



# Light-induced lifetime degradation in high-performance multicrystalline silicon: Detailed kinetics of the defect activation

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## ARTICLE INFO

### Keywords:

Multicrystalline silicon

Carrier lifetime

Degradation

## ABSTRACT

We examine the defect activation kinetics in block-cast high-performance multicrystalline silicon (HP mc-Si) under illumination at elevated temperature. Our lifetime analysis shows that the observed light-induced lifetime degradation consists of two separate stages: a fast stage followed by a slow stage. Our experiments reveal that both degradation stages can be fitted using a sum of two exponential decay functions. The resulting degradation rate constants depend both on the temperature and the light intensity applied during degradation. For the fast component, we determine an activation energy of  $(0.89 \pm 0.04)$  eV from an Arrhenius plot of the degradation rate and for the slow component we determine a value of  $(0.94 \pm 0.06)$  eV. The activation energies are relatively large, leading to a very pronounced dependence of the degradation rates on temperature. We also observe that both degradation rates show a linear dependence on the applied light intensity during degradation in the examined intensity range between 0.25 and 1.5 suns.

## 1. Introduction

The degradation of solar cells fabricated on block-cast **multicrystalline silicon (mc-Si)** wafers under illumination at elevated temperature has recently attracted great attention by the PV community. Ramspeck et al. [1] discovered that mc-Si solar cells exhibit a pronounced degradation in efficiency of up to 6% relative at an illumination intensity of  $40 \text{ mW/cm}^2$  at an elevated temperature of  $75^\circ\text{C}$  on a timescale of about 400 h. They observed that especially solar cells with an  $\text{Al}_2\text{O}_3/\text{SiN}_x$ -passivated rear surface are prone to this novel degradation mechanism and were not able to explain this mechanism by known light-induced degradation processes such as the boron-oxygen defect activation [2–4] or the iron-boron pair dissociation [5,6]. Similar results were later reported by Fertig et al., who examined the degradation behaviour of passivated emitter and rear cells (PERC) fabricated on mc-Si wafers at 0.15 suns and  $70^\circ\text{C}$  on even larger timescales [7,8]. Measurements on mc-Si lifetime samples and mc-Si PERC solar cells were conducted by Kersten et al., who observed the degradation mechanism in both solar cells and lifetime samples. Interestingly, after full degradation, they observed a complete *regeneration* in the cell efficiency after about 1000 h of illumination at 0.3 suns and  $95^\circ\text{C}$  [9]. More recently, several studies on mc-Si lifetime samples reported on a **pronounced degradation and a subsequent regeneration of the carrier lifetime during illumination at elevated temperature** [10–13], clearly

indicating that the mc-Si degradation is largely a bulk effect. However, recent publications of Sperber et al. raise the possibility of a change in surface passivation quality to contribute a small signal to the observed degradation [14]. In a previous publication, we showed that the mc-Si degradation takes place only after firing the mc-Si wafer at a sufficiently high peak temperature and that the lifetime degradation proceeds in two stages: a fast and a slow degradation stage, followed by the regeneration stage [12]. However, the exact defect activation kinetics has not been examined until today. A qualitative study on both the temperature and the illumination intensity dependence was conducted by Kersten et al. [9]. Most recently, Chan et al. showed that the degradation kinetics in multicrystalline PERC solar cells can be modulated by a previous dark anneal [15]. Within this study, we examine the lifetime degradation of high-performance mc-Si wafers as a function of temperature and applied light intensity during degradation. In the first experiment, we degrade our samples at constant illumination intensity and vary the sample temperature to determine the temperature dependence of the defect activation kinetics. In the second experiment, we examine the dependence on the applied light intensity. Our experimental results provide important information to pin down the physical degradation mechanism.

