantly for lower injections in the first phase, whereas the higher injection dominates in the second phase.

The first phase suggests the formation of a deep-level defect which forms (degradation) and vanishes (regeneration) again. In the second phase, surface defects are formed, which also vanish again. For most investigations in this work, the treatment of samples is stopped after the first phase has ended, since surface-related degradation (SRD) is not the priority in this work and with the used testing conditions of 130 °C, observing complete SRD and following regeneration is expected to take over a year.

Under the assumption of a deep bulk defect in p-type, data can be fitted with Equation (2.6) which yields the symmetry factor τ_p/τ_n , maximal bulk-related lifetime equivalent defect density $\Delta N_{\text{leq}}^* = \sigma_n v_{\text{th},n} \Delta N_{\text{def}}$ (ΔN_{leq} for $\Delta n \rightarrow 0$) and the change in surface-related saturation current density Δj_0 . Figure 2.2b displays the derived fit parameters, including the saturation current density j_0 evaluated via Kimmerle's slope-based approach ($j_{0,\text{Kimmerle}}$) and plotted alongside the fitted Δj_0 values. For direct comparison, the y-axis for Δj_0 is shifted by the initial j_0 value determined by the slope-based method of $\sim 11 \text{ fA cm}^{-2}$. The calculation of j_0 incorporates the current Auger correction model [26] assuming maximal photon recycling conditions. For the symmetry factor, open symbols are used for data points with $\Delta N_{\text{leq}}^* < 4 \text{ ms}^{-1}$, where the first term ($\Delta N_{\text{def}}/f_{\text{def}}$) of Equation (2.6) does not yield reliable data. This can be legitimated as the fit gets less reliable for low amounts of recombination active defects. It makes sense that

τ_p/τ_n only stabilizes between 25 to 37 when enough defects have formed. This is consistent with LeTID observations in literature [36, 39, 67, 191]. Note that the evaluated Δj_0 values are not noticeably impacted by the inferior fit quality of the first term as the Δj_0 related term dominates for low ΔN_{leq}^* values. The separation of bulk and surface-related defects enables the separation of two degradation phases with different observable features. During the initial phase, degradation and regeneration are exclusively detectable through changes in ΔN_{leq}^* , while the second phase only impacts Δj_0 and $j_{0,\text{Kimmerle}}$. Notably, the emergence of bulk defects in

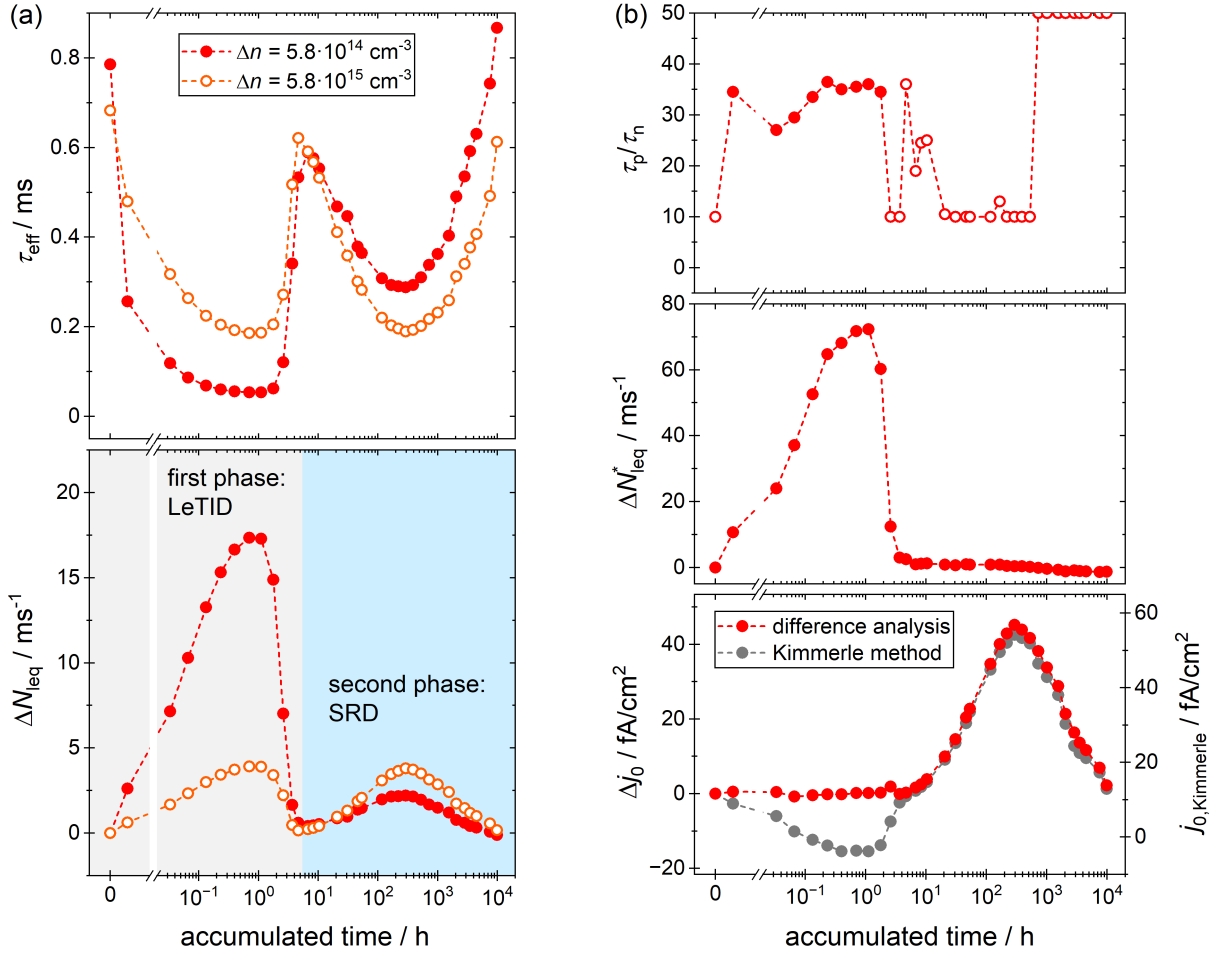


Figure 2.2: (a) Evolution of τ_{eff} and ΔN_{leq}^* , respective to the initial lifetime, during LeTID testing of a Ga-doped sample at 130 °C and 1 sun, evaluated at two different injection levels corresponding to $0.1 \cdot p_0 = 5.8 \cdot 10^{14} \text{ cm}^{-3}$ and $p_0 = 5.8 \cdot 10^{15} \text{ cm}^{-3}$. (b) Evolution of the fit parameters: symmetry factor τ_p/τ_n , maximal bulk-related lifetime equivalent defect density ΔN_{leq}^* and change in surface-related saturation current density Δj_0 . The symmetry factor τ_p/τ_n is constrained between 10 and 50 for the fit, with open symbols indicating data points where $\Delta N_{\text{leq}}^* < 4 \text{ ms}$. Additionally, j_0 is evaluated using Kimmerle’s slope-based method and plotted alongside Δj_0 , which values are offset to match the initial $j_{0,\text{Kimmerle}}$ value obtained from the slope-based approach. The shown sample corresponds to the group A1-1 in Chapter 3.

the first phase apparently enhances the surface passivation quality in $j_{0,\text{Kimmerle}}$ measurements, while Δj_0 remains unaffected by these changes in the bulk. Thus, Δj_0 remains relatively stable throughout this first phase. As the system transitions into the second phase and bulk defects have regenerated, both surface evaluation methods converge to consistent results with the respect to the change in j_0 .

For any p-type sample in this work, evaluation is performed with this difference analysis, assuming a deep bulk defect (LeTID). For most of the discussions, the symmetry factor is excluded from consideration as it consistently fell within the expected range of 25–37 and provided negligible additional insight into the defect behavior.

For n-type material, the injection dependence stemming from the defect evolving during LeTID testing is less pronounced, making reliable fits more difficult. Discussion is therefore limited to τ_{eff} , ΔN_{leq} and j_0 , evaluated by the use of Equation (2.5). As discussed in Section 1.4.2, the position of the energy level for the evolving defect(s) (see Section 4.1) and corresponding symmetry factor(s) remain uncertain. Nevertheless, n-type material generally exhibits higher lifetimes, which improves the applicability of the Kimmerle Method.

2.3.3 Detection of Iron in p-Type Si

Iron is among the most common metallic impurities and another deep level defect in silicon. Typically, iron is already introduced during crystal growth (see Section 2.1) and can therefore accumulate in the silicon as it will be discussed in Section 3.2.

Iron can exist as two species (if not clustered), either as interstitial (Fe_i) or paired with acceptors, differing in their recombination behavior [54, 171]. These iron atoms can be positively charged in p-type silicon, which leads to the formation of neutral iron acceptor pairs [55]. Since gallium is the only acceptor dopant used throughout this work, FeGa will be used for acceptor-iron pairing. Iron can be purposefully toggled between the metastable FeGa and Fe_i by storage in darkness (mainly FeGa pairs) and strong illumination at room temperature (mainly Fe_i) [48, 55].

Both species are strongly recombination active with the FeGa inducing a weak injection-dependence in defect lifetime. For Fe_i , the injection-dependence becomes more steep but lifetime above the crossover point (not visible here) is increased [54, 192] as it can be observed in Figure 2.3. This crossover point occurs at a specific injection where $\tau_{\text{eff,FeGa}} = \tau_{\text{eff,Fe}_i}$ which is typically well below an injection of $1 \cdot 10^{14} \text{ cm}^{-3}$ [193, 194]. Above this crossover point the effective lifetime is more limited by the FeGa pairs than Fe_i .

The change in recombination and thus effective lifetime τ_{eff} in the respective state can be used

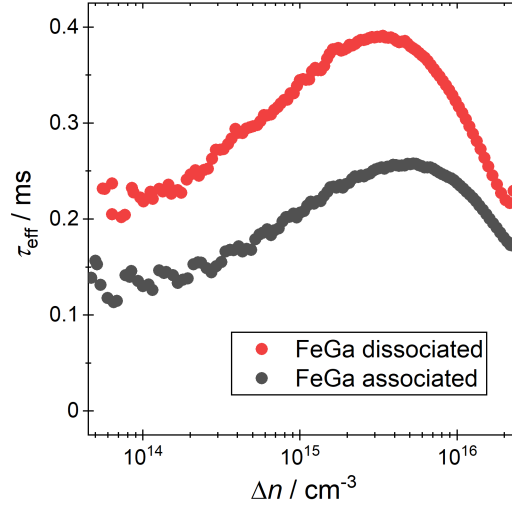


Figure 2.3: Injection dependence of τ_{eff} of a Ga-doped sample in the two states of FeGa association and dissociation. The measurement from sample A1-1 (Section 3.2) is used to illustrate the impact on the effective lifetime.

to quantify the interstitial iron concentration

$$[\text{Fe}_i] = C \left(\frac{1}{\tau_{\text{eff,FeGa}}} - \frac{1}{\tau_{\text{eff,Fe}_i}} \right) \quad (2.8)$$

The calibration factor C follows from the SRH theory of point defects (see Equation (1.15)) using parameters from Schmidt and Macdonald [193]. The calculation is performed at an injection level of $5 \cdot 10^{14} \text{ cm}^{-3}$. The absolute concentrations may depend on the chosen parameters as there are slight variations across various works [194, 195]. However, this should not impact discussions in Section 3.2, since the observed trends are more important.

This lifetime-based approach offers the possibility to detect iron at very low concentration levels below 10^{10} cm^{-3} . Experimentally, $\tau_{\text{eff,FeGa}}$ is determined after having samples stored in the dark for 24 h to have the majority of FeGa-pairs associated. The samples are then illuminated for 60 s at room temperature and a photon-flux equivalent to 1 sun using a halogen lamp to access $\tau_{\text{eff,Fe}_i}$. The treatment duration leads to saturation with no further change in carrier lifetime by longer illumination periods. Since stable dopant-iron pairs are only present in p-type material this technique for iron quantification cannot be used for n-type silicon.

For the used treatment conditions of 130 °C and an illumination of 1 sun, typically an increase in lifetime during the first 30 s was observed even though LeTID defects are already emerging. Hence, samples are illuminated under the aforementioned 1 sun at room temperature with a constant nitrogen flow for 40 s prior to LeTID testing. With this treatment the equilibrium is shifted towards more Fe_i . For all results from LeTID testing with p-type material, initial

lifetime is therefore always given after the prior illumination at room temperature.

2.3.4 Acceptor-Hydrogen Pair Formation

Hydrogen in silicon is a widely studied topic in literature. It is known that hydrogen can be present in different forms which is atomic, molecular, acceptor-hydrogen pairs, vacancy/impurity-hydrogen pairs or platelets [196] because of hydrogen accumulation. Atomic hydrogen may exist as interstitial in positive, negative or neutral charge state (H^+ , H^- and H^0) [197] enabling H to act as both, donor and acceptor, respectively. By the quenching of the sample during high-temperature processing such as the firing process described above, a significant part of hydrogen bonds into hydrogen dimers (H_2) [198]. Additionally, hydrogen may bind with dopant p- or n-type elements. While donor-hydrogen such as phosphorus hydrogen (PH) pairs are not thermally stable at room temperature [199], acceptor hydrogen pairing can be exploited through the neutralization of the dopant atom [200].

The hydrogen content introduced into the bulk by diffusion from a $SiN_x:H$ layer during firing can then be assessed by determining the change of hole concentration p with resistivity measurements at a temperature of 25 °C [185]. Consequently, the change in hole concentration changes the conductivity according to Equation (1.30). The absolute temperature is not critical, however, temperature stabilization is essential to ensure consistent results. For p-type material the equation simplifies to the bulk resistivity

$$\rho_{\text{bulk}} = \frac{1}{\sigma} = \frac{1}{q \cdot p_0 \cdot \mu_p} \quad (2.9)$$

However, this is only true for negligible injection, making it necessary to measure resistivity in darkness. The mobility is hereby calculated by the models of Klaassen [201, 202], available via PV Lighthouse [35].

After firing, hydrogen is mainly present as either H_2 dimer or as an overall neutral acceptor-hydrogen pair [203, 204]. Even though any electron accepting dopant other than Ga can form those pairs, be it B, Al or In, this work focuses on GaH pairs and the following discussion will only be made in that regard. Yet, the reaction mechanisms can be very similar for the other acceptors in group III. Due to the consumption of holes by formation of neutral GaH-pairs it is possible to track resistivity changes in the bulk. The change in p_0 occurs according to an overall reaction



that consumes holes (h^+) during dark annealing, where GaH pairs form [205, 206], and subsequent illuminated annealing, where nearly all GaH pairs dissociate [207]. The change in GaH

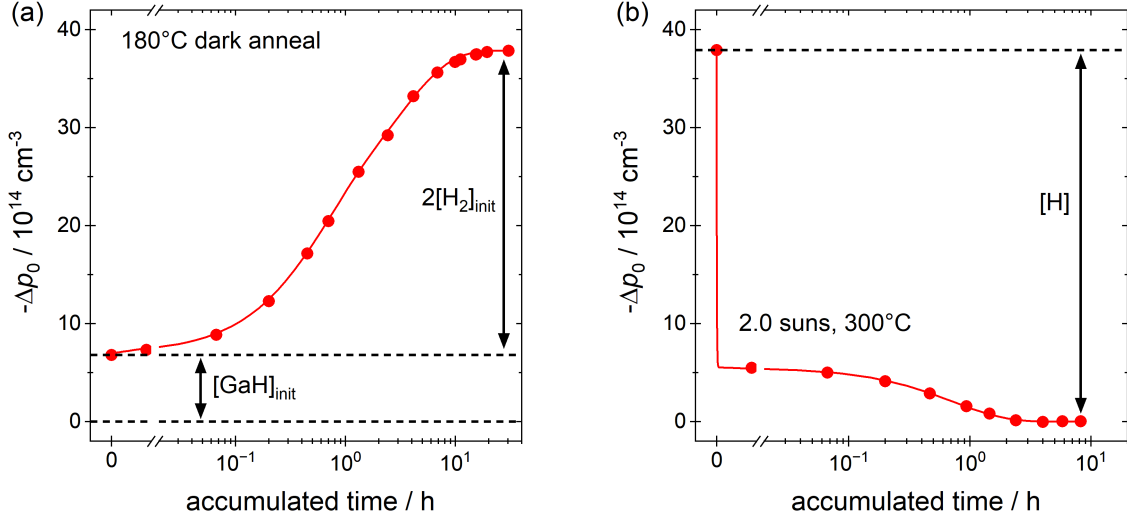


Figure 2.4: (a) Change in p_0 during dark annealing at 180 °C. (b) Change in p_0 during treatment at 2 suns and 300 °C. Sample A1-1 from Section 3.2 is shown as an example. After dissociation of GaH pairs using injection and elevated temperature in (b), the measured change in hole concentration for the association is shifted to match the initial value during dissociation. The graphical extraction of hydrogen species concentrations $[\text{H}_2]_{\text{init}}$, $[\text{GaH}]_{\text{init}}$ and $[\text{H}]$ is also shown. Data is fitted with exponential functions in both graphs. The shown sample corresponds to the group A1-1 in Chapter 3.

concentration is therefore given by $\Delta[\text{GaH}] = -\Delta p_0$. The initial concentration of GaH pairs $[\text{GaH}]$ and hydrogen dimers $[\text{H}_2]$ can be concluded from the initial hole concentration $p_{0,\text{init}}$, that after dark annealing $p_{0,\text{da}}$ and that after illuminated annealing $p_{0,\text{il}}$. The initial concentrations are then given by

$$[\text{GaH}]_{\text{init}} = p_{0,\text{init}} - p_{0,\text{il}} \quad (2.11)$$

$$[\text{H}_2]_{\text{init}} = \frac{1}{2} (p_{0,\text{init}} - p_{0,\text{da}}) \quad (2.12)$$

with the factor $\frac{1}{2}$ accounts for the formation of two GaH-pairs from one dimer. Total hydrogen concentration is then given by

$$[\text{H}] = 2 [\text{H}_2]_{\text{init}} + [\text{GaH}]_{\text{init}} \quad (2.13)$$

In this work, formation of GaH pairs is induced during dark annealing at 180 °C with interruptions to measure the change in hole concentration. Illuminated annealing at 300 °C and a photon-flux equivalent of 2 suns is employed to dissociate GaH-pairs [207]. The duration of these treatments varies slightly for the different sample types but the association of GaH pairs was finished within 20 h of dark annealing, whereas all pairs were dissolved within 10 h of illuminated annealing. The association kinetics can be described by an exponential rise-to-

saturation curve, whereas dissociation requires fitting with a sum of two exponential decays of different reaction rates and amplitudes, reflecting its two-step nature [207]. In Figure 2.4 the association and dissociation process is exemplarily shown for the sample A1-1 from Section 3.2. Hereby, the parameters $[H_2]_{init}$, $[GaH]_{init}$ and $[H]$ can be extracted. These parameters are always extracted for this type of measurement while the actual change in hole concentration will not be shown.

Several studies, where the hydrogen concentration is varied on the same material by different means, suggest a correlation between total hydrogen concentration and the extent of degradation [107, 111, 112, 117] with a more pronounced defect formation the more hydrogen is present. In recent studies [105, 106], this is narrowed down to a correlation with $[H_2]_{init}$ implying that the presence of hydrogen dimers promotes the formation of LeTID defects while GaH pairs act as hydrogen sink. Therefore, this method can be exploited to investigate various impacts on the hydrogen content in the bulk such as different passivation layers and solar cell precursor structures in Chapter 5.

2.3.5 Fourier-Transform Infrared Spectroscopy

Even though Fourier-transform infrared (FTIR) spectroscopy [208] is not directly a tool to detect LeTID, it offers the possibility to determine hydrogen and oxygen concentrations in silicon. Especially hydrogen is hereby known to be at least indirectly involved in the formation of LeTID defects (see Section 1.4). Usually, a Michelson interferometer is used to split IR light into two beams of which one is reflected at a movable mirror and creates a dynamic interference with the second beam. The interfered beam is directed through the sample. Due to the light passing through the sample, absorption occurs at specific wavelengths depending on vibrational modes of specific bonds in the material. By the use of a Fourier-transformation, an absorption spectrum can be calculated from the time-varied transmission spectrum.

The interstitial oxygen concentration $[O_i]$ can be calculated using the ASTM F1188 standard [209] according to

$$[O_i] = 2.45 \cdot 10^{17} \text{ cm}^{-2} \cdot \alpha \quad (2.14)$$

related to the an absorption coefficient α of the stretching mode of the Si-O-Si bond at $\sim 1107 \text{ cm}^{-1}$. The absorption coefficient is calculated from the measured peak and base transmittance and is dependent on the samples thickness. For this standard measurement, typically 2 mm silicon slabs are used. Usually, the integral over the peak is taken to improve accuracy.

While it is sufficient to measure the transmission for $[O_i]$ at room temperature, the detection of hydrogen in the form of H_2 or as vacancy complexes such as VH_4 benefits from cryogenic temperatures.

2.3.6 Characterization of Solar Cells

The current density-voltage characteristic ($j(V)$ curve) of an ideal solar cell can be approximated by the Shockley diode model

$$j(V) = j_0 \left[\exp \left(\frac{q \cdot V}{k_B \cdot T} \right) - 1 \right] - j_{ph} \quad (2.15)$$

with the photocurrent density j_{ph} and the diode saturation current density j_0 [210]. This saturation current density can be calculated as

$$j_0 = \frac{q \cdot D_n \cdot n_i^2}{L_{n,eff} \cdot N_A} + \frac{q \cdot D_p \cdot n_i^2}{L_{p,eff} \cdot N_D} \quad (2.16)$$

with the amount of acceptor atoms N_A and donor atoms N_D , respectively. In Figure 2.5 the current density is measured while sweeping the voltage over a defined range. The short-circuit current density j_{SC} is obtained at zero applied voltage ($V = 0$) and corresponds to j_{ph} , while the open-circuit voltage V_{OC} corresponds to the condition of no external load ($j = 0$). The V_{OC} is the maximal voltage that a solar cell under illumination can produce. While V_{OC} can be limited by a reduced effective carrier lifetime as described by Section 1.2.3, j_{SC} remains independent of τ_{eff} as long as the diffusion length is sufficiently large for charge carriers to reach the contacts and is then only limited by optical absorption. Once the diffusion length itself becomes limiting, j_{SC} scales with $\sqrt{\tau_{eff}}$.

Additionally, it is possible to extract the maximum power point from Figure 2.5 by calculation of the power density, which can be described by a corresponding current density at the maximum power point j_{MPP} and voltage V_{MPP} respectively. Obviously, a solar cell should always be operated as close to the maximum point to maximize the yield. How soft the $j(V)$ curve is increasing can then be expressed by the fill factor FF according to

$$FF = \frac{V_{MPP} \cdot j_{MPP}}{V_{OC} \cdot j_{SC}} \quad (2.17)$$

The power conversion efficiency η of a solar cell can be calculated from the fraction of the power density at the maximum power point P_{MPP} and the power of the incoming light P_{ph} so that

$$\eta = \frac{P_{MPP}}{P_{ph}} = \frac{FF \cdot j_{SC} \cdot V_{OC}}{P_{ph}} \quad (2.18)$$

In a real solar cell, there are always resistance losses, that reduce the overall solar cell performance. The inclusion of an ideality factor in the Shockley diode model may be necessary to properly account for recombination effects within the space charge region of the pn-junction.

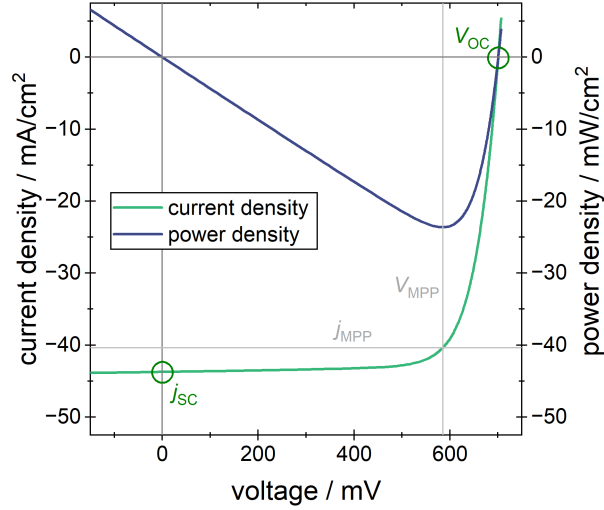


Figure 2.5: Current density-voltage characteristic ($j(V)$ curve) and power density of a solar cell measured using a flasher tool. The short-circuit current density j_{SC} and the open-circuit voltage V_{OC} are obtained from the intersections with the y-axis and x-axis, respectively. Parameters at the maximum power point are determined from the maximum power density, with the corresponding current and voltage denoted as j_{MPP} and V_{MPP} .

When recombination in this region is explicitly considered, the current-voltage characteristic requires modification through the addition of a second diode term. This extended model captures both the ideal diffusion current and the space-charge recombination current components and can be expressed as [211]

$$j(V) = j_{01} \left[\exp \left(\frac{q \cdot V}{m_1 \cdot k_B \cdot T} \right) - 1 \right] + j_{02} \left[\exp \left(\frac{q \cdot V}{m_2 \cdot k_B \cdot T} \right) - 1 \right] + \frac{V - j \cdot R_S}{R_{Sh}} - j_{ph} \quad (2.19)$$

Further, the series resistance R_S and the shunt resistance R_{Sh} are included in the third term. They account for resistive losses due to charge extraction at the contacts (R_S) and leakage currents across the pn-junction (R_{Sh}). For an ideal cell, the ideality factor is $m_1 = 1$. The second term captures recombination losses in the space charge region, with its ideality factor typically close to $m_2 \approx 2$. Comprehensive discussions of solar cell operating principles can be found in [17, 212].

All solar cell measurements were carried out using a cetis PV flasher tool from *H.A.L.M.*, equipped with a temperature-controlled, water-cooled measurement chuck set to 25 °C and a xenon flash lamp. Owing to the back-contact architecture of the solar cells, vacuum pressure was applied to press the cell busbars onto the contacts of the measurement chuck. For $j(V)$ curve measurements, a 1000 W m⁻² flash of 100 ms duration was applied while sweeping the voltage and simultaneously recording the current. From the resulting data, the solar cell parameters described above were extracted.

3 LeTID in Ga-Doped Cz-Si with Melt Recharging

This chapter discusses the impact of crystal growth conditions on the material quality and observed degradation extent during LeTID testing. Most of the findings presented here are published in [127]^{3.1}.

The photovoltaic industry has transitioned from boron to gallium as the standard p-type dopant for monocrystalline silicon grown via the Cz method (see Section 2.1). In Section 1.4.1 a comprehensive review on LeTID in Ga-doped silicon is given. Concentrations of the active LeTID defect are estimated to be below 10^{12} cm^{-3} [36], placing it below the detection limit for many analytical techniques. If the defect precursor concentration lies below this threshold, its direct observation becomes exceedingly challenging and quantitative analysis nearly impossible. Additionally, it is still unknown what the nature of the defect is.

Nevertheless, if this precursor is associated with a specific impurity, its distribution should follow established segregation behavior during Cz crystal growth. One could formulate the working hypothesis that a LeTID-active contamination is incorporated into the crystal, which can be described using the Scheil equation and monitored by other species with similar segregation behavior. Several assumptions are required. First, there should be no, or only negligible, evaporation from the melt. While the concept of segregation at the melt/solid interface remains valid, adjusted boundary conditions would otherwise need to be considered. Second, the incorporated contamination must not be redistributed within the crystal while the ingot remains high temperature. Third, it is assumed that the source of the contamination lies within the melt with an initial concentration already present. This assumption would no longer be valid if the contamination originated from an external source, such as the crucible.

Supporting the segregation hypothesis, solar cells fabricated from silicon ingots with elevated impurity concentrations in the melt have been shown to exhibit enhanced LeTID severity [134]. This suggests that LeTID magnitude may vary along the length of a Cz ingot when exposed to comparable hydrogen concentrations. However, this relationship may be obscured by other

^{3.1} Conceptualization, sample preparation, investigation, formal analysis and main writing were carried out by the author.

ingot properties that also vary during standard Cz growth, such as oxygen concentration gradients [213, 214].

Section 3.1 explores the incorporation of atoms during recharged Czochralski-silicon growth in theory with a focus on the incorporation of gallium as a dopant and the accumulation of impurities.

In Section 3.2 the material quality is assessed by the iron quantification for samples taken throughout two distinct RCz-Si processes. Additionally, the degradation extent is monitored during LeTID testing. In the end, the relationship between the accumulated impurities and the LeTID defect concentration is discussed.

3.1 Properties of Recharged Cz-Si Crystal Growth

The modern photovoltaic industry has increasingly adopted the recharged Czochralski (RCz) process, wherein multiple ingots are pulled sequentially from a single crucible through periodic melt replenishment. In Figure 3.1 a general schematic for this repeated melt recharging and ingot pulling is depicted. In comparison to the well established standard Cz batch process the melt recharging approach offers significant cost advantages and improved production throughput, due to minimization of non-productive set-up, heat-up and cool down times [215–217].

Even though this concept is not new, the process has not been adopted in industry for a long time due to the need for long-lasting crucibles and affordable recharge systems with lasting reliability [215, 218]. While many bulk properties remain consistent across consecutively pulled ingots, metallic impurity concentrations in both the melt and solidified ingots rise with each

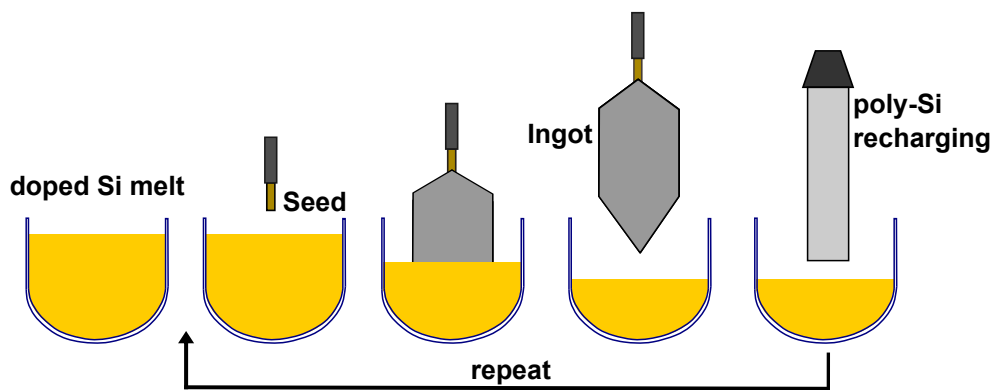


Figure 3.1: Schematic for the Czochralski process with melt recharging. A doped silicon melt is heated, and an ingot is pulled by dipping a seed into the melt. After a fraction of the melt volume is consumed, the crucible is recharged with silicon chunks or poly-Si, and a new seed is used to pull the next ingot. This cycle is repeated several times, typically yielding 8–11 ingots, before the process is fully restarted with a new crucible and melt. Inspired by [152].

subsequent pull (see Section 3.1.2), leading to a progressive reduction in bulk carrier lifetime (τ_{bulk}) [219]. Iron, in particular, serves as a useful marker for impurity monitoring owing to its well-characterized impact on lifetime (see Section 2.3.3) [171, 220, 221]. The study by Basnet *et al.* [221] uses material from a very similar RCz-Si process and therefore provides a good reference for calculated iron concentrations in current wafer material.

Another cost-efficient approach is to continuously refill the melt during crystal growth. This also benefits the crucible by reducing heating and cooling cycles. Nevertheless, it will not be discussed here, as the ingots used in this work are all produced by melt recharging after pulling each ingot.

Despite the growing industrial focus on n-type Cz silicon [222], Ga-doped p-type material remains economically attractive, especially for advanced cell architectures such as IBC solar cell designs (see Section 5.4) [173, 223].

The properties of RCz-Si growth concerning impurities were widely studied before, e.g. in the study by Hopkins *et al.* [224], but a short discussion is given here in the context of Cz crystal growth with melt recharging.

The incorporation of impurities at the growth front between the liquid melt and the solidified crystal is determined by the segregation coefficient $\kappa = C_S/C_L$ which is the equilibrium ratio of concentrations in the solidified phase C_S and the liquid melt C_L (directly at the growth front). It is important to note that limited transport within the melt can lead to the accumulation of impurities with $\kappa < 1$ near the growth front. Therefore, the effective segregation coefficient which depends on growth conditions, such as melt circulation and pulling speed, provides a better description of incorporation. For silicon, many impurity species have segregation coefficients smaller than unity, indicating a preference for remaining in the melt. The segregation behavior is described by the well-known Scheil equation

$$C_S(f) = C_{S0} \cdot (1 - f)^{\kappa-1} \quad \text{with} \quad C_{S0} = \kappa \cdot C_{L0} \quad (3.1)$$

This equation describes the impurity concentration in the solid phase as a function of the solidified fraction f , assuming the initial concentration in the melt was C_{L0} . If κ is unity, incorporation is homogeneous. Conversely, if κ is smaller than unity, C_S increases monotonically from the seed end to the tail end.

3.1.1 Dopants

The increase in dopant concentration along the crystal is somewhat unfavorable, as it leads to variations in resistivity. If the dopant concentration of the wafers cut along the crystal must be

within a certain range, i.e., the allowed ratio C_S/C_{S0} is limited, only a fraction

$$f = 1 - (C_S/C_{S0})^{\frac{1}{\kappa-1}} \quad (3.2)$$

of the melt can be utilized, with the remainder being discarded. To illustrate, one can consider an example where the dopant concentration is allowed to double, i.e., $C_S(f) = 2 \cdot C_{S0}$. For boron, with $\kappa_B = 0.8$ [225], approximately ~97 % of the melt can be used. In contrast, gallium's substantially lower segregation coefficient ($\kappa = 0.008$ [225]) limits usable melt to just 50 %, making conventional Cz growth economically unviable. This is where melt recharging becomes essential.

