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## Understanding the light-induced lifetime degradation and regeneration in multicrystalline silicon

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### Abstract

In this contribution, we focus on improving the fundamental understanding of the carrier lifetime degradation and regeneration observed in block-cast multicrystalline silicon (mc-Si) wafers under illumination at elevated temperature. We observe a pronounced degradation in lifetime at 1 sun light intensity and 75°C after rapid thermal annealing (RTA) in a belt-firing furnace at a set peak temperature of 900°C. However, almost no lifetime instability is detected in mc-Si wafers which are fired at a peak temperature of only 650°C, clearly showing that the firing step is triggering the degradation effect. Lifetime spectroscopy reveals that the light-induced recombination centre is a deep-level centre with an asymmetric electron-to-hole capture cross section ratio of  $20 \pm 7$ . After completion of the degradation, the lifetime is observed to recover and finally reaches even higher carrier lifetimes compared to the initial state. While the lifetime degradation is found to be homogeneous, the regeneration shows an inhomogeneous behaviour, which starts locally and spreads later laterally throughout the sample. Furthermore, the regeneration process is extremely slow with time constants of several hundred hours. We demonstrate, however, that by increasing the regeneration temperature, it is possible to significantly speed up the regeneration process so that it might become compatible with industrial solar cell production. To explain the observed lifetime evolution, we propose a defect model, where metal precipitates in the mc-Si bulk dissolve during the RTA treatment and the mobile metal atoms bind to a homogeneously distributed impurity. Restructuring and subsequent dissociation of this defect complex is assumed to cause the lifetime degradation, whereas a subsequent diffusion of the mobile species to the sample surfaces and crystallographic defects explains the regeneration.

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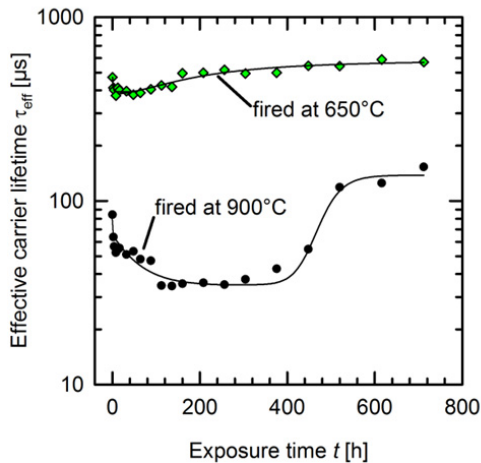


Fig. 1. Effective carrier lifetime measured at  $\Delta n = 10^{15} \text{ cm}^{-3}$  by the PCD (diamonds) and the QSSPC (circles) techniques of mc-Si lifetime samples plotted versus the exposure time of illumination at 1 sun at 75°C. The lifetime evolution is subdivided into three stages: (1) fast degradation, (2) slow degradation and (3) regeneration. The solid lines are guides to the eyes.

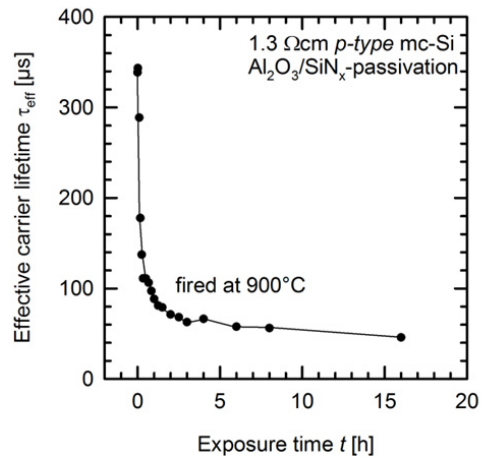


Fig. 2. Effective carrier lifetime of an mc-Si lifetime sample with  $\text{Al}_2\text{O}_3/\text{SiN}_x$ -passivation measured at  $\Delta n = 10^{15} \text{ cm}^{-3}$  by the PCD technique and plotted versus the exposure time of illumination at 1 sun at 75°C.

## 1. Introduction

Ramspeck et al. [1] showed that multicrystalline silicon (mc-Si) solar cells loose up to 6% relative in their efficiency at an illumination intensity of 40  $\text{mW}/\text{cm}^2$  (0.4 suns) at 75°C, which he was not able to explain by known light-induced degradation processes such as the boron-oxygen defect activation [2] or the iron-boron pair dissociation [3]. This new type of light-induced degradation (LID) was found to be most pronounced in PERC-type solar cells and was observed to a lesser extent on solar cells with a full-area aluminum back surface field (Al-BSF). Similar results were more recently reported by Fertig et al. [4]. Most recently, Kersten et al. [5] observed the degradation effect on both passivated mc-Si lifetime samples as well as on PERC solar cells. Interestingly, they also observed a complete regeneration of the cell efficiency after approximately 150 hours of illumination at 0.3 suns at 95°C. In this contribution, we perform a series of experiments to elucidate the underlying physical mechanisms behind the observed LID effect in mc-Si solar cells.

