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Impact of LeTID in Industrial P- and Sb-Doped n-Type Cz-Si With Melt Recharging

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Abstract. In this study the impact of treatments under illumination at elevated temperatures on the long-term stability of excess carrier lifetime in state-of-the-art melt recharging Czochralski-grown silicon with n-type dopants is investigated. For samples that are treated at elevated temperatures and illumination only, it is found that bulk regeneration dominates until surface related degradation becomes limiting. If an additional light-soaking treatment at room temperature is previously applied, both bulk degradation and regeneration can be observed for P- and Sb-doped Cz-Si. An increase in degradation extent is observed for subsequently pulled ingots which is very similar for both dopant species. It is therefore assumed that the accumulation of impurities in n-type Cz-Si may be involved in an increase of defects that form during treatment at elevated temperatures and illumination. Furthermore, it is shown for Sb-doped material that the applied high temperature processing steps do not have an impact on degradation extent or kinetics.

Keywords: Degradation, Charge Carrier Lifetime, Silicon, Melt Recharging

1. Introduction

In recent years, the solar industry has undergone a significant shift from p-type cell architectures to those based on n-type Czochralski-grown silicon (Cz-Si) [1]. To align with this transition, crystal growers have adopted n-type doping while also leveraging the Czochralski process with melt recharging (RCz-Si) to enhance cost efficiency and throughput [2,3]. Historically, phosphorus (P) has been the preferred n-type dopant. However, one of the largest wafer suppliers for photovoltaics has recently introduced a product that utilizes antimony (Sb) doping [4]. For such dopants, research on light- and elevated temperature-induced degradation (LeTID) remains limited. Studies from recent years suggest that n-type Si may exhibit some degree of degradation after firing, depending on the process parameters [5]. This results in a noticeable initial improvement in carrier lifetime during subsequent treatments, which is also influenced by firing temperature [6]. For p-type it is known that there it is possible to mitigate or minimize LeTID through optimized processing – such as adjusting the hydrogen concentration in the bulk [7,8]. However, the precise nature of the underlying defect in p-type Si remains unclear. In n-type Si a correlation between firing temperature and degradation extent seems also to be present [9], suggesting a dependence on hydrogen content as well. It has been observed by the authors that lifetime equivalent defect densities in Ga-doped RCz-Si are found to increase within each crystal pulled and with the number of subsequent pulls after melt recharging, suggesting a correlation of LeTID defect density and impurity concentration rising due to segregation effects [10]. Since it is reasonable to assume that impurities are also accumulating during

RCz-Si with n-type dopants, this work investigates industrial n-type P-doped and Sb-doped wafers from seed positions throughout RCz-Si processes regarding their long-term stability of excess carrier lifetime. Additionally, the influence of high temperature processing steps like Tabula Rasa (TR) [11] and $POCl_3$ diffusion gettering (PDG) on Sb-doped Cz-Si regarding long-term stability is evaluated.

2. Experimental

Sample processing was conducted on P-doped (approx. 1 Ω cm) and Sb-doped wafers with lower doping concentration ~12 Ω cm (Sb_L) and higher doping ~0.7 Ω cm (Sb_H). Prior to processing, all wafers were cut to M0 size. All samples underwent saw-damage removal followed by standard cleaning procedures. Wafers from the tail position of the last pulled ingot from Sb_L process then also underwent high-temperature treatments, such as TR and PDG. The TR is carried out at a peak temperature of 1050°C in an oxygen (TRO) or nitrogen (TRN) atmosphere. A 75 nm thick SiN_x:H passivation layer was deposited on both sides using plasma-enhanced chemical vapor deposition. Subsequently, the wafers were fired at a sample peak temperature of 800°C with a cooling rate of ~100 K/s.

Interstitial oxygen concentration [O_i] was calculated from Fourier-transform infrared spectroscopy measurements using a conversion factor of $2.45 \cdot 10^{17}$ cm^2 according to the ASTM F 121-83 standard. Base resistivity is extracted from 4-point probe measurements, which were used to calculate the net doping n_0 for all samples in this work.