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## 2. Experimental details

We use block-cast boron-doped industrially available high-performance (HP) mc-Si wafers with a resistivity of  $\rho = (1.66 \pm 0.03) \Omega \text{ cm}$  determined via four-point-probe measurements and with a size of  $15.6 \times 15.6 \text{ cm}^2$ . The as-cut HP mc-Si wafers are first cleaned with a surface-active agent and subsequently etched in a potassium hydroxide solution to remove the saw damage. A phosphorus diffusion is then performed in a quartz-tube furnace at a process temperature of  $\sim 850^\circ\text{C}$  resulting in  $n^+$ -layers on both wafer surfaces with a sheet resistance between 50 and  $60 \Omega/\text{sq}$ . The  $n^+$ -layers are chemically removed by a solution of hydrofluoric acid and nitric acid using a chemical polishing process. The surfaces are then passivated by an  $\text{Al}_2\text{O}_3/\text{SiN}_x$  stack, where the 10 nm thick  $\text{Al}_2\text{O}_3$  layers are deposited by plasma-assisted ALD (FlexAL<sup>TM</sup>, Oxford Instruments). The  $\text{SiN}_x$  layers with a thickness of 100 nm and a refractive index of 2.05 are deposited using an industrial-type plasma-enhanced chemical vapor deposition (PECVD) process (Roth & Rau, SiNA). All samples receive a rapid thermal annealing (RTA) firing treatment at a set peak temperature of  $900^\circ\text{C}$  and a belt speed of 6.8 m/min using an industrial conveyor belt furnace (centrotherm photovoltaics, DO-FF-8.600-300). Under these conditions, we measured the actual wafer temperature during RTA and found that the peak temperature reached during the firing step is  $(788 \pm 10)^\circ\text{C}$ . On parallel-processed float-zone silicon (FZ-Si) reference samples we determined the surface recombination velocity of our fast-fired samples to be smaller than  $5 \text{ cm/s}$ . As a final process step the wafers are cut into  $5 \times 5 \text{ cm}^2$  samples, which are then kept in the dark at room temperature to prevent any degradation prior to the actual experiments. The final thickness of the samples used throughout this study is  $d = (158 \pm 4) \mu\text{m}$ . All experiments are conducted on neighbouring samples, so the results become comparable and are not affected by effects stemming from different sample structures. Note that lateral variations on the mc-Si wafers are largely excluded in our study by using  $5 \times 5 \text{ cm}^2$  samples from the same lateral position on the initial  $15.6 \times 15.6 \text{ cm}^2$  neighbouring wafers.

Injection-dependent carrier lifetimes are measured using the photoconductance decay (PCD) technique (Sinton Lifetime Tester WCT-120) [16]. We extract the lifetimes at a fixed excess carrier density of  $\Delta n = 10^{15} \text{ cm}^{-3}$ . For each measurement we removed the sample from the degradation site and measured the lifetime at  $(29.4 \pm 1.1)^\circ\text{C}$ . The samples are illuminated with halogen lamps and the illumination intensity is adjusted by changing the distance between halogen lamp and sample. We measure the illumination intensity with a calibrated reference solar cell and achieve an accuracy of the set illumination intensity of  $\pm 0.08$  suns over the sample's surface. All experiments are carried out on a hot-plate and the actual sample temperature is measured using a type-K thermocouple. During all experiments the sample temperature is measured and held constant with an accuracy of  $\pm 2.5^\circ\text{C}$ . To exclude possible effects from a dark storage of our samples, we continuously illuminated the samples once the experiment started. Additionally, we checked for possible effects stemming from iron-boron pair dissociation by flashing exemplary samples 10 times with a high-intensity flashlight ( $> 100$  suns) before the actual degradation measurements. Since we were not able to observe any changes in the injection-dependent lifetimes related to the iron-boron dissociation with increasing flash count, we conclude that our measurements are not affected by iron-boron pair dissociation.

## 3. Temperature dependence of degradation kinetics

The data shown in Figs. 1 and 2 were measured at a constant illumination intensity of 0.5 suns at temperatures ranging from 75 to  $120^\circ\text{C}$ . The normalized defect concentration  $N^*$  is determined from the measured lifetime values using Eq. (1) with  $\tau(t)$  being the measured lifetime at time  $t$  and  $\tau_0$  the initial lifetime before degradation:

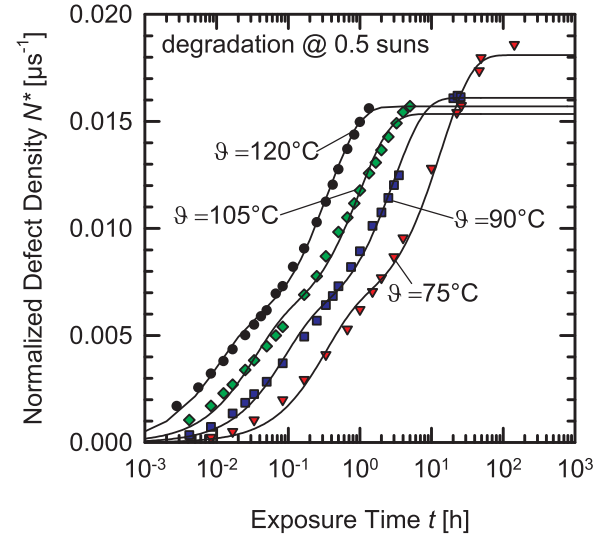


Fig. 1. Measured normalized defect densities  $N^*$  calculated from PCD measurements versus the exposure time  $t$  in hours with double-exponential rise-to-maximum fits (solid lines). Degradation conditions are 0.5 suns light intensity and temperatures ranging from 75 to  $120^\circ\text{C}$ .