After the fraction f has crystallized from the melt with initial volume V_0 and concentration C_L in the remaining melt with volume $V_L = V_0 \cdot (1 - f)$ has risen to

$$C_L(f) = C_S/\kappa = C_{L0} \cdot (1 - f)^{\kappa-1} \quad (3.3)$$

Consequently, the total amount of dopants N_L remaining in the melt is given by

$$N_L(f) = V_L \cdot C_L = V_0 \cdot C_{L0} \cdot (1 - f)^\kappa \quad (3.4)$$

where $N_{L0} = V_0 \cdot C_{L0}$ represents the total amount of dopants in the original melt. Thus, $N_L/N_{L0} = (1 - f)^\kappa$ is the fraction of dopants remaining in the melt and $1 - N_L/N_{L0}$ is the fraction incorporated into the crystal. For instance, given $C_S(f) = 2 \cdot C_{S0}$, only ~6 % of the initial boron atoms remain in the melt after ~97 % of the melt has been crystallized, while ~94 % are incorporated into the crystal. In contrast, for gallium, after ~50 % of the melt has crystallized, ~99.4 % of the initial gallium atoms remain in the melt, with only ~0.6 % incorporated into the crystal. A corresponding graphical illustration is given in Figure 3.2a, showing the comparison of gallium and boron incorporation into the solidified crystal for a solidified fraction of 90 %. Hereby, the concentration of gallium varies by a factor of ten along the ingot, making it unsuitable for mass production. In Figure 3.2b, the dopant concentration is only allowed to vary by a factor of two.

The difference in dopant incorporation can be understood by comparing the initial melt concentrations required for boron and gallium. To achieve the same target concentration C_{S0} in the crystal, the initial melt concentrations must follow the relation $C_{L0,Ga} = \kappa_B/\kappa_{Ga} \cdot C_{L0,B}$. Since the segregation coefficient of gallium (κ_{Ga}) is two orders of magnitude smaller than the one of boron (κ_B), the gallium doped melt must start with a correspondingly higher dopant concentration.

For a target crystal concentration of $C_{S0} = \kappa \cdot C_{L0} = 1 \cdot 10^{16} \text{ cm}^{-3}$, the required initial melt concentration is $1.25 \cdot 10^{16} \text{ cm}^{-3}$ for boron but $1.25 \cdot 10^{18} \text{ cm}^{-3}$ for gallium. While the crystallization

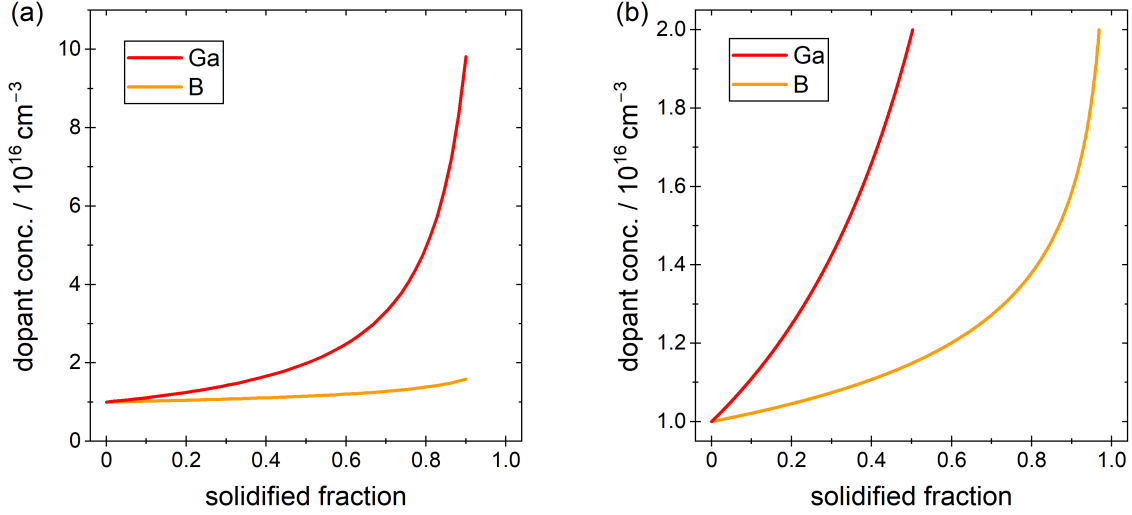


Figure 3.2: Calculated gallium and boron concentrations along a crystal, assuming an initial concentration $C_{S0} = 1 \cdot 10^{16} \text{ cm}^{-3}$. (a) Dopant concentration profiles for both species during crystal pulling up to a solidified fraction of 90 %. (b) Case where the maximum variation in dopant concentration is limited to a factor of two for both gallium and boron.

fractions differ significantly ($\sim 97\%$ for boron versus $\sim 50\%$ for gallium), both dopants reach similar concentrations in the crystal. As a result, the gallium melt retains much more dopant which has not been incorporated in the crystal as it is the case for the boron melt after growth. When the melt is recharged to its initial volume V_0 , the remaining volume $V_0 \cdot (1 - f)$ with concentration $C_L(f)$ is mixed with an added volume $V_0 \cdot f$ of concentration $C_{L,\text{add}}$. The total dopant quantity $N_{L,\text{new}}$ in the replenished melt is then given by

$$N_{L,\text{new}} = V_0 \cdot C_L \cdot (1 - f) + V_0 \cdot C_{L,\text{add}} \cdot f \quad (3.5)$$

To maintain the initial conditions of the first growth, the new melt concentration $C_{L,\text{new}} = N_{L,\text{new}}/V_0$ must equal the original concentration C_{L0} , which means

$$C_{L,\text{add}} = C_{L0} \cdot \frac{1 - (1 - f)^k}{f} \quad (3.6)$$

In the case of gallium in the aforementioned example, this corresponds to a recharge concentration $C_{L,\text{add}}$ of $\sim 1\%$ of C_{L0} . This small value reflects that only the dopant fraction incorporated into the crystal needs replacement. Consequently, optimal recharging should use lowly doped silicon such as scrap portions from the crystal itself matching the removed dopant concentration.

Using higher-doped silicon for replenishment would cause progressive dopant accumulation

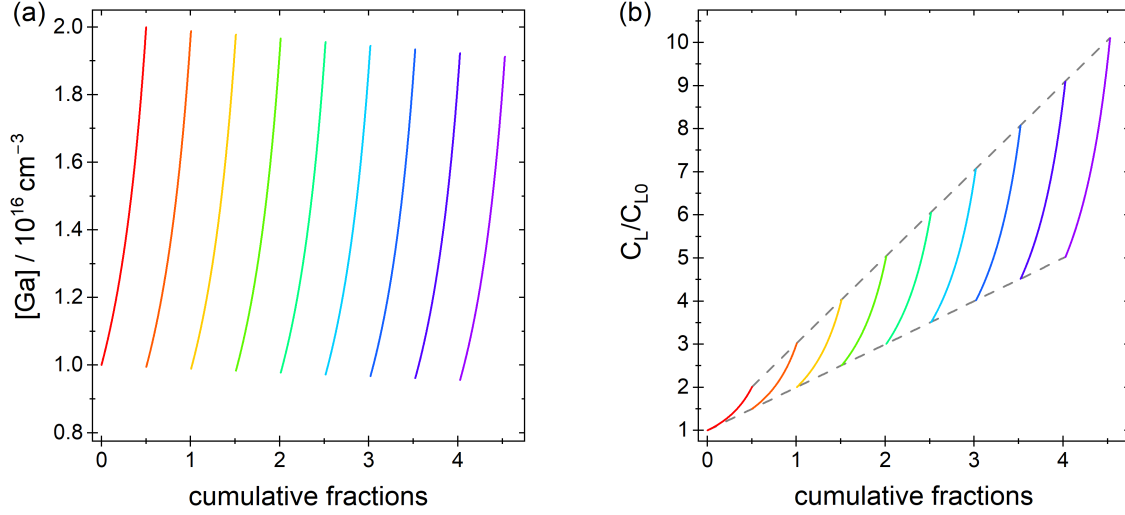


Figure 3.3: (a) Calculated gallium concentration along nine consecutively pulled crystals, assuming an initial concentration $C_{S0} = 1 \cdot 10^{16} \text{ cm}^{-3}$ and recharging with undoped silicon after a fraction of $\sim 50\%$ of the melt has crystallized for each crystal. (b) Normalized concentration relative to the initial value for a species with $\kappa = 10^{-6}$ along nine consecutively pulled crystals, again using $\sim 50\%$ of the melt and assuming that each recharge introduces a constant amount of the species. Adapted from [127].

(and resistivity reduction) at the seed end with successive ingot growth. Conversely, employing lower-doped or undoped material would gradually decrease dopant concentrations (increasing resistivity). However, since only about $\sim 0.6\%$ of dopants are incorporated into each crystal, even undoped recharge material would produce minimal concentration shifts. This effect is demonstrated for nine consecutively pulled crystals for an initial dopant concentration of $1 \cdot 10^{16} \text{ cm}^{-3}$ in Figure 3.3a.

Reducing ingot lengths and recharging the melt therefore allows a relatively tight doping distribution even for elements with very small segregation coefficients such as gallium. This enables to compete with boron in cost and production efficiency.

3.1.2 Impurities

The discussion of impurity incorporation is basically the same as for dopants, only that doping specifications determine the boundary conditions such as the crystallized fraction f . Metallic impurities in silicon typically exhibit very small segregation coefficients, often differing by orders of magnitude, e.g., $6.4 \cdot 10^{-6}$ for iron compared to $6.9 \cdot 10^{-4}$ for copper [224]. This raises the question of how such differences in κ influence impurity distributions under the conditions of RCz crystal growth.

For gallium which already has a small segregation coefficient of 0.008, the condition $\kappa \ll 1$ holds. In this regime, the Scheil Equation (3.1) simplifies to

$$C_S(f) \approx C_{S0} \cdot (1 - f)^{-1} \quad \text{for } \kappa \ll 1 \quad (3.7)$$

The incorporation in this case is virtually independent of κ . This explains why gallium shows a doubling of concentration ($C_S(f) = 2 \cdot C_{S0}$) at approximately $f \sim 50\%$. This is a direct consequence of the simplified Scheil equation for $\kappa \ll 1$.

Numerically, in the given example, the iron concentration would increase by a factor of 2.0112 along the crystal, while copper would increase by a factor of 2.0102, despite differing in κ by two orders of magnitude. This difference is not reliably detectable. Thus, it can be stated that the accumulation of impurities with $\kappa \ll 1$ within ‘short’ crystals is not specific to the species.

Consequently, monitoring a single impurity (like gallium or iron) can provide meaningful information on other low-segregation species, assuming no significant diffusion alters their profiles. However, this approach could fail for fast-diffusing elements like copper [226]. Additionally, resistivity measurements may inaccurately reflect gallium concentration due to compensation effects from thermal donors or unintended n-type co-doping.

Besides impurity accumulation during individual crystal growth, the progressive accumulation in the melt during repeated recharge and growth cycles requires consideration. The contamination source plays a critical role in this process. When contamination originates from the raw silicon feedstock which maintains a fixed impurity concentration C_{L0} , the initial concentration C_{Ln} for the n -th recharge cycle can be derived by combining Equation (3.3) and Equation (3.5) (with $C_{L,\text{new}} = N_{L,\text{new}}/V_0$) yielding

$$C_{Ln} = C_{L(n-1)} \cdot (1 - f_{(n-1)})^\kappa + C_{S0} \cdot f_{(n-1)} \quad (3.8)$$

In this expression, $n = 1$ corresponds to the first recharge cycle ($n = 0$ representing the original melt). The term $f_{(n-1)}$ identifies the crystallized fraction from the previous growth. When each pull maintains the same crystallization fraction, C_{Ln} reduces to

$$C_{Ln} = C_{L0} \cdot \left[(1 - f)^{n\kappa} + f \cdot \sum_{m=0}^{n-1} (1 - f)^{m\kappa} \right] \quad (3.9)$$

$$\approx C_{L0} \cdot [1 + n \cdot f] \quad \text{for } \kappa \ll 1 \quad (3.10)$$

For impurity species in relatively short crystals which are characterized by $\kappa \ll 1$, the accumulation in the melt exhibits linear scaling with $n \cdot f$, demonstrating independence from the specific κ value. This behavior indicates that during sequential crystal growth with intermediate melt

replenishment, the accumulation process becomes non-specific to the impurity species. As a result, monitoring a particular impurity (e.g. iron) can provide meaningful information about unidentified contaminants present in the system. This principle is illustrated in Figure 3.3b for the case of ~50 % melt consumption, showing a linear progression of both seed and tail end concentrations (dashed lines). The concentration profile in the n -th crystal can be obtained by applying the Scheil equation with C_{Ln} substituted for the initial concentration C_{L0} .

The overall accumulation remains limited for species with $\kappa \ll 1$ in short crystals, as each melt recharge substantially mitigates impurity buildup. As shown in Figure 3.3b, nine consecutive growth cycles produce less than a fivefold increase in seed to end concentrations and under a tenfold difference between the first seed and final tail end. Since this accumulation depends mainly on the solidified fraction f rather than the specific κ value, an impurity like iron can effectively serve as an indicator for other species, assuming sufficiently slow diffusion of these contaminants within the crystal lattice.

3.2 Material Quality and LeTID Susceptibility

3.2.1 Material Characterization

In this investigation, state-of-the-art (2023) industrial Ga-doped RCz-Si wafers were utilized. These wafers were taken from ingots produced via two distinct RCz-Si growth processes which were designed to yield varying resistivities, labeled, in the following A and B. Throughout both processes, nine ingots of differing lengths were drawn each. Diamond wire sawing was employed to slice the wafers, resulting in thicknesses of 170 μm for process A and 160 μm for process B. For ingots from process A, wafers were extracted from the seed, center, and tail of both the first (A1) and ninth (A9) ingots. The resistivity along A1 ranged from 2.45 $\Omega\text{ cm}$ to 1.71 $\Omega\text{ cm}$, and for A9, it ranged from 2.68 $\Omega\text{ cm}$ to 1.49 $\Omega\text{ cm}$. It should be noted that the final ingot nine was deliberately pulled longer and sliced into wafers for this study to facilitate a more pronounced accumulation of impurities towards the tail end. Usually this part would be recycled.

The lengths of ingots A1 and A9 were 2.17 m and 5.1 m, respectively, leading to different absolute positions of wafers from the center and tail, as shown in Table 3.1. The factor g denotes the ratio of the weight incorporated in the ingots to the weight of the material before each crystal growth. For ingots B, the resistivity varied between 0.90 $\Omega\text{ cm}$ and 1.06 $\Omega\text{ cm}$ for seed wafers of the first (B1), sixth (B6), and ninth (B9) subsequently pulled ingots. By means of the factor g in Table 3.1, it can be noticed that not even 50 % of the melt is used to pull the first ingot A1. However, in practice, ingot lengths always vary throughout the RCz-Si process out

Table 3.1: Position and ingot lengths for all materials used in this chapter. The factor g is the ratio of the ingot weight after crystallization to the weight of the material in the crucible before each new Cz-growth. Additionally the base resistivity is given from which the net doping p_0 is calculated. Reproduced from [127].

ingot label	A1			A9			B1	B6	B9
ingot length (mm)	2166			5085			1490	2923	3153
position	A1-1	A1-2	A1-3	A9-1	A9-2	A9-3	B1-1	B6-1	B9-1
resistivity (Ω cm)	2.45	2.07	1.71	2.68	1.82	1.49	0.9	0.93	1.06
g	0.024	0.279	0.348	0.005	0.476	0.864	0.005	0.005	0.005

of various reasons e.g. losing of mono-crystallinity can lead to process abortion.

The net dopant concentration p_0 , determined from base resistivity measurements, and the interstitial oxygen concentration $[O_i]$, characterized by FTIR spectroscopy^{3,2}, are presented in Figure 3.4. The data include samples cut from different positions of ingots A1 and A9, as well as from the seed of ingots B1, B6, and B9. As previously described, p_0 increases towards the tail of the ingot. After recharging the melt with undoped poly-Si, p_0 near the seed of the ingot is similar to that of the prior grown ingots (see Section 3.1). During each RCz-Si pull, the interstitial oxygen concentration increases and is highest for the last pulled ingot in both processes, as also observed by Basnet et al. [221]. However, oxygen concentrations are only slightly increased at the seed positions for both processes. Overall, $[O_i]$ ranges from $4.5 \cdot 10^{17}$ to $7 \cdot 10^{17} \text{ cm}^{-3}$, with the lowest concentration at the tail positions and is comparable to trending industrial material [227, 228].

For each ingot, half of the samples were exposed to a phosphorus diffusion treatment to reduce mobile impurities like iron. After PSG removal, all samples were subjected to KOH etching to remove the emitter and achieve a uniform thickness for samples in the same group, resulting in a final wafer thickness of approximately $150 \mu\text{m}$ for A and $140 \mu\text{m}$ for B. Sample thicknesses were determined by weighing and averaging over the full sample. After symmetrical deposition of dielectric surface passivation layers (see Section 2.2.3), different set temperatures were used to realize a sample peak temperature of 800°C in an industrial belt furnace. Because of the $10 \mu\text{m}$ thickness difference between the wafers from ingots A and B, both groups were fired separately. The maximum cooling rate after reaching the peak temperature was set to approximately 100 K s^{-1} within the temperature range between 750°C and 400°C . This condition was chosen to increase the amount of hydrogen retained in the bulk of the sample, which is known to enhance the susceptibility to LeTID [106, 107]. A more detailed discussion of the influence of peak firing temperature and cooling rate is provided in Section 5.1.

^{3,2} FTIR characterization and determination of sample resistivity were carried out by the Cz producer

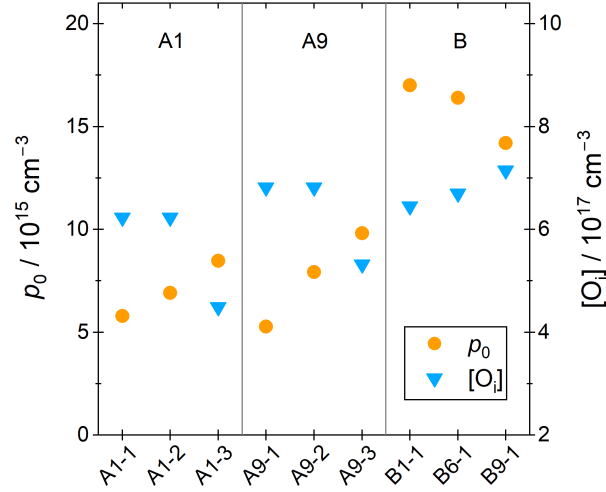


Figure 3.4: Comparison of net dopant concentration and interstitial oxygen concentration in as-cut samples from all positions of the five investigated RCz-Si ingots. A1 and B1 denote the first ingots of new RCz-Si processes at different doping concentrations. The second number in each label refers to the wafer position within the ingot: seed (1), center (2) and tail (3). Reproduced from [127].

3.2.2 Interstitial Iron Concentration

As described in Section 3.1.2, it is expected that the metal impurity concentration in the melt increases with each recharging process and so should the concentration in the consecutively pulled ingots. Iron provides a practical way to detect even low concentrations via a lifetime-based approach. The metal exists as two species, either as interstitial (Fe_i) or paired with gallium (FeGa), differing in their recombination behavior. As iron can be purposefully toggled between FeGa and Fe_i by storage in darkness (mainly FeGa pairs) and strong illumination (mainly Fe_i), the change in recombination and thus effective lifetime τ_{eff} in the respective state can be used to quantify the interstitial iron concentration (see Section 2.3.3).

Effective lifetimes in the state of associated FeGa pairs $\tau_{\text{eff,FeGa}}$ and in the dissociated state $\tau_{\text{eff,Fe}_i}$ after illumination are shown in Figure 3.5a for all samples. The data is shown at an injection corresponding to $0.1 \cdot p_0$. Hereby, those exposed to an additional PDT, indicated by (P), show lower initial effective lifetimes for wafers of process A and a higher τ_{FeGa} for B compared to their sister samples which did not receive any additional treatment. For Process A, an improvement in lifetimes due to PDT is only observable for the center and tail positions of A9. Eventually the purity of A samples was already sufficiently good, so that the additional PDT resulted in a reduction of lifetime. All reported lifetime values represent the mean of measurements taken from at least four samples, with these samples distributed across a minimum of two distinct wafers to improve reliability.

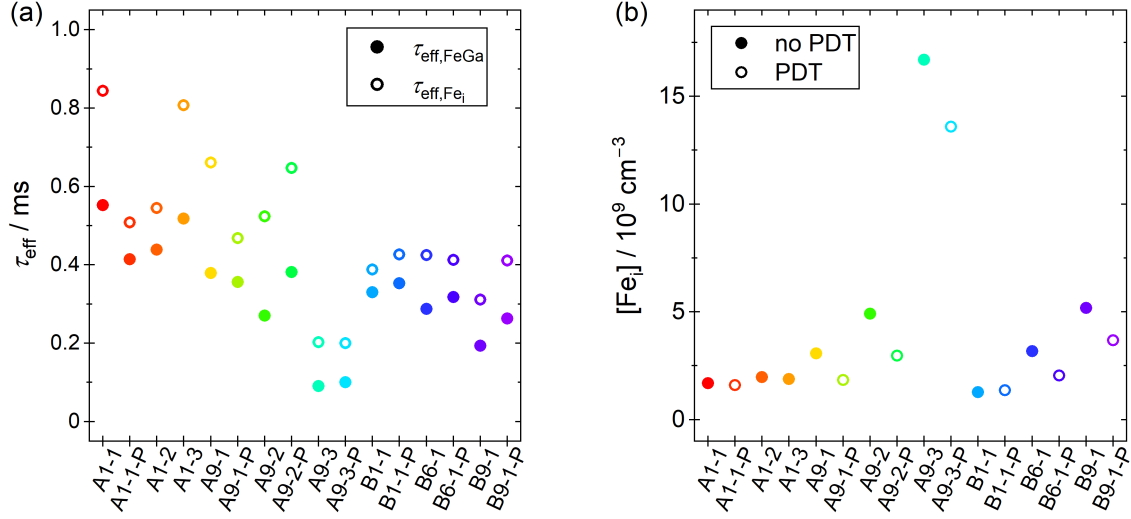


Figure 3.5: (a) Measured effective lifetimes after dark storage and after illumination for samples that received a PDT (P) and samples without PDT across all ingots used in this work. Lifetimes are evaluated at an injection level equal to one tenth of the net doping. (b) Calculated interstitial iron concentrations for samples with a PDT (P) and samples without additional treatment for all ingot positions. Reproduced from [127].

Iron concentration, calculated by the use of Equation (2.8), is comparatively low ($\sim 2 \cdot 10^9 \text{ cm}^{-3}$) in samples from the first ingots of both RCz-Si processes as shown in Figure 3.5b. Along the first grown ingot A1, no significant increase of iron can be observed, whereas the concentration massively increases in A9. Of course, this is also due the increased length of this ingot (see Table 3.1) leading to a significant increase in iron incorporation into the crystal. At seed positions of process B, an increase for ingots six and nine can be observed. This can be attributed to the increase of iron by the melt replenishing between each crystal growth cycle. For samples with iron concentration exceeding $3 \cdot 10^9 \text{ cm}^{-3}$, the applied PDT could lower it to a certain degree. Evaluation at different injections yields the same trends with offsets of $\sim 0.5 \cdot 10^9 \text{ cm}^{-3}$ which can be interpreted as the uncertainty for Fe_i .

It can be concluded that the PDT serves as an effective gettering step to remove iron from the wafer as long as contamination is sufficiently high.

3.2.3 Long-Term Stability Experiments

Degradation Extent along Ingots with Varying Impurity Concentrations

Having evaluated the accumulation of impurities during the RCz-Si process concerning $[\text{Fe}_i]$, samples from different ingot positions were subjected to long-term stability tests. LeTID testing was conducted on a hotplate at 130°C with illumination being photon-flux equivalent to 1 sun.

The treatment was periodically interrupted for PCD measurements to monitor the lifetime.

Figure 3.6 illustrates the measured τ_{eff} and calculated ΔN_{leq} on the left side and the parameters ΔN_{leq}^* and Δj_0 , derived from fitting Equation (2.6) to the measured injection-dependent lifetime data during LeTID testing for wafers from RCz-Si process A, on the right side. All Δj_0 are shifted to the initial value of $j_{0,\text{Kimmerle}}$ (see Section 2.3.2). For the first grown ingot, minimal change in degradation extent is observed, whereas maximal degradation extent $\Delta N_{\text{leq,max}}$ significantly increases up to 95 ms^{-1} towards the tail end of ingot A9. It should be noted that A9 was deliberately pulled longer in this study than usual to accumulate impurities towards the tail of the last pulled crystal.

Comparing the seed positions of ingot A1 and A9 also shows an increase of degradation extent, suggesting that the LeTID triggering species is increased due to several melt replenishing cycles. Throughout the LeTID treatment, surface passivation quality remains relatively constant and is only deteriorated once the regeneration of the bulk defect is complete, as it can be observed by the comparison of ΔN_{leq}^* and Δj_0 .

Additionally, the maximum defect density is shifted to increasing accumulated treatment times, likely related to the iso-generative treatment conditions. As the carrier lifetime is lowered as a consequence of other lifetime limiting impurities such as iron or as a consequence of the formation of LeTID defects during the treatment, the resulting injection in the sample is reduced, since the generation is kept constant. This then leads to slowed down reaction kinetics and will be investigated and discussed in more detail within Section 3.2.3. A more qualitative analysis of the correlation between iron accumulation and LeTID extent will be given

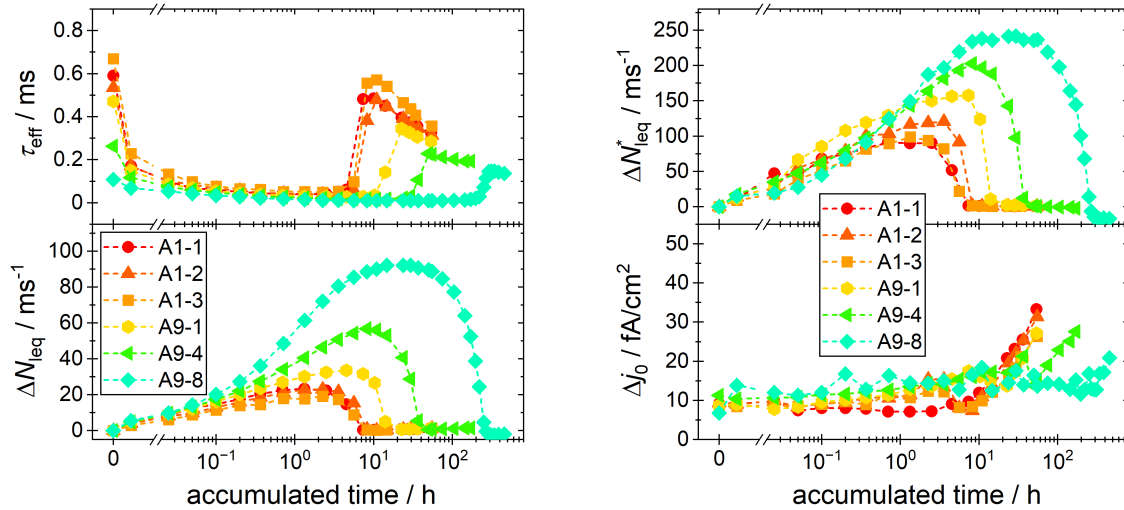


Figure 3.6: Change in τ_{eff} , ΔN_{leq} , ΔN_{leq}^* and Δj_0 (shifted to the initial $j_{0,\text{Kimmerle}}$ as described in Section 2.3.2) during treatment under 1 sun at 130°C for samples along the ingots A1 and A9. Both ΔN_{leq} and ΔN_{leq}^* are referenced to the initial lifetime. Adapted from [127].

in Section 3.2.4.

Influence of the PDT

In another experiment the influence of an additional PDT on the degradation and regeneration behavior is examined. This time, only the wafers from the seed positions of both RCz-Si processes are investigated.

In Figure 3.7, the accelerated degradation and regeneration behavior under iso-generative illumination at 130(1) °C is depicted with a comparison of samples that did receive an additional PDT to sister samples without a PDT. Two exponential functions for the degradation and one for the regeneration were fitted to each data set to enhance clarity. Given the different thicknesses and doping concentrations between samples from ingots A and B, direct comparisons of maximum defect densities are not advisable. Thus, the two processes are presented separately

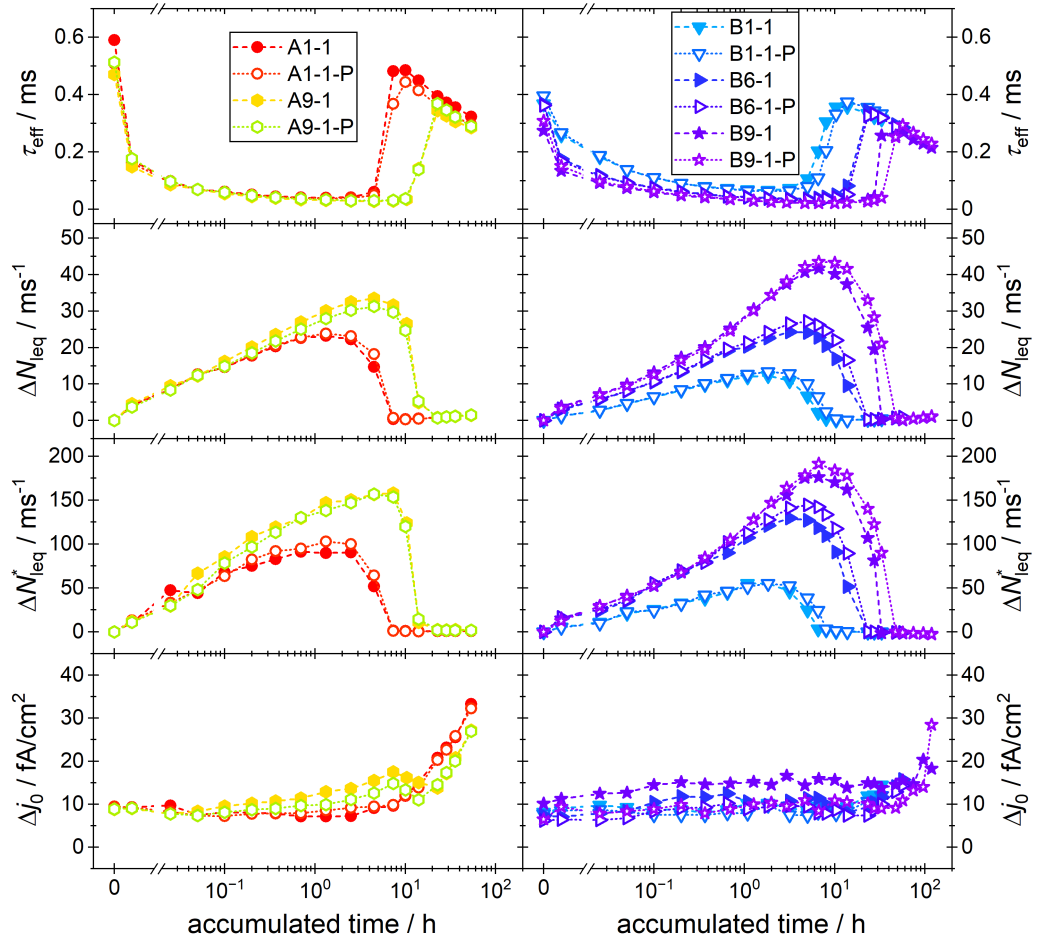


Figure 3.7: Evolution of τ_{eff} , ΔN_{leq} , ΔN_{leq}^* and Δj_0 for seed-position wafers with a PDT (P) and samples without PDT for ingots from process A (left) and process B (right) under illumination with a photon-flux equivalent to 1 sun at 130 °C. Adapted from [127].

in this graph. A trend of increasing $\Delta N_{\text{leq,max}}$ with each melt recharge is observed in both RCz-Si processes for subsequently pulled ingots as it was already noted in the previous section for process A.

The B1-1 sample, being slightly thinner, exhibits a lower defect density than A1-1. This correlation aligns with previous studies reporting a matching relationship between thinner wafer thickness and lower degradation extent [122]. Consequently, another degradation experiment is conducted with the final thickness matched at $\sim 147(5) \mu\text{m}$ for all samples. The resulting parameters from LeTID testing are shown in Figure 3.8. Despite the similar thickness of all wafers, significant differences in $\Delta N_{\text{leq,max}}$ persist. Particularly for the comparison of wafers from the seed end of ingots A and B, a similar degradation extent would be expected given the comparable iron contamination.

While it is expected that the purity of the melt at the beginning of a new RCz-Si process should be of the same purity, variations may occur. One possible reason for variations could be the initially present impurity concentrations of the melt which is usually put together by recycled materials and relatively pure poly-Si. This could lead to different initial amounts of LeTID defects already present in the beginning of the process and therefore altered observed $\Delta N_{\text{leq,max}}$ when comparing process A and B.

