

Light-induced degradation in indium-doped silicon

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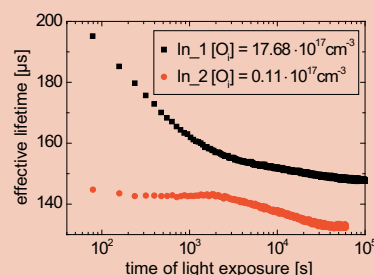
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Light-induced degradation of charge carrier lifetime was observed in indium-doped silicon. After defect formation, an annealing step at 200 °C for 10 min deactivates the defect and the initial charge carrier lifetime is fully recovered. The observed time range of the defect kinetics is similar to the well known defect kinetics of the light-induced degradation in boron-doped samples. Differences between defect formation in boron- and indium-doped silicon are detected and discussed. A new model based on an acceptor self-interstitial $A_{Si}-Si_i$ defect is proposed and established with experimental findings and existing ab-initio simulations.



Charge carrier lifetime degradation during light soaking of indium-doped samples with different oxygen concentrations.

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1 Introduction The most frequent lifetime limiting recombination center in state of the art boron-doped Czochralski (CZ) silicon solar cells occurs at high boron and oxygen amounts in the crystal. The complex forms under illumination or electron injection in the dark and degrades the conversion efficiency of p-type solar cells by 1% to 2% (absolute). Already discovered in 1973 [1], the advent of compensated low cost (solar-grade) silicon leads to a new understanding of the physical processes during defect formation [2–5]. However, the defect itself is still unclear [6].

As aforementioned, light-induced degradation (LID) takes place in boron-doped silicon and is the object of topical research. In gallium-doped CZ silicon no LID was found [7]. CZ silicon co-doped with gallium and boron shows a significantly reduced LID [8]. Aluminum-doped silicon shows degradation due to an aluminum–oxygen complex after thermal treatment above 900 °C [9]. Light-induced lifetime degradation was not observed at room temperature. To the knowledge of the authors only one investigation on indium-doped silicon is published in the literature [10]. Unfortunately, only a lifetime measurement

without any further sample information is denoted. On the basis of the published literature data, light-induced degradation is only expected in boron-doped silicon.

In this Letter, time dependent excess charge carrier lifetime measurements during light soaking of boron-, gallium- and indium-doped silicon samples are presented. Lifetime was measured with microwave-detected photoconductance decay (MWPCD) and the quasi-steady-state photoconductance (QSSPC) technique.

2 Experimental details The samples used for the lifetime degradation study were cut from different indium- and gallium-doped silicon crystals. The crystals were grown out of electronic grade silicon either by Czochralski (CZ) or float-zone (FZ) process by Zulehner from Wacker Siltronic AG. The boron-doped reference was out of a crystal grown by Bosch Solar Energy AG. Specific resistivity was measured with a 4-point-probe setup [11]. The interstitial oxygen content was determined by Fourier transform infrared spectroscopy (FTIR) [11]. To verify the indium doping, the indium concentration was measured us-

Table 1 Samples investigated in this study. CZ designates a Czochralski silicon sample, FZ a float-zone silicon sample.

sample	method/ orientation	dopant	ρ (Ω cm)	N_A (10^{15} cm $^{-3}$)	$[O_i]$ (10^{17} cm $^{-3}$)
B	CZ/100	boron	5.80	2.4	9.84
Ga	CZ/100	gallium	3.41	4.1	8.39
In_1	CZ/100	indium	7.82	1.8	17.68
In_2	FZ/111	indium	8.61	1.6	0.11

ing a low-temperature FTIR setup at CiS according to ASTM F 1630-95 as well as by low-temperature photoluminescence spectroscopy using the setup described in Ref. [12]. In the indium-doped samples no amount of other dopants like boron, gallium, phosphorous, etc. was detected. Details of the investigated samples are given in Table 1.

Before charge carrier lifetime measurements, the samples were etched to remove the saw damage by potassium hydroxide (50 μ m/site) and cleaned by standard RCA followed by a PECVD silicon nitride layer for surface passivation [13].

