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# Influence of hydrogen on interstitial iron concentration in multicrystalline silicon during annealing steps

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The influence of in-diffusing atomic H into an annealed multicrystalline silicon (mc-Si) wafer on the concentration of interstitial iron [$Fe_i$] was investigated. Neighboring wafers with similar initial [$Fe_i$] were annealed with and without in-diffusing H. In-diffusion was realized by exposing the samples to a microwave induced remote hydrogen plasma at 400 °C. [$Fe_i$] was detected based on lifetime measurements before and after dissociating the FeB complex. Surface passivation was achieved by a quinhydrone-methanol solution at room temperature to avoid further temperature steps or in-diffusion of H during surface passivation. From [$Fe_i$] measurements before and after the annealing steps with and without H, the influence of H alone on [$Fe_i$] could be accessed. The results were compared to previous experiments where the same $SiN_x$:H layers were used as surface passivation for multiple [$Fe_i$] measurements of mc-Si samples before and after several anneals at 400 °C. It could be shown that a H plasma atmosphere has a strong additional effect on the reduction of [$Fe_i$] compared to temperature effects alone. A formation of H-$Fe_i$ complexes associated with the passivation of the electrical activity of $Fe_i$ could be shown to be improbable because no depassivation of $Fe_i$ could be observed in subsequent annealing steps at 400 °C.
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## I. INTRODUCTION

Hydrogenation is known to significantly improve the average effective bulk minority charge carrier lifetime of multicrystalline silicon (mc-Si) wafers.[1–3] This improvement is explained by the passivation of defects by atomic H. There are on-going discussions not only about the exact underlying mechanisms,[1,3,4] but also about which defects and impurities can be passivated. One of the most detrimental impurities to wafer quality is interstitial iron ($Fe_i$)—both because of the very high recombination rate of electron-hole pairs at this type of defect[4] and because it is a main constituent in equipment for Si wafer production and a common contaminant in chemicals used for processing.[5] The present analysis is dedicated to the question of whether or not $Fe_i$ in standard industrial B doped mc-Si can be passivated by H. This question is of great interest not only because of the improvement potential of material quality by H in-diffusion, but also because $Fe_i$ could be used as a tracer for H diffusion analyses in B doped mc-Si if a formation of H-$Fe_i$ pairs associated with a passivation of the recombination activity of $Fe_i$ took place.[6,7]

Previous experiments on different Si materials (Fe-contaminated float-zone Si,[7,8] Fe-contaminated Czochralski-grown Si,[3,9–11] standard mc-Si (Refs. 6–8, 12, and 13)) have come to different conclusions. All analyses report a decrease of [$Fe_i$] after the hydrogenation process, but while some authors explain this with the temperature driven formation of Fe precipitates alone,[3,10,12] others assume mainly hydrogenation of $Fe_i$ associated with the formation of H-$Fe_i$ complexes to be responsible for this effect.[6–9] Another investigation states that $Fe_i$ (in n-type Si) can build a complex with H but that the recombination rate of this complex is even higher than the one of $Fe_i$ alone.[11] This is supported by theoretical calculations.[14]

## II. EXPERIMENTAL CONSIDERATIONS

### A. $Fe_i$ measurement

The afore mentioned results of previous experiments are either based on deep-level transient spectroscopy (DLTS)[9–11] or based on the determination of [$Fe_i$] via minority charge carrier lifetime measurements.[6–8,12] A summary of the results gained from DLTS measurements can be found in Ref. 4. It is remarkable that both measurement methods generated both data that imply the formation of a H-$Fe_i$ complex and data that exclude this possibility.

The present analysis uses lifetime measurements to determine [$Fe_i$]. The average [$Fe_i$] of B doped mc-Si wafers can be determined from two minority charge carrier lifetime measurements taken with the quasi steady state photoconductance (QSSPC) method.[15] Spatially resolved [$Fe_i$] mappings are gained from two lifetime calibrated photoluminescence imaging (PLI) pictures.[16–18] These methods are based on the fact that the $Fe_i$ content of a B doped Si wafer can be deliberately cycled between being mostly present as either $Fe_i$ or FeB pairs.[15] Because of the different recombination properties of these two forms of dissolved Fe in Si, the lifetime is influenced significantly by the present state of the complex. Measurements are taken before and after dissociating the FeB complexes by optical activation. According to the following relation, the [$Fe_i$] can be calculated as[15]

$$[\mathrm{Fe_i}] = C(\Delta n, N_A)\left[\left(\frac{1}{\tau_d(\Delta n, N_A)} - \frac{1}{\tau_a(\Delta n, N_A)}\right)\right]. \qquad (1)$$

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$\tau_d$ refers to the lifetime in the dissociated state, and $\tau_a$ to the lifetime in the associated state of the FeB complex. The conversion factor C depends on the excess minority charge carrier density $\Delta n$ and the B doping density $N_A$. C is determined by the energy levels and the capture cross sections of the $Fe_i$ and the FeB states. Those values for the determination of C were taken from Ref. 19.

### B. Hydrogenation

Previous experiments from other authors used different methods to hydrogenate the bulk of silicon wafers. Those basically are H ion implantation,[9] annealing $SiN_x$:H layers deposited by plasma enhanced chemical vapor deposition (PECVD),[6–8,12] etching with H containing acids,[11] and exposure of samples to a H plasma.[10,13]

H ion implantation can produce material damages that can influence the [$Fe_i$] by gettering $Fe_i$ at the damaged sites.[9,20] Therefore, it was excluded as a method to incorporate H into the Si bulk. Etching with H containing acids only affects regions very close to the surface. It has to be doubted that the small effect could be detected with the applied measurement method in a proper way.