As shown in Figure 3.7, the τ_{eff} , ΔN_{leq} , and ΔN_{leq}^* of PDT-treated samples closely follow the defect kinetics of untreated samples, suggesting that the defect cannot be effectively gettered with the applied PDT. While slight changes in surface passivation may occur, the evolution of bulk defects remains largely unchanged. Comparing the degradation extents in Figure 3.7 with the

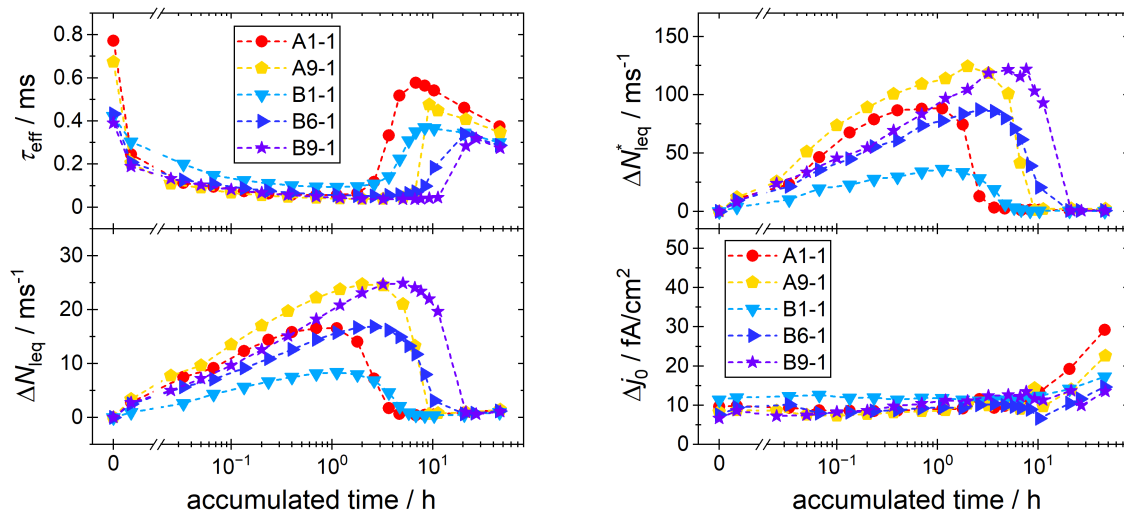


Figure 3.8: Change in τ_{eff} , ΔN_{leq} , ΔN_{leq}^* and Δj_0 during treatment under 1 sun at 130°C for seed-position wafers without PDT, matched by thickness. Adapted from [127].

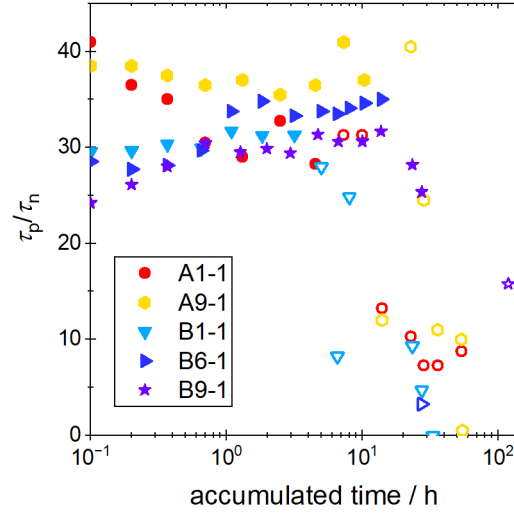


Figure 3.9: Defect specific τ_p/τ_n for all samples from Figure 3.7 without an additional PDT. Open symbols indicate data points with $\Delta N_{leq} < 4 \text{ ms}^{-1}$, where the fit does not yield reliable results. Reproduced from [127].

calculated iron concentrations in Figure 3.5b shows that ingots with higher Fe_i concentrations also exhibit increased degradation. However, in PDT-treated samples, Fe_i is reduced while degradation remains essentially unchanged, indicating that interstitial iron is not involved in LeTID. Other Fe species, e.g., bound in complexes and not removed by PDT, could still contribute to the defect reaction.

Assuming a deep-level defect species, the injection-dependent data from Figure 3.7 can also be used to evaluate the defect-specific ratio τ_p/τ_n .

Figure 3.9 shows the resulting τ_p/τ_n ratio for seed-position samples during LeTID testing. Reliable values are obtained only once sufficient defects have formed, as discussed in Section 2.3.2. Ratios for samples matched in thickness show similar behavior and are omitted for clarity. The symmetry factor τ_p/τ_n ranges from approximately 27 to 37 after 1 h, consistent with previous LeTID reports [39].

The bulk-related degradation can therefore be attributed to the LeTID defect for all samples, independent of impurity concentrations. Since the degradation extent is increased for subsequently pulled ingots, it seems reasonable to assume that more LeTID defects or precursors have accumulated due to melt recharging.

Iso-Injective Illumination

As mentioned before, a noticeable shift in the time required to reach maximum degradation extent $\Delta N_{leq,max}$ is evident in Figure 3.7 for subsequently pulled ingots. However, the effective

lifetime varies between samples, particularly as degradation approaches its maximum extent $\Delta N_{\text{leq,max}}$, implying varying injection under constant generation conditions applied during treatment.

Both LeTID-related degradation and regeneration in B-doped material are known to slow down with lower injection [88], suggesting that the observed delayed development of maximum degradation extent and the extent itself could be side effects of the (partially degradation-related) injection mismatch between samples. It is not completely trivial to argue that despite changing kinetics throughout the treatment, the observed maximal degradation extent should not be influenced by it. Therefore, another treatment is performed at a constant injection $\Delta n = 1.5 \cdot 10^{15} \text{ cm}^{-3}$, using an 805 nm wavelength laser with adjustable power, widened to cover the entire sample using a beam homogenizer. During iso-injective illumination, the laser is adjusted to maintain a constant injection $\Delta n \approx 0.1 \cdot p_0$ in the bulk of the sample [88]. To determine the generation needed to maintain constant injection in the sample throughout the treatment, the effective lifetime must be monitored separately at the treatment temperature of 130 °C.

For samples of ingots B1 and B9, the evolution of τ_{eff} , ΔN_{leq} , ΔN_{leq}^* and Δj_0 during iso-injective treatment at 130 °C is shown in Figure 3.10. The maximal degradation extent aligns with that observed previously in Figure 3.7 with B9 showing a significantly higher $\Delta N_{\text{leq,max}}$ compared to B1. In spite of that, regeneration occurs more rapidly, particularly for B9. Thus, the maximum degradation extent occurs roughly at the same accumulated time despite having a factor of 4 difference in $\Delta N_{\text{leq,max}}$. In this case, the data can be fitted with one exponential function for

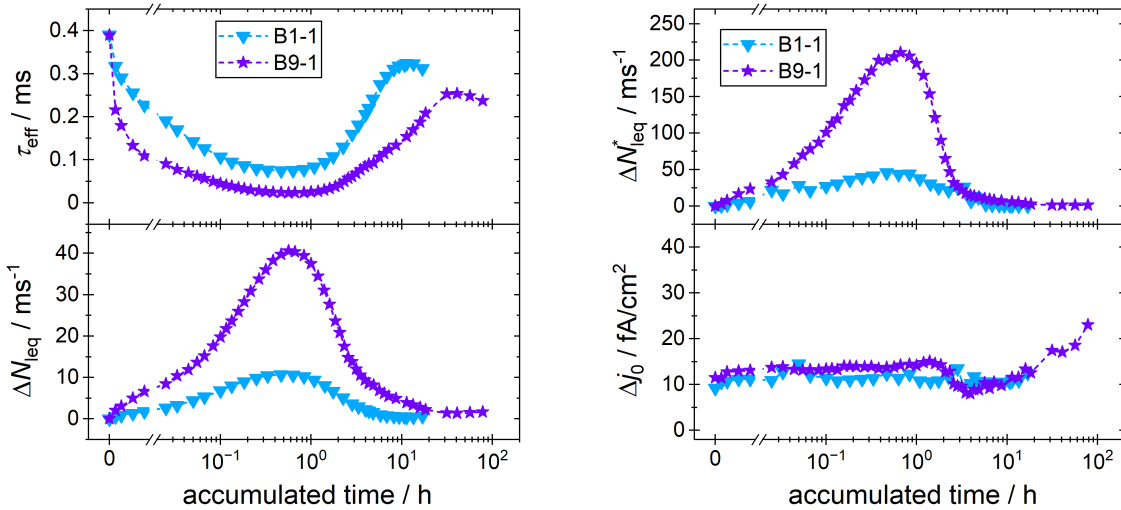


Figure 3.10: Change τ_{eff} , ΔN_{leq} , ΔN_{leq}^* and Δj_0 for seed-position wafers from the first and last ingot of process B at a constant charge carrier injection of $\Delta n = 1.5 \cdot 10^{15} \text{ cm}^{-3}$ and a temperature of 130 °C. Adapted from [127].

degradation and regeneration each.

Thus, it can be concluded that the delayed occurrence of maximum degradation extent in Figure 3.7 under iso-generative conditions is primarily due to an injection mismatch which becomes more pronounced as more defects form. Conversely, the observed difference in $\Delta N_{\text{leq,max}}$ remains almost the same even under iso-injective conditions, indicating consistent behavior as in Section 3.2.3. These results underscore that the defect formation rate is primarily dictated by the injection level rather than the applied generation. Consequently, comparisons between samples with varying initial carrier lifetimes or defect densities may yield differing defect formation rates.

3.2.4 Correlation of LeTID with Hydrogen and Impurities

So far, the accumulation of impurities is discussed separately from the observed lifetime equivalent defect densities. In order to check a correlation between hydrogen concentrations and impurity concentrations, the maximum of bulk-related lifetime equivalent defect density $\Delta N_{\text{leq,max}}^*$ for all samples that did not receive an additional PDT are plotted respective to the corresponding calculated interstitial iron concentrations in Figure 3.11a. Samples that did receive a PDT are excluded because the interstitial iron concentration itself did not influence LeTID, reducing the clearance of the graph.

Even though iron contamination can be very low, around 10^9 cm^{-3} as it is observed in Figure 3.5b, LeTID can still be observed. While interstitial iron was already sorted out as a possible candidate for the formation of LeTID defects, it can still serve as a tracker for other impurities that accumulate during the RCz-Si crystal growth. However, this can only work if no measures such as a PDT are taken to reduce iron contamination. By performing an effective gettering treatment for iron, insight about species with similar segregation coefficients as iron are lost. While there is still the possibility that other gettering treatments could also reduce the amount of the LeTID related defect species, the applied treatment in this work did not have any effect. Since the measured iron concentrations are close to realistically detectable iron concentrations with this technique and observed $\Delta N_{\text{leq,max}}^*$ are not close to zero, there might be a range where iron will not be usable as a tracker for other species that accumulate.

A linear fit is applied to all samples except for A9-3 to highlight the linear relationship between accumulated interstitial iron and the observed degradation extent. This linear trend does not seem to be able to describe the observed defect density in the tail part of ingot A9. It is possible that hydrogen becomes a limiting factor in this case. Furthermore, an offset appears to be present, as the linear trend suggests that measurable degradation occurs even when hardly any interstitial iron can be detected. In the most trivial case, one would expect the

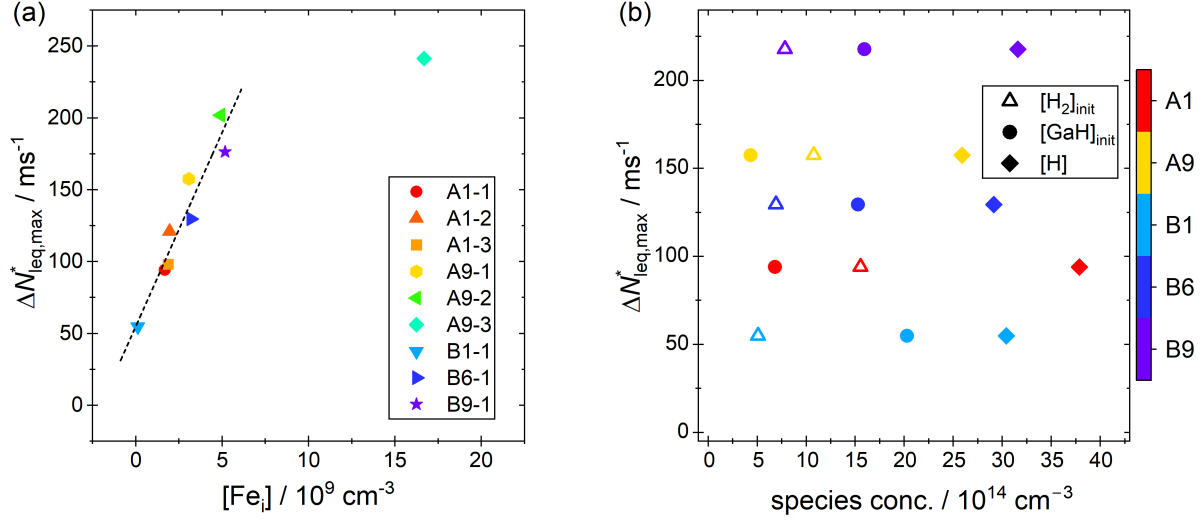


Figure 3.11: (a) Correlation between the maximum bulk-related lifetime equivalent defect density and the corresponding calculated interstitial iron concentrations for samples from all ingot positions investigated that did not receive an additional PDT. (b) Relationship between $\Delta N_{leq,max}^*$ and the concentrations of $[\text{H}_2]_{init}$, $[\text{GaH}]_{init}$ and $[\text{H}]$ for all seed wafer positions. Panel (b) is adapted from [127].

linear fit to pass through the origin, with no observable degradation in the absence of defects. A possible explanation for this offset could simply be the choice of parameter used for the calculation. Depending on the selected parameter, the absolute values may shift while the overall trends remain unaffected. Of course, the case may not be trivial, allowing for more complex dependencies than the simple linear correlation assumed here.

To investigate the correlation between hydrogen concentration and LeTID, resistivity samples were prepared from the seed wafers of processes A and B using the method described in Section 2.3.4. This allowed for the evaluation of total hydrogen concentration and the initial distribution of $[\text{H}_2]$ and $[\text{GaH}]$.

Figure 3.11 illustrates the correlation between the initial hydrogen dimers, GaH pairs and the corresponding total hydrogen in the non-gettered samples from seed positions of all investigated ingots and their corresponding $\Delta N_{leq,max}^*$, as shown in Figure 3.7. Samples from process A exhibit higher $[\text{H}_2]_{init}$ levels compared to those from process B, likely due to lower doping concentrations, which results in fewer initial GaH pairs. This difference in hydrogen concentration may explain the higher $\Delta N_{leq,max}^*$ observed in A1-1 compared to B1-1, as previously discussed in Section 3.2.3.

The doping concentration affects the formation of GaH during the cooling process of rapid thermal anneal, which in turn could reduce the initial amount of H_2 and lead to lower degradation extents. However, for samples originating from the same RCz-Si process, the increase in

$\Delta N_{\text{leq,max}}^*$ cannot be attributed to a higher hydrogen content introduced into the silicon bulk during firing, as $[\text{H}_2]_{\text{init}}$ shows only a slight increase in process B, while a strong increase in degradation extent is observed. In process A, even a decrease in $[\text{H}_2]_{\text{init}}$ is observed, accompanied by an increase in $\Delta N_{\text{leq,max}}^*$ for the last pulled ingot. There is no clear correlation between the hydrogen content and the degradation extent. Therefore, the rise in $\Delta N_{\text{leq,max}}^*$ is likely related to different defect species, which accumulates during crystal growth.

3.3 Conclusions

The analysis of electronic properties using wafers from two recharged Cz-Si processes (five ingots in total) revealed interstitial iron concentrations ranging from $1 \cdot 10^9 \text{ cm}^{-3}$ to $1.7 \cdot 10^{10} \text{ cm}^{-3}$. The $[\text{Fe}_i]$ is hereby increased in wafers from subsequently pulled ingots. For wafers with elevated iron levels, phosphorus diffusion treatment (PDT) effectively reduced iron concentrations.

Accelerated long-term stability testing showed the PDT used in this study did not significantly influence the observed maximum lifetime equivalent defect density. Notably, $\Delta N_{\text{leq,max}}^*$ increased with higher ingot numbers, likely due to accumulating impurities or crystal defects in later-stage ingot pulls. The responsible defect matches literature-reported LeTID characteristics, showing a defect-specific τ_p/τ_n ratio between approximately 27 and 37.

Iso-injective treatments revealed that delayed maximum degradation extent in higher-numbered ingots during iso-generative treatment stems from reduced injection levels leading to a delayed regeneration. However, these delayed kinetics did not affect the ultimate maximum degradation extent.

While $[\text{H}_2]_{\text{init}}$ typically correlates with LeTID degradation severity in affected samples, this study found no such correlation with degradation extent. This suggests the observed $\Delta N_{\text{leq,max}}^*$ increase results from impurity/defect accumulation in later RCz-Si ingots, consistent with the correlation between $\Delta N_{\text{leq,max}}^*$ and $[\text{Fe}_i]$. The applied PDT showed no significant effect on maximum lifetime equivalent defect densities.

In summary, these results emphasize that with current materials produced via the RCz process, impurity levels and maximum LeTID related defect densities may vary depending on the specific ingot from which the investigated material is sourced. Therefore, any comparison of RCz-Si should be approached with caution if this specific information is missing. The findings also show that hydrogen content alone does not fully explain LeTID behavior and the concentration of an unknown reaction partner appears linked to material quality.

For solar cell manufacturing, this variation presents a practical challenge. While dopant distri-

butions can be maintained consistently across different ingot pulls, as discussed in Section 3.1, cells fabricated with identical base resistivities but differing impurity levels may experience different LeTID degradation extents. Even when initial performance appears equivalent, this difference in degradation could lead to reduced module performance over time. Yet, precise control of the hydrogenation during firing and the choice of passivation layers could cover these downsides as it will be further discussed in Chapter 5.

The monitoring of impurity accumulation through iron tracking, while valuable, is limited by the inability to distinguish between impurities exhibiting segregation coefficients of $k \ll 1$. This limitation prevents the extraction of specific information regarding potential LeTID defect precursors. To address this constraint, the influence of different high-temperature processing treatments such as PDT on degradation behavior could be systematically examined. Hereby, the focus should be the correlation of certain temperature regimes that could lower the observed defect concentration during LeTID testing. Further, the phenomenon could be characterized across a wider range of materials, including n-type Cz-Si, as will be presented in the following Chapter 4.

4 LeTID in n-Type Silicon

Degradation during prolonged exposure to elevated temperature and illumination is not limited to p-type material but has also been observed in n-type Cz-Si, as discussed in Section 1.4.2. Overall, the degradation in n-type material has not been extensively studied so far since the market share of cell architectures using n-type wafers was comparatively low. Until recently, the solar industry was dominated by p-type silicon, but a rapid shift toward n-type Cz-Si solar cell architectures has occurred [222].

At first glance, the degradation extent observed by ΔN_{leq} in n-type material appears significantly smaller than in p-type. Some architectures based in n-type base materials require higher lifetimes to ensure efficient charge carrier collection at the contacts [229]. With more advanced surface passivation techniques (e.g. passivating contacts that will be discussed in Section 5.2), the bulk material quality becomes more relevant [230]. Consequently, even a less pronounced degradation of bulk lifetime may be harmful for such devices.

Caused by the adoption of melt recharging in the photovoltaic industry, the impact of impurity accumulation on defect formation during light and elevated temperature treatment has become of increased interest. Additionally, the leading wafer producer for photovoltaic applications (Longi), has transitioned to producing n-type doped Cz-Si using antimony instead of the traditionally employed phosphorus [228]. So far, LeTID studies on n-type material have almost exclusively been carried out on P-doped material, raising the question of how defect kinetics behave in Sb-doped materials.

In Section 4.1, a fundamental investigation of the reaction kinetics is presented, using a qualitative analysis based on a three-state defect model to describe the degradation process.

Building on this foundation, Section 4.2 applies the acquired insights into defect evolution to evaluate the degradation extent during LeTID testing of phosphorus-doped and antimony-doped RCz-Si. The correlation between impurity accumulation and the extent of degradation is examined, followed by a discussion on the influence of high-temperature processing on long-term stability.

4.1 Distribution of Defect States during LeTID

This section discusses LeTID in n-type Cz-Si using a three-state defect model analogous to that proposed for LeTID in p-type Si [69]. The model describes a defect in one of three states: annealed (A), degraded (B) or regenerated (C) following the reaction scheme $A \rightleftharpoons B \rightleftharpoons C$. States A and C are assumed to exhibit little or no recombination activity, while state B is recombination-active. Thus, degradation corresponds to transitions $A \rightarrow B$, whereas regeneration involves transitions $B \rightarrow C$. The total defect density $[N_{\text{total}}]$ is conserved, satisfying

$$[A] + [B] + [C] = [N_{\text{total}}] \quad \text{and} \quad \frac{[A] + [B] + [C]}{[N_{\text{total}}]} = N_A + N_B + N_C \quad (4.1)$$

where N_A , N_B and N_C are normalized densities [32].

In general, transitions between different defect states are described by their respective reaction rates as

$$\frac{d}{dt} \underline{N} = \hat{\lambda} \cdot \underline{N} \quad (4.2)$$

by the use of a conversion state matrix $\hat{\lambda} \in \mathbb{R}^{3 \times 3}$ and the state vector $\underline{N} = (N_A, N_B, N_C)^T \in \mathbb{R}^3$ [32]. For example, a coefficient λ_{AB} describes the reaction rate between state A and B and could be used to describe the change in the corresponding defect states by

$$\frac{d}{dt} N_A = -\lambda_{AB} \cdot N_A + \lambda_{BA} \cdot N_B = -\frac{d}{dt} N_B \quad (4.3)$$

For simplicity, only the transition between states N_A and N_B is considered, while the transition to state N_C is neglected. Without the consideration of any injection dependence of λ_{AB} the above equation can be solved by separation of the variables and integration with the solution being proportional to exponential decay functions [32]. For LeTID in p-type, these reaction rates are known to depend not only on temperature but also on injection and hydrogen concentrations.

The experiments presented here focus on the reversibility of the partial reaction $A \rightleftharpoons B$ under varying treatment conditions. The goal is to qualitatively assess the reaction equilibrium without requiring quantitative knowledge of specific reaction rates, as these are more challenging to determine and demand precise control over injection conditions in the sample.

Sample preparation was performed on uncompensated phosphorus-doped n-type Cz-Si wafers with base resistivities ranging from $0.7 \, \Omega \, \text{cm}$ to $6 \, \Omega \, \text{cm}$. The wafers were processed according to Section 2.2.1, followed by $\text{SiN}_x\text{:H}$ deposition and firing. Experiments were conducted on different materials to demonstrate that the observed behavior is not material-specific but occurs across various wafers produced in different years (different impurity content) and with varying dopant concentrations. The measurements discussed in the following were performed during a

Bachelor thesis supervised by the author [231].

4.1.1 Impact of Light Soaking on LeTID Testing

In a first approach, samples were tested for long-term stability under identical conditions to those used for p-type sample evaluation. Figure 4.1 shows the evolution of effective lifetime and ΔN_{leq} for two samples with 6 Ω cm resistivity. The middle graphs show LeTID testing at 130°C, while the outer graphs depict light soaking treatments at 20°C and 2 suns. One sample underwent direct testing after firing (circles), while the other received a light soaking treatment (open triangles), as visible in the left graphs. Both samples were subsequently subjected to additional light soaking after the LeTID testing phase.

During LeTID testing, significant degradation is observed only in the light-soaked sample, though both ultimately reached comparable regenerated lifetime levels. Notably, a negative defect density of -0.6 ms^{-1} occurs, indicating that more defects vanished than initially formed. Following bulk lifetime regeneration and the onset of SRD after approximately 2 h of LeTID testing, both samples exhibit exceptional stability during the subsequent light soaking treatment (right graphs), with minimal lifetime variations throughout the testing period.

The initial light soaking treatment reveals the emergence of an additional defect that limits effective lifetime most significantly after approximately ~ 30 min of illumination before subsequently regenerating. A rapid lifetime increase is also observed within the first 30 s of treatment. Notably, this characteristic behavior appears both during initial light soaking and during LeTID testing when no prior light soaking has been applied. The additional defect occurring after ~ 30 min of light soaking is examined in greater detail in Section 4.1.2.

Overall, the lifetime during light soaking (left graph) stabilizes after ~ 24 h of illumination, which appears related both to the regeneration of this transient defect and the equilibrium between states $A \leftarrow B$. This observation supports the hypothesis that after firing, defects initially exist in a mixture of states A and B , predominantly in the recombination-active state B , as previously proposed in [139]. After light soaking, most defects transition to state A , leading to the steep reduction of τ_{eff} during subsequent LeTID testing (middle graph) through $A \rightarrow B$ transitions. However, this model cannot explain the initial rapid lifetime increase observed during both light soaking and LeTID testing without prior light soaking.

From the previous experiment, prolonged light soaking is expected to shift more defects toward state A . The impact of varying this parameter in subsequent LeTID testing is shown in Figure 4.2a through the lifetime-equivalent defect density for material with 0.7 Ω cm base resistivity. For all light soaking durations, ΔN_{leq} during LeTID testing is referenced to the post light soaking lifetime.

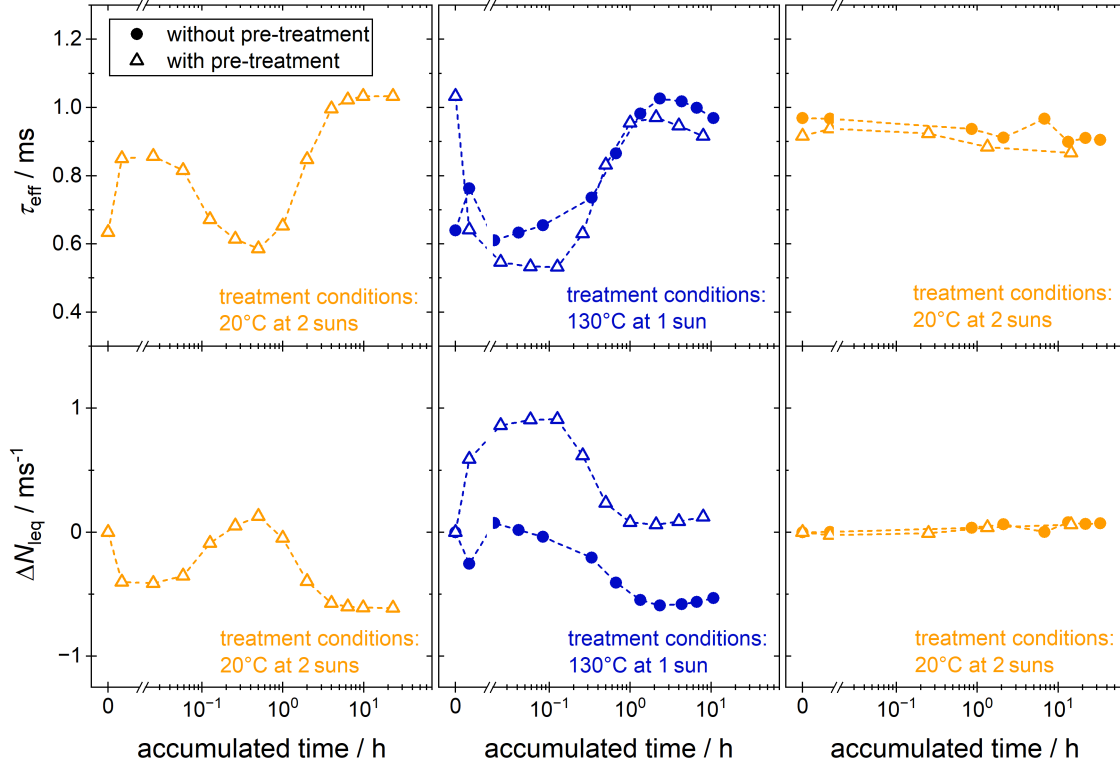


Figure 4.1: Development of τ_{eff} and ΔN_{leq} during LeTID testing (middle graph) without (closed circles) and with (open triangles) prior light soaking at 20 °C and a photon-flux equivalent of 2 suns (left graphs) for 6 Ω cm n-type Cz-Si. In both cases, light soaking at 20 °C is continued (right graphs) after most defects are regenerated and SRD begins to dominate. Blue color indicates LeTID testing and orange indicates light soaking treatments. Adapted from [231].

Notably, regeneration appears strongest without prior light soaking, as previously observed in Figure 4.1, with the fast initial regeneration diminishing as light soaking duration increases. For durations up to 200 s, regeneration dominates. Longer light soaking leads to visible degradation. After 13 h of light soaking, when lifetimes stabilize, subsequent LeTID testing yields more pronounced degradation. In all cases, regeneration becomes dominant around ~ 1 h, while SRD emerges after ~ 10 h of treatment, marked by renewed ΔN_{leq} increase and (not shown here) significant j_0 rise.

Figure 4.2b displays the effective lifetime parameters before light soaking (τ_0), after light soaking (τ_{ill}), and after regeneration during LeTID testing (τ_{reg}). The data show that τ_{reg} remains remarkably consistent across all samples, independent of light soaking duration, confirming the earlier observation in Figure 4.1. Notably, lifetimes are substantially lower than in previous experiments, which can most likely be attributed to the higher doping concentration in these samples.

Examining τ_{ill} more closely reveals no discernible minimum, unlike the light-soaking behavior shown in Figure 4.1. However, lifetime regeneration slows after ~ 0.02 h of treatment, potentially

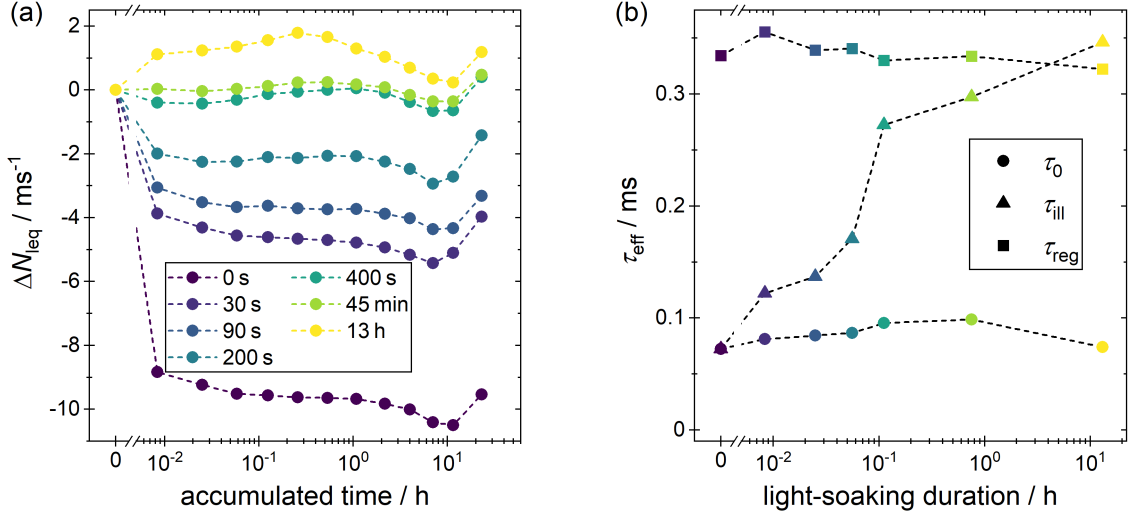


Figure 4.2: (a) Lifetime equivalent defect density ΔN_{leq} during LeTID testing for samples with a base resistivity of $0.7 \, \Omega \, \text{cm}$ subjected to varying durations of prior light soaking. (b) Effective carrier lifetimes before light soaking (τ_0), after light soaking (τ_{ill}) and following LeTID testing (τ_{reg}). The corresponding LeTID testing is shown in (a) using the same color code. Adapted from [231].

due to the formation of an additional defect as previously discussed.

Within the 3-state model framework, the ΔN_{leq} increase suggests that extended light soaking promotes more frequent $A \leftarrow B$ transitions, thereby enhancing the subsequent $A \rightarrow B$ conversion capacity during LeTID testing [231]. Light soaking appears to preferentially drive $A \leftarrow B$ transitions, while LeTID testing first induces $A \rightarrow B$ followed by $B \rightarrow C$ transitions. Consequently, greater accumulation of defects in state A during light soaking leads to more severe subsequent degradation at elevated temperatures, which is consistent with the observations in Figure 4.1.

4.1.2 Temporary Recovery by Light Soaking

The first two experiments indicate that it is possible to transition defects $A \leftarrow B$ through light soaking at low temperatures and $A \rightarrow B$ during LeTID testing at elevated temperature. To explicitly verify the reversibility of the partial reaction $A \rightleftharpoons B$, an additional cyclic experiment was performed, subjecting a sample to alternating light soaking and LeTID testing phases. Degradation beyond the maximum of ΔN_{leq} is carried out three times in a way that regeneration occurs but is not fully complete.