According to Fischer et al. [1], an annealing step at 200 °C for 10 min was used to deactivate the defect complex. The photoconductance decay was measured with the Semilab WT-2000 MWPCD device. The lifetime of the excess charge carriers was calculated from the MWPCD signal at a carrier density of $\Delta n = 5 \times 10^{14}$ cm $^{-3}$ and calibrated by comparison with a QSSPC measurement [14]. Charge carrier lifetime change due to defect formation by illumination was induced by a 200 ns laser pulse with a wavelength of 904 nm and an average intensity of 8500 W/m 2 . Additionally, excess charge carrier dependent lifetime measurements were executed with the Sinton BCT-120 QSSPC setup at an excess charge carrier density of $\Delta n = 1 \times 10^{15}$ cm $^{-3}$. The QSSPC measurements determine the photoconductance using a calibrated inductively coupled coil [15]. For light soaking the flash of the QSSPC setup (illumination for the first five minutes) and a halogen lamp with an intensity of ~ 100 W/m 2 were used.

3 Results The change in the charge carrier lifetime of the boron-, gallium- and indium-doped silicon samples due to illumination is shown in Fig. 1. Complete defect formation takes place after about 40 hours. With an annealing step at 200 °C for 10 min the initial value of the lifetime is recovered (inset of Fig. 1). The strength of degradation is dependent on the interstitial oxygen concentration. Degradation strength increases with increasing interstitial oxygen concentration. In sample B lifetime is decreased by 29% relative, In_1 by 35% and In_2 by 8% after light soaking. The charge carrier lifetime in gallium-doped silicon stays constant during illumination – this reproduces earlier findings [7, 8]. In the following discussion only the In_1 and the B sample are considered.

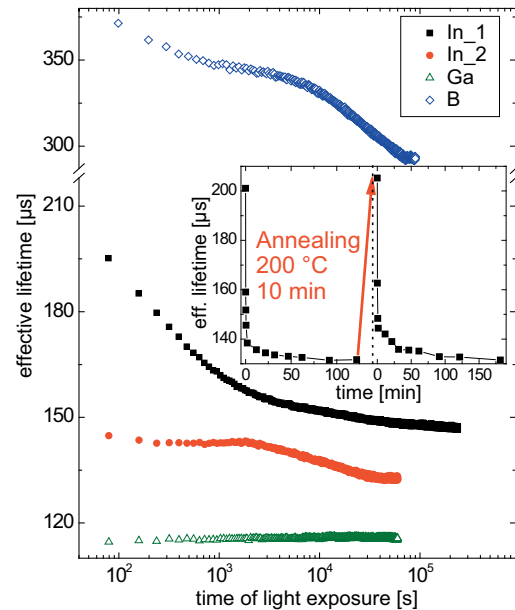


Figure 1 Effective charge carrier lifetime during illumination as a function of time for boron-, gallium- and indium-doped samples measured with the MWPCD setup at room temperature after annealing at 200 °C for 10 min. The inset shows two consecutive cycles of lifetime degradation due to illumination and fully recovered lifetime after annealing. Lifetime cycles in the inset were determined with the QSSPC setup after the MWPCD cycle. Light soaking was done with the QSSPC flash (first five points) and a halogen lamp.

The normalized defect concentration $N_t = 1/\tau_d - 1/\tau_0$ calculated from data depicted in Fig. 1 for boron- and indium-doped samples is displayed in Fig. 2. In this connection, τ_0 is the initial charge carrier lifetime after annealing and τ_d is the measured carrier lifetime during illumination. The time response of the formation process is similar to the well known defect kinetics of the boron–oxygen complex and can be distinguished by two components [7].

The fast forming recombination center (FRC) takes place in the first minutes of light soaking (about 2×10^3 s in Fig. 2). Boron-doping causes a weak degradation while

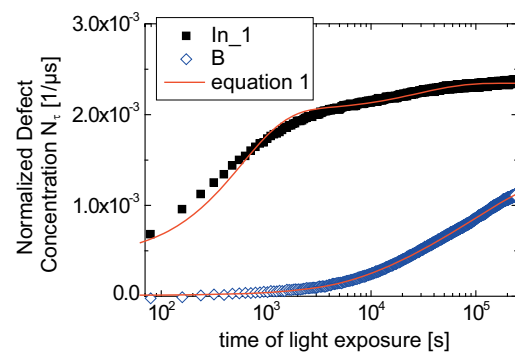


Figure 2 Time dependent normalized defect concentration N_t of the boron- and indium-doped sample.