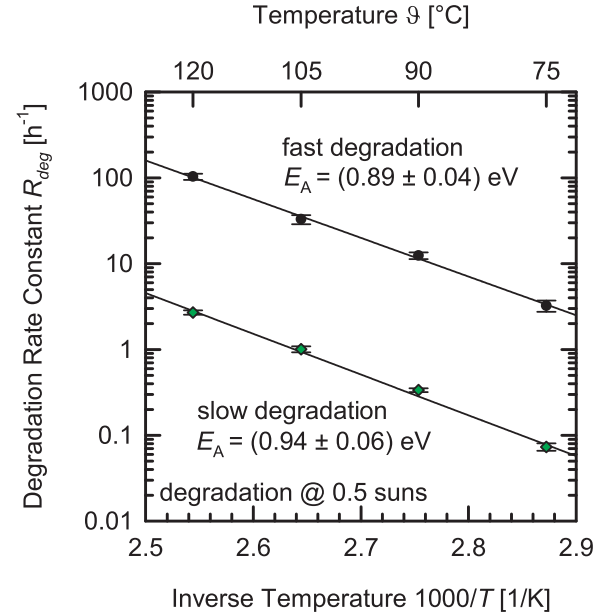


Fig. 2. Degradation rate constants  $R_{\text{deg}}$  of the fast and slow stages of degradation plotted versus the inverse temperature  $1/T$  with fits according to the Arrhenius law.

$$N^*(t) = \frac{1}{\tau(t)} - \frac{1}{\tau_0}. \quad (1)$$

For all temperatures, we observe two stages of lifetime degradation: a fast stage and a subsequent slow stage. Thus, it is not possible to fit the  $N^*(t)$  evolution with a mono-exponential rise-to-maximum fit. However, using a sum of two exponential rise-to-maximum fits, an excellent agreement with the experimental  $N^*(t)$  evolution is observed. Using the fit function

$$N^*(t) = a(1 - \exp(-R_{\text{deg,fast}} t)) + b(1 - \exp(-R_{\text{deg,slow}} t)), \quad (2)$$

with  $a$  and  $b$  being pre-factors determining the maximum defect concentration, we are hence able to extract the degradation rates of the two processes. Fig. 2 shows an Arrhenius plot of the respective degradation rate constants  $R_{\text{deg,fast}}$  and  $R_{\text{deg,slow}}$  according to Eq. (2) with the temperature-independent pre-factor  $\kappa_0$ , the activation energy  $E_A$ , the Boltzmann constant  $k_B$  and the absolute temperature  $T$ :

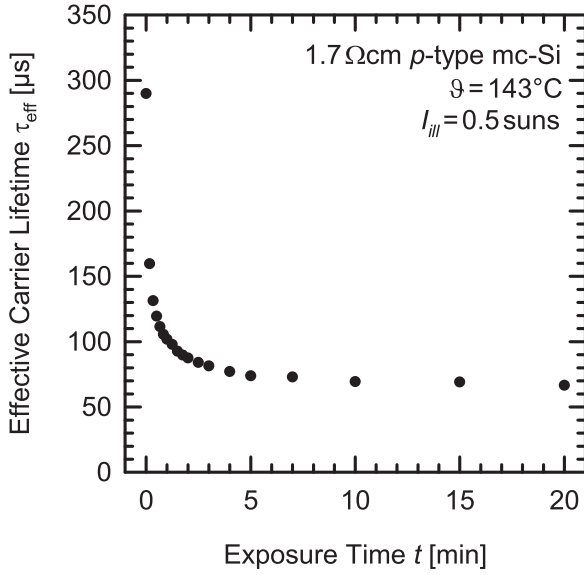


Fig. 3. Evolution of the effective carrier lifetime  $\tau_{\text{eff}}$  under illumination at 0.5 suns light intensity and a temperature of 143°C. The lifetime drops from initially 290  $\mu\text{s}$  to 60  $\mu\text{s}$  within 20 min.