The resulting τ_{eff} , ΔN_{leq} and j_0 for these experiments are shown in Figure 4.3 with the sample initially being exposed to light soaking before the exposure to LeTID testing. Lifetime after this

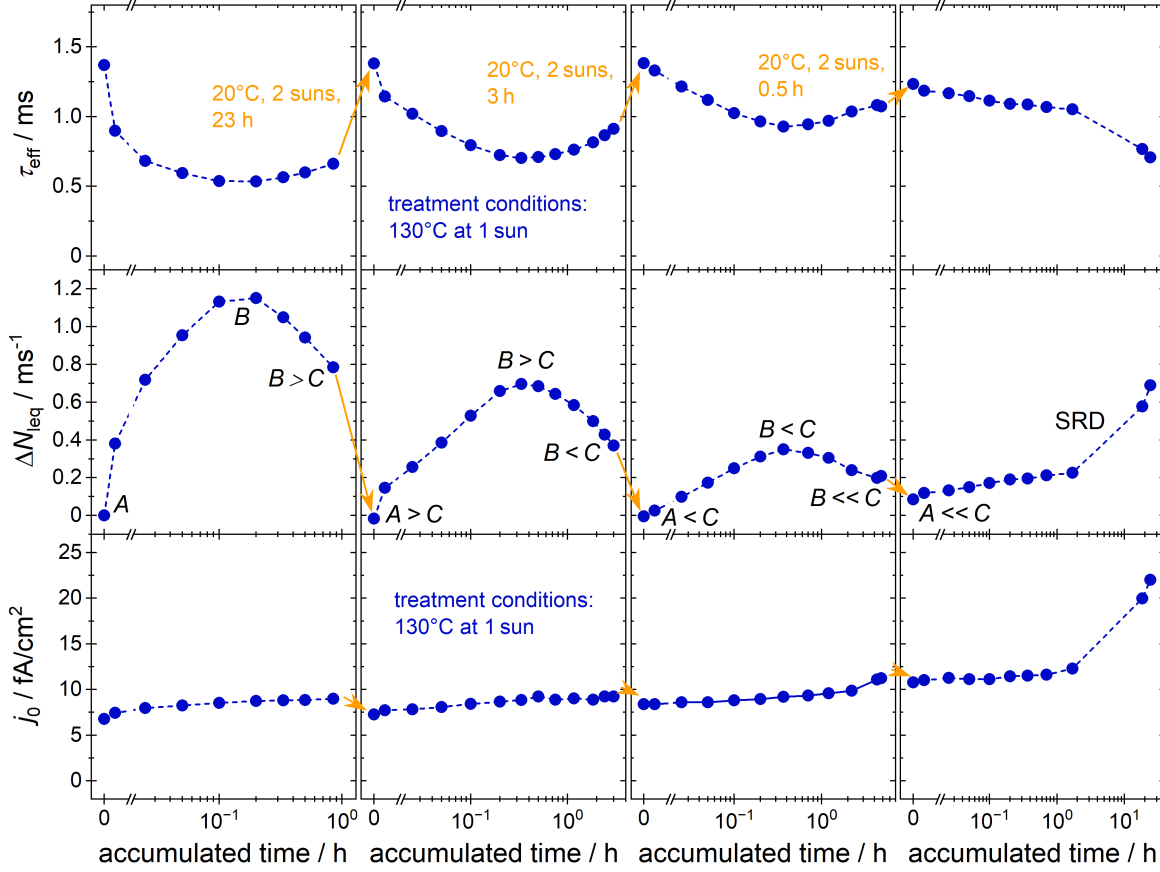


Figure 4.3: Evolution of τ_{eff} , ΔN_{leq} and j_0 of a 1.1 Ω cm n-type Cz-Si sample during LeTID testing beyond the point of maximum defect density, followed by light soaking at 20 °C under 2 suns. The cycle of LeTID testing (blue) and light soaking (orange arrows) is repeated three times until no further bulk degradation occurs, after which only SRD is observed. The first data point in the left graph corresponds to the sample after an initial light soaking for 24 h. This sample underwent an additional tabula rasa treatment followed by a PDT. Adapted from [231].

initial light soaking serves as the reference point for calculation of ΔN_{leq} . It should be noted that the light soaking duration (orange arrows) does not indicate the actual illumination time but the time until lifetime is constant. To make sure that lifetime is stabilized, measurement points beyond the annealing duration are recorded.

Notably, after each LeTID testing and subsequent light soaking, lower maximum extents of ΔN_{leq} are reached. With each degradation beyond $\Delta N_{\text{leq,max}}$, a reduction in degradation extent during the following LeTID testing is observed. As more defects transition $B \rightarrow C$, the required light soaking duration to achieve a stable lifetime decreases. This behavior cannot be explained by the simple approach presented in Section 4.1, as the timescale would be expected to be independent from the observed amplitude. The most plausible explanation is that the coefficient for the temporary recovery during light soaking, λ_{BA} , strongly depends on the injection level. Alternatively, the system may not be adequately described by this simplified equation, and a

more complex dependency might be required.

It appears that defects which have transitioned to the regenerated state C are recombination-inactive and cannot be re-activated during subsequent light soaking. In the graph on the right the majority of defects are in state C and only slight degradation can be observed until SRD is dominating (increase in j_0) after ~ 3 h of LeTID testing. Lifetime is only slightly degrading throughout this last LeTID testing because barely any defects are left in state A that can transition towards state B . During the first three LeTID testing treatments shown in Figure 4.3 it can be seen that lifetime is approximately the same after each light soaking treatment. Thus, state C seems to be equally non-recombination active as state A .

At this stage, key observations regarding SRD merit summary. The initial LeTID testing reveals a minor j_0 increase, followed by surface passivation recovery (to $j_0 \sim 7 \text{ fA cm}^{-2}$) after subsequent light soaking. This cyclic behavior repeats after each LeTID treatment and light soaking sequence. Notably, a slight increase in j_0 is observed during each cycle of LeTID testing.

This phenomenon may stem from prior $B \rightarrow C$ transitions during earlier LeTID testing. A species (e.g. hydrogen) previously involved in LeTID mechanisms could now contribute to SRD by migrating to the surface and altering surface charge, thereby degrading passivation. Since only a fraction of defects reach state C , SRD's impact remains limited initially. However, once most defects transition to C , j_0 rises markedly after ~ 3 h of LeTID testing. This delayed onset suggests that SRD precursors require time to diffuse to the surface following light soaking. In summary, these findings demonstrate that defects remaining outside state C can undergo unlimited $A \rightleftharpoons B$ transitions [231].

4.1.3 Proposed Three-State Models

The discussion has thus far focused on the primary defect observed during LeTID testing. However, equal consideration must be given to the additional defect observed during light soaking, as shown in the left panels of Figure 4.1. To investigate this secondary defect, another experiment is performed with samples subjected to light soaking (left), followed by LeTID testing until most defects reach state B (middle) and successive light soaking (right) similar to the experiment in Figure 4.3. The resulting ΔN_{leq} is shown in Figure 4.4 with ΔN_{leq} being referenced to the as-fired lifetime.

At this stage, an additional three-state defect model comprising states A' , B' , and C' is introduced to characterize the secondary defect. The maximum population of the recombination-active state B' is observed to be reached after approximately 10 min of illumination during light soaking, consistent with the earlier results presented in Figure 4.1. The subsequent LeTID testing is maintained until the majority of defects have transitioned to state B , with the degradation

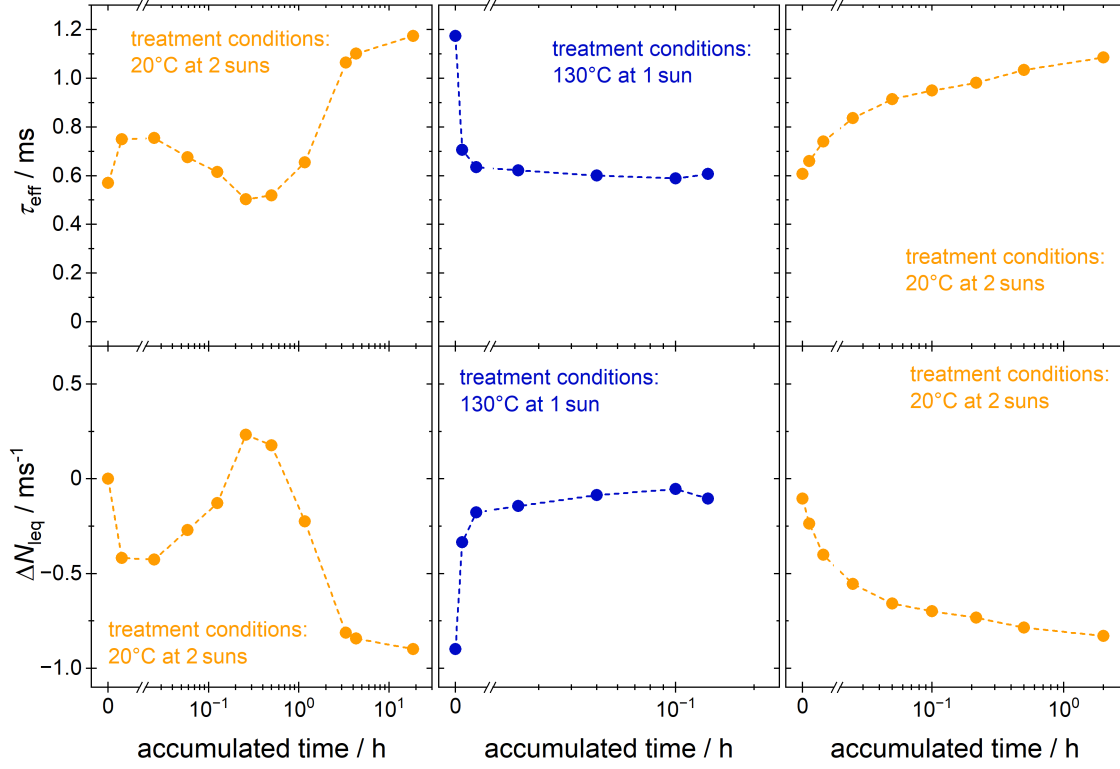


Figure 4.4: Evolution of τ_{eff} and ΔN_{leq} for a 6 Ω cm n-type Cz-Si sample during subsequent light-soaking (orange) and LeTID testing (blue). Adapted from [231].

extent slightly surpassing the maximum degradation point. During the following light soaking phase (right graph), transitions between states $A \leftarrow B$ are observed until lifetime stabilization is achieved, reaching values comparable to those obtained after the initial light soaking treatment.

During this annealing phase, no occurrence of the additional defect is observed. This absence suggests that regeneration (transition $B' \rightarrow C'$) may have occurred following the initial light soaking treatment, with the resulting state C' remaining stable throughout subsequent LeTID testing. These observations indicate that isolation of the primary LeTID defect from the secondary light soaking defect can potentially be achieved through complete regeneration ($B' \rightarrow C'$). However, isolation of the secondary defect itself appears more complex and would require more thorough characterization of the corresponding transition kinetics.

In principle, defect characterization through SRH-formalism could provide defect-specific parameters including the symmetry factor τ_n/τ_p and corresponding energy levels within the bandgap. However, as discussed in Section 1.2.3, such analysis proves problematic for the observed defects. The primary challenge lies in the clear differentiation between variations in surface passivation quality and modifications of bulk defects, particularly given their relatively weak injection-dependence in the lower injection regime. As discussed with Figure 1.2, this

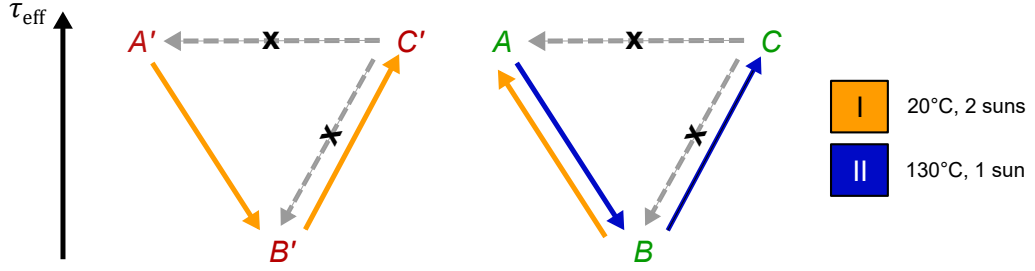


Figure 4.5: Two 3-state defect models illustrating defect evolution during long-term stability experiments of n-type Cz-Si. The left model with states A' , B' and C' represents the defect primarily observed during light soaking at 20 °C. The right model shows states A , B and C , with transitions between $A \rightleftharpoons B$ depending on the treatment conditions. Gray arrows indicate transitions that have not been observed under the applied experimental conditions.

limitation has thus far prevented the acquisition of reliable quantitative data. Consequently, the defect kinetics are described herein using a qualitative approach.

From these experimental results, several conclusions regarding the three-state model can be drawn. First, it is observed that LeTID-defects present after firing exist in a mixed configuration of states A and B . The relative population of these states may be influenced by processing parameters such as firing temperature and cooling rate. For the specific firing conditions employed in this work, state B appears to be preferentially populated in n-type material. The observed behavior during both light soaking and LeTID testing is best explained through two distinct three-state models, as illustrated in Figure 4.5. This separation of models accounts for the different defect dynamics observed under these two experimental conditions.

As previously indicated, transitions between states $A \leftarrow B$ are observed during light soaking, while elevated temperatures predominantly induce degradation followed by subsequent regeneration ($A \rightarrow B \rightarrow C$). The regenerated state C is found to remain stable under the employed treatment conditions. However, a single three-state model proves insufficient to fully describe the experimental observations in this work.

An additional defect system is identified, being particularly evident during light soaking treatments but potentially occurring during LeTID testing if not previously regenerated. This secondary defect system is characterized by states A' , B' , and C' . As discussed in Section 4.1.2, the regenerated state C' appears stable under the present experimental conditions. Nevertheless, complete separation of this additional defect system from the primary LeTID defect system remains uncertain based on the current data. Under the specific conditions employed in this investigation, clear separation of these defect systems could not be achieved.

For subsequent investigations of n-type Cz-Si, the findings from this section will be utilized to achieve at least partial separation between the additional defect system and LeTID through implementation of initial light soaking treatments. This approach offers two significant ad-

vantages for quantitative analysis of the LeTID cycle ($A \rightarrow B \rightarrow C$). First, the maximum degradation extent can be determined more reliably when referenced to the post-light soaking state rather than the as-fired condition. This eliminates potential variability introduced by differing initial distributions of defects between states A and B across samples. Second, while referencing ΔN_{leq} to the fully regenerated state C might appear advantageous, this method is complicated by the concurrent onset of surface-related degradation. The SRD phenomenon obscures the true regenerated bulk lifetime, making the post light soaking reference (state A) a more robust reference to calculate $\Delta N_{\text{leq,max}}$.

4.2 LeTID in n-Doped RCz-Si

As demonstrated in Chapter 3, an increase in ΔN_{leq} has been observed in Ga-doped RCz-Si with each successive crystal pull and across multiple pulls following melt recharging. This correlation suggests a relationship between LeTID defect density and accumulating impurity concentrations [127]. Given that similar impurity accumulation is expected during RCz-Si growth with n-type dopants, the current investigation focuses on industrial-grade P-doped and Sb-doped wafers obtained from seed positions throughout RCz-Si processes, with particular emphasis on their excess carrier lifetime stability. Hereby, it is of interest whether the extent of the LeTID defect does also correlate with the accumulated impurity as well. Additionally, the influence of high-temperature processing steps like tabula rasa and a phosphorus diffusion treatment (PDT) on Sb-doped Cz-Si regarding long-term stability is evaluated.

In contrast to the RCz-Si process previously described for gallium doping, the dopant incorporation for n-type material can be different. If the incorporation of dopants is governed solely by segregation, the following considerations can be applied. Phosphorus ($\kappa_{\text{P}} = 0.35$ [225]) exhibits segregation characteristics that differ from both boron and gallium. Nevertheless, relatively tight resistivity distributions can still be achieved in melt-recharged Czochralski growth through the pulling of shorter ingots. Antimony demonstrates segregation behavior nearly identical to gallium, despite possessing a slightly higher segregation coefficient ($\kappa = 0.023$ [225]). The calculated dopant concentrations presented in Figure 4.6a for 90 % solidified fraction reveal that significantly tighter resistivity distributions would be obtained for all dopants except boron when shorter ingots are pulled.

For phosphorus, the incorporation is mainly governed by the segregation. In contrast, antimony exhibits significant volatility, leading to evaporation from the melt that alters the expected segregation-based incorporation. In modern RCz-Si growth processes, precise control of Sb evaporation is achieved through careful regulation of chamber pressure and gas flow rates. This controlled environment enables either compensation or over-compensation of segregation

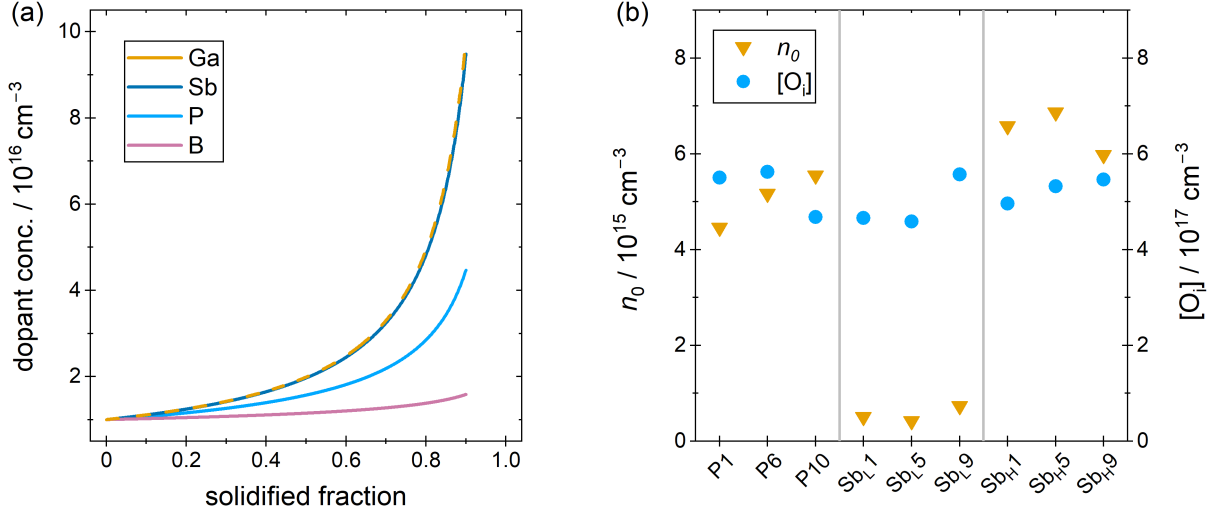


Figure 4.6: (a) Calculated dopant concentrations for B, Ga, P and Sb along a crystal assuming an initial concentration $C_{S0} = 1 \cdot 10^{16} \text{ cm}^{-3}$ and a solidified fraction of 90 %, derived using Equation (3.1). Ga data is shown with a dashed line for clarity. (b) Comparison of n_0 and $[O_i]$ for seed-position samples of three different RCz-Si processes. One process uses P-doping, while the other two use Sb-doping with different resistivity ranges. The number in the x-axis label indicates the ingot sequence during RCz-Si growth. Graph (b) is reproduced from [232].

effects [228], resulting in tight resistivity distributions along the crystal ingot. Consequently, for the purposes of this investigation, Sb-doping concentration cannot be considered a reliable indicator for the accumulation of impurities characterized by $\kappa \ll 1$.

The utilization of iron as a tracer impurity is ruled out in n-type material, as the lifetime-based detection method relies fundamentally on the iron-acceptor pairing mechanism exclusive to p-type silicon. In n-type material, these pairs are not formed in sufficient concentrations to produce measurable changes in τ_{srh} . Other characterization techniques may not be able to detect such low iron concentrations. Consequently, the monitoring of impurity accumulation is more challenging in n-type materials. However, the fundamental accumulation process of impurities with $\kappa \ll 1$ still occurs in principle [219]. Based on this understanding, an increase in degradation extent would be anticipated if the defect formation mechanism in n-type material follows similar principles to that observed in p-type silicon. The findings in this chapter are mainly based on a publication which can be found in [232]^{4.1}.

^{4.1} Conceptualization, sample preparation, formal analysis and writing were carried out by the author.

4.2.1 Material Characterization

For the following experiments, $\sim 1 \Omega \text{ cm}$ P-doped and Sb-doped wafers from the seed end with two different doping concentrations from a total of three industrial RCz-Si processes are investigated. Hereby, lowly doped material $\sim 12 \Omega \text{ cm}$ (Sb_L) and material with a higher doping concentration of $0.7 \Omega \text{ cm}$ is used. An overview of the material properties is provided in Figure 4.6b, which displays both the net dopant concentration (n_0) and interstitial oxygen concentration. The $[\text{O}_i]$ values were determined through FTIR spectroscopy measurements following the ASTM F 121-83 standard protocol (see Section 2.3.5). Base resistivity values were obtained via four-point probe measurements, from which the n_0 was subsequently calculated for all specimens.^{4.2}

The interstitial oxygen concentration is found to be comparable across all samples, measuring approximately $\sim 5 \cdot 10^{17} \text{ cm}^{-3}$, which represents a slight reduction compared to the Ga-doped material shown in Figure 3.4. A progressive increase in dopant concentration is observed in subsequently pulled ingots, suggesting that the recharged material contributes additional phosphorus to the melt. For the antimony-doped ingots, concentration variations are noted throughout the RCz-Si process, primarily attributed to dopant additions during melt recharging.

Wafers obtained from the tail position of the final Sb_L process ingot were subjected to high-temperature treatments, including both tabula rasa (TR) and phosphorus diffusion treatment (PDT). These wafers exhibit similar base resistivities to those taken from the seed, indicating that Sb incorporation does not follow segregation behavior but is most likely controlled by the growth atmosphere. The TR process was performed at a peak temperature of 1050°C using either oxygen (TRO) or nitrogen (TRN) atmospheres, as detailed in Section 2.2.2.

4.2.2 Long-Term Stability Experiments

P-doped Material

First, the long-term stability behavior of the excess carrier lifetime of P-doped samples from seed positions of ingot 1, 3 and 10 of a RCz-Si process is investigated. Figure 4.7 shows the evolution of τ_{eff} , ΔN_{leq} and j_0 for LeTID testing at 130°C and 1 sun illumination directly after firing (a), and after a prior light soaking treatment at 20°C and 2 suns (b). Additionally, an iso-injective treatment at 130°C is performed for samples that received a light soaking treatment (c).

For as-fired samples (Figure 4.7a), lifetime regeneration is observed until approximately 10 h of

^{4.2} FTIR characterization and determination of sample resistivity were carried out by the Cz producer

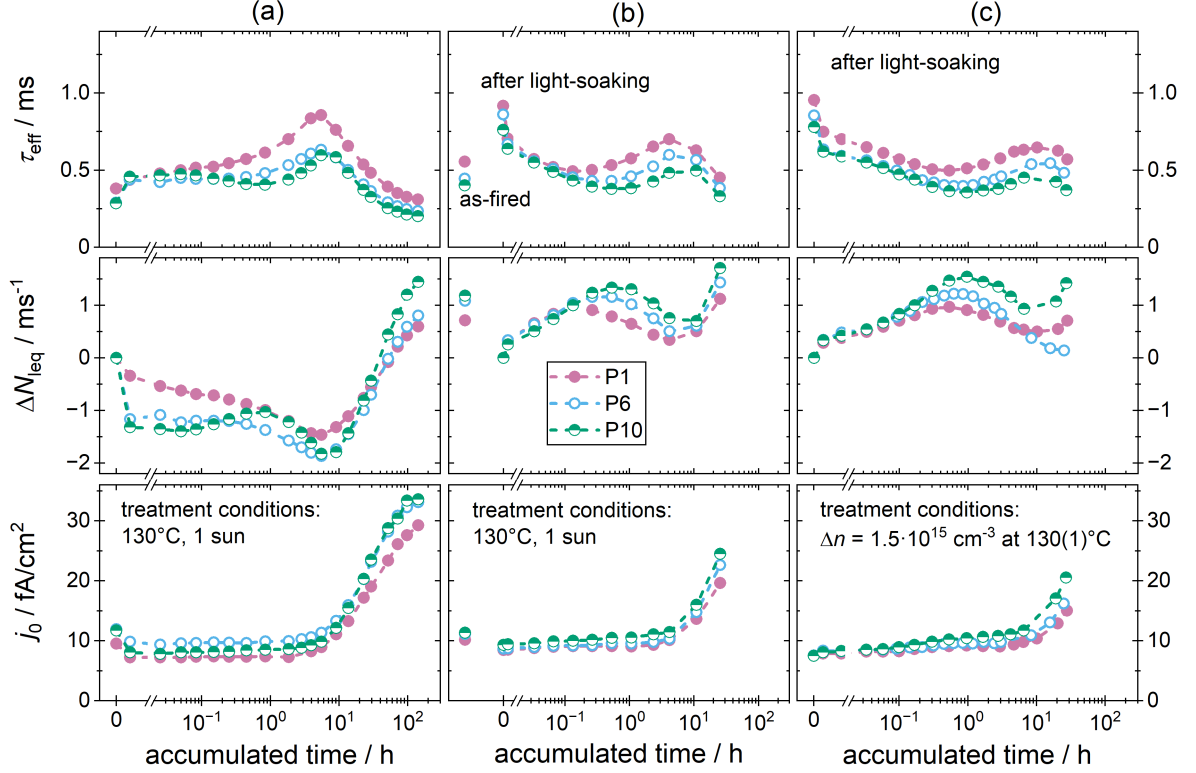


Figure 4.7: Extracted τ_{eff} , ΔN_{eq} and j_0 for P-doped samples during treatment at 130 °C under 1 sun illumination. Panel (a) shows samples measured directly after firing, (b) shows samples after light soaking at 20 °C under 2 suns, and (c) shows previously light-soaked samples subjected to an iso-injective treatment with $\Delta n = 1.5 \cdot 10^{15} \text{ cm}^{-3}$ at 130 °C. Adapted from [232].

treatment, after which degradation occurs. This subsequent lifetime reduction is attributed to surface-related degradation (SRD), as evidenced by the substantial increase in j_0 . These findings are consistent with previous observations (see Figure 4.1).

While bulk-related regeneration is observed in all samples prior to the onset of SRD, distinct short-term behaviors are noted among wafers from different ingot positions. Continuous regeneration is exhibited by the first ingot sample, whereas the final ingot sample displays slight degradation between ~ 0.1 h and ~ 1 h of treatment. For the sixth ingot sample, lifetime stagnation is observed during this interval. In this case, a comparison of degradation extent might become difficult as it is not clear which point in time would be a good reference to do so. Furthermore, certain samples lack a clearly defined degradation maximum. Thus, the previously discussed light soaking is now applied to shift defects from B to A which is accompanied with the changes in the second defect system (A' , B' and C') as discussion in Section 4.1.3.

A marked improvement in lifetime compared to the initial as-fired state is observed immediately following an additional light soaking treatment (20 °C, 2 suns, 24 h), as demonstrated in Figure 4.7b. Subsequent LeTID testing was performed under identical conditions (130 °C, 1 sun),

with the temporal evolution of τ_{eff} , ΔN_{leq} , and j_0 being monitored.

In this case, all samples show a degradation and regeneration behavior. The degradation maximum $\Delta N_{\text{leq,max}}$ is shifted towards longer treatment times for higher ingot numbers. Additionally, the degradation extent is also increased for samples from subsequently pulled ingots with the lowest degradation for P1 and greatest extent for P10. Surface-related degradation, indicated by j_0 , again sets in after ~ 10 h of treatment. However, a slight increase in j_0 appears to occur already before that point in time. This is consistent with the observations in Figure 4.3, where a gradual increase in j_0 was observed during each LeTID testing cycle. If this were an artefact of the evaluation, an intermediate maximum coinciding with the lifetime minimum would be expected. While the overall impact on j_0 appears to be small compared to the inset of SRD, the origin of this surface deterioration remains unclear.

Variations in initial lifetime prior to LeTID testing are observed across ingot positions, likely attributable to progressively accumulated impurities in higher-numbered ingots. These differences may influence reaction kinetics through injection-level changes. In p-type material, LeTID dynamics are known to decelerate with lifetime degradation due to injection-dependent rates (see Section 3.2.3).

To enable direct comparison, iso-injective conditions were used (see discussion in Section 2.3.1), ensuring identical injection during degradation and regeneration across all samples. Following 24 h of light soaking, the same sample set was subjected to LeTID testing under fixed injection conditions ($\Delta n = 1.5 \cdot 10^{15} \text{ cm}^{-3}$). The resulting evolution of τ_{eff} , ΔN_{leq} , and j_0 is presented in Figure 4.7c.

The maximum defect density is observed to occur after ~ 1 h of treatment for all samples, with only minor temporal delays noted for higher-numbered ingots. The degradation extent under iso-injective conditions is found to be comparable to that observed in the iso-generative treatment (b). Given the relatively limited impact on bulk lifetime throughout the treatment, the injection level remains largely stable during iso-generative testing, resulting in minimal overall differences between the two treatments.

Consistent with previous observations, SRD occurs after ~ 10 h of treatment, as indicated by rising j_0 values. The observed delays in $\Delta N_{\text{leq,max}}$ cannot be conclusively explained. Although limitations in laser adjustability for small lifetime variations must be considered, the potential influence of accumulated impurities on regeneration kinetics cannot be excluded. While analogous behavior was not observed in Ga-doped material (Figure 3.10), prior studies have demonstrated aluminum-induced delays in LeTID regeneration for boron-doped silicon for Al concentrations of $\sim 3 \cdot 10^{14} \text{ cm}^{-3}$ [233].

There might be a connection between $\Delta N_{\text{leq,max}}$ in phosphorus-doped material and impurity ac-

cumulation during melt recharging, mirroring previous findings in Ga-doped RCz-Si. However, the overall degradation extent is significantly lower compared to p-type counterparts. This may be attributed either to a generally lower defect concentration in the material or to different defect-specific parameters. While it is possible that the same microscopic defect is responsible for LeTID in both n- and p-type material, its energy level may differ between the two, leading to the distinct injection dependencies observed in the excess charge carrier lifetime.

It should be noted that the immediate post-firing light soaking treatment employed in this study may not represent standard industrial practice, despite documented use of intense light treatments at elevated temperatures [234]. Under typical operating conditions, conventional n-type solar cells might initially exhibit performance improvement rather than degradation. This apparent benefit is counterbalanced by two implications. First, initial cell efficiency may be inherently limited by the presence of LeTID defects. Second, application of regeneration treatments directly after firing could potentially induce more severe degradation during field operation due to the annealing of state *B*. The exact defect distribution might strongly depend on the used treatment conditions. Consequently, minimization of recombination-active defect formation is still desired.

Sb-doped Material

Figure 4.8 presents the evolution of τ_{eff} , ΔN_{leq} , and j_0 during LeTID testing for Sb-doped samples from RCz-Si processes, comparing two doping concentrations. Hereby, a higher-doped variant (Sb_H, $\sim 0.7 \Omega \text{ cm}$) and a lower-doped variant (Sb_L, $12 \Omega \text{ cm}$) is compared. All samples were subjected to identical treatment conditions with prior light soaking (20 °C, 2 suns, 24 h) followed by LeTID testing (130 °C, 1 sun). As expected, the initial lifetime ($t = 0$) following light soaking is observed to be higher for Sb_L samples, consistent with their reduced dopant concentration.

During LeTID testing, both dopant concentrations show a similar trend of increasing degradation extent with higher ingot numbers. However, the time at which $\Delta N_{\text{leq,max}}$ occurs is shifted to longer treatment durations for samples from the Sb_H RCz-Si process. In the lower-doped material, this delayed regeneration is less pronounced but still evident. The effect cannot be explained by differences in injection levels, since Sb_H1 reaches its degradation maximum earlier than Sb_L, despite exhibiting a lower overall effective lifetime. A comparable behavior is observed when comparing Sb_H1 with Sb_H9, where regeneration is delayed in the latter. This suggests that the accumulation of certain species in the melt may be responsible for the observed regeneration delay. With the exception of Sb_L9, the overall degradation extent does not appear to be strongly influenced by the doping concentration.

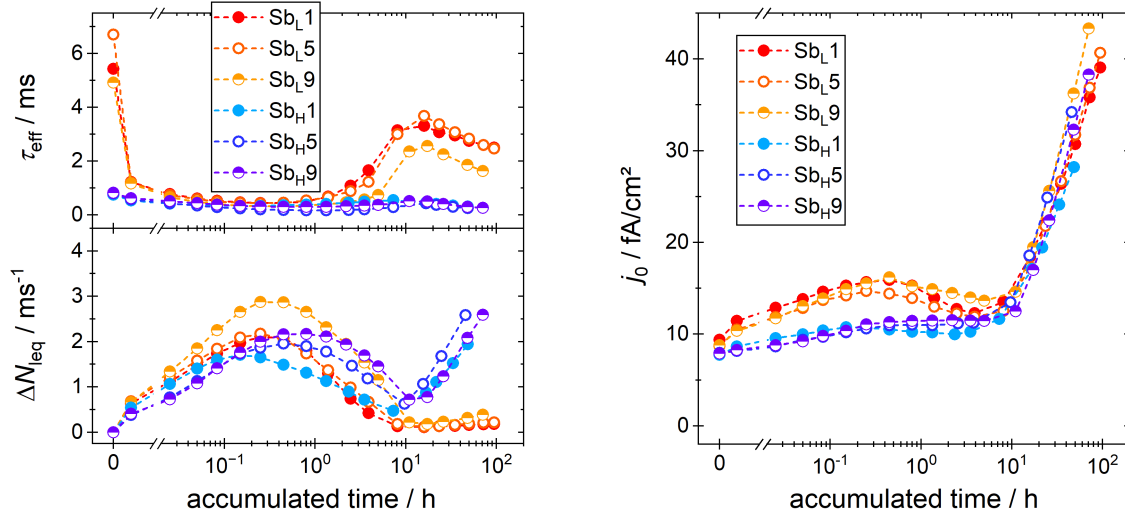


Figure 4.8: Extracted τ_{eff} , ΔN_{leq} and j_0 for Sb-doped material with lower (Sb_L) and higher (Sb_H) doping concentration during treatment at 130 °C at 1 sun illumination, following light soaking at 20 °C and 2 suns. Adapted from [232].