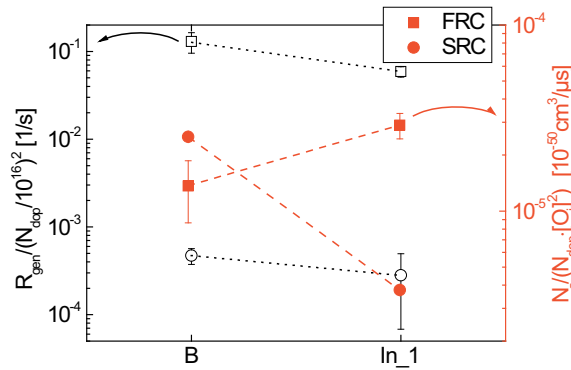


Figure 3 Defect generation rate R_{gen} (empty symbols) and normalised defect concentration N_r (filled symbols) of the fast and slow recombination center for the boron- and indium-doped silicon sample. The errors are the standard deviation out of three measurement cycles. The lines are guide to the eyes.

indium-doping causes a strong degradation in this time range. The slowly forming recombination center (SRC) caused a strong degradation during light soaking in boron-doped samples and takes place during up to 40 hours. In indium-doped samples the SRC caused only a weak degradation. Both, FRC and SRC, follow a single exponential function:

$$N_{\text{FRC/SRC}}(t) = N_{\text{FRC/SRC}}(t \rightarrow \infty) \{1 - \exp(-t \cdot R_{\text{gen FRC/SRC}})\}. \quad (1)$$

R_{gen} is the defect generation rate. The result of the fit is shown in Fig. 2.

Figure 3 shows the defect generation rate R_{gen} (empty symbols) and the normalized defect concentration N_r (filled symbols) of the boron- and indium-doped sample. The defect generation rate is comparable for both dopants. This indicates identical formation processes for the FRC and the SRC in the material. The normalized defect concentration indicates the density of the FRC or SRC recombination center. In the boron-doped sample the earlier seen [7] stronger influence of the SRC is visible. In the indium-doped sample the FRC causes a stronger degradation than the SRC.

Light-induced degradation takes place in both boron- and indium-doped silicon and not in gallium-doped silicon. Similar defect generation rates are found for FRC and SRC independent of the dopant. A difference between boron- and indium-doped silicon is observed in the normalized defect concentration. SRC concentration is more pronounced in boron-doped silicon, whereas in indium-doped silicon the FRC concentration is the larger component.

4 Discussion A possible explanation for the observed phenomena can be found if the lattice sites with the lowest formation energy for interstitial acceptor atoms in silicon are compared. It has been found by ab-initio simulations of silicon containing different types of acceptor atoms that interstitial boron [16] and interstitial indium [17] are forming complexes with silicon interstitials in its lowest energy

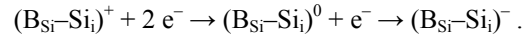
configuration. In the case of boron, the favourable configuration is $\text{B}_{\text{Si}}\text{-Si}_i$ in a C_{1h} or C_{3v} symmetry, dependent on charge state. Thereby the boron stays close to its substitutional position, and a silicon interstitial is trapped at a nearby tetrahedral site [16]. Also, in indium-doped silicon the favourable configuration has C_{1h} symmetry [17]. However, gallium [18] and aluminium [19] are forming pure interstitials on tetrahedral sites in the lowest formation energy case without Si_i . From this we propose that the light-induced degradation is caused by an acceptor–silicon interstitial defect $\text{A}_{\text{Si}}\text{-Si}_i$. This notation was chosen following Ref. [16].

Below, some main experimental results of the LID are discussed in view of the proposed model.

During silicon crystal growth interstitial oxygen precipitates. Two interstitial oxygen atoms induce one silicon interstitial atom Si_i . This concept is well established [20]. Hence, the concentration of $[\text{O}_i]$ is directly correlated to the amount of Si_i . Further, the reaction constants for reactions between substitutional boron and silicon self-interstitials are three magnitudes higher than the reaction constants for reaction between other impurities like e.g. carbon and self-interstitials [21, 22].