In most cases, light-soaking at 20°C and 2 suns [12] was performed for a total of 24 h on all wafers to bring defects from the recombination-active state B into the recombination-inactive state A [13]. Further insights to this procedure are given in [14]. A water-cooled chuck is used to ensure that temperature remains stable during illumination. Afterwards, samples were treated at 130°C with an illumination equivalent of 1 sun provided by halogen lamps for LeTID testing (iso-generative). Additionally, iso-injective stability tests are carried out using an 805 nm laser with adjustable power [15]. Treatment was repeatedly interrupted to measure the injection dependent effective carrier lifetime $\tau_{eff}(\Delta n)$ using photoconductance decay [16,17] at 30°C with a WCT-120 system from Sinton Instruments. The degradation extent during LeTID testing is evaluated by the calculation of a lifetime equivalent defect density

$$\Delta N_{\mathrm{leq}} = \frac{1}{\tau_{\mathrm{eff}}(t)} - \frac{1}{\tau_{\mathrm{eff}}(0)} \qquad (1)$$

which serves as a good measure of changing defect density emerging in the bulk, without any knowledge about specific defect levels [18]. All effective lifetimes and ΔN_{leq} are evaluated at an injection level of $N_{dop}/2$. Evaluation of the surface related saturation current density j_0 is performed by the slope-based approach [19], using the parametrization from Niewelt et al. [20].

3. Results and Discussion

The calculated net dopant concentration n_0, and interstitial oxygen concentration [O_i] for the P-doped (left side) and the Sb-doped (centre and right side) material used for this investigation is shown in Fig. 1. For all samples the [O_i] is very similar in a range of $9–11 \cdot 10^{17}$ cm^{-3}. The dopant concentration during each RCz-Si process for P- and Sb-doped material only varies slightly which is related to the recharging of dopants. Obviously, this doping concentration is mostly influenced by the amount of dopants added during the recharging before reseeding of a new ingot.

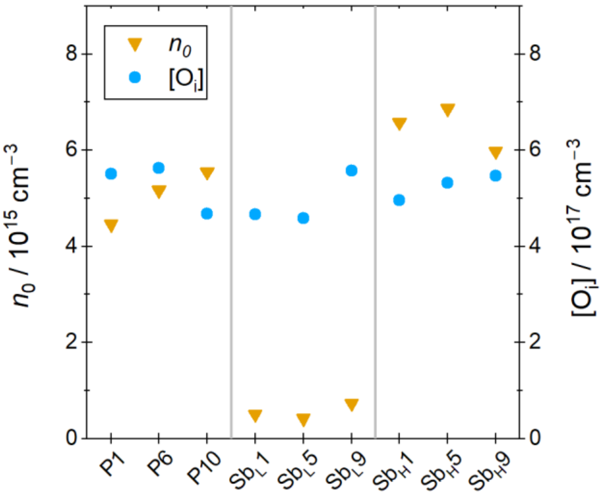

Figure 1. *Comparison of n_0 and $[O_i]$ for samples from the seed position of three different RCz-Si processes. One process used P-doping while the other two used Sb-doping with two different resistivity ranges. The number in the label on the x-axis labels the ingot number during RCz-Si growth.*

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. Fig. 2 shows 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). In case of LeTID testing of as-fired samples (a), lifetime regenerates until ~10 h of treatment.