## 2. Experimental details

We use block-cast boron-doped mc-Si wafers with a resistivity of 1.2-1.3  $\Omega\text{cm}$  of two different ingots grown under the same conditions. The mc-Si materials were grown in a G1 lab-size crucible and contain the typical broad variety of metallic impurities, as examined by inductively-coupled plasma mass spectrometry (ICP-MS) [6].

The as-cut 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 853°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 5 nm thick  $\text{Al}_2\text{O}_3$  layer is deposited by spatial atomic layer deposition (ALD) in an InPassion LAB System (SolayTec). The samples used for the fast-regeneration experiments are passivated by 10 nm  $\text{Al}_2\text{O}_3$  layers deposited by plasma-assisted ALD (FlexAL<sup>TM</sup>, Oxford Instruments). The  $\text{SiN}_x$  layers have a thickness of 100 nm and a refractive index of 2.05 and are deposited using an industrial-type plasma-enhanced chemical vapor deposition (PECVD) tool (Roth&Rau, SiNA).

As final step, the wafers receive an RTA firing treatment at two different set peak temperatures using an industrial conveyor belt furnace (centrotherm photovoltaics, DO-FF-8.600-300). One part of the samples is fired at a set peak temperature of 900°C and the other one at 650°C. Those peak temperatures are chosen to cover the range of relevant temperatures in a typical solar cell fabrication process and to clearly separate the impact of different firing conditions on the light-induced degradation and regeneration processes.

Injection-dependent carrier lifetimes are measured at room temperature using the photoconductance decay (PCD) and the quasi-steady-state photoconductance (QSSPC) techniques [7]. Spatially resolved lifetime measurements are carried out using the photoconductance-calibrated photoluminescence imaging (PC-PLI) method [8].

### 3. Experimental results

The samples are illuminated with halogen lamps at 1 sun light intensity at 75°C. The mc-Si lifetime samples fired at a set peak temperature of 900°C show a pronounced degradation in the lifetime, as can be seen in the lifetime measurements shown in Fig. 1, which we attribute to bulk lifetime instabilities, as discussed in more detail in a parallel paper [9]. The observed mc-Si-specific lifetime degradation can be subdivided into two stages. The first stage proceeds within the first hour and is characterized by a fast and pronounced reduction in lifetime. This stage is followed by a slower exponential degradation, taking place within ~100 hours. For longer periods, the lifetime increases ('regeneration') and finally reaches lifetimes even higher than the initial lifetime. Note, however, that the regeneration process is extremely slow and it takes ~500 hours to fully regenerate the lifetime under the conditions applied in Fig. 1. One of our most important findings is the observation that the samples fired at a reduced peak temperature of 650°C show only a negligible degradation, as can be seen in Fig. 1 (upper curve). Reducing the peak firing temperature would hence be an easy-to-implement measure to avoid LID in industrially produced mc-Si solar cells.

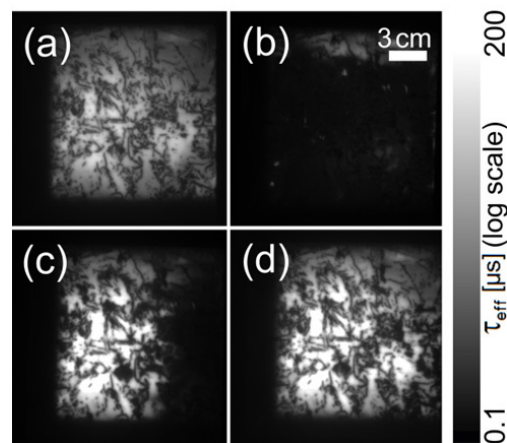


Fig. 3. Lifetime images measured by PC-PLI of an mc-Si lifetime sample at different timesteps during illumination at 1 sun light intensity and 75°C. (a) Initial state, (b) after 48 hours of illumination, (c) after 448 hours, (d) after 616 hours.