Consistent with the behavior observed in phosphorus-doped material, SRD occurs after ~ 10 h of treatment indicated by an increasing j_0 . It is unclear, why the j_0 does follow the course of ΔN_{leq} for all Sb_L and Sb_H1 . It is possible that the evaluation of j_0 is influenced by the change in bulk defects. Comparing the increase of j_0 after ~ 10 h of treatment and the course of j_0 before that point in time with ΔN_{leq} , it can be observed that there are only minor changes in ΔN_{leq} during SRD while a significant degradation is visible during the first hours of treatment. It is therefore not possible to explain the bulk-related degradation by these comparatively small changes in j_0 .

The degradation kinetics are found to be remarkably similar for both phosphorus- and antimony-doped materials. This consistency suggests that the observed LeTID behavior is not uniquely associated with either n-type dopant species, nor does it appear to correlate with absolute dopant concentrations.

Correlation of Defects with Accumulated Impurities

Even though the impurity concentration cannot be monitored directly easily, a general approach was used to estimate the impurity accumulation by the total amount of recharged silicon. Throughout a RCz-Si process, roughly 3000 kg of material is used. In Figure 4.9, the extracted ΔN_{leq} from LeTID testing for P-doped (a) (see Figure 4.7b) and Sb-doped (b) (see Figure 4.8) samples from seed positions of different ingots throughout the melt recharging process are correlated with the accumulated recharged fraction. An accumulated fraction of

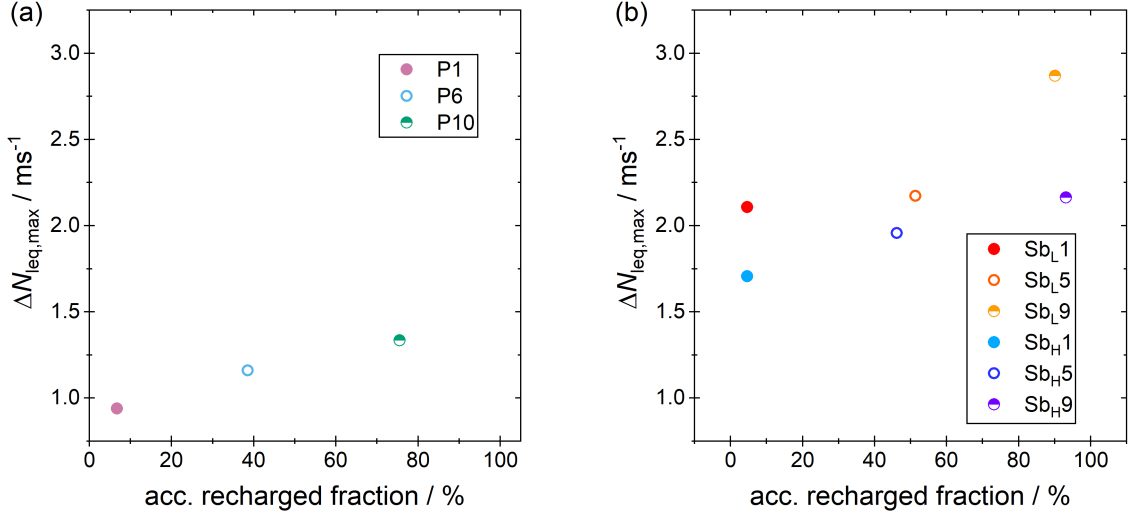


Figure 4.9: Extracted $\Delta N_{\text{leq,max}}$ for P-doped (a) and Sb-doped material with lower (Sb_L) and higher (Sb_H) doping concentrations (b) during LeTID at 130 °C under 1 sun illumination, following light soaking, shown in correlation with the accumulated recharged fraction. An accumulated fraction of 100 % corresponds to a total added poly-Si load of approximately 3000 kg, used throughout the RCz-Si process.

100 % corresponds to the complete use of the total poly-Si load of the corresponding RCz-Si process.

A systematic increase in $\Delta N_{\text{leq,max}}$ with higher accumulated recharged fractions is observed for both P-doped and Sb-doped samples. While this trend is clearly evident in the higher-doped materials (exhibiting nearly linear correlations), the pattern appears less distinct for the lower-doped Sb_L samples, particularly given the unexpectedly low $\Delta N_{\text{leq,max}}$ value observed for Sb_L5 .

The established correlation between degradation extent and recharged fraction closely resembles the previously reported relationship between defect density and interstitial iron concentration in Ga-doped p-type material (see Figure 3.11). However, it should be noted that the accumulated recharged fraction metric possesses inherent limitations in accuracy, particularly for RCz-Si processes employing variable ingot lengths. When ingots are grown beyond 50 % solidified fraction, impurity accumulation patterns become more complex, potentially leading to increased impurity concentrations at seed positions of subsequently pulled ingots compared to earlier ones. This effect, combined with unknown ingot length parameters in the current study, could account for the anomalous $\Delta N_{\text{leq,max}}$ value observed for Sb_L5 .

It seems reasonable to assume that for n-type material, the RCz-Si can have a very similar impact on the LeTID extent as it is the case for the Ga-doped material in Chapter 3. While it is unclear if an accumulated impurity is directly involved in the defect formation, this mechanism

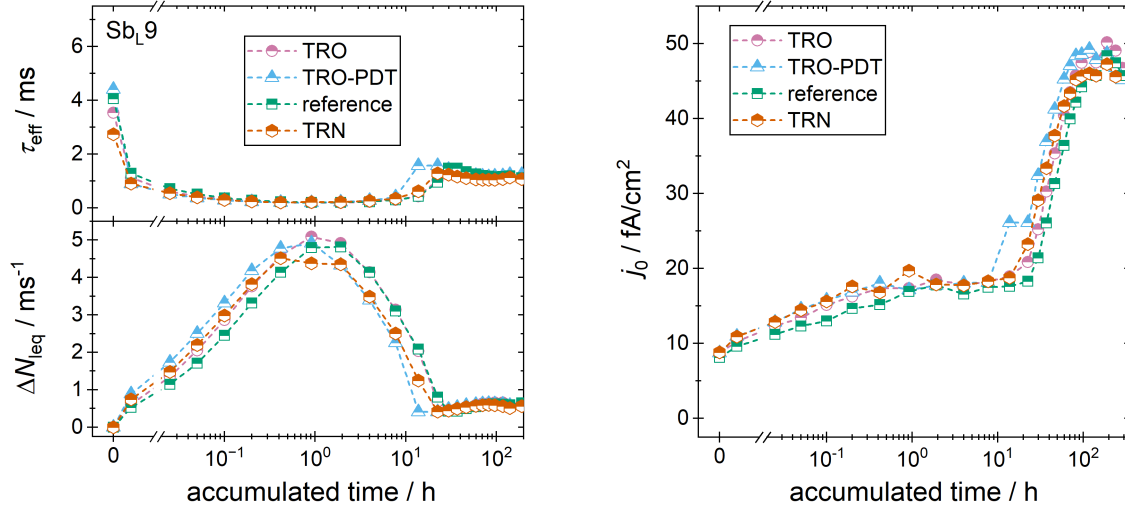


Figure 4.10: Extracted τ_{eff} , ΔN_{leq} and j_0 during LeTID testing at 130 °C under 1 sun illumination for tail-position wafers of Sb-doped material subjected to different high-temperature processing steps. All samples are light soaked prior to LeTID testing. Adapted from [232].

appears to be independent of the specific dopant species. Despite these parallel observations in both p-type and n-type materials, the possibility of distinct defect species participation cannot be excluded. The fundamental defect formation mechanisms may differ while yielding similar phenomenological behavior.

4.2.3 High-Temperature Processing

Lastly, the impact of high-temperature processing steps on the long-term stability of Sb-doped material is investigated. The evolution of τ_{eff} , ΔN_{leq} , and j_0 for a 6 Ω cm sample taken from the tail end of Sb_L9 is presented in Figure 4.10. In this case, the tail section of the final ingot pulled from the melt was selected for analysis, as it is expected to exhibit the highest impurity concentrations. Samples subjected to tabula rasa (TR) treatments under different ambient conditions are compared to a reference sample that did not undergo any additional high-temperature treatment. For one sample, the tabula rasa treatment in oxygen atmosphere (TRO) is followed by a phosphorous diffusion treatment (PDT). Prior to LeTID testing at 130 °C under 1 sun illumination, all samples were exposed to light soaking at 20 °C and 2 suns for 24 h.

It can be observed that the highest τ_{eff} after light soaking is achieved in the sample that underwent TRO followed by PDT. This improvement could be attributed to a reduced concentration of metallic impurities. However, conclusions based on individual samples must be treated with caution.

A statistical analysis of the TRO treatment, involving at least 4 samples from two wafers per

group, shows that TRO can slightly improve both effective and illuminated lifetimes, as shown in Figure 4.11. Effective lifetimes were evaluated for wafers from the seed and tail ends of Sb_L1 directly after firing (τ_0) and after extended light soaking (τ_{ill}). Samples either served as references without additional high-temperature processing or were subjected to a tabula rasa treatment in oxygen. Error bars represent the standard error of the mean.

Nevertheless, the overall degradation extent observed in Figure 4.10 remains unchanged, as was also observed for PDT in Ga-doped material (see Section 3.7). In general, the observed $\Delta N_{\text{leq,max}}$ appears to be independent of the applied high-temperature processing. Aside from the onset of SRD after approximately 20 h of treatment, a slight increase in j_0 is observed during the bulk-related degradation phase. This may be an artifact resulting from the formation of bulk defects. A comparable trend was previously noted in Figure 4.8 for Sb_L. Overall, the initial lifetime can be affected by the high-temperature processing steps, while the extent of LeTID degradation appears to remain constant.

A comparison of the maximum degradation extent between the reference sample and the seed position of Sb_L9 in Figure 4.8 shows an increase in defect concentration toward the tail. This trend is most likely caused by impurity accumulation in the melt due to recharging, as discussed in Section 3.1, since all samples were prepared identically.

A related study by Mehler *et al.* [140] investigated the effect of TRO in phosphorus-doped FZ silicon. In their work, enhanced regeneration during LeTID testing was observed and correlated with a reduced signal of the vacancy complex VH_4 , as measured by FTIR. Additionally, a two-

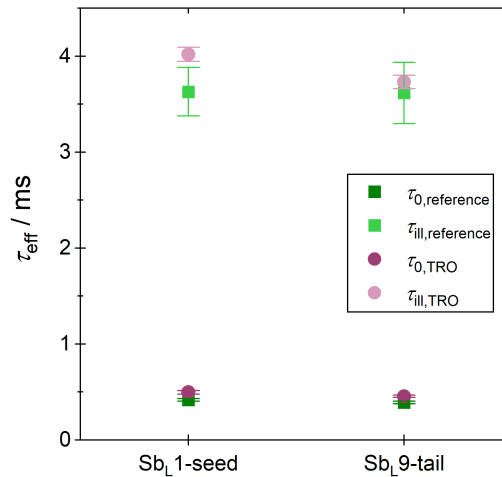


Figure 4.11: Averaged effective lifetimes after firing (τ_0) and after light soaking at 2 suns and 20 °C (τ_{ill}), determined for wafers from the seed position of Sb_L1 and the tail position of Sb_L9. Samples were either left untreated (reference) or subjected to a TRO treatment. Error bars represent the standard error of the mean, calculated from at least six samples across two wafers. Adapted from [231]

step regeneration is observed when the TR in oxygen atmosphere was applied. Their findings are therefore not directly comparable to those presented here, as no initial light soaking was applied and a significantly purer material was used. In the present study, no clear correlation is found between high-temperature processing steps such as TRO or PDT and a reduction in the degradation extent during LeTID testing.

4.3 Conclusions

The first part of this chapter can be summarized by the concept of two (independent) three-state models used to describe the observed defects during light soaking and LeTID testing of n-type Cz-Si wafers. In contrast to p-type material, most defects in n-type samples appear in the recombination-active state B directly after firing. In addition, another defect is predominantly found in the annealed state A' . Light soaking at lower temperatures can anneal the defect that forms at elevated temperatures, with the duration of treatment influencing the fraction of defects transitioning between $A \leftarrow B$. At the same time, this treatment induces degradation and subsequent regeneration in the additional defect system $A' \rightarrow B' \rightarrow C'$.

Transitions between states $A \rightleftharpoons B$ can be controlled by alternating light soaking at 20 °C and LeTID testing at 130 °C. However, the regeneration process $B \rightarrow C$, observed during LeTID testing, appears to be permanent and is not reversed by subsequent light soaking. In contrast, the additional defect seems to fully regenerate ($B' \rightarrow C'$) during light soaking and does not reappear in subsequent thermal or illumination treatments. It remains uncertain whether the transition $A' \rightarrow B'$ is reversible. Overall, the treatment temperature appears to be the dominant factor governing the occurrence of these different transitions.

During these experiments, it is also observed that surface-related degradation tends to occur only after a significant fraction of defects have transitioned into state C . A detailed study investigating changes in surface charge at various stages of LeTID testing could provide further insights into this phenomenon.

From a practical standpoint, these findings highlight the need for a standardized LeTID testing procedure for solar cells. In this context, incorporating a pre-treatment via light soaking may prove beneficial. However, the suitability of such a pre-treatment likely depends on the specific objectives of the testing protocol and the nature of the applied processing steps, particularly regeneration treatments following firing. For evaluating the maximum degradation extent, prior light soaking may offer a practical and consistent approach within LeTID studies.

Many open questions remain for future work. First, it is not yet fully understood whether the secondary defect ($A' \rightleftharpoons B' \rightleftharpoons C'$) is truly independent of the LeTID defect, or whether

some interaction exists between the two. Separating these defect systems may be necessary to enable more precise defect characterization, as the simultaneous evolution of at least two distinct defect types complicates the analysis. While the current data suggest a degree of independence, the role of hydrogen, whether direct or indirect, in each defect system remains unclear. Additionally, a systematic study of injection-dependent kinetics could provide deeper insights into the reaction rates and mechanisms governing both defect models.

In experiments with phosphorus- and antimony-doped RCz-Si samples that did not undergo any light soaking prior to degradation, regeneration-dominated behavior was observed during treatment at 130 °C under 1 sun until the onset of SRD. In contrast, samples subjected to light soaking at 20 °C and 2 sun prior to LeTID testing exhibited a more pronounced degradation response, with an increased degradation extent observed for ingots pulled later in the crystallization process. These results suggest, that LeTID in n-type material is influenced by impurity accumulation during the RCz-Si growth process, consistent with observations in p-type material discussed in Chapter 3. The implications for solar cell manufacturing are thus comparable for both dopant types and ultimately depend on the requirements of the specific cell design.

Changes in degradation and regeneration kinetics can partly be attributed to variations in excess carrier injection during iso-generative treatments. A trend of delayed regeneration is also evident in subsequently pulled ingots. For phosphorus-doped samples from such ingots, degradation and regeneration kinetics become more similar under iso-injective conditions, although a slight shift of the degradation maximum toward longer treatment times can still be observed. Overall, the LeTID behavior in this chapter appears very similar for both dopant types, suggesting a common underlying mechanism driven by injection level rather than dopant species.

The delay in regeneration may be relevant for industrial applications. Typically, regeneration is applied immediately after firing, either by strong illumination over a short duration or by current injection combined with thermal annealing. In the illumination-based approach, the lifetime is mainly limited by surface and Auger recombination due to the very high intensities. The time required for complete regeneration is therefore not expected to vary because of different impurity induced degradation differences. In contrast, the current injection approach operates at significantly lower injection levels, which may result in different regeneration times for samples with varying impurity levels. For p-type cells, the current-based approach is preferred by solar cell manufacturers due to its easier integration into mass production [235], which makes it likely that this method will also be adopted for n-type cell architectures.

One potential approach for ingot growers to estimate the possible degradation extent is through the monitoring of impurity accumulation. In principle, changes in impurity concentration along the ingot can be assessed by calculating impurity incorporation ($\kappa \ll 1$) and the accumulated

recharged fraction. However, since impurity levels in silicon are typically very low, absolute concentrations are likely to remain below the detection limit.

Furthermore, this study finds that additional high-temperature processing steps, such as tabula rasa and phosphorus diffusion treatments, can influence material quality but do not appear to significantly alter the degradation extent or kinetics during illumination at elevated temperatures.

Future research could therefore focus on identifying effective mitigation strategies aimed at improving the long-term stability of the material. Hereby, the impact of alternative passivation techniques can be investigated, which are expected to influence the hydrogen concentration in the wafer after firing. Additionally, further research could focus on finding a correlation between the vacancy concentration and the observed degradation extent. If the applied tabula rasa does not effectively modify the vacancy concentration in the investigated material, an alternative approach would be to adjust the pulling speed during crystal growth, thereby influencing the amount of crystal defects present in the as-grown crystal [236, 237].

Since electron paramagnetic resonance has already been applied to investigate LeTID in p-type silicon [2], the technique could yield additional insights in n-type silicon, where the hyperfine interaction between the donor-bound electron and the donor nucleus gives rise to characteristic splitting. If the defect formed during LeTID interacts with the donor, such coupling may provide complementary information about the microscopic nature of the underlying defect.

5 Impact of Solar Cell Processing on LeTID

Up to this point, the impact of impurity accumulation during crystal growth on long-term stability has been discussed. It has been demonstrated that wafer production can significantly influence the LeTID behavior. In solar cell manufacturing, however, an additional set of processing steps is applied, which may also affect LeTID characteristics. As outlined in Section 1.4, the degradation extent is strongly correlated with the bulk hydrogen concentration, which plays a critical role in p-type Cz-Si.

This chapter addresses the manipulation of hydrogen content in the bulk of Ga-doped material. Precise control of the hydrogen concentration is required to enhance passivation [238] while avoiding the (most likely) hydrogen-induced bulk and surface degradation. Data presented in [135] indicate that the degradation extent in n-type Cz-Si also depends on hydrogen concentration. It is therefore plausible that the techniques developed to control hydrogen in Ga-doped p-type silicon can likewise be effective to n-type material. Nevertheless, despite this similarity, the defect state distribution and associated LeTID kinetics differ between p-type and n-type material, as discussed in the previous chapter.

Several approaches exist to control the excess hydrogen concentration in the silicon bulk. Section 5.1 examines the role of the firing process, while Section 5.2 addresses the impact of different passivation layer stacks. Since tunnel oxide passivating contact (TOPCon) is currently the most widely implemented technology in solar cell manufacturing, sample structures relevant to this architecture are of particular interest. Finally, in Section 5.4, the methods developed in this work are applied to a p-type interdigitated back-contact (pIBC) solar cell, demonstrating the effect of LeTID on key device parameters during accelerated long-term stability testing.

5.1 Influence of the Firing Process

In solar cell processing, the firing process typically serves multiple purposes. One of the primary functions is the formation of electrical contacts following the screen-printing of metal pastes onto dielectric passivation layers. In conventional silicon solar cells, $\text{SiN}_x\text{:H}$ is commonly used not only as a passivation layer but also as an anti-reflective coating. During the rapid thermal ramp-up to peak temperatures of several hundred degrees Celsius, hydrogen from the passivation layer can diffuse toward the Si/SiO_2 interface. This excess hydrogen can saturate dangling bonds, thereby reducing surface recombination [239]. Moreover, hydrogen also diffuses into the silicon bulk, where it can passivate defects within the crystal, further enhancing the electrical quality of the material.

This section investigates the influence of the peak firing temperature on the wafer's cooling rate R_c . Since the LeTID defect is known to correlate with the hydrogen content introduced during the firing process [105, 106], appropriate long-term stability experiments are conducted. The degradation extent is then compared to the hydrogen species present in the material after firing.

Sample preparation was carried out as described in Section 2.2, including preprocessing and the deposition of $\text{SiN}_x\text{:H}$. Samples intended for resistivity measurements were prepared according to the procedure outlined in Section 2.2.5. Some of the measurements presented in this section were conducted as part of a Master's thesis supervised by the author [240].

5.1.1 Cooling Ramp and Peak Firing Temperature

Firstly, the actual peak firing temperature on the wafer ($T_{\text{sample,peak}}$) for a range of set peak firing temperatures ($T_{\text{set,peak}}$) between 740 °C and 1000 °C is measured. This temperature range is selected as it includes the typical firing conditions used in standard solar cell production between 750 °C and 850 °C [241]. The corresponding measured thermal profiles are presented in Figure 5.1a. While the first ~20 s of firing are critical for the outgassing of organic components and the etching of metal pastes [242], they are not the focus of this study. Instead, only the set peak firing temperature is varied, which consequently determines the actual peak temperature reached by the sample. After reaching this peak at 22 s, the wafer begins to cool. Below 400 °C, no significant hydrogen out-diffusion from the bulk is expected [243]. However, the relative distribution between different hydrogen species, $[\text{H}_2]_{\text{init}}$ and GaH , may still change, as part of the dimers can dissociate and subsequently bind to additional acceptor atoms [244].

Although the change in peak firing temperature is the most apparent variable, it also influences the cooling rate, which plays a crucial role in the quenching behavior of hydrogen following

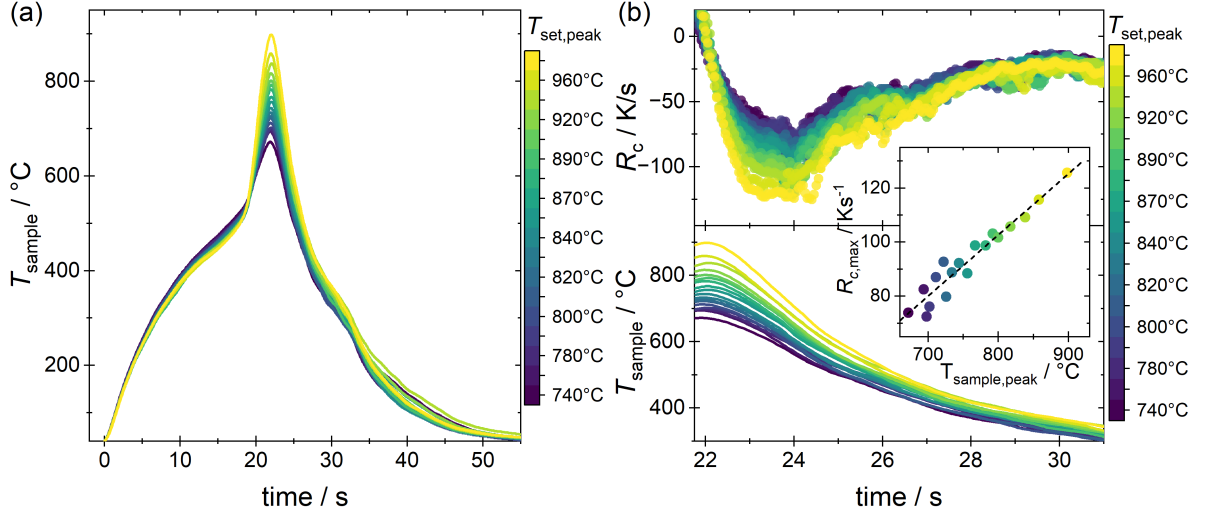


Figure 5.1: Measured firing temperatures of non-metallized samples processed in a belt furnace with set peak temperatures ranging from 740 °C to 1000 °C. (b) Temperature profiles after reaching the peak firing temperature at 22 s, shown until cooling below 400 °C (bottom), and corresponding cooling rates R_c obtained by differentiating the temperature profiles (top) for different set peak firing temperatures. The inset shows the maximum cooling rate $R_{c,max}$ as a function of the achieved peak firing temperature of the samples, with a linear fit added as a guide to the eye. The inset in (b) is adapted from [240], with the data also published in [246].

high-temperature processing [204, 245]. Specifically, higher cooling rates limit the time available for atomic hydrogen to diffuse out of the crystal, thereby retaining more hydrogen within the silicon bulk.

Figure 5.1b displays the firing profiles after reaching the various peak firing temperatures until cooling below 400 °C (bottom). The corresponding cooling rate R_c , obtained by differentiating the temperature profile, is shown in the top part. It can be seen that, at ~24 s a maximum cooling rate $R_{c,max}$ is reached. Here, the variation between the different set firing temperatures is the greatest which is diminishing over the next few seconds, until ~27 s when all profiles show a similar cooling rate. The inset in Figure 5.1b depicts the maximum cooling rate as a function of the achieved sample peak firing temperature.

Within the investigated temperature range, an approximately linear relationship is observed between $R_{c,max}$ and $T_{sample,peak}$. This correlation makes sense due to the radiative and convective cooling which is expected to increase with rising temperatures. The default firing profile used in prior experiments corresponds to a maximum cooling rate of approximately 100 K s⁻¹ with a measured peak temperature of 800 °C. However, in this study, the focus lies on evaluating how variations in peak firing temperature influence both long-term stability and bulk hydrogen content.

In many degradation studies, only the peak firing temperature is reported [39, 78, 247]. This parameter alone is insufficient, as the remaining hydrogen content in the crystal is strongly influenced by the quenching behavior, which is governed by the cooling rate within a specific temperature range. While the peak temperature determines how much hydrogen initially enters the wafer, knowledge of the maximum cooling rate alone is not sufficient to predict the final hydrogen concentration either.

In practice, the cooling rate is not only a function of peak temperature but also depends on the firing furnace design, for example, the number and temperature of individual heating zones and the belt speed. Slower belt speeds typically result in lower cooling rates. The influence of belt speed on cooling behavior is further discussed in Section 5.1.3. For simplicity, only the peak firing temperature is reported here. Nonetheless, as long as the same firing furnace and belt speed are used, the corresponding cooling rates can be referenced from Figure 5.1b.

5.1.2 Impact of Peak Firing Temperature on LeTID and Hydrogen Content

The impact of peak firing temperature on both long-term stability and the initially present hydrogen concentration after firing is investigated in this section. Four firing temperatures, resulting in $T_{\text{sample,peak}}$ between 700 °C and 850 °C, are applied to equivalently processed samples. The long-term stability treatment at 130 °C is evaluated using the parameters τ_{eff} , ΔN_{leq} , as well as the fitted values ΔN_{leq}^* and Δj_0 as shown in Figure 5.2.

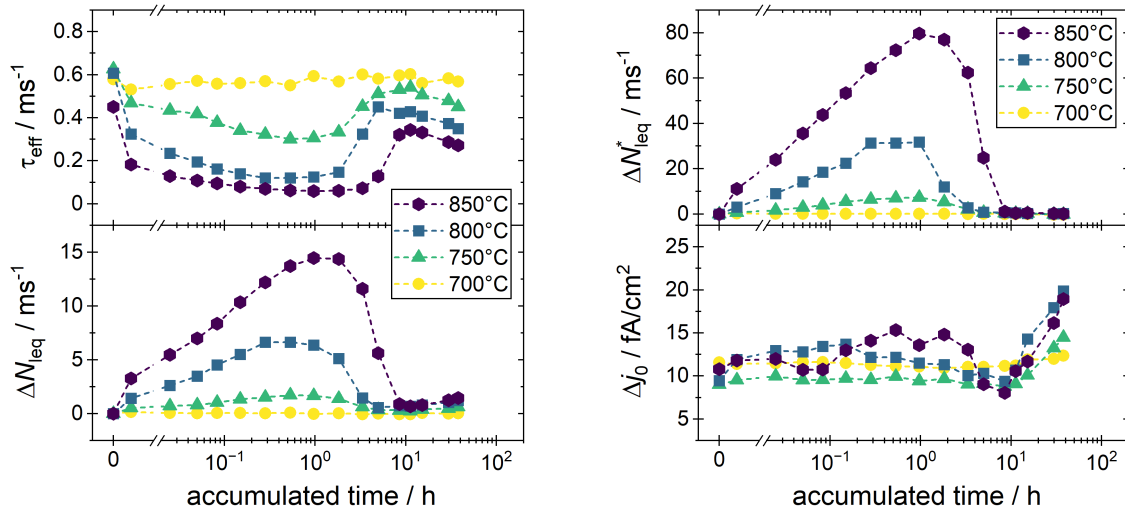


Figure 5.2: Evolution of τ_{eff} , ΔN_{leq} as well as the fit parameter ΔN_{leq}^* and Δj_0 during treatment at 130 °C under 1 sun illumination for different peak sample temperatures $T_{\text{sample,peak}}$. The Ga-doped base material has a resistivity of $\sim 1 \, \Omega \, \text{cm}$.

The initial τ_{eff} after firing is approximately 0.6 ms for samples fired up to 800 °C, while a slight reduction is observed for the sample fired at 850 °C. This decrease is likely related to bulk material degradation as indicated by the relatively constant Δj_0 around 10 fA cm⁻².

During the first ~1 h of treatment, ΔN_{leq} and ΔN_{leq}^* increase, followed by a regeneration phase lasting until approximately 10 h. During this period, Δj_0 remains relatively stable and only shows a significant increase once regeneration is complete. The bulk-related defect density increases more strongly with higher firing temperatures. In terms of SRD, the differences between firing conditions are less pronounced, although a slight reduction in Δj_0 is observed for peak firing temperatures below 750 °C.

The observed increase in bulk-related degradation is further investigated by determining the hydrogen content present in the silicon bulk immediately after firing, using resistivity measurements. From these measurements, the concentrations of individual hydrogen species $[\text{H}_2]_{\text{init}}$, $[\text{GaH}]_{\text{init}}$ and $[\text{H}]$, are extracted as it is described in Section 2.3.4. In Figure 5.3, the $\Delta N_{\text{leq,max}}^*$ is plotted against each of the species concentrations for different $T_{\text{sample,peak}}$ values.

At higher peak firing temperatures, the total hydrogen content in the samples increases significantly. A nearly linear trend is observed for the increase of $[\text{H}_2]_{\text{init}}$, indicating that the extent of bulk-related degradation is proportional to the initial concentration of hydrogen dimers [106]. The linear fit does not include the data point for the peak firing temperature of 700 °C, as it is not clear whether the $[\text{H}_2]_{\text{init}}$ concentration must reach zero to completely prevent LeTID. In a review by Hammann *et al.* [72], it was discussed that total hydrogen

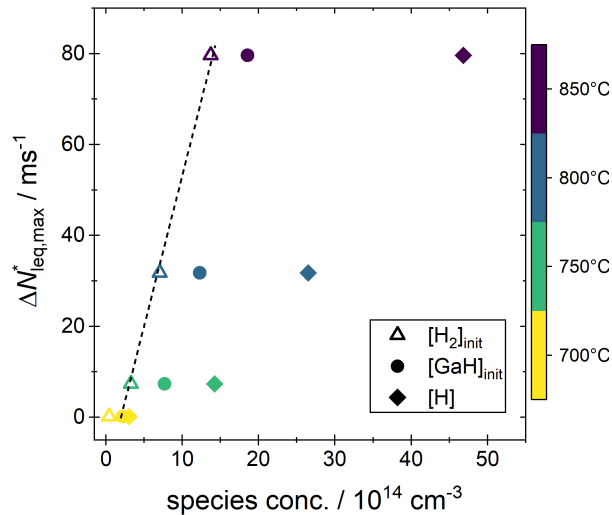


Figure 5.3: (a) Maximal bulk-related degradation extent $\Delta N_{\text{leq,max}}^*$ derived from Figure 5.2 as a function of the corresponding species concentrations $[\text{H}_2]_{\text{init}}$, $[\text{GaH}]_{\text{init}}$ and $[\text{H}]$ for different peak firing temperatures. A linear fit is applied to the $[\text{H}_2]_{\text{init}}$ data, excluding the peak firing temperature of 700 °C.

concentrations below approximately $5 \cdot 10^{14} \text{ cm}^{-3}$ completely suppress LeTID. While the exact $[\text{H}_2]_{\text{init}}$ threshold at which the LeTID extent becomes negligible remains uncertain, it must lie well below $5 \cdot 10^{14} \text{ cm}^{-3}$, depending on the ratio between GaH and H_2 . The extrapolation of the linear fit to the x-axis yields a $[\text{H}_2]_{\text{init}}$ concentration of $\sim 3 \text{ cm}^{-2}$.

The higher firing temperature enhances hydrogen diffusion from the $\text{SiN}_x\text{:H}$ layer into the silicon bulk. At the same time, the increased cooling rate reduces hydrogen out-diffusion and promotes the formation of H_2 dimers through quenching, thereby increasing the susceptibility to LeTID. Because of the increased amount of hydrogen molecules the formation of GaH-pairs is promoted as well.

This experiment clearly demonstrates that the peak firing temperature plays a critical role in determining the hydrogen concentration in the silicon bulk and, consequently, the long-term stability of the material. While the linear correlation between degradation extent and $[\text{H}_2]_{\text{init}}$, as well as the correlation between peak firing temperature and the observed cooling rate, align quite well, it remains unclear whether the peak temperature itself or the maximum cooling rate is the more decisive factor.

In the experiment presented here, a direct correlation with the cooling ramp cannot be established due to its strong dependence on the peak temperature. Moreover, the cooling rate is determined not only by the belt speed but also by the furnace design. This suggests that, depending on the belt speed required for optimal contact formation, a well-engineered cooling phase can still mitigate LeTID in solar cells by limiting hydrogen retention in the wafer bulk. Therefore, in the next section, both varying belt speeds and two different furnace designs will be employed to investigate the effect of different cooling rates at comparable peak firing temperatures.

5.1.3 Firing in Different Belt Furnaces

Depending on the metal paste used for screen printing, different belt speeds and therefore different firing profiles may be required to achieve optimal contact formation [248]. In this section, two different belt furnaces are compared at two belt speeds to investigate their impact on hydrogen incorporation in the silicon bulk and the implications for long-term material stability.