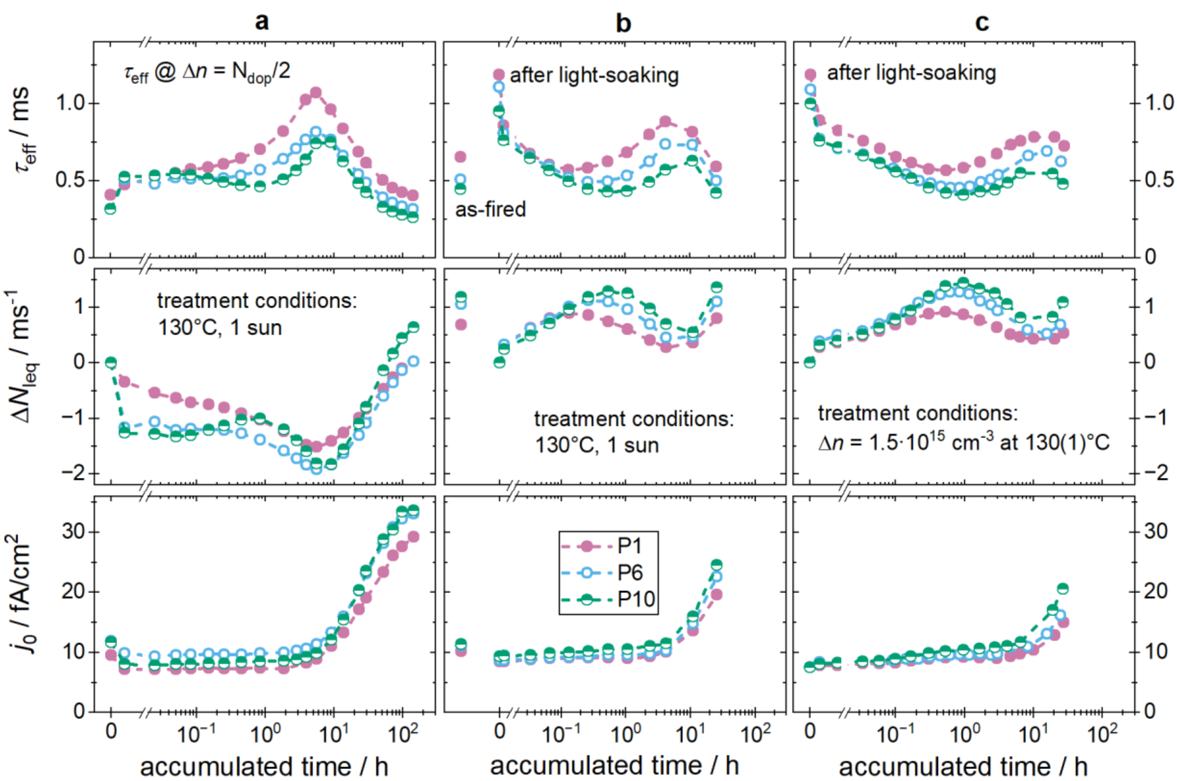

Figure 2. *Extracted τ_{eff}, ΔN_{leq} and j_0 for P-doped samples during accumulated treatment at 130°C at 1 sun illumination either directly after firing (a) or after light soaking at 20°C and 2 suns (b). In addition, previously light-soaked samples underwent an iso-injective treatment with Δn = 1.5·10^{15} cm^{-3} at 130°C (c).*

Lifetime reduction after this time can be attributed to a surface related degradation (SRD) indicated by the significant increase of j_0. While all samples show a bulk-related regeneration in mid-term before SRD sets in, differences between wafers from different ingot numbers can be noticed in short-term. The sample from the 1st ingot continuously regenerates, whereas a slight degradation for the sample from the 10th ingot between ~0.1 h and ~1 h of treatment can be observed. For the sample from the 6th ingot a stagnation of lifetime during this time frame is observed.

An improvement of lifetime compared to the initial as-fired lifetime is visible right after the application of an additional light-soaking treatment (b). Again, LeTID testing at 130°C at 1 sun is conducted after the light-soaking. This time all samples show a degradation and regeneration behavior. The degradation maximum ($\Delta N_{leq,max}$) is shifted to longer treatment times for higher ingot numbers. Additionally, the degradation extent is also increased for samples from subsequently pulled ingots. SRD, indicated by j_0, again sets in after ~10 h of treatment.

Since the initial lifetime prior to LeTID testing differs for samples from different ingots (probably due to higher accumulated impurity concentration for higher ingot numbers) another experiment is executed with iso-injective conditions during illumination (c). In p-type it is known that LeTID dynamics are slowed down when lifetime degrades as rates are injection-dependent [10]. With the iso-injective treatment, degradation and regeneration rates should be the same for all samples and can be compared. It can be seen that $\Delta N_{leq,max}$ occurs almost after the same treatment time around ~1 h of treatment with a slight delay for samples with higher ingot numbers. Additionally, the observed degradation extent is comparable with the iso-generative treatment in (b). Since the degradation does not seem to massively impact lifetime throughout the treatment, the injection during iso-generative treatment is not impacted too much. Therefore, the difference between iso-generative and iso-injective treatment is not that significant overall. In summary, the observed $\Delta N_{leq,max}$ seems therefore to be correlated with the accumulation of impurities during melt recharging.