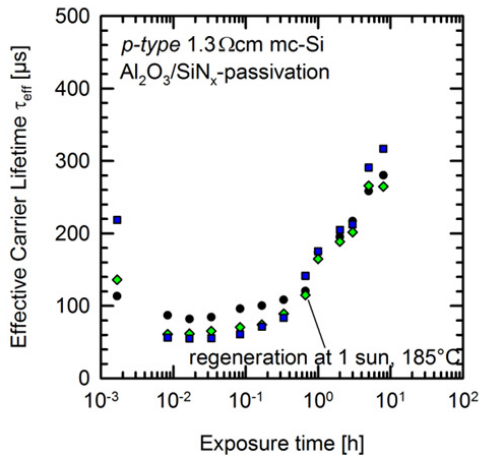


Fig. 4. Effective carrier lifetime measured at  $\Delta n = 10^{15} \text{ cm}^{-3}$  by the PCD technique of mc-Si lifetime samples plotted versus the exposure time of illumination at 1 sun at 185°C. The lifetime decreases within less than an hour and finally increases again to higher lifetime values than in the initial state. The different symbols indicate three different spots on the same wafer with a size of each  $5 \times 5 \text{ cm}^2$ .

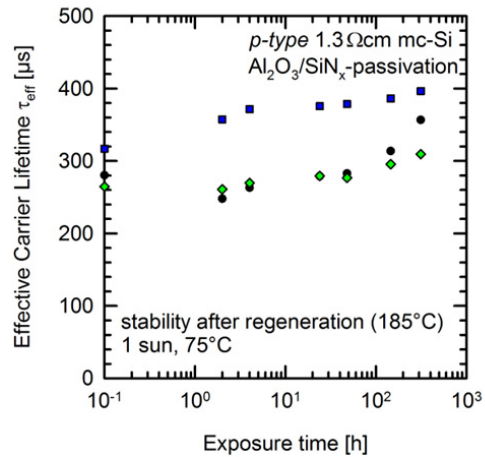


Fig. 5. Effective carrier lifetime measured at  $\Delta n = 10^{15} \text{ cm}^{-3}$  by the PCD technique of mc-Si lifetime samples plotted versus the exposure time of illumination at 1 sun at 75°C. The lifetimes of the samples which underwent the regeneration process in Fig. 3 show no degradation under illumination at 1 sun at 75°C. The different symbols indicate the same three spots on the same wafer as in Fig. 4.

We verified the presence of at least two stages of degradation – a fast and a slow one – by additional measurements on mc-Si wafers of a different ingot grown under comparable conditions as the one used in Fig. 1. Figure 2 shows the lifetime evolution of those mc-Si lifetime samples, which were recorded with a higher time resolution compared to Fig. 1. It is obvious from Fig. 2 that the lifetime evolution cannot be described by a single-exponential decay function. The fast component of degradation is clearly visible to be terminated after less than 1 hour.

Figure 3 shows PC-PLI lifetime measurements of the degradation and regeneration on the same sample as shown in Fig. 1. The excitation level is chosen to result in an area-averaged excess carrier concentration of  $10^{14} \text{ cm}^{-3}$  during the measurements. While the degradation occurs relative homogeneously over the wafer area, the regeneration is a rather inhomogeneous process. As can be seen in Fig. 3, the regeneration starts locally and is then spreading out over the wafer area. Note that we have verified via reference samples processed on monocrystalline silicon wafers that the observed lifetime evolution is not related to changes in the surface passivation of our samples.

In order to speed up the rather slow regeneration process, we have increased the temperature during illumination to 185°C, leading to an accelerated degradation as well as regeneration, as can be seen in Fig. 4. The lifetime degradation takes now less than one hour and the regeneration is finished after 8 hours (compared to ~500 hours at 75°C). We investigate the stability of the regenerated state under illumination at 1 sun and 75°C. As shown in Fig. 5, the regenerated lifetime does not show any degradation over the examined period of 314 hours. The weak increase in lifetime in Fig. 5 might be due to the fact that the regeneration at 185°C was not completely saturated in Fig. 4. Further investigations are underway to examine possibilities to further speed up the regeneration process (by e.g. further increasing the regeneration temperature and the illumination intensity), in order to develop an industrially feasible process to fully eliminate LID in mc-Si solar cells and modules.

In order to further elucidate the nature of the light-induced defect, we have performed injection-dependent lifetime measurements in the initial state (lifetime  $\tau_i$ ) and the fully degraded state (lifetime  $\tau_d$ ), as shown in Fig. 6. Figure 7 shows a plot of the Shockley-Read-Hall (SRH) lifetime  $\tau_{\text{SRH}} = (1/\tau_d - 1/\tau_i)^{-1}$  of the light-induced recombination centre as a function of the electron-to-hole concentration ratio  $n/p$ . From the linear behavior observed in Fig. 7, we conclude that the light-induced centre is a deep-level centre with a capture cross section ration of  $\sigma_n/\sigma_p = 20 \pm 7$ .