$$R_{\text{deg}} = k_0 \exp\left(-\frac{E_A}{k_B T}\right) \quad (3)$$

We determine the activation energy of the fast degradation stage  $E_{A,\text{fast}} = (0.89 \pm 0.04) \text{ eV}$  and of the slow stage  $E_{A,\text{slow}} = (0.94 \pm 0.06) \text{ eV}$ . Note that the difference in the two activation energies are within the respective measurement uncertainties. Hence, both activation energies are very similar or even identical. The pre-exponential factors determined at 0.5 suns illumination intensity differ however significantly by one order of magnitude:  $\kappa_{0,\text{fast}} = 8.26 \times 10^9 \text{ s}^{-1}$  for the fast stage and  $\kappa_{0,\text{slow}} = 9.37 \times 10^8 \text{ s}^{-1}$  for the slow stage of degradation. As can be seen in Fig. 3, the relatively large activation energy of the slow degradation leads to a full degradation at 143°C within 20 min on the examined sample. The lifetime drops from initially 290–66  $\mu\text{s}$  after 20 min. Upon further illumination at elevated temperature the lifetime regeneration sets in, which is however, not part of this study.

#### 4. Illumination intensity dependence of degradation kinetics

The experiments to determine the impact of the applied illumination intensity on the degradation kinetics are carried out at a constant sample temperature of 143°C. The illumination intensity is varied from 0.25 to 1.5 suns. As can be seen in Fig. 4, the degradation rate constants  $R_{\text{deg,fast}}$  and  $R_{\text{deg,slow}}$  show a linear dependence on the applied illumination intensity  $I_{\text{ill}}$  at constant temperature (in this case 143°C). With  $a_{\text{slow}} = (29.4 \pm 4.9) \text{ suns}^{-1}$ ,  $a_{\text{fast}} = (271.9 \pm 99.3) \text{ suns}^{-1}$ ,  $b_{\text{slow}} = (2.6 \pm 4.7) \text{ h}^{-1}$ ,  $b_{\text{fast}} = (99.3 \pm 33.3) \text{ h}^{-1}$ , the illumination dependence can be expressed as follows:

$$\begin{aligned} R_{\text{deg,fast}} &= a_{\text{fast}} \cdot I_{\text{ill}} + b_{\text{fast}}, \\ R_{\text{deg,slow}} &= a_{\text{slow}} \cdot I_{\text{ill}} + b_{\text{slow}}. \end{aligned} \quad (4)$$

#### 5. Discussion

In a previous study, we proposed a first possible defect model which is consistent with our experimental observations [12]. In this model, we assume that during the high-temperature firing step, precipitates of a so far unknown metal dissolve into interstitial impurities  $M_i$ , which during cooling are captured by another homogeneously distributed impurity  $X$  to form an  $M_i\text{-}X$  complex. During illumination at elevated temperature,

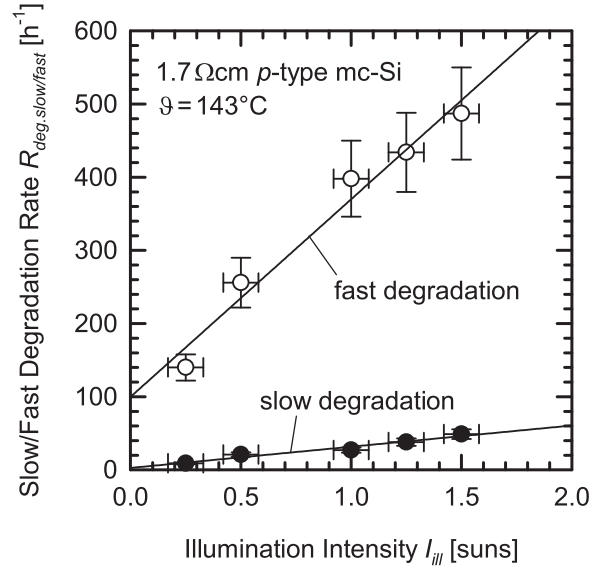


Fig. 4. Degradation rate constants  $R_{\text{deg,slow}}$  and  $R_{\text{deg,fast}}$  at 143°C of the slow and fast degradation component versus the illumination intensity  $I_{\text{ill}}$  in suns (filled and unfilled circles) with a linear fit (solid line).

the  $M_i\text{-}X$  complex changes its configuration into a more recombination-active form  $M_i\text{-}X^*$ , which subsequently dissociates into isolated  $M_i$  and  $X$ . While the reconfiguration of the  $M_i\text{-}X$  complex is according to this model responsible for the fast degradation stage, the dissociation of the  $M_i\text{-}X^*$  complex is made responsible for the slow stage. The kinetics of both types of processes are naturally described by an Arrhenius law. However, our observation that the two involved activation energies are almost identical might indicate that both stages are just different forms of one and the same defect reaction.