Figure 5.4 displays sections of the firing profiles after reaching the peak firing temperatures for two furnaces (F1 and F2), each operated at two belt speeds: 3 m min^{-1} (profile 1, P1) (a) and 6 m min^{-1} (profile 2, P2) (b). Additionally, both graphs feature the derived cooling rate R_c . Unless otherwise stated, the standard configuration used throughout this work is furnace F1 operated at belt speed P2.

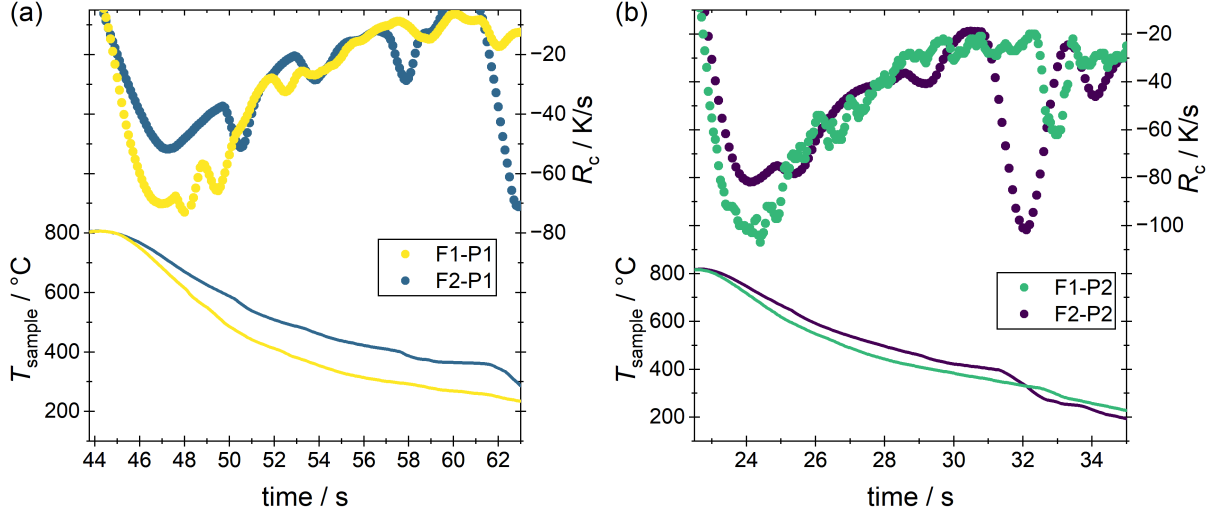


Figure 5.4: Firing profiles T_{sample} (lines) and derived cooling rate R_c (points) from two different belt furnaces (F1 and F2) using two belt speeds each ((a): P1 $\sim 3 \text{ m min}^{-1}$ and (b): P2 $\sim 6 \text{ m min}^{-1}$). For the faster belt speed, the peak firing temperature was increased to achieve a similar measured $T_{\text{sample,peak}}$.

Because faster belt speeds reduce the time available for the sample to reach thermal equilibrium, the set peak firing temperature must be adjusted to achieve comparable actual wafer temperatures. In this case, the set temperature is chosen such that the resulting sample peak temperatures are approximately $T_{\text{sample,peak,P1}} \sim 806 ^\circ\text{C}$ and $T_{\text{sample,peak,P2}} \sim 817 ^\circ\text{C}$. As a consequence of the slower belt speed in P1, the cooling rate after reaching peak temperature is significantly lower than in the faster P2 configuration.

Further, the results show that the design of the furnace also has a significant impact on the cooling rate. With similar wafer peak temperature at same belt speed the cooling rate and thus hydrogen retention is expected to be different for the two furnaces. This highlights the importance of considering both process conditions and furnace design when evaluating long-term stability effects related to hydrogenation by firing.

Long-term stability testing of wafers fired in the two different furnaces (F1 and F2) at different belt speeds (P1 and P2) was conducted under conditions of $130 ^\circ\text{C}$ and 1 sun illumination. The measured τ_{eff} and derived ΔN_{leq} , ΔN_{leq}^* and Δj_0 are presented in Figure 5.5a. Regardless of the firing conditions, all samples exhibit good surface passivation. However, the initial effective lifetime appears slightly reduced for the F1-P1 configuration, and the recovered lifetime is also lower compared to samples fired with other profiles. Moreover, the degradation extent is generally higher for furnace F1 compared to F2 when using the same belt speed. For both furnaces, the faster belt speed (P2) leads to a more pronounced degradation extent than the slower belt speed (P1).

To further investigate these effects, resistivity measurements were used to determine the hydrogen species present after firing. The correlation between $\Delta N_{\text{leq,max}}^*$ (taken from Figure 5.5a) and the hydrogen species concentrations is shown in Figure 5.5b. For relating the species concentrations to the firing profile, the $T_{\text{sample,peak}}$ values are taken from Figure 5.4. The maximum cooling rate is determined by taking the derivative of the thermal profile after the peak temperature has been reached. The relationship between these two firing parameters and the

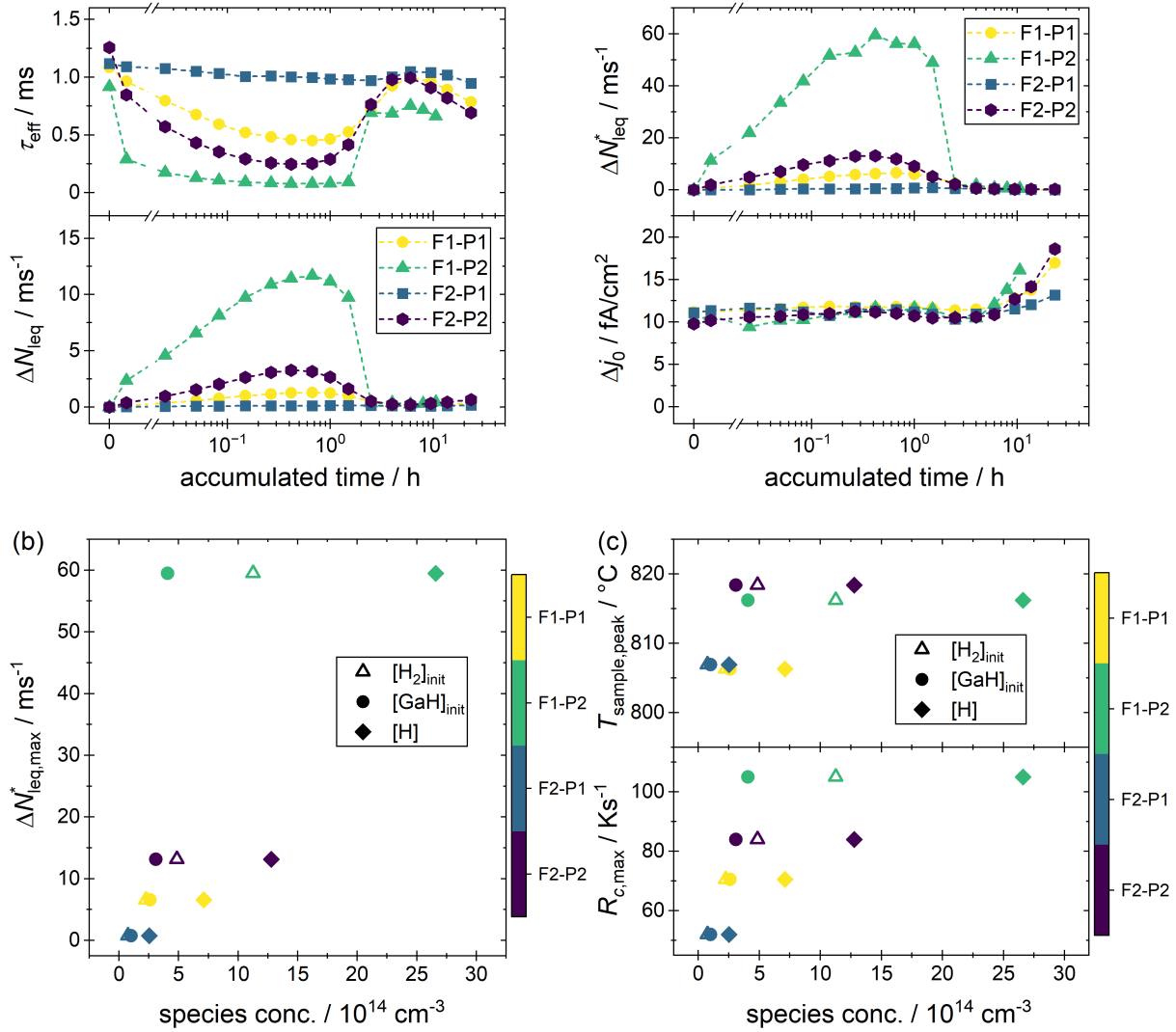


Figure 5.5: (a) Evolution of τ_{eff} , ΔN_{leq} and the fit parameters ΔN_{leq}^* and Δj_0 during treatment at 130 °C and 1 sun for samples exposed to the firing profiles shown in Figure 5.4. The base material has a resistivity of $\sim 1.7 \Omega \text{ cm}$. (b) Maximum bulk-related degradation extent $\Delta N_{\text{leq,max}}^*$ derived from Figure 5.5a as a function of the corresponding species concentrations $[\text{H}_2]_{\text{init}}$, $[\text{GaH}]_{\text{init}}$ and $[\text{H}]$ for the different firing profiles in Figure 5.4. (c) Maximum peak firing temperature $T_{\text{sample,peak}}$ and cooling rate $R_{\text{c,max}}$ plotted versus the corresponding species concentrations. Both parameters are derived from the firing profiles in Figure 5.4. Adapted from [240].

hydrogen species concentrations is presented in Figure 5.5c.

As observed in the experiment with varying peak firing temperatures (see Figure 5.3a), $\Delta N_{\text{leq,max}}^*$ increases almost linearly with rising $[\text{H}_2]_{\text{init}}$. Alongside this trend, both $[\text{GaH}]_{\text{init}}$ and $[\text{H}]$ also show an increase. However, Figure 5.5c reveals no clear correlation between $T_{\text{sample,max}}$ and $[\text{H}_2]_{\text{init}}$. In contrast, a linear increase in $[\text{H}_2]_{\text{init}}$ is observed with increasing $R_{\text{c,max}}$.

The concentrations of the final hydrogen configurations are more dependent on the temperature profile at lower temperatures than on the maximal cooling rate, as it was mentioned in the previous section. It still serves as a good quantity for this experiment because the cooling rate at lower temperatures will be relatively impacted by the different belt speeds as it is the case for $R_{\text{c,max}}$.

Comparing the hydrogen species $[\text{H}_2]_{\text{init}}$ and $[\text{GaH}]_{\text{init}}$ at the faster belt speed (P2) between the two furnaces reveals a significant increase in $[\text{H}_2]_{\text{init}}$ for F1, accompanied by only a slight increase in $[\text{GaH}]_{\text{init}}$. This behavior can be attributed to the markedly different cooling rates at lower temperatures (below 500 °C) shown in Figure 5.4b. The data also indicate that the main factor influencing the total hydrogen content in the bulk is the temperature range between approximately 750 °C and 600 °C. Due to the higher cooling rate in F1, hydrogen has less time to diffuse out of the bulk, resulting in a higher amount of quenched hydrogen.

These findings suggest that for degradation studies known to correlate with hydrogen, such as LeTID, reporting only the peak firing temperature [39, 90, 184] is insufficient for ensuring comparability across different institutions. Including the maximum cooling rate within specific temperature intervals would provide a more complete and reproducible characterization. Ideally, the full temperature profile should be reported, as it contains all relevant information. Of course, even with similar cooling rates, material quality and passivation layer design must be consistent to fully reproduce results. In this study, the cooling ramp of furnace F2 demonstrates a more favorable design for reducing bulk hydrogen content and thereby mitigating LeTID.

5.2 Stability of the TOPCon Architecture

The photovoltaic industry is currently undergoing a significant transition, with TOPCon technology increasingly replacing the traditional passivated emitter and rear cell (PERC) design due to its potential for higher cell efficiencies [25, 249, 250]. This shift to n-type TOPCon solar cells, however, raises concerns regarding rising silver consumption, a critical and finite resource [251, 252]. While n-type Cz-Si dominates recent production trends [222], Ga-doped Si remains a cost-effective alternative, enabling high-efficiency designs such as p-type interdigitated back-contact (pIBC) solar cells [173, 174, 223]. Silver consumption can be reduced

in these cells by contacting the base with aluminum. Additionally, adopting POCl_3 -diffusion instead of BCl_3 or BBr_3 may further enhance gettering efficacy. Nevertheless, regardless of the cell architecture, ensuring long-term stability remains a persistent challenge for the photovoltaic sector.

Additionally, surface-related degradation has been observed to significantly reduce the effective excess carrier lifetime (τ_{eff}) in TOPCon structures [253, 254]. Another source of degradation is the occurrence of LeTID which is the main focus of this work. While high-temperature processing (e.g., reducing bulk hydrogen content [102, 117]) can mitigate LeTID, the long-term stability of diverse sample configurations remains an active area of investigation.

This section examines the impact of peak firing temperature on hydrogen concentration in Ga-doped Cz-Si featuring symmetrically deposited (n)poly-Si layers. The study correlates defect formation during accelerated aging tests with measured hydrogen concentrations. Furthermore, the degradation behavior of various sample structures, including symmetrical and asymmetrical configurations, is systematically evaluated. Hereby, a variation of symmetrical and asymmetrical TOPCon layer stacks and a variation of AlO_x layer thickness is examined. The goal is to examine the impact of the TOPCon layer stack in Ga-doped interdigitated back-contact (pIBC) solar cells. This section is mainly based on the publications [184]^{5.1} and [247]^{5.2}.

5.2.1 IBC Solar Cell Architecture

The fundamental concept behind a back-contacted solar cell design is to minimize metal-induced shading on the front side by relocating the front contact grid to the rear of the cell [255, 256]. A schematic of the resulting pIBC solar cell architecture is shown in Figure 5.6. A brief overview of the necessary layer stacks is provided below.

After saw-damage etching and cleaning, the front side of the solar cell is textured to enhance light coupling. A SiO_x layer is then thermally grown, followed by deposition of (n)a-Si:H on the back side of the wafer. During the subsequent POCl_3 diffusion step, the amorphous silicon crystallizes into (n)poly-Si, simultaneously forming an additional front-floating emitter (FFE) on the front side. The resulting (n)poly-Si layer functions as the n^+ emitter while providing excellent surface passivation and maintaining low contact resistance [257, 258].

Laser ablation is used to locally open the (n)poly-Si on the rear side [223], which is then coated with a thin interfacial oxide, followed by an $\text{AlO}_x/\text{SiN}_x\text{:H}$ stack. Local openings are created by laser ablation, allowing screen-printed aluminum to form contacts with the silicon base. Silver contacts are printed directly onto the dielectric passivation stack. During the firing

^{5.1} Conceptualization, main investigation, formal analysis, and writing were carried out by the author.

^{5.2} Investigation, formal analysis and writing were carried out by the author.

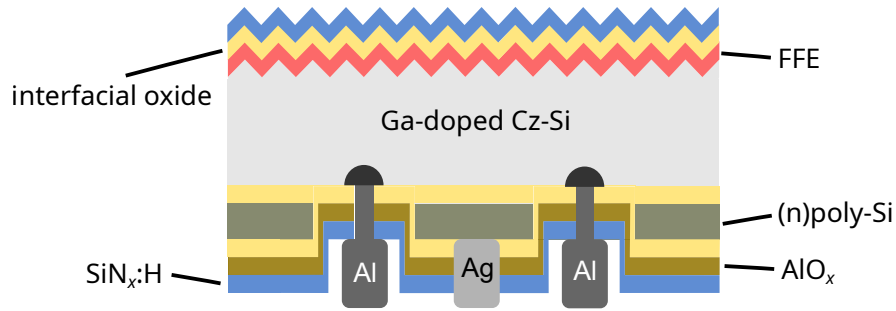


Figure 5.6: Schematic of the investigated p-type interdigitated back-contact (pIBC) solar cell based on Ga-doped Cz-Si. The design includes a front-floating emitter (FFE) on the front side and a patterned TOPCon stack positioned between the silver contacts and the silicon base on the back side.

process, electrical contacts are established between the aluminum and the silicon base, as well as between the silver and the (n)poly-Si layer, respectively. The front side is passivated by a stack of SiO_x and $\text{SiN}_x\text{:H}$, which also serves as an anti-reflection coating.

In IBC solar cells, minority carriers, especially those generated near the front surface, must travel longer distances to reach the rear-side contacts. Therefore, sufficiently high carrier lifetimes are essential to reduce recombination losses.

5.2.2 Design of Experiments and Sample Preparation

This section provides a brief overview of the process parameters used to obtain the various sample structures, including lifetime samples corresponding to the previously presented pIBC solar cell. For this study, Ga-doped wafers with a resistivity of $1.6 \, \Omega \, \text{cm}$ underwent pre-processing as described in Section 2.2.1, resulting in sample thicknesses of approximately $150 \, \mu\text{m}$. Depending on the targeted sample structure shown in Figure 5.7, a thermal tunnel oxide was grown, followed by the deposition of a $\sim 240 \, \text{nm}$ -thick P-doped amorphous silicon ((n)a-Si:H) layer via PECVD, applied either on both sides or only on a single side of the wafer.^{5.3} The (n)a-Si:H layers were crystallized during a subsequent POCl_3 -diffusion step. On planar c-Si surfaces, this diffusion resulted in a sheet resistance of approximately $320 \, \Omega \, \text{sq}^{-1}$, with minimal impact on the doping concentration of the resulting (n)poly-Si.

Following phosphorus silicate glass removal, an optimized $\text{SiN}_x\text{:H}$ passivation and anti-reflective coating were deposited via PECVD. For some samples, a thin PECVD AlO_x layer ($\sim 4 \, \text{nm}$) was additionally deposited between a thermally grown oxide and the $\text{SiN}_x\text{:H}$ layer. The four main sample groups, together with two reference groups lacking (n)a-Si:H or POCl_3 -treatment, are

^{5.3} All processing and passivation steps, except for firing, were carried out externally by either the Fraunhofer Institute for Solar Energy Systems (ISE) or the International Solar Energy Research Center (ISC) Konstanz.

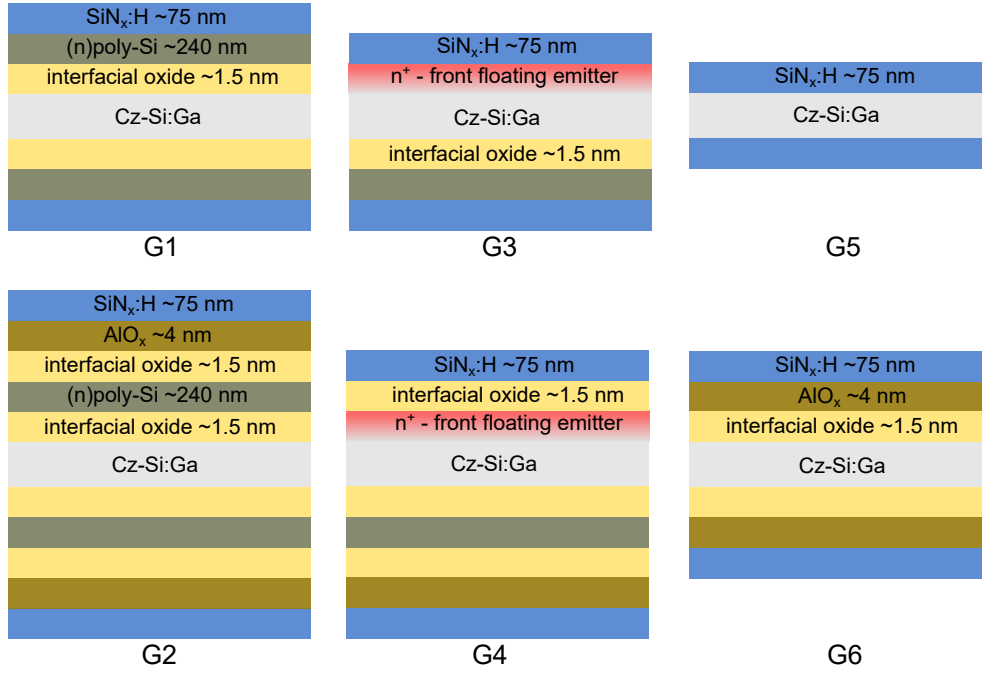


Figure 5.7: Overview of sample configurations. Groups G1/G2 feature both-sided (n)a-Si layers, whereas G3/G4 contain a single-sided layer. Crystallization of (n)a-Si:H during POCl_3 -diffusion introduces an additional front floating emitter. G5 serves as a reference without (n)poly-Si, whereas G2, G4, and G6 include an interfacial oxide and AlO_x beneath $\text{SiN}_x\text{:H}$, in contrast to G1, G3 and G5. Reproduced from [184].

depicted in Figure 5.7. All wafers were fired in an industrial belt furnace at a measured peak sample temperature of 800°C , a condition expected to introduce sufficient hydrogen into the bulk to induce LeTID, as observed in Section 5.1.

For peak temperature variation studies, G2 samples bypassed POCl_3 -diffusion for crystallization, instead undergoing an equivalent-temperature annealing step. The samples were then fired at four measured sample temperatures of $T_1 = 700^\circ\text{C}$, $T_2 = 750^\circ\text{C}$, $T_3 = 800^\circ\text{C}$, and $T_4 = 850^\circ\text{C}$. Four $5\text{ cm} \times 5\text{ cm}$ samples were cut from each wafer before further treatment. Sample preparation for resistivity measurements is described in Section 2.2.5.

5.2.3 Edge-Related Recombination

The study revealed that some of the investigated sample structures, in particular those that feature a layer that collects excess carriers like (n)poly-Si on a p-type substrate, may suffer from long-range edge-related recombination which was already observed by others [259, 260]. Figure 5.8 demonstrates this effect through injection-dependent τ_{eff} measurements of a G2 sample (see Figure 5.7) at varying sizes. The wafers were progressively trimmed on all sides while maintaining the measurement position at the center.

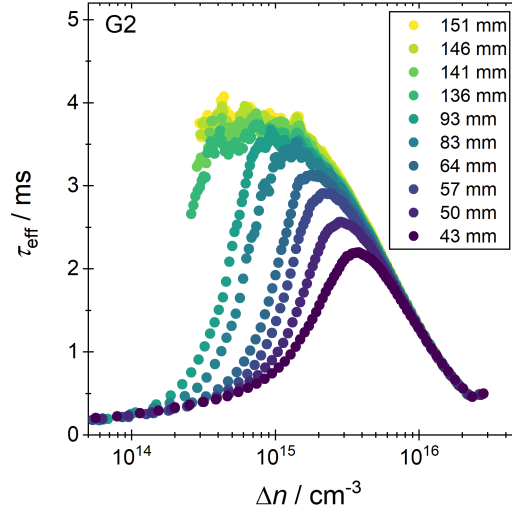


Figure 5.8: Injection-dependent τ_{eff} measurements for a G2 sample with side length reduced from 151 mm to 43 mm. Material was removed equally from all sides while maintaining the original measurement position in the middle of the wafer. Reproduced from [184].

The results show that carrier lifetime remains stable for intact wafers when measurement spots are sufficiently far from edges. However, τ_{eff} decreases substantially at lower injection levels as sample size reduces, with similar findings recently reported via photoluminescence imaging studies [261]. While it is possible to simply use the full wafer after firing without cutting smaller pieces from the sample, this becomes a problem for LeTID studies where space on hotplates can become limited for bigger samples. Potential mitigation strategies are presented in recent works [262, 263], which could be applied for further investigations because they require a more extensive processing approach to prevent recombination at the edges of samples featuring a induced pn-junction.

Since all LeTID testings are executed with 50 mm samples, evaluation of effective charge carrier lifetime will primarily be conducted at $\Delta n = 5 \cdot 10^{15} \text{ cm}^{-3}$ to minimize edge recombination effects. This value is chosen because it represents the lowest injection level at which only marginal differences in τ_{eff} are observed with respect to sample size, as shown in Figure 5.8. However, it should be noted that the injection-dependence of ΔN_{leq} for a deep-level defect, in particular with a high τ_p/τ_n ratio which is around 30 for LeTID [36, 39], implies increasing ΔN_{leq} values when evaluated at lower injection levels [187]. This makes cross-comparisons between datasets with different injection levels (Δn) or $\Delta n/p_0$ ratios potentially problematic (see Section 2.3.1).

Since the lifetime-equivalent defect density is derived from the differences in effective lifetime during degradation, all constant recombination components that remain unchanged during treatment cancel out, as discussed in Section 2.3.1. It remains unclear, however, whether edge-related recombination changes during LeTID testing as the lifetime degrades. A comparison of

long-term stability between two G2 samples, one kept as a full wafer and the other cut to a side length of 5 mm. revealed comparable degradation behavior. The only notable difference was a higher mean square error in the fitted parameters ΔN_{leq}^* , Δj_0 , and τ_p/τ_n (not shown here). Because a higher injection level was chosen for evaluation, the overall degradation extent reported in this section may appear lower than in other sections, where different injection conditions were used. Moreover, the determination of the maximum bulk-related lifetime-equivalent defect density ΔN_{leq}^* carries an increased risk of misinterpretation due to greater fit uncertainties. Nevertheless, correlations with the observed hydrogen species are drawn.

5.2.4 Variation of Sample Structures

As-Fired Characterization

The parameters τ_{eff} , j_0 , implied open-circuit voltage iV_{OC} are evaluated for symmetrical (n)poly-Si samples with a $\text{SiO}_x/\text{AlO}_x/\text{SiN}_x\text{:H}$ layer stack (G2) following firing at peak temperatures ranging from 700 °C to 850 °C. For each peak temperature, measurements are taken at nine positions across at least two wafers. The excess carrier lifetime (at $\Delta n = 5 \cdot 10^{15} \text{ cm}^{-3}$) remains relatively constant at $\sim 2.5 \text{ ms}$ up to a firing temperature of 800 °C, where a drop of $\sim 400 \mu\text{s}$ occurs. Surface-related j_0 remains at $\sim 2 \text{ fA cm}^{-2}$, but variation across the wafer is increased for 800 °C. Implied open-circuit voltage is slightly reduced from $\sim 743 \text{ mV}$ to $\sim 741 \text{ mV}$ at 800 °C.

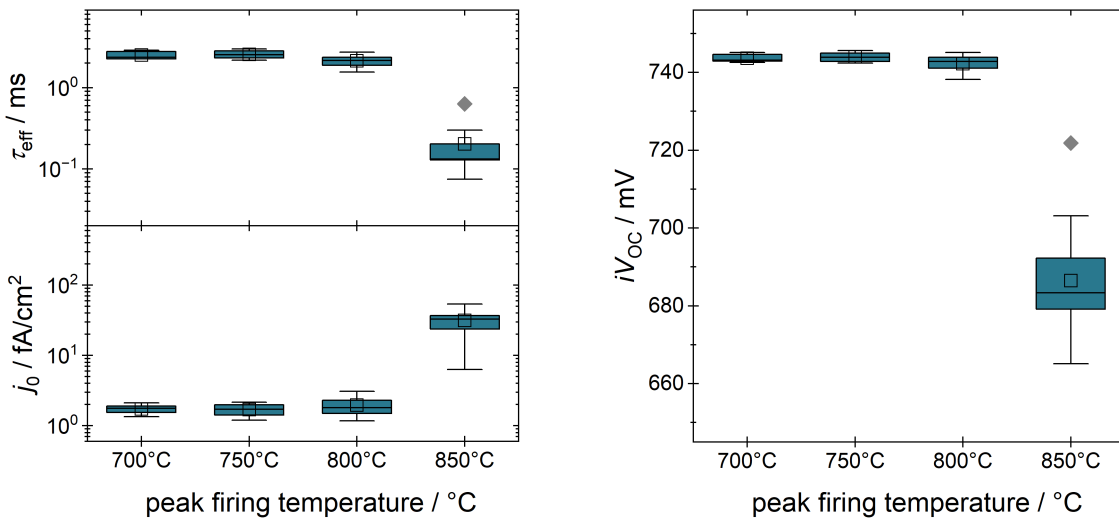


Figure 5.9: Post-firing characteristics of symmetrical $\text{SiO}_x/\text{AlO}_x/\text{SiN}_x\text{:H}$ -capped (n)poly-Si samples on Ga-doped Cz-Si, showing τ_{eff} , j_0 , and iV_{OC} across different peak firing temperatures. As mentioned, τ_{eff} is evaluated at $\Delta n = 5 \cdot 10^{15} \text{ cm}^{-3}$ and j_0 is determined with the Kimmerle method as described in Section 2.3.2. Adapted from [184].

Notably, samples fired at 850 °C exhibited significant performance degradation and loss of homogeneity, consistent with previous observations for (n)poly-Si on B-doped substrates [264]. This deterioration correlates with visible blistering, particularly near sample edges, likely caused by hydrogen accumulation at the (n)poly-Si/c-Si interface leading to layer delamination [265]. These findings suggest that peak firing temperatures should not substantially exceed 800 °C.

Complementary experiments on $\text{SiO}_x/\text{SiN}_x\text{:H}$ -capped samples (G1) without an AlO_x interlayer showed comparable trends, though these results are omitted as a consequence of limited statistical significance.

Impact of Firing on Long-Term Stability in Symmetrical TOPCon Samples

The long-term stability of samples from groups G1 and G2 was evaluated for peak firing temperatures of $T_1 = 700^\circ\text{C}$, $T_2 = 750^\circ\text{C}$, and $T_3 = 800^\circ\text{C}$. Samples fired at 850 °C were excluded by reason of insufficient homogeneity. Figure 5.10 depicts the evolution of τ_{eff} , ΔN_{leq} , ΔN_{leq}^* and j_0 during LeTID testing with 1 sun at 130 °C for the samples G1 and G2. Effective lifetime measurements show that the initial lifetime is lowest for T_3 as already observed in Figure 5.9. After ~ 0.2 h of treatment a minimum in lifetime for both sample types fired at 800 °C can be observed, which is visible as a maximum in ΔN_{leq} . For the peak temperature T_2 the degradation extent is significantly reduced and for T_1 barely any defects are formed or dissolved during the first hour of the treatment.

After ~ 4 h of illuminated anneal, ΔN_{leq} is rising for all samples which can be explained by an increase of j_0 . The degradation and regeneration (especially for T_2 and T_3) during the first few

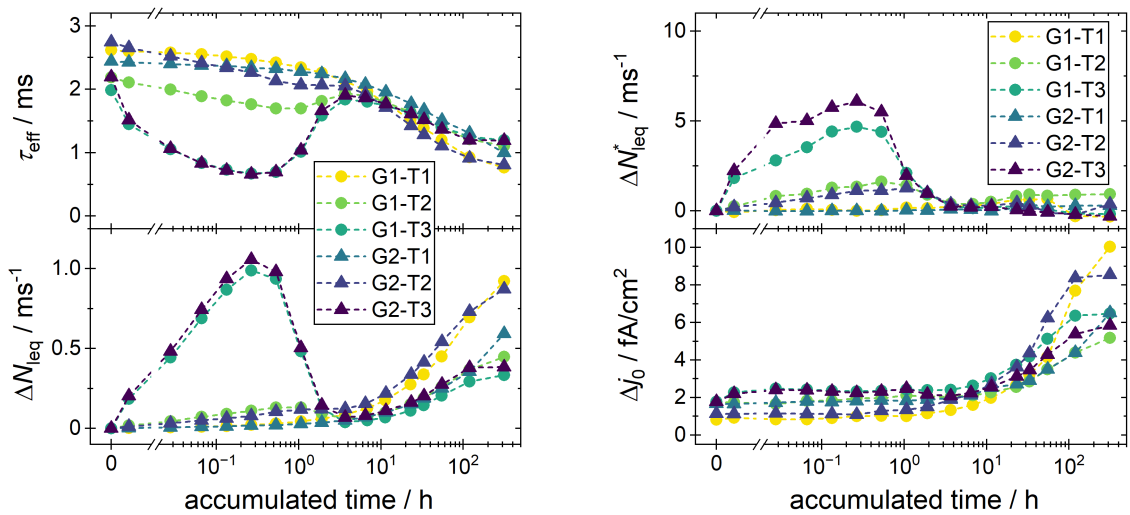


Figure 5.10: Evolution of τ_{eff} , ΔN_{leq} (evaluated at $\Delta n = 5 \cdot 10^{15} \text{ cm}^{-3}$) and Δj_0 for G1 and G2 samples during treatment under 1 sun illumination at 130 °C. Adapted from [184].