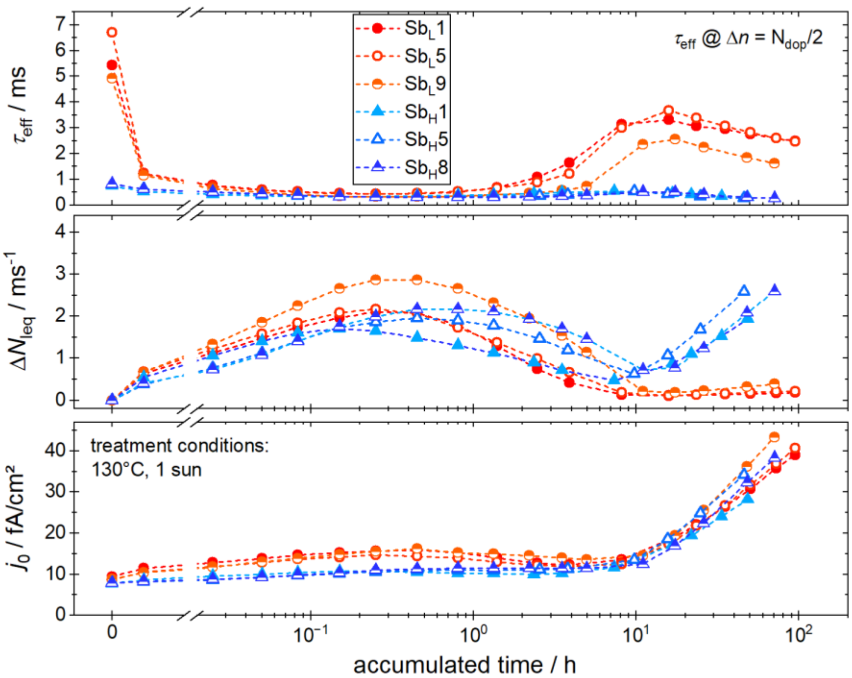

Figure 3. *Extracted τ_{eff}, ΔN_{leq} and j_0 for Sb-doped material with lower (Sb_L) and higher (Sb_H) doping concentration during accumulated treatment at 130°C with 1 sun illumination after light-soaking at 20°C and 2 suns.*

In general, it should be noted that the shown data for degradation are only from single wafer experiments and absolute levels of $\Delta N_{\mathrm{leq,max}}$ may vary depending on the processing conditons. Yet, the observed trends remain reproducible.

With Sb as dopant for state-of-the-art Cz grown ingots, the long-term stability of excess carrier lifetime of this current industrial material is of interest. The results from LeTID testing for Sb-doped samples from RCz-Si processes with higher and lower dopant concentrations Sb_H and Sb_L resulting in a base resistivity of ~0.7 Ω cm (Sb_H) and ~12 Ω cm (Sb_L) are shown in Fig. 3. The parameters τ_{eff}, ΔN_{leq} and j_0 are shown for an LeTID testing at 130°C with 1 sun illumination after light-soaking is carried out for samples from seed positions of subsequently pulled ingots. Lifetime after light soaking is obviously higher for Sb_L due to the lower dopant concentration. During LeTID testing a similar trend in degradation extent for higher ingot number is present for both dopant concentrations. The time after which $\Delta N_{\mathrm{leq,max}}$ appears is shifted towards longer treatment times for Sb_H. Just like it is observed for the P-doped material before, SRD occurs after ~10 h of treatment indicated by an increasing j_0. The overall degradation kinetics seems to be very similar for both types of dopants. The observed LeTID may therefore not be correlated to a specific type of n-type dopant.