The observed linear dependence of the degradation rates on the illumination intensity is most likely due to a linear dependence of  $R_{\text{deg}}$  on the excess carrier concentration  $\Delta n$ . However, note that further studies are needed to examine a possible direct impact of the photons, which could, however, not explain the observed y-offset of the fast degradation stage in Fig. 4. Since in this study we used a minimum illumination intensity of 0.25 suns, the  $R_{\text{deg,fast}}(I_{\text{ill}})$  dependence might be either stronger for lower intensities or the fast degradation also occurs without illumination. Future experiments are needed to verify which of the two possibilities holds true. Note that a previous study of Kersten et al. showed that both illumination and current injection lead to the same degradation behaviour on mc-Si solar cells [9]. Furthermore, it is rather surprising to us that the increase in the normalized defect concentration can be fitted by using a double-exponential rise-to-maximum fit. Since  $R_{\text{deg}}$  depends most likely linearly on  $\Delta n$  and the excess carrier concentration is changing with lifetime in the course of degradation, one would expect a more complex relationship. Furthermore, the measured degradation rates are affected by the regeneration as well, which most likely proceeds in parallel to the degradation. However, as the regeneration kinetics is much slower compared to the degradation kinetics, the impact is assumed to be small and is neglected within this study.

Our results explain why in the initial paper of Ramspeck et al. [1] a full degradation was only observed for temperatures much larger than 25°C. One major reason is obviously that the degradation time constants were too large to be observable within the timeframe of their study. Using our Eq. (3), we would expect a degradation rate of the slow stage  $R_{\text{deg,slow}}$  of  $3.83 \times 10^{-4} \text{ h}^{-1}$  at 25°C and 0.5 suns, which would correspond to a time constant of 2608 h. As the experiments of Ramspeck et al. were terminated after 400 h at 40 mW/cm<sup>2</sup> illumination intensity, they did not observe the complete degradation at 25°C. Note, however, that the maximum defect concentration could in fact be

dependent on the degradation temperature, as has recently been suggested by Kersten et al. [17].

The degradation rate constants of both the slow stage and the fast stage determined at an illumination intensity of 0.5 suns and a temperature of 143°C are not included in the Arrhenius plot shown in Fig. 2, because the experiments regarding the temperature dependence have been conducted on samples stemming from different positions on the examined neighbouring wafers than the samples used in the experiment which examined the illumination intensity dependence. Furthermore, the used type-K thermocouples have not been the same in both cases. So we do not mix up the results to avoid influences from additional systematic measurement errors. Nevertheless, the degradation rates measured at a temperature of 143°C do fit well into the Arrhenius plot in Fig. 2 within the given uncertainties of the activation energies.

## 6. Summary

Within this study, we have performed experiments on industrial HP mc-Si lifetime samples and examined the dependence of the degradation kinetics on both the temperature and the applied light intensity during degradation. We have shown that the degradation takes place in two stages, a slow and a fast one, and that the temperature dependence of the corresponding degradation rate constants can both be described using an Arrhenius law. For the fast degradation stage we have determined an activation energy of  $E_{A,fast} = (0.89 \pm 0.04)$  eV and for the slow stage of  $E_{A,slow} = (0.94 \pm 0.06)$  eV. Both values are relatively large and are within their uncertainties similar or even identical. The pre-factors differ, however, by one order of magnitude, leading to significantly different time constants for both stages. For the dependence on the applied illumination intensity during degradation on the degradation rates of both stages, we have observed a linear dependence in the range from 0.25 up to 1.5 suns, which would be consistent with an electronically stimulated defect activation process. One possible defect model explaining the presence of the two stages was discussed. Further theoretical and experimental work is needed to clarify the detailed physical mechanisms behind the observed two-stage degradation process in mc-Si material.

## Acknowledgements

The authors thank C. Marquardt for sample processing. This work was funded by the German State of Lower Saxony and the German Federal Ministry of Economics and Energy and by industry partners

within the research project “SolarLIFE” (Contract no. 0325763C). The content is the responsibility of the authors.

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