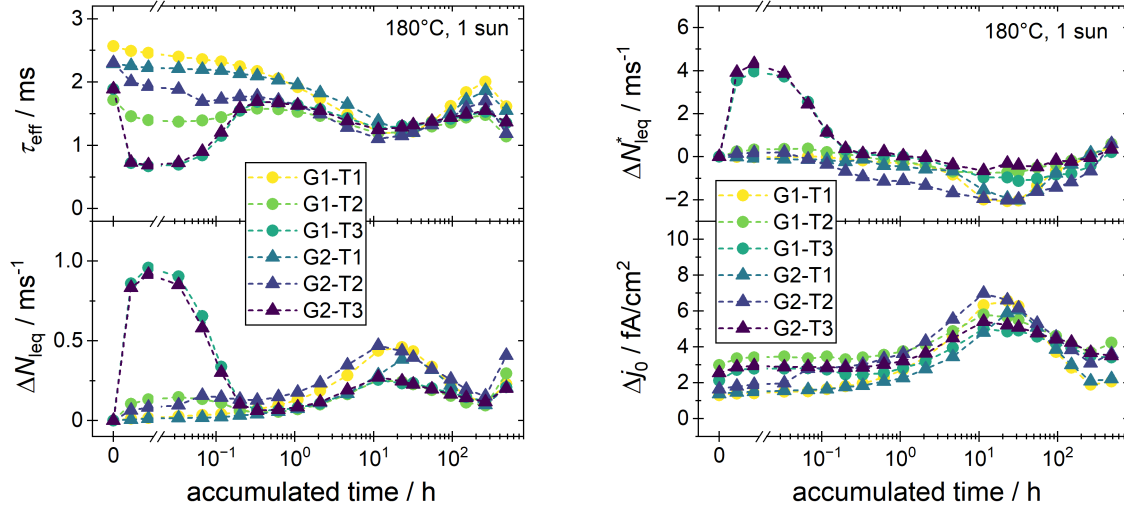


Figure 5.11: Evolution of Δj_0 for samples of G1 and G2 during a treatment under an illumination of 1 sun on a hotplate at 180 °C. Both sample groups were fired at the peak firing temperatures T_1 , T_2 and T_3 . Adapted from [184].

hours of treatment can be attributed to the bulk as j_0 is barely affected.

Complementary experiments with an increased temperature of 180 °C and an illumination of 1 sun revealed minimal differences in surface degradation dynamics between G1 and G2 across different firing temperatures. The evolution of τ_{eff} , ΔN_{leq} , ΔN_{leq}^* and j_0 during these accelerated LeTID tests is shown in Figure 5.11 for the three different peak firing temperatures. During this accelerated LeTID testing, bulk related degradation and regeneration is already finished after ~ 0.3 h of treatment and SRD can be observed.

Overall, the degradation extent observed in Δj_0 appears to be very similar across all firing temperatures. Since the primary difference between these two experiments lies in the passivation layer stack, a direct comparison between these sample types will be discussed in Section 5.2.4. Furthermore, ΔN_{leq}^* remains relatively low throughout the treatment, indicating a reduced susceptibility to LeTID.

Correlation with the Hydrogen Content in Symmetrical TOPCon Samples

It has already been shown in Figure 5.3 that the hydrogen concentration in the Si bulk can be changed by the dependence of peak firing temperature with the maximal cooling rates that affect hydrogen effusion during sample cooling. Therefore, resistivity samples were processed according to Figure 2.1 for G1 and G2 with a variation of peak firing temperatures T_1 , T_2 and T_3 to investigate the influence of (n)poly-Si on the bulk hydrogen concentration.

In Figure 5.12 the initial concentrations $[\text{H}_2]_{\text{init}}$ and $[\text{GaH}]_{\text{init}}$ as well as the total hydrogen

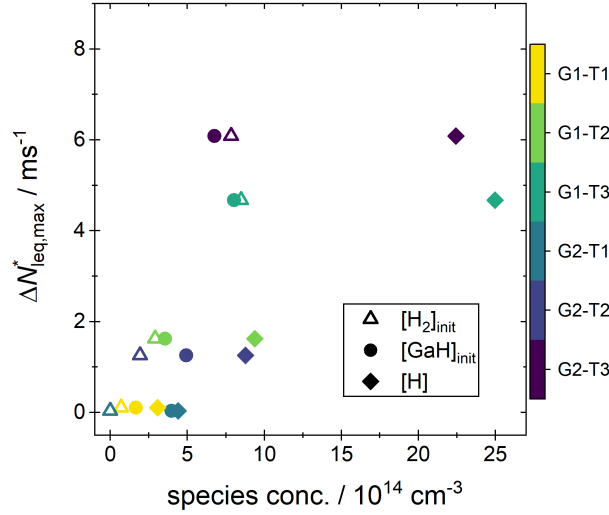


Figure 5.12: Correlation between hydrogen species concentrations ($[H_2]_{\text{init}}$, $[GaH]_{\text{init}}$ and $[H]$) and the maximum bulk-related defect density ($\Delta N_{\text{leq,max}}^*$) for samples with (n)poly-Si passivation and two different stack configurations. Data are shown for three peak firing temperatures: $T_1 = 700^\circ\text{C}$, $T_2 = 750^\circ\text{C}$ and $T_3 = 800^\circ\text{C}$. $\Delta N_{\text{leq,max}}^*$ values are extracted from Figure 5.10. The base material has a base resistivity of $\sim 1.6 \Omega \text{ cm}$. Adapted from [184].

concentration are shown over the observed ΔN_{leq}^* . The latter increases for both sample types with rising peak fire temperature up to $2.5 \cdot 10^{15} \text{ cm}^{-3}$. A similar trend is observed for the initial species concentrations $[H_2]_{\text{init}}$ and $[GaH]_{\text{init}}$.

For the samples fired at T_1 , hardly any $[H_2]_{\text{init}}$ was found. Interestingly, these are also the samples where hardly any degradation in the c-Si bulk occurs. This matches the hypothesis that hydrogen dimers, not GaH pairs, are the main source of hydrogen responsible for LeTID [106].

There is barely any difference in the initial dimer concentration between the sample groups G1 and G2. Since this difference is very small, it is possible that the AlO_x layer does not significantly influence the hydrogen concentration in the bulk. This could be attributed to the use of the PECVD deposition tool, which has been shown to provide a reduced hydrogen barrier compared to ALD [116]. Overall, samples with symmetrical (n)poly-Si appear to show a reduced total hydrogen content or at least $[H_2]_{\text{init}}$ for lower peak firing temperatures. An almost linear correlation between $\Delta N_{\text{leq,max}}^*$ and $[H_2]_{\text{init}}$ is present, as observed before for samples without TOPCon-like structures [105, 106]. In Section 5.2.4, the amount of $[H_2]_{\text{init}}$ compared to references without TOPCon structures will be discussed for a peak temperature of 800°C .

Comparison of Long-Term Stability for Various Layer Stacks

Now, asymmetrical samples resembling real pIBC solar cells, but without metallization, are investigated. To assess the impact of different layer stacks on long-term stability and hydrogen

content, various stack configurations are prepared.

Therefore, the different sample structures shown in Figure 5.7, involving samples with at least one side of (n)poly-Si for G1 to G4 and reference samples only capped with $\text{SiN}_x\text{:H}$ (G5) or $\text{SiO}_x/\text{AlO}_x/\text{SiN}_x\text{:H}$ (G6), are fired at a measured peak sample temperature of $800(10)^\circ\text{C}$. The evolution of τ_{eff} , ΔN_{leq} , ΔN_{leq}^* and j_0 during LeTID testing for these samples is depicted in Figure 5.13. The initial excess carrier lifetime for the symmetrical groups G1 and G2 is similar to that of samples shown in Figure 5.10. Blistering occurring on asymmetrical samples with (n)poly-Si on the backside and a front floating emitter (G3 and G4) during firing may be the reason for reduced lifetimes. For the reference samples, an additional $\text{SiO}_x/\text{AlO}_x$ capping improved the initial lifetime compared to passivation with only $\text{SiN}_x\text{:H}$.

The observed maximum lifetime equivalent defect density seems to be lowest for the first three groups G1 to G3 at $\sim 0.8 \text{ ms}^{-1}$ and is increased for the other groups with the reference that is only capped by $\text{SiN}_x\text{:H}$ showing the highest degradation extent. However, j_0 is improving for some groups during the first $\sim 4 \text{ h}$ of the treatment, in particular G3 and G4, which lowers the observed ΔN_{leq} during this phase.

Symmetrical (n)poly-Si samples maintain the lowest bulk defect densities (ΔN_{leq}^*), with asymmetrical structures showing intermediate values and references displaying the highest susceptibility to degradation. Notably, samples featuring additional $\text{SiO}_x/\text{AlO}_x$ layers consistently outperform their counterparts with only $\text{SiN}_x\text{:H}$ passivation in bulk stability.

Surface-related degradation emerges after approximately 4 h of treatment, most pronounced in samples with single-layer $\text{SiN}_x\text{:H}$ passivation. Symmetrical (n)poly-Si structures (G1, G2)

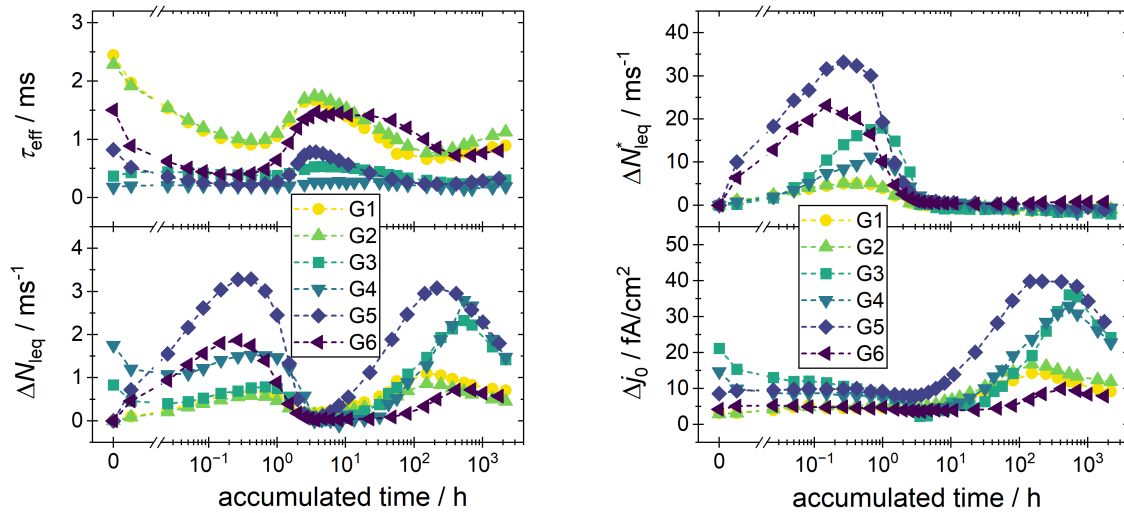


Figure 5.13: Evolution of ΔN_{leq} , ΔN_{leq}^* and Δj_0 during treatment under 1 sun illumination at $130(1)^\circ\text{C}$ for sample groups G1 to G6. Adapted from [184].

demonstrate reduced SRD, while the reference sample G6 with an $\text{AlO}_x/\text{SiN}_x\text{:H}$ passivation exhibits the least change in surface passivation quality throughout the testing period.

Correlation with the Hydrogen Content in Different Layer Stacks

The hydrogen content in the different sample structures is again accessed as described in Section 2.2.5. The species concentrations of $[\text{H}_2]_{\text{init}}$, $[\text{GaH}]_{\text{init}}$ and $[\text{H}]$ for all six groups in correlation with the evaluated maximal bulk-related lifetime equivalent defect density are shown in Figure 5.14. The use of $\Delta N_{\text{leq,max}}^*$ is still preferred in this context despite the limitations discussed in Section 5.2.3 because of the influence of surface-related improvement of samples G3 and G4 during the first few hours of treatment.

Total hydrogen concentration $[\text{H}]$ and $[\text{H}_2]_{\text{init}}$ is highest for the $\text{SiN}_x\text{:H}$ reference G5, which also shows the highest degradation extent. For the AlO_x reference group G6, degradation extent and hydrogen content is already reduced. This can be explained by earlier studies regarding the role of AlO_x as a hydrogen diffusion barrier [116–118, 247] during firing (see Section 5.2.5). As already mentioned in the previous section, this effect is not visible by the comparison between the symmetrical (n)poly-Si samples G1 and G2. The role of AlO_x in combination with (n)poly-Si is likely more complex, and it remains unclear whether the AlO_x layer provides an additional barrier function in this case.

Overall, the (n)poly-Si seems to have more advantageous properties regarding hydrogen content in the c-Si as bulk-related degradation is significantly reduced. The usage of a one-sided (n)poly-Si already lowers the hydrogen content and therefore its degradation extent. An explanation

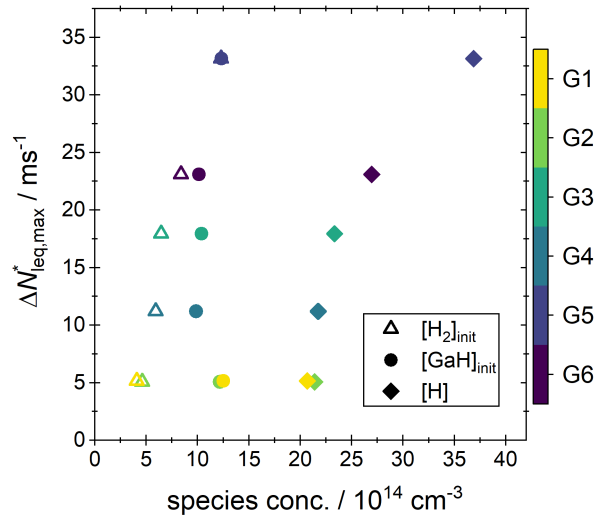


Figure 5.14: Correlation between the maximum bulk-related defect density $\Delta N_{\text{leq,max}}^*$ and the concentrations of hydrogen species $[\text{H}_2]_{\text{init}}$, $[\text{GaH}]_{\text{init}}$, and $[\text{H}]$ for sample structures G1 to G6. Adapted from [184].

might be that the poly-Si is acting as a H sink, leaving less hydrogen in the c-Si that could be harmful due to the involvement in the formation of the LeTID defect and subsequent SRD. Interestingly, the concentration of initially present GaH pairs is highest for the samples G1 and G2 but is rather relatively constant for all sample variations. An interpretation could be that the (n)poly-Si supports an increase of initially present GaH pairs. During or after GaH-pair formation, atomic hydrogen (possibly released from residual H_2) might be removed from the system. As a result, [GaH] would represent a “frozen” concentration, while $[H_2]$ could be reduced afterwards.

Comparing the symmetrical (n)poly-Si samples with those fired at a peak temperature of 800 °C in Figure 5.12, the total hydrogen concentration in both cases remains slightly above $\sim 2.2 \cdot 10^{15} \text{ cm}^{-3}$. However, the present experiment shows a lower $[H_2]_{\text{init}}$ and a higher $[GaH]_{\text{init}}$. This discrepancy aligns with the degradation trends observed in Figure 5.13 compared to Figure 5.10. Since both experiments share the same firing process and base doping concentration, the origin of these deviations remains unclear.

5.2.5 Influence of AlO_x Layer Thickness

The following section builds upon the findings reported in [247], but incorporates a re-evaluation of the original data in light of more recent insights gained over the course of the present work. This re-analysis ensures greater consistency with the current understanding of hydrogen-related degradation phenomena.

Following the investigation of different TOPCon precursor structures, the influence of the AlO_x layer thickness is now addressed. Previous studies have demonstrated that increasing the thickness of the AlO_x layer beneath the $SiN_x:H$ can lead to a reduction in hydrogen content in the silicon bulk, thereby lowering the extent of LeTID, particularly in B-doped materials [116, 117].

In this study, samples were fabricated by depositing AlO_x layers of varying thicknesses (5–25 nm) via ALD. A $SiN_x:H$ layer was subsequently deposited by PECVD, after which all samples were fired at a measured peak temperature of 800(5) °C with a maximal cooling rate of $\sim 100 \text{ K s}^{-1}$. Following processing, the samples underwent LeTID testing on a hotplate under 1 sun illumination at 100 °C. The sample structure therefore corresponds to the reference structure G6 shown in Figure 5.7.

As a consequence of the lower temperature of this treatment compared to previous experiments, the degradation and regeneration dynamics differ, and the absolute extent of LeTID may not be directly comparable to earlier results [92]. Nevertheless, within this set of experiments, a comparative evaluation of LeTID extent as a function of AlO_x layer thickness is valid. The outcomes of the long-term stability testing under these conditions are presented in Figure 5.15.

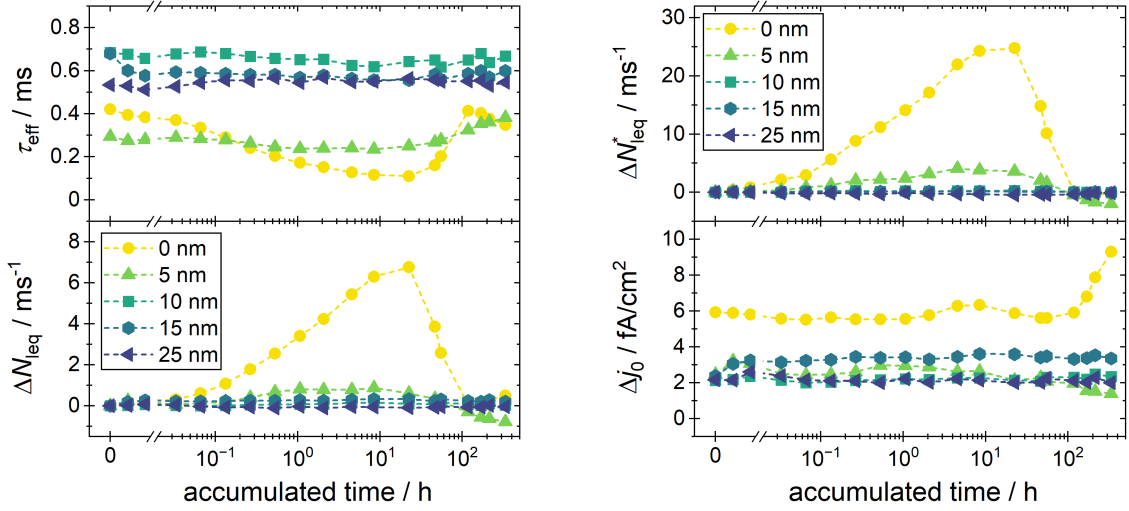


Figure 5.15: Evolution of τ_{eff} , ΔN_{leq} , ΔN_{leq}^* , and j_0 for samples with varying AlO_x layer thicknesses compared to a reference sample without an AlO_x layer during treatment under 1 sun illumination at 100 °C. Samples have a base resistivity of 0.7 $\Omega \text{ cm}$. Data are previously published in [247] and have been reevaluated for this work.

The measurement data of the reference samples without AlO_x layer is evaluated in more detail in [188].

For all samples incorporating an AlO_x layer, the initial τ_{eff} is higher than that of the reference sample without AlO_x , with the exception of the sample featuring a 5 nm AlO_x layer. This improvement can be attributed to enhanced surface passivation, as evidenced by a lower initial j_0 . The reduced initial lifetime in the 5 nm sample may result from insufficient surface passivation or possible introduction of additional bulk defects during processing. Passivation homogeneity may be particularly affected in the case of thin AlO_x layers.

During the LeTID stability testing at 100 °C, a clear degradation is only observed in the reference sample and the 5 nm AlO_x sample. Moreover, for the latter, the extracted ΔN_{leq}^* becomes negative during regeneration, indicating that more defects become recombination-inactive than were initially active. This observation supports the hypothesis that the initially lower lifetime arises at least in parts from temporary defect activation that vanishes upon extended treatment.

All samples passivated with AlO_x exhibit no signs of SRD after ~100 h of illumination treatment. In contrast, the reference sample without AlO_x shows a distinct increase in Δj_0 , a signature of SRD. While the absence of SRD in AlO_x -passivated samples may in part be due to the limited duration of the experiment, it aligns with previous results shown in Figure 5.13, where sample G6 (with AlO_x) exhibited delayed or absent SRD compared to reference sample G5 (without AlO_x). This behavior has also been reported for B-doped samples featuring similar passivation stacks [38, 144].

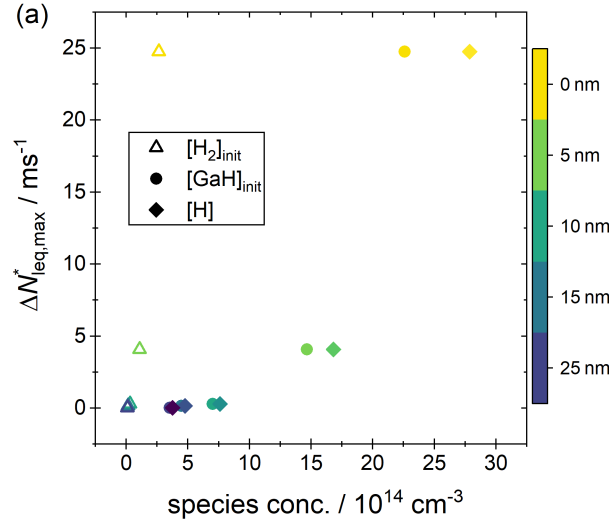


Figure 5.16: Correlation between $\Delta N_{\text{leq,max}}^*$ and concentrations of the hydrogen species $[\text{H}_2]_{\text{init}}$, $[\text{GaH}]_{\text{init}}$ and $[\text{H}]$ for samples with varying AlO_x interlayer thicknesses. Data were previously published in [247] and have been reevaluated for this work.

To verify the suppression of SRD, additional accelerated LeTID testing at 200 °C was conducted (data not shown), and no SRD was observed in any of the AlO_x -passivated samples within 10 h of treatment. These findings reinforce the conclusion that the $\text{AlO}_x/\text{SiN}_x\text{:H}$ stack not only reduces the LeTID extent but also lowers the susceptibility to SRD, as previously observed [38, 144].

These results suggest that an AlO_x layer thicker than 10 nm is sufficient to fully suppress LeTID. A potential explanation for this effect is illustrated in Figure 5.16a, where the maximum defect concentration $\Delta N_{\text{leq,max}}^*$ is plotted against the hydrogen species concentrations $[\text{H}_2]_{\text{init}}$, $[\text{GaH}]_{\text{init}}$ and $[\text{H}]$, all derived from resistivity-measurements. Previous work has already demonstrated, by varying the AlO_x layer thickness, that the resulting hydrogen concentration is strongly influenced by the peak firing temperature [118]. However, it is likely that the cooling rate is also increased in such cases, as discussed in Section 5.1. Overall, this suggests that the barrier function depends on the specific firing profile and therefore cannot be applied universally.

In Figure 5.16, it becomes evident that all hydrogen-related species concentrations decrease significantly with increasing AlO_x layer thickness. Notably, $[\text{H}_2]_{\text{init}}$ approaches zero once the AlO_x thickness exceeds 5 nm, which correlates well with the observed suppression of LeTID. Interestingly, the reference sample, despite exhibiting LeTID, still shows a comparatively low $[\text{H}_2]_{\text{init}}$. This apparent discrepancy can likely be explained by the higher base doping concentration used in this study. A larger dopant concentration increases the availability of acceptor sites for acceptor-hydrogen pair formation, thereby reducing the amount of H_2 remaining in the bulk after firing. This observation will be discussed in more detail in the following section.

5.3 Distribution of Hydrogen Species After Firing

Throughout this chapter, experiments have been conducted to investigate the concentration of hydrogen species in materials with varying base resistivities and layer stacks. This section provides an overview of how changes in material properties influence the configuration of hydrogen species initially present after firing.

In Figure 5.17, the fraction of initially present GaH-pairs relative to the total hydrogen concentration $[\text{GaH}]_{\text{init}}/[\text{H}]$, is plotted as a function of the total hydrogen concentration $[\text{H}]$ for samples with different base doping levels. The data are taken from the respective experiments discussed in this chapter, representing base resistivities of $0.7 \, \Omega \text{ cm}$ (from Figure 5.16), $1 \, \Omega \text{ cm}$ (from Figure 5.3), $1.6 \, \Omega \text{ cm}$ (sample G1 in Figure 5.12), and $1.7 \, \Omega \text{ cm}$ (from Figure 5.5b).

Across all doping levels, the data points with the lowest total hydrogen concentration correspond to the samples that exhibit the least degradation extent, as indicated by the smallest values of ΔN_{leq}^* . As the total hydrogen concentration increases, the degradation extent rises correspondingly. Notably, the relative share of GaH pairs decreases with increasing total hydrogen concentration. This trend suggests that as more hydrogen is quenched into the bulk during firing, a greater fraction exists as H_2 , rather than in the form of electrically inactive GaH pairs. Consequently, the ratio $[\text{GaH}]_{\text{init}}/[\text{H}]$ declines, indicating an increase of LeTID-active hydrogen species that contribute to degradation phenomena such as LeTID.

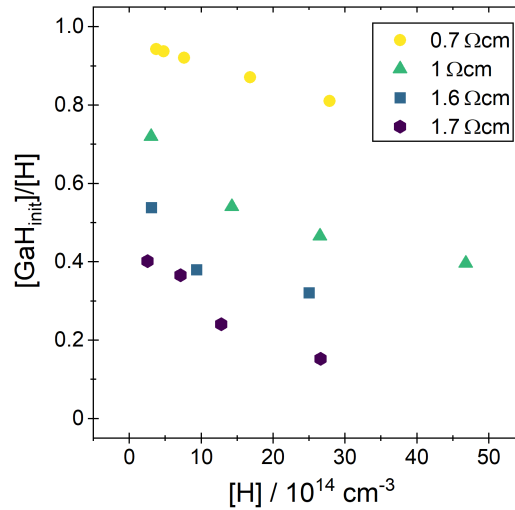


Figure 5.17: Fraction of initially present GaH pairs relative to the total hydrogen concentration plotted versus $[\text{H}]$ for samples with different doping levels. The $0.7 \, \Omega \text{ cm}$ material corresponds to the AlO_x thickness variation, the $1 \, \Omega \text{ cm}$ material comes from the peak firing temperature variation in Figure 5.3, the $1.6 \, \Omega \text{ cm}$ material is from the peak firing-temperature variation with (n)poly-Si/ $\text{SiN}_x\text{:H}$ layer stacks (Figure 5.12) and the $1.7 \, \Omega \text{ cm}$ material is from the furnace comparison experiment in Figure 5.5b.

For higher dopant concentrations (lower base resistivity), the fraction of $[\text{GaH}]_{\text{init}}$ relative to the total hydrogen concentration $[\text{H}]$ increases due to the greater availability of acceptor sites for hydrogen pairing. The data for the $\sim 1 \Omega \text{ cm}$ sample align well with the findings of [106], where the $[\text{GaH}]_{\text{init}}/[\text{H}]$ ratio similarly approaches a value of 0.4 as $[\text{H}]$ increases. It is important to note, however, that while this plot compares the $[\text{GaH}]_{\text{init}}/[\text{H}]$ ratio across varying dopant concentrations, the methods used to induce different hydrogen concentrations differed between experiments, for example, through the variation of AlO_x layer thickness. As a result, the observed trends might not strictly follow the same course for all hydrogenation approaches.

In general, given the observed proportionality between ΔN_{leq}^* and $[\text{H}_2]_{\text{init}}$, using wafers with higher base doping concentrations may be advantageous for mitigating degradation. In such cases, a larger fraction of hydrogen may be bound in the form of GaH pairs, thereby reducing the concentration of free H_2 dimers in the bulk. This reduction in $[\text{H}_2]_{\text{init}}$ could lead to a lower LeTID susceptibility and an overall reduced degradation extent.

5.4 Stability of pIBC Solar Cells

Now that the impact of various TOPCon structures on long-term stability has been evaluated for p-type base materials, this section shifts focus to the actual performance loss of a solar cell during LeTID testing. Specifically, an interdigitated back contact (IBC) solar cell^{5.4} is fabricated using a layer stack shown in Figure 5.6. Many advantages of this cell architecture, particularly in the context of LeTID mitigation, have already been discussed in Section 5.2. Experiments using higher belt speeds, and thus faster cooling rates, showed that the pIBC solar cell exhibits LeTID during illumination at 130°C , with degradation kinetics similar to those observed in the previous lifetime sample experiments. For the following investigation, a firing profile with a slower cooling ramp (3 m min^{-1}) is applied to examine whether LeTID can be effectively suppressed.

This section provides a short overview of the long- and short-term stability of pIBC solar cells during LeTID testing and subsequent measurements. Standard solar cell parameters are evaluated (see Section 2.3.6), while Suns- V_{OC} measurements offer deeper insight by enabling extraction of the injection-dependent effective carrier lifetime (see Section 1.3.1). All pIBC cell investigations in this part are conducted on Ga-doped Cz-Si wafers with a base resistivity of $1 \Omega \text{ cm}$.

^{5.4} Solar cells for this investigation were provided by ISC Konstanz.

5.4.1 Light Soaking

During the measurement of pIBC solar cells using a flasher with a water-cooled measurement chuck, it is observed that repeated flashing leads to an improvement in solar cell performance. As shown in Figure 5.18a, a cyclic measurement of the open-circuit voltage is conducted at 6 s intervals over a total of 600 flashes. A steep increase in V_{OC} is seen during the initial flashes, which gradually flattens and eventually saturates. An overall improvement of ~ 4 mV is observed during this light soaking process. This behavior has also been reported by another study [266]. The improvement can be observed consistently across all solar cell parameters.

One possible hypothesis for this improvement is the dissociation of FeGa-pairs, which can enhance carrier lifetime, as previously observed in Ga-doped RCz-Si wafers (see Section 3.5). However, the observed dynamics in this case do not necessarily align with the known association/dissociation behavior of FeGa pairs. Specifically, in the saturated, light-soaked state, the pIBC cell reverts relatively quickly to its initial performance after about one hour of dark storage.

To gain further insight into the observed performance improvement during light soaking, an additional experiment is conducted. A second pIBC solar cell is subjected to cyclic light soaking for a total of 600 flashes. The resulting injection-dependent τ_{eff} , derived from Suns- V_{OC} measurements, is shown in Figure 5.18b. With an increasing number of flashes, the τ_{eff} curve shifts consistently toward higher lifetimes. The absence of significant injection dependence

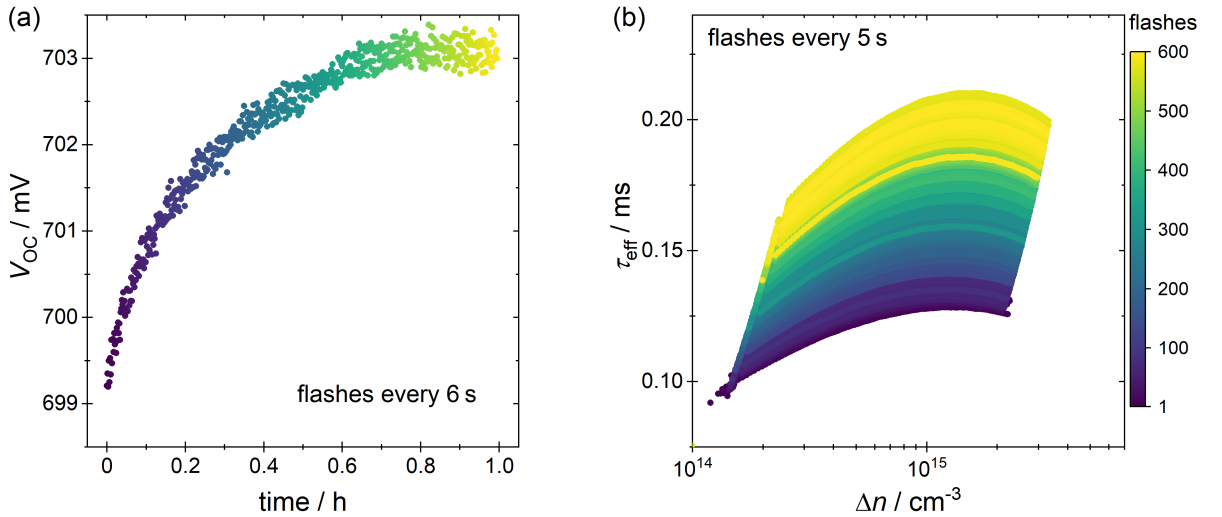


Figure 5.18: (a) Consecutive open-circuit voltage measurements with 6 s pauses between flashes, recorded over a total of 600 flashes. (b) Injection-dependent τ_{eff} derived from Suns- V_{OC} measurements with 5 s pauses between flashes, likewise recorded over 600 flashes. In both cases, the initial measurement was performed after storing the cell in the dark for more than 24 h.

suggests that iron-acceptor pair dissociation is not the cause.

Instead, the observed behavior could be attributed to an improvement in surface passivation quality. Based on an analysis using Equation (2.6), a reduction of $\sim 10 \text{ fA cm}^{-2}$ in the surface-related saturation current density is calculated. However, this effect was not observed in the non-metallized samples discussed in earlier sections, despite reports of similar light-soaking behavior in such samples by others [266]. Their findings also indicate that this phenomenon is present in n-type TOPCon solar cells, albeit to a lesser extent.

When testing V_{OC} during different measurement cycle intervals between 5 s and 10 s, as shown in Figure 5.19a, higher equilibrium states are reached with shorter cycling intervals. Conversely, monitoring the relaxation of V_{OC} from a light-soaked state using longer cycling intervals of 20 s to 50 s, as illustrated in Figure 5.19b, reveals that the equilibrium state depends on the time between each flash. The equilibrium therefore depends on the illumination interval and the accumulated light dose.

A possible explanation for the observed light-soaking behavior is a change in surface charge states induced by illumination, which gradually relax back to their initial configuration when the cell is stored in the dark. This suggests that the light-soaking effect may result from the excitation or reaction of a certain species at the solar cell surface, occurring on a short timescale under illumination and reversing once the illumination ceases. However, it remains unclear what exactly triggers this process and which component of the surface passivation stack is involved.