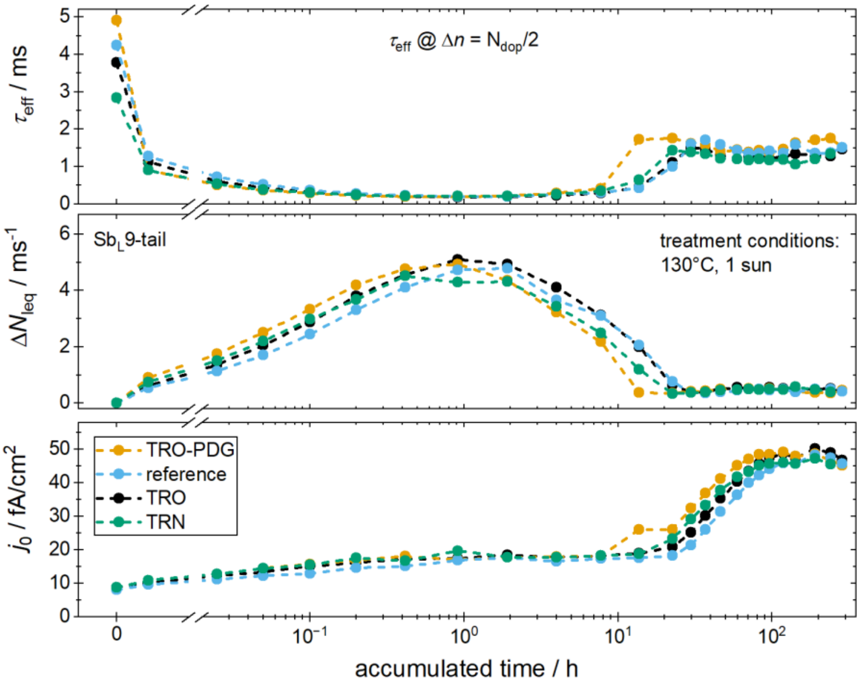

Figure 4. *Extracted τ_{eff}, ΔN_{leq} and j_0 during treatment at 130°C and 1 sun illumination for samples from the tail position of Sb-doped material that received different high temperature processing steps. All samples received an additional light-soaking prior to LeTID testing.*

Lastly, the impact of high temperature processing steps on the long-term stability in Sb-doped material is investigated. The results for τ_{eff}, ΔN_{leq} and j_0 for a 6 Ω cm sample from the tail position Sb_L9 are shown in Fig. 4. This time the tail part of the last ingot pulled from the melt is chosen to study the impact of high temperature steps as it is expected that impurity concentrations are the highest there. Samples that underwent TR treatments (in different ambients) are compared to a sample that did not receive any additional high temperature treatment. For one sample, the TRO treatment is followed by a PDG step. Again, all samples are exposed to light-soaking prior to LeTID testing at 130°C and 1 sun illumination. It can be seen that τ_{eff} after light-soaking is highest for the sample that received the TRO followed by PDG which could be explained by a reduced concentration of metallic impurities. However, this cannot be reliably discussed with a single sample each.

The observed $\Delta N_{leq,max}$ seems to be very similar independent of the applied high-temperature processing. Besides the occurrence of SRD after ~20 h of treatment there seems to be a slight increase in j_0 during the bulk related degradation which may be an artefact due to the emergence of bulk defects. A similar behavior is also visible in Fig. 3 for Sb_L. Overall, it seems that the material quality indicated by the initial lifetime may be changed by the applied processing steps, whereas the extent of LeTID remains unchanged. Eventually the fixed evaluation at Δn = $N_{dop}/2$ is not fair in this case as no thermal donor killing is considered here.

4. Conclusions

P- and Sb-doped RCz-Si samples that did not receive any light-soaking prior to degradation display a regeneration dominated behaviour until SRD sets in when treated at 130°C and 1 sun. If a light-soaking treatment at 20°C and 2 suns prior to LeTID testing is applied, it is observed that the P-doped as well as Sb-doped RCz-Si material show a more pronounced degradation with an increased degradation extent $\Delta N_{leq,max}$ for subsequently pulled ingots. Changes in degradation and regeneration kinetics are mainly attributed to injection changes during iso-generative treatment. For P-doped samples from subsequently pulled ingots it was found that the degradation and regeneration kinetics are very similar when treating the samples under iso-injective condition. Overall, the observed LeTID effect seems to be very similar for both dopant types, P and Sb, investigated in this work. Additionally, it was found that additional high temperature processing steps such as Tabula Rasa (TR) and phosphorous diffusion gettering (PDG) can impact material quality but do not seem to significantly change the observed degradation extent or kinetics during treatment under illumination at elevated temperatures.

Data availability statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Author contributions

J. Kamphues: formal analysis, investigation, validation, data curation, visualization, conceptualization, writing - original draft; **S. M. Warmbold:** investigation; **J. Miech:** investigation; **W. Han:** investigation; **Y. Wang:** resources; **A. Herguth:** writing – review and editing; **G. Hahn:** resources, writing - review and editing; **F. Geml:** conceptualization

Competing interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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