#### 4. Defect model

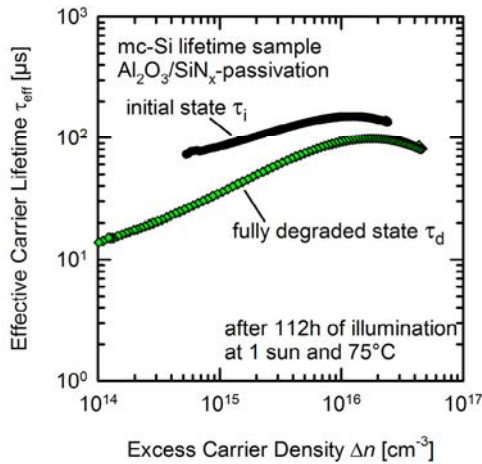


Fig. 6. Injection-dependent carrier lifetime measured by the PCD technique in both the initial state ( $\tau_i$ ) and the fully degraded state ( $\tau_d$ ).

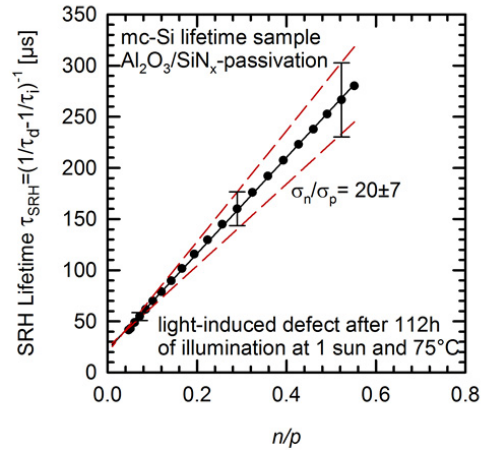


Fig. 7. SRH lifetime of the light-induced recombination centre  $\tau_{SRH}$  plotted versus the ratio of electron and hole concentration  $n/p$ .

We have recently proposed a defect model [9] which consistently explains all our experimental observations. However, note that further experiments are required to verify or falsify the various aspects of our model. In this model, we assume that latent precipitates of a particular metal ( $M_p$ ) are the root cause of the observed LID effect in mc-Si. Since we observe the degradation and regeneration cycle only after belt-firing at sufficiently high temperature (900°C), we assume that the precipitates  $M_p$  dissolve during the high-temperature RTA into mobile, probably interstitial metal atoms  $M_i$ , whereas the precipitates  $M_p$  do not dissolve at the lower firing temperature of 650°C. The  $M_i$  are captured by a homogeneously distributed impurity X (e.g.  $O_i$ ,  $C_s$ ,  $N_2$ ,  $H$ ) to form an  $M_i$ -X complex. During illumination at elevated temperature, the  $M_i$ -X complex changes its configuration into a more recombination-active form  $M_i$ -X\*, which subsequently dissociates into isolated  $M_i$  and X. While the reconfiguration of the  $M_i$ -X complex is responsible for the fast component of the lifetime degradation, the isolated  $M_i$  is assumed to be highly recombination active, thus explaining the slow degradation of the bulk lifetime of our samples. During prolonged illumination at elevated temperature, the mobile  $M_i$  atoms diffuse to the wafer surfaces, where the  $M_i$  are trapped. Due to the inhomogeneous wafer thickness and therefore a spatially inhomogeneous period for the  $M_i$  to diffuse to the wafer surface, the lifetime regeneration is strongly position-dependent. The wafer surfaces are not the only possible sink for the fast diffuser  $M_i$ . Another category of sinks are the inhomogeneously distributed crystallographic defects in the mc-Si material.

#### 5. Summary

Within this contribution, we have conducted degradation and regeneration experiments on mc-Si lifetime samples under illumination at elevated temperature. Our measurements clearly revealed that the most crucial process step in mc-Si solar cell fabrication is the firing step. Only if the peak firing temperature exceeds a certain critical firing temperature, the lifetime degradation and regeneration can be observed. Our experimental results suggest an easy-to-implement approach to avoid degradation in industrially produced mc-Si solar cells by reducing the peak firing temperature below the critical temperature. A problem of this approach to suppress LID in mc-Si solar cells might be that the required firing temperature might not be compatible with the optimal firing temperature of the screen-printing pastes applied. This problem could be overcome by a regeneration treatment at higher temperatures (>250°C), as our lifetime results show that higher temperatures during the regeneration speed up the required regeneration process. Our experimental results show that regeneration at 185°C and 1 sun illumination intensity lead

in fact to high and stable lifetimes. Finally, we have proposed a defect model, where the degradation/regeneration effects were attributed to metal precipitates, which dissolve above a critical firing temperature. Lifetime spectroscopy has shown that the recombination centre activated during illumination in mc-Si is a deep-level SRH center with an asymmetric capture cross section ratio of  $\sigma_n/\sigma_p = 20 \pm 7$ , which is a frequent property of interstitial metallic impurities in crystalline silicon.

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