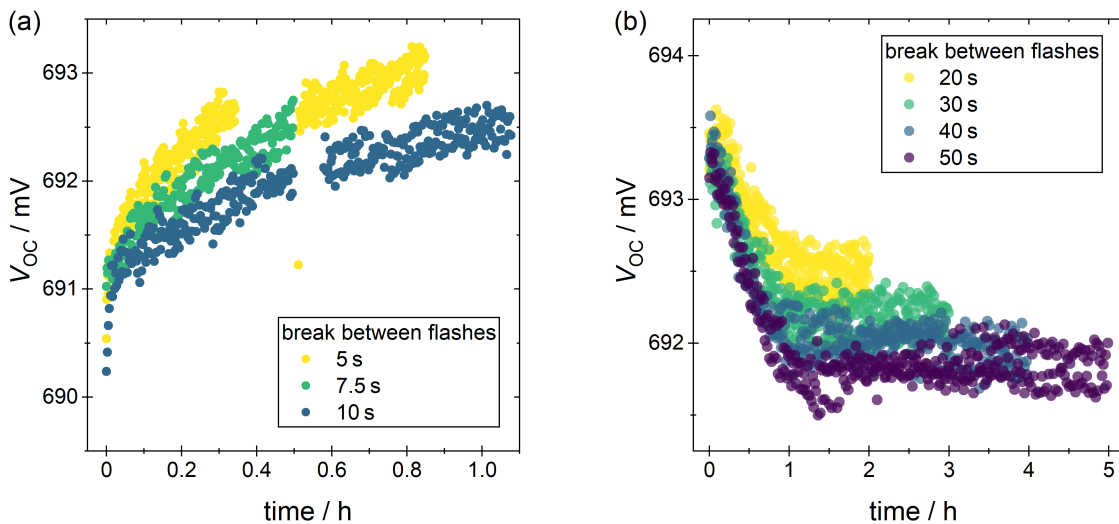


Figure 5.19: (a) Consecutive open-circuit voltage measurements with varying pauses between flashes. The measurement cycle is interrupted by a longer break after ~ 0.35 h for the 5 s cycle and after ~ 0.5 h for the 10 s cycle. (b) Consecutive open-circuit voltage measurements with varying pauses between flashes after reaching a stable V_{OC} during light soaking.

An additional observation is that light soaking using a halogen lamp at 1 sun intensity while keeping the cell at room temperature results in a smaller performance improvement compared to flashing with 1000 W m^{-2} . Since the accumulated photon-flux is reached much faster with the halogen lamp, this suggests that the spectral composition plays a crucial role. The main difference between the flasher and halogen spectra lies in the photon flux at shorter wavelengths, implying that high-energy photons absorbed near the surface are likely responsible for the temporary improvement. Furthermore, this light-soaking effect appears independently of LeTID behavior, and changes in bulk hydrogen content do not influence the observed dynamics. Another notable, though not yet extensively studied, observation is the localized improvement of certain nonspecific spots on the solar cell during light soaking with infrared LEDs in a PLI setup. In Figure 5.20, the change in photoluminescence intensity is shown by pixel-wise subtraction in PL images 1–9 recorded during progressive LED illumination. Between each image, the cell was exposed to approximately 800 ms of light soaking using a photon-flux of $2.1 \cdot 10^{17} \text{ cm}^{-2} \text{ s}^{-1}$. The reference image was taken after storing the cell in the dark for more than 24 h. While a few regions exhibit significant improvement, the overall photoluminescence intensity of the cell increases only slightly. This suggests that the effect may be confined to localized defects rather than reflecting a global enhancement of cell performance.

In terms of field application, the impact of this light-soaking effect is likely negligible since the

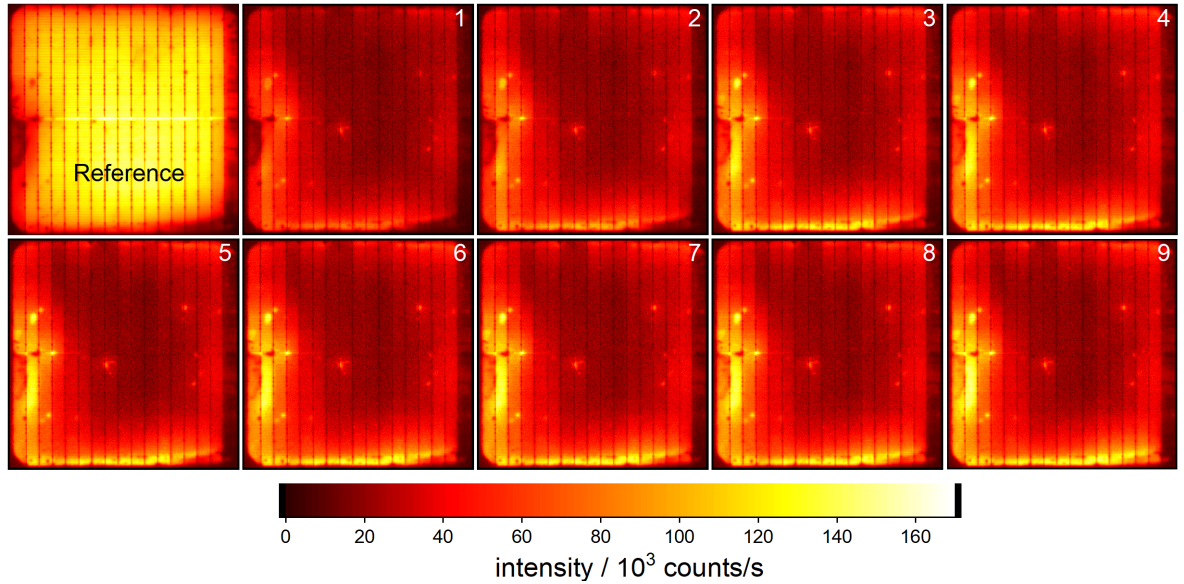


Figure 5.20: Photoluminescence images of a pIBC solar cell during light soaking using LEDs. The top-left image represents the first measurement after dark storage. The cell is oriented such that the LEDs illuminate the rear side while photoluminescence is recorded from the front. Images 1–9 show the pixel-wise difference relative to the reference image, illustrating progressive changes during light soaking. Between each measurement, the cell is illuminated for 800 ms with LEDs at a photon flux of $2.1 \cdot 10^{17} \text{ cm}^{-2} \text{ s}^{-1}$.

improvement occurs over very short timescales. For example, the saturation in Figure 5.18a is reached only after approximately one hour due to the use of 100 ms flashes with 5 s intervals. Under continuous illumination, the light-soaked state might be attained within seconds. However, this transient behavior should be carefully considered during testing to ensure measurement consistency and comparability.

5.4.2 Long-Term Stability

More relevant for operation of pIBC solar cells is the long term stability which is discussed in the following. For this investigation the previous learnings are applied and a slow belt speed at 3 m min^{-1} is used to reduced the hydrogen content in the sample. Throughout the testing, solar cell parameters are repeatedly measured over a series of flashes, followed by a Suns- V_{OC} measurement using a decaying flash. Figure 5.21 shows the evolution of V_{OC} , j_{SC} , FF , and η during LeTID testing at 130°C of the pIBC solar cell. During LeTID testing, the cell shows an initial drop in all parameters. It then stays relatively stable until about 10 h of treatment. At this point, a strong degradation of V_{OC} sets in. After $\sim 100 \text{ h}$, j_{SC} also begins to decrease. In contrast, the FF changes only slightly and even improves during the V_{OC} drop. Overall, V_{OC} suffers more strongly than j_{SC} . Comparing the inset of V_{OC} degradation with earlier lifetime experiments, the timing matches well with the onset of surface-related degradation in those samples.

To gain deeper insights, injection-dependent lifetimes are derived from Suns- V_{OC} measurements, and the evolution of τ_{eff} during LeTID testing is analyzed using Equation (2.6). The

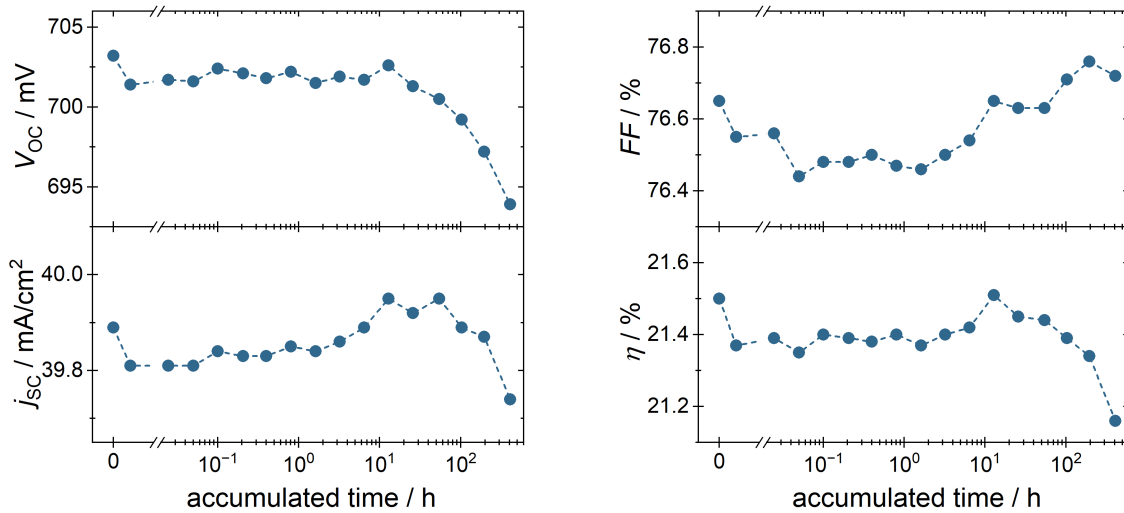


Figure 5.21: Evolution of the solar cell parameter V_{OC} , j_{SC} , FF and η during LeTID testing of a pIBC solar cell at 130°C under 1 sun illumination.

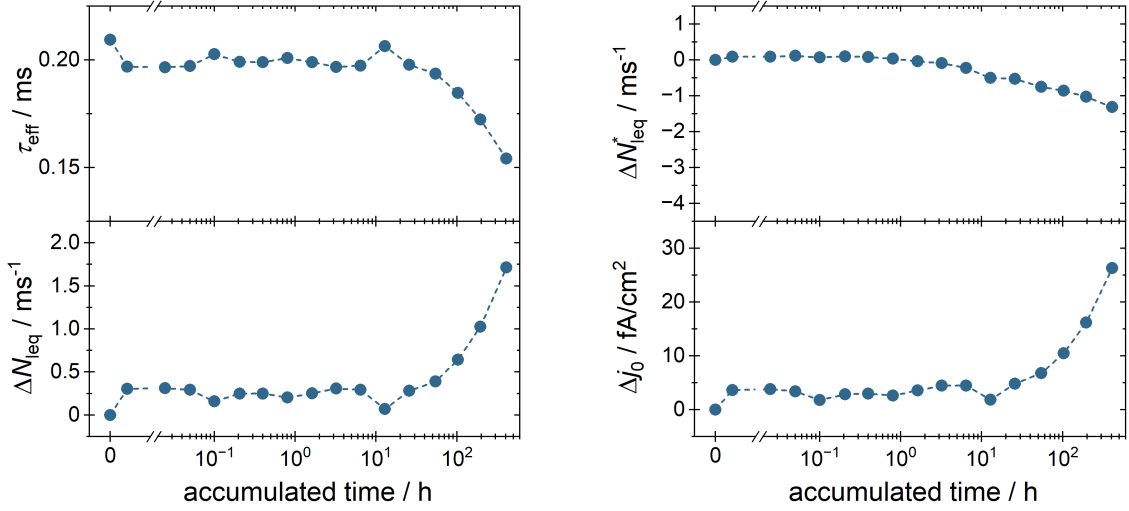


Figure 5.22: Evolution of τ_{eff} , ΔN_{leq} , ΔN_{leq}^* and Δj_0 of a pIBC solar cells treated at 130 °C under 1 sun illumination. The initial j_0 from the slope-based approach could not be reliably determined owing to a lack of data in the higher injection range.

effective lifetime and related parameters obtained from the difference analysis for the pIBC solar cell is shown in Figure 5.22. Because of the reduced lifetime, the limitation imposed by the maximal generation intensity of 1000 W m^{-2} makes it difficult to access higher injection ranges. Consequently, it is not possible to calculate an absolute value for j_0 , and the change in surface passivation quality cannot be normalized to the initial value as was done in previous investigations with precursor samples.

The initial drop in solar cell parameters (see Figure 5.21) can be attributed to a change in surface passivation quality, as seen in Figure 5.22 by the rise in Δj_0 , while the bulk-related ΔN_{leq}^* appears less affected. Since the cell is preconditioned by light soaking, the equilibrium state under halogen lamp illumination may be lower. After the first 30 s of LeTID testing, the surface remains relatively stable until about 10 h, when a steep increase in Δj_0 indicates SRD. At the same time, ΔN_{leq}^* decreases, which is likely an evaluation artifact caused by the limited injection range. During the first few hours of treatment, ΔN_{leq}^* stays nearly constant, indicating the absence of LeTID in this period.

It should be noted that for this specific cell and more precisely for this metal paste, a relatively slow belt speed during firing is necessary, leading to a slow cooling ramp after reaching the peak temperature. As discussed in Section 5.1.3, this processing condition reduces the LeTID extent by lowering the hydrogen content in the wafer bulk. Consequently, the pIBC solar cell investigated here is largely immune to LeTID. Precise control of the firing profile is therefore sufficient for effective LeTID mitigation. However, the slower firing process may be unfavorable for industrial production as it lowers throughput. Enhancing the silicon wafer

purity could increase the hydrogen tolerance, thereby enabling the use of faster belt speeds while maintaining long-term stability.

Even though LeTID could be effectively mitigated, surface-related degradation still occurs. The underlying cause of this degradation remains unclear at this stage. However, investigating this phenomenon lies beyond the scope of the present work and represents an opportunity for future research.

5.5 Conclusions

Variation of firing profiles revealed a correlation between the peak firing temperature and the maximum cooling rate of a wafer. Further analysis showed that the maximum cooling rate is the more reliable parameter for estimating the degradation extent during LeTID testing. This finding is consistent with the observed concentration of initially present hydrogen dimers, which are known to correlate with the severity of LeTID. As a consequence of the observations made in this work, it is recommended to apply a comparatively low firing temperature combined with a low maximum cooling rate. This approach reduces the amount of hydrogen quenched into the silicon bulk. Furthermore, adjusting the temperature profile at lower temperatures may prove beneficial, as it could shift the initial species distribution toward a higher fraction of GaH pairs, thereby lowering the susceptibility to LeTID.

The results further suggest that the role of the maximum cooling rate at higher temperatures, where atomic hydrogen diffusion determines the bulk concentration, can likely be transferred to n-type material. However, further research should investigate the influence of the cooling rate at lower temperatures (below $\sim 400^\circ\text{C}$) to evaluate whether degradation susceptibility can be reduced. Since donor-hydrogen pairs are not stable, dopant atoms cannot be expected to lower $[\text{H}_2]_{\text{init}}$.

TOPCon stacks featuring (n)poly-Si show an improved surface passivation quality compared to p-type samples passivated with $\text{SiN}_x\text{:H}$ only. The firing stability of such stacks is given up to a peak sample temperature of 800°C . Higher temperature may result in blistering. Overall, the hydrogen concentration is significantly reduced for samples featuring TOPCon symmetrical on both sides of the sample. Thus, reduced degradation extent can be observed during LeTID testing compared to samples featuring a TOPCon stack only on the back side of a wafer.

A comparison of different capping layers such as a $\text{SiO}_x/\text{SiN}_x\text{:H}$ or a $\text{SiO}_x/\text{AlO}_x/\text{SiN}_x\text{:H}$ stack showed no further reduction in degradation extent or hydrogen content. Yet, a variation of AlO_x layer thickness on $[\text{H}_2]_{\text{init}}$ and observed $\Delta N_{\text{leq,max}}^*$ on plain Ga-doped Cz-Si wafer showcased the barrier function of AlO_x against hydrogen.

It can be concluded that TOPCon structures, such as the ones used in this work, are less susceptible to LeTID compared to samples which do not feature such TOPCon structures. With the current trend towards cell architectures relying on this technology, a further reduction of LeTID extent is to be expected.

The transfer to fully metallized Ga-doped IBC solar cells demonstrated that a combination of suitable firing conditions and the use of TOPCon structures can effectively mitigate LeTID in cell applications. Nevertheless, SRD was still observed after extended treatment times.

In addition, short-term instabilities appeared during light soaking. To gain deeper insight, it would be valuable to investigate light-soaking effects in n-type solar cells, which also rely on TOPCon technology. In such cells, a surface-related improvement similar to that observed in the pIBC solar cell may occur, though changes in bulk defects are also likely, as indicated by the findings in Section 4.1. Overall, the light-soaking effect in the pIBC solar cell is not yet fully understood and leaves room for further investigation, for example by varying the illumination spectrum or passivation stacks. However, this phenomenon appears to be of limited relevance for field applications.

Summary

In this work, the process influences during solar cell production on the light and elevated temperature-induced degradation (LeTID) are explored. A special focus lies on the impact of state-of-the-art crystal growth by the Czochralski method with melt recharging (RCz-Si) and on the stability of p-type interdigitated back-contact (pIBC) solar cells.

Chapter 3 discusses the fundamentals of segregation in the RCz-Si process. Interstitial iron concentrations ranging from $1 \cdot 10^9 \text{ cm}^{-3}$ to $1.7 \cdot 10^{10} \text{ cm}^{-3}$ were determined, confirming the expected accumulation of impurities both along individual crystals and in crystals subsequently pulled after melt recharging. Phosphorus diffusion treatment effectively reduced iron levels, demonstrating its gettering efficacy. The maximum defect density $\Delta N_{\text{leq,max}}$ is found to increase progressively in later ingot pulls, likely due to impurity incorporation or intrinsic defect generation. This behavior aligns with LeTID characteristics, particularly the asymmetric minority carrier lifetimes (symmetry factor τ_p/τ_n between 27 and 37). However, no correlation is found between initially present hydrogen dimers ($[\text{H}_2]_{\text{init}}$) and degradation extent, ruling out hydrogen as the primary driver. Instead, an unknown species accumulating in the melt is suspected to cause the increased degradation. While iron tracking provides useful insights into impurity accumulation, its usefulness is constrained by the inability to distinguish between impurities with segregation coefficients $\kappa \ll 1$.

Chapter 4 focuses on the defect kinetics in n-type Cz-Si under light soaking and LeTID conditions, which seem to follow two independent three-state models. In contrast to p-type Si, where defects stabilize mostly in recombination-inactive states post-firing, n-type defects remain predominantly in recombination-active state B after firing. Light soaking at reduced temperatures simultaneously anneals a LeTID defect ($A \leftarrow B$) while activating an additional defect ($A' \rightarrow B'$). While $A \rightleftharpoons B$ is reversible, the pathway $B \rightarrow C$ (LeTID regeneration) is irreversible. The metastable B' state fully converts into C' during prolonged illumination without recurrence, indicating a single-pass activation process.

Both phosphorus- and antimony-doped RCz-Si exhibit regeneration-dominated long-term stability behavior at 130°C under 1 sun illumination, with surface-related degradation appearing a secondary phase in samples passivated with $\text{SiN}_x\text{:H}$. Prior light soaking enhances the subsequent LeTID degradation later-ingot wafers, reflected by increased $\Delta N_{\text{leq,max}}$. Compared

to p-type material, n-type shows an overall reduced lifetime degradation. High-temperature treatments such as PDT or TR have only minor influence on the long-term LeTID kinetics, suggesting that the mitigation of the secondary defect precursor, beside hydrogen, is not easily possible.

Chapter 5 demonstrates a correlation between peak firing temperature and maximum cooling rate. The cooling rate determines LeTID severity by quenching mobile atomic hydrogen and promoting hydrogen dimer formation, which correlates with degradation extent. Optimal suppression of LeTID is achieved with reduced peak firing temperatures combined with slow cooling. Moreover, the temperature profile at lower temperatures (below $\sim 400^\circ\text{C}$) also plays a critical role, as it defines the initial hydrogen species distribution.

TOPCon structures with (n)poly-Si on Ga-doped Cz-Si exhibit performance losses at measured peak firing temperatures above 800°C , caused by blistering. Pronounced degradation occurs only for $T_{\text{peak}} > 750^\circ\text{C}$. The maximum defect density ($\Delta N_{\text{leq,max}}$) correlates with initial H_2 dimer concentration, independent of the capping layer composition, indicating (n)poly-Si alone serves as an effective hydrogen sink. Thus, the lowest degradation occurred in symmetrical (n)poly-Si structures, consistent with their lowest $[\text{H}_2]_{\text{init}}$. In comparison, asymmetric TOPCon structures with $\text{SiO}_x/\text{AlO}_x$ capping showed reduced degradation relative to $\text{SiN}_x\text{:H}$ -only samples.

Lastly, a pIBC solar cell on Ga-doped Cz-Si with TOPCon passivation and slow belt speed during firing showed strong LeTID suppression. Transient light-soaking effects were observed independently of bulk degradation and may be linked to localized improvements in surface passivation.

In summary, the influence of solar cell processing on degradation phenomena such as LeTID can be divided into two key aspects. The first concerns the intrinsic material quality, which is primarily determined by the purity of crystal growth process. While subsequent high-temperature treatments may alter this initial quality, they do not change the degradation extent during LeTID testing. Instead, the degradation behavior appears to be governed by an as-yet unidentified precursor species linked to impurity accumulation during crystal growth.

The second critical aspect involves all process-related factors of hydrogen incorporation, particularly those steps that determine the final hydrogen concentration and configuration in the silicon bulk. Here, the composition of the passivation stack and the exact firing conditions are decisive, with the post-firing cooling rate identified as a key parameter, as it strongly influences hydrogen retention and distribution within the wafer.

Although intrinsic material quality and hydrogen-related processing factors often act independently, their combined effect ultimately determines the overall extent of degradation in silicon solar cells. The findings of this work highlight that targeted optimization of hydrogen

incorporation is essential to mitigate degradation phenomena in modern high-efficiency devices. At the same time, the crystal growth process remains the decisive factor in determining how susceptible a given material is to LeTID.

Zusammenfassung

In dieser Arbeit wurden die Einflüsse von Produktionsprozessen auf die licht- und temperaturinduzierte Degradation (LeTID) von Solarzellen untersucht. Ein besonderer Schwerpunkt lag auf den Auswirkungen moderner Kristallzüchtungsverfahren mittels Czochralski-Methode mit Schmelznachfüllung (RCz-Si) sowie auf der Stabilität von p-Typ-Solarzellen mit ineinandergreifenden Rückkontakten (pIBC Solarzellen).

Kapitel 3 behandelte die Grundlagen der Segregation im Kontext des RCz-Si-Prozesses. Im untersuchten Material wurden interstitielle Eisenkonzentrationen zwischen $1 \cdot 10^9 \text{ cm}^{-3}$ und $1.7 \cdot 10^{10} \text{ cm}^{-3}$ festgestellt, was die erwartete Akkumulation von Verunreinigungen während der Kristallzucht bestätigt. Die Phosphordiffusionsbehandlung reduzierte die Eisenwerte effektiv und bestätigt damit ihre Getterwirkung. Die maximale LeTID-Defektdichte $\Delta N_{\text{leq,max}}$ stieg in späteren Ingot-Ziehungen progressiv an, vermutlich aufgrund kumulativer Verunreinigungsaufnahme oder intrinsischer Defektbildung. Dieses Verhalten entspricht den LeTID-Charakteristika, insbesondere den asymmetrischen Minoritätsträgerlebensdauern (Symmetriefaktor τ_p/τ_n zwischen 27 und 37). Ein Zusammenhang zwischen initial vorhandenen Wasserstoffdimeren ($[\text{H}_2]_{\text{init}}$) und dem Degradationsausmaß konnte hingegen nicht festgestellt werden, sodass Wasserstoff als primärer Treiber ausgeschlossen wird. Stattdessen wird eine unbekannte Spezies, die sich in der Schmelze anreichert, für die verstärkte Degradation verantwortlich gemacht. Die Bestimmung der Eisenkonzentrationen lieferte zwar wertvolle Einblicke in die Verunreinigungsakkumulation, ihre Aussagekraft ist jedoch durch die Unfähigkeit eingeschränkt, Verunreinigungen mit sehr kleinem Segregationskoeffizienten ($\kappa \ll 1$) zu unterscheiden.

Kapitel 4 beschäftigte sich mit der Defektkinetik in n-Typ Cz-Si unter Lichtbestrahlungs- und LeTID-Bedingungen. Die Kinetik lässt sich vermutlich durch zwei unabhängige Drei-Zustands-Modelle beschreiben. Im Gegensatz zu p-Typ Si, bei dem Defekte nach dem Feuerschritt überwiegend in einem rekombinationsinaktiven Zustand verbleiben, befinden sich n-Typ-Defekte nach thermischer Behandlung überwiegend im rekombinationsaktiven Zustand B . Lichtbestrahlung bei reduzierten Temperaturen treibt gleichzeitig die Ausheilung eines LeTID-Defekts ($A \leftarrow B$) sowie die Aktivierung eines zusätzlichen Defekts ($A' \rightarrow B'$) voran. Dabei ist der Übergang $A \rightleftharpoons B$ reversibel, während $B \rightarrow C$ (LeTID-Regeneration) irreversibel verläuft. Der metastabile Zustand B' wandelt sich während längerer Beleuchtung vollständig in C' um, ohne

dass eine Rückbildung erfolgt, was auf einen Einweg-Aktivierungsprozess hindeutet.

Sowohl phosphor- als auch antimondotiertes RCz-Si zeigten bei 130 °C und 1 sun eine regenerationsdominierte Degradation, wobei oberflächenbezogene Degradation eine sekundäre Phase darstellt. Vorherige Lichtbestrahlung verstärkte die Degradation in nachfolgenden LeTID-Tests bei späteren Ingot-Wafern, was sich in einem erhöhten Degradationsausmaß widerspiegelte. Im Vergleich zu p-Typ weist n-Typ eine geringere Lebensdauerverminderung auf. Hochtemperaturbehandlungen wie PDT oder TR beeinflussen die langfristige LeTID-Kinetik nur minimal, was darauf hindeutet, dass die Minderung anderer Defektvorläufer neben Wasserstoff die LeTID-Phänomene nicht einfach reduzieren kann.

Kapitel 5 zeigte eine direkte Korrelation zwischen der Spitzentemperatur T_{peak} und der maximalen Abkühlrate. Die Abkühlrate bestimmt die LeTID-Stärke, indem sie mobile Wasserstoffatome einfriert und dadurch die Bildung von Wasserstoffdimeren begünstigt, die bekanntermaßen mit dem LeTID-Ausmaß korrelieren. Optimale Feuerbedingungen kombinieren reduzierte Spitzentemperaturen mit langsamer Abkühlung, um den Wasserstoffgehalt im Wafer zu minimieren. Zudem spielt auch das Temperaturprofil bei niedrigeren Temperaturen (unterhalb von ~400 °C) eine entscheidende Rolle, da es die anfängliche Verteilung der Wasserstoffspezies bestimmt.

TOPCon-Strukturen mit (n)poly-Si auf Ga-dotiertem Cz-Si zeigten Leistungsverluste bei $T_{\text{peak}} > 800$ °C aufgrund von Blisterbildung. Signifikante Degradation trat nur oberhalb von $T_{\text{peak}} > 750$ °C auf, während niedrigere Temperaturen die oberflächenbezogene Degradation verstärkten. Die maximale Defektdichte ($\Delta N_{\text{leq,max}}$) korrelierte mit der initialen H_2 -Konzentration, unabhängig von der Deckschichtzusammensetzung, was darauf hinweist, dass (n)poly-Si allein als effektive Wasserstoffsенke wirkt. Asymmetrische TOPCon-Strukturen mit $\text{SiO}_x/\text{AlO}_x$ -Schichten wiesen eine geringere Degradation auf als $\text{SiN}_x\text{:H}$ -only-Proben, während symmetrisches (n)poly-Si die niedrigsten $[\text{H}_2]_{\text{init}}$ -Werte und somit die geringste Degradation zeigte.

Schließlich zeigten pIBC-Solarzellen auf Ga-dotiertem Cz-Si mit TOPCon-Passivierung eine deutliche LeTID-Unterdrückung. Transiente Lichtbestrahlungseffekte traten unabhängig von der Volumendegradation auf und deuten auf eine lokale, metastabile Rekombination an der Grenzfläche hin

Zusammenfassend lässt sich der Einfluss der Solarzellenprozessierung auf Degradationsphänomene wie LeTID in zwei zentrale Aspekte unterteilen. Der erste betrifft die intrinsische Materialqualität, die hauptsächlich durch die Reinheit des Kristallzuchtprozesses bestimmt wird. Zwar können nachfolgende Hochtemperaturprozesse die Materialqualität beeinflussen, das Degradationsverhalten bleibt jedoch weitgehend unverändert. Das Ausmaß der Degradation hängt zudem von einer bisher unbekannten Vorläuferspezies ab, die mit der Verunreinigungsakkumulation während der Kristallzüchtung verknüpft ist.

Der zweite Aspekt umfasst alle prozessbedingten Faktoren der Wasserstoffeinbringung, insbesondere solche Schritte, die die endgültige Wasserstoffkonzentration und -konfiguration im Siliziumvolumen bestimmen. Hier spielen vor allem die Zusammensetzung der Passivierungsstapel und die genauen Feuerungsbedingungen eine entscheidende Rolle. Die Abkühlrate beim Feuerschritt erwies sich dabei als kritischer Parameter, da sie die Wasserstoffretention und -verteilung im Wafer maßgeblich steuert.

Obwohl diese beiden Mechanismen häufig unabhängig wirken, bestimmen sie in ihrer Kombination das Gesamtausmaß der Degradation in Siliziumsolarzellen. Die Ergebnisse dieser Arbeit verdeutlichen, dass eine gezielte Prozessoptimierung der Wasserstoffkonzentration essenziell ist, um Degradationsphänomene in modernen Hochleistungssolarzellen effektiv zu minimieren. Die materialbedingte Komponente lässt sich hingegen primär durch die Kristallzüchtung beeinflussen und stellt somit einen weiteren zentralen Faktor für die Anfälligkeit gegenüber LeTID dar.

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List of Publications and Supervision

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Peer-reviewed Journals

A. Herguth, **J. Kamphues**, *On the impact of bulk lifetime on the quantification of recombination at the surface of semiconductors*, IEEE J. of Photovolt., 13(5) (2023) doi:10.1109/JPHOTOV.2023.3291453

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Conference Proceedings

J. Kamphues, A. Schmid, R. Fischer-Süßlin, G. Hahn F. Geml, *Influence of AlO_x interlayers on LeTID kinetics in Ga-doped Cz-Si*, SiliconPV Conf. Proc. 1 (2023) doi:10.52825/siliconpv.v1i.84

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Presentations at Scientific Conferences and Workshops

J. Kamphues, A. Schmid, R. Fischer-Süßlin, G. Hahn F. Geml, *Influence of AlO_x interlayers on LeTID kinetics in Ga-doped Cz-Si*, 13th SiliconPV Conf., 12.04.2023, Delft, Poster (2023)

J. Kamphues, J. Miech, Y. Wang, X. Bai, G. Hahn F. Geml, *Extent of LeTID in industrial Ga-doped Cz-Si ingots with melt recharging*, SiliconFOREST workshop, 28.02.2024, Falkau, Talk (2024)

J. Kamphues, J. Lison, J.-I. Polzin, A. Wolf, J. Lossen, G. Hahn F. Geml, *Long-term stability of TOPCon solar cell precursor structures based on Ga-doped Cz-Si*, 14th SiliconPV Conf., 15.04.2024, Chambéry, Talk (2024)

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J. Kamphues, A. Herguth, J. Miech, X. Bai, Y. Wang, G. Hahn F. Geml, *LeTID in industrial Ga-doped Cz-Si with melt recharging*, 41st EU PVSEC, 23.09.2024, Vienna, Talk (2024)

J. Kamphues, J. Miech, S. M. Warmbold, W. Han Y. Wang, A. Herguth, G. Hahn F. Geml, *Impact of LeTID in industrial P- and Sb-doped n-type Cz-Si ingots with melt recharging*, SiliconFOREST workshop, 25.02.2025 Falkau, Talk (2025)

J. Kamphues, J. Miech, S. M. Warmbold, W. Han Y. Wang, A. Herguth, G. Hahn, F. Geml, *Impact of LeTID in industrial P- and Sb-doped Cz-Si ingots with melt recharging*, 15th SiliconPV Conf., 08.04.2025, Oxford, Talk (2025)

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Other

J. Kamphues, T. Okker, F. Geml, J. Lison, E. Kusari, R. Fischer-Süßlin, J. Miech, G. Hahn, *Produktionstechnologien für hochperformante IBC-Solarzellen (POPEI): Teilprojekt 3 der Universität Konstanz: Materialuntersuchungen und Defektreaktionen von Ga-dotiertem kristallinem Silizium für IBC-Solarzellen*, Final Report, Project duration: 01.05.2021–30.10.2023 (2025) doi:10.34657/19124

Supervision

Endrit Kusari, *Einfluss der Behandlungsbedingungen auf die Langzeitstabilität von Ga-dotiertem c-Si unter isoinjektiven Messbedingungen*, Bachelor Thesis, Universität Konstanz (2023)

Sarah Marie Warmbold, *Pretreatment and long-term stability under illumination and elevated temperature in n-type Cz-Si*, Bachelor Thesis, Universität Konstanz (2024)

Juri Miech, *Investigation of long-term stability and defect characterization of RCz n-type silicon using lifetime spectroscopy methods*, Master Thesis. Universität Konstanz (2025)

Ann-Kristin Becker: *Langzeitstabilitätsverhalten der Ladungsträgerlebensdauer in n-Typ Cz-Si bei Variation der Prozessbedingungen*, Bachelor Thesis, Universität Konstanz (2026)

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