The generation rate of interstitial acceptor atoms, which are thought to be the origin of the $\text{A}_{\text{Si}}\text{-Si}_i$ defect, depends on the one hand on the concentration of self-interstitials [23]. On the other hand it is known for boron that this generation rate increases with increasing hole density [24]. Thus, the $\text{A}_{\text{Si}}\text{-Si}_i$ defect density is, via the oxygen induced silicon interstitials, a function of the oxygen content and, via the dependency on the hole density, correlated to the boron content. At the end of the crystallisation as well as crystal cooling process the $\text{A}_{\text{Si}}\text{-Si}_i$ configuration, which is thought to induce the LID, will form in boron- and indium-doped silicon, as this is the energetic favourable configuration.

During illumination a two step defect formation process takes place. It is possible that this can be explained by a charge induced configuration change of the $\text{A}_{\text{Si}}\text{-Si}_i$ defect. For boron it is known that the $\text{B}_{\text{Si}}\text{-Si}_i$ can capture two electrons in two consecutive steps [16]:



It was assumed [16, 25] that the negative-U defect of interstitial boron, observed by Harris et al. [26], is identical with the $\text{B}_{\text{Si}}\text{-Si}_i$ defect. The first electron capture converts the $(\text{B}_{\text{Si}}\text{-Si}_i)^+$ (C_{3v} configuration, probably a shallow donor) in the neutral metastable state (C_{1h} or C_{3v} configuration, $E_i \sim 0.15$ eV [26]). The second electron capture transfers the $(\text{B}_{\text{Si}}\text{-Si}_i)^0$ in the stable negatively charged C_{1h} configuration, $E_i \sim 0.37$ eV [26]. The lifetime decrease during defect formation is caused by the different energy levels (and defect parameters) of the configurations. The slow lifetime degradation behaviour can be explained by the charge induced configuration change of the $\text{B}_{\text{Si}}\text{-Si}_i$ defect complex from C_{3v} to C_{1h} configuration [16]. It is thinkable that a temperature step converts the C_{1h} back into the C_{3v} con-

figuration. Unfortunately, no experimental and theoretical studies of configuration changes in indium-doped silicon are available in the literature.

The observed differences in normalised defect concentration between boron- and indium-doped samples are probably caused by the size difference of the dopants and different SRH parameters of the defect.

Enhancement of LID due to ion implantation of silicon self-interstitials was not observed [27]. This is in accordance with our proposed model because the amount of implanted Si_i of 10^{12} cm^{-3} [27] is much lower compared to the Si_i introduced during CZ crystal growth. If about 1% of the interstitial oxygen in standard CZ silicon forms precipitates, around 10^{15} cm^{-3} Si_i are present in the crystal. From this point of view it is improbable to see an enhancement of LID by implantation of 10^{12} cm^{-3} Si_i .

Some experimental results, like the situation in boron-doped silicon co-doped with gallium [8], the defect deactivation during illumination and subsequent annealing [28] and the similar annealing properties of boron- and indium-doped silicon, are not promptly explainable but seem not impossible in the proposed acceptor–interstitial model.

5 Summary Light-induced degradation (LID) of charge carrier lifetime was investigated in boron-, gallium- and indium-doped silicon. LID takes place in boron- and indium-doped silicon, the lifetime of the gallium-doped sample does not degrade during light soaking. An annealing step at 200°C for 10 min deactivates the detrimental LID defect on the lifetime in boron- and indium-doped silicon and the lifetime is fully recovered. A comparison of the defect kinetic in indium- and boron-doped silicon shows comparable defect generation rates R_{gen} of the slow and the fast component of the defect independent of the dopant species. This leads to the assumption that similar physical processes occur, independent on dopant species. Out of the experimental results and ab-initio calculations a model based on an interstitial acceptor self-interstitial $\text{A}_{\text{Si}}\text{-Si}_i$ defect is proposed. The model is discussed in relation to the known experimental findings of the LID.

The discovery that indium leads to a light-induced degradation leads to new explanation approaches for the origin of the light-induced defect formation process.

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