

Contents lists available at ScienceDirect

# Solar Energy Materials and Solar Cells

journal homepage: www.elsevier.com/locate/solmat



# 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 mW/cm<sup>2</sup> at an elevated temperature of 75°C on a timescale of about 400 h. They observed that especially solar cells with an Al2O3/SiNx-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°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°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

http://dx.doi.org/10.1016/j.solmat.2017.08.007

Received 31 March 2017; Received in revised form 20 July 2017; Accepted 4 August 2017 Available online 16 August 2017 0927-0248/ © 2017 Elsevier B.V. All rights reserved. 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  $\rho = (1.66 \pm 0.03) \Omega$  cm determined via four-point-probe measurements and with a size of 15.6  $\times$  15.6 cm<sup>2</sup>. The as-cut HP mc-Si wafers are first cleaned with a surfaceactive 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  $\sim 850^{\circ}$ C resulting in  $n^+$ -layers on both wafer surfaces with a sheet resistance between 50 and 60  $\Omega$ /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 Al<sub>2</sub>O<sub>3</sub>/SiN<sub>x</sub> stack, where the 10 nm thick Al<sub>2</sub>O<sub>3</sub> layers are deposited by plasma-assisted ALD (FlexAL<sup>™</sup>, Oxford Instruments). The SiN<sub>x</sub> layers with a thickness of 100 nm and a refractive index of 2.05 are deposited using an industrialtype 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°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  $(788 \pm 10)^{\circ}$ 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 cm/s. As a final process step the wafers are cut into 5  $\times$  5 cm<sup>2</sup> 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  $d = (158 \pm 4)$ µm. 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  $5 \times 5$  cm<sup>2</sup> samples from the same lateral position on the initial 15.6  $\times$  15.6 cm<sup>2</sup> 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  $\Delta n$ =  $10^{15}$  cm<sup>-3</sup>. For each measurement we removed the sample from the degradation site and measured the lifetime at  $(29.4 \pm 1.1)^{\circ}$ 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°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 highintensity 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°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°C.



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

$$N^{*}(t) = \frac{1}{\tau(t)} - \frac{1}{\tau_{0}}.$$
(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

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

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