The two remaining methods both involve annealing of the samples. Depending on the initial [$Fe_i$], as well as on the applied temperature and on the annealing time, the [$Fe_i$] in B doped mc-Si can decrease drastically during a temperature treatment.[21–23] That is why the main challenge of this investigation concerning the hydrogenation of $Fe_i$ is the separation between the influence of H and the influence of temperature. It is known that already the $SiN_x$:H deposition process during PECVD introduces H into the wafer bulk.[24] The desired H in-diffusion mainly takes place during a subsequent anneal. The H flux during this in-diffusion is not constant.[25] Because diffusion temperature and time can be controlled better and to realize a constant H flux, in this analysis a microwave-induced remote hydrogen plasma (MIRHP) is used to introduce atomic H into the silicon crystal.[26]

### C. Effusion of H after hydrogenation

Hydrogenation associated with the formation of a H-defect complex is a competition between the H supply of defects to be hydrogenated and the temperature induced reactivation of already hydrogenated defects. It is important to recognize that a higher local flux of H should enhance defect passivation in mc-Si, because it can compete more effectively with the dehydrogenation process.[25] If the H supply is interrupted and the temperature is still high enough to dissociate H-defect-pairs, a dehydrogenation takes place.

The suggested binding energy between substitutional Fe and H is, at 1.5 eV, rather small.[3] The value for $Fe_i$ could be in the same range.[11] A first-order reaction kinetics model for dissociation leads to the following relationship:[3,27,28]

$$\frac{N}{N_0} = \exp\left[-t\nu \exp\left(-\frac{E_D}{k_B T}\right)\right], \qquad (2)$$

where $N_0$ and N are the densities of passivated defects before and after an annealing step, t the annealing time, $\nu$ the attempt frequency, $E_D$ the binding energy, T the annealing temperature, and $k_B$ the Boltzmann constant.

Fig. 1 shows a plot of the fraction of $Fe_i$ defects $N/N_0$ being still H passivated after 5 s long temperature steps for different temperatures (without temperature ramps taken into account). It is assumed that all $Fe_i$ was passivated by H via formation of H-$Fe_i$ complexes at the beginning of the temperature treatment and that the binding energy of the H-$Fe_i$ complex is 1.5 eV. This graph clarifies that all H-$Fe_i$-complexes can be dissociated by a 5 s long exposure to temperatures above 250 °C. When samples are removed directly from the MIRHP reactor after a 400 °C hydrogenation step, they endure temperatures above 250 °C for much more than 5 s while no further hydrogen supply is present.

After dissociating such H-$Fe_i$ complexes, a repassivation of $Fe_i$ could be possible, if the H stays in the sample. To clarify, if this is the case, the diffusion of H in the Si sample has to be considered. The diffusion coefficient D of H in mc-Si is not reliably known. The diffusion length $L = (Dt)^{1/2}$ at 400 °C for t = 2 min (this is roughly the time to remove samples from the reactor) should be between 15 µm and 170 µm according to the diffusion coefficients taken from Refs. 1 and 29. For that reason, there is a possibility that H originating from possibly dissociated H-$Fe_i$ complexes diffuses out of the sample during removing the samples at temperatures around 400 °C and no repassivation at all takes place. If all $Fe_i$ defects are dehydrogenated and no repassivation occurs, effectively no bulk passivation is observed in the removed samples.

To investigate this question, some samples were not removed from the hydrogen atmosphere until the reactor was cooled down to 150 °C. A cool down to even lower temperatures could lead to H passivation of B, as can be seen in Fig. 1 (H-B binding energy is 1.1 eV (Refs. 3 and 28)). This would influence the determination of the $Fe_i$ concentration by measurements with QSSPC and PLI before and after dissociating FeB complexes by optical activation and therefore has to be avoided.

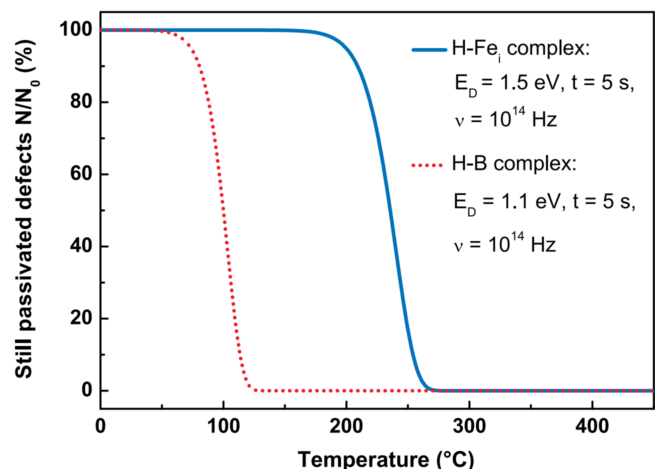


FIG. 1. Fraction of $Fe_i$ and B which are still H passivated after 5 s long temperature steps simulated with Eq. (2).

## III. EXPERIMENTS

The basic idea of the present analysis is to measure [$Fe_i$] before and after a H in-diffusion step at a defined temperature and to compare these two results with neighboring samples (with very similar $Fe_i$ concentration and distribution) that were treated with the same thermal budget but without in-diffusion of H. This experiment is described in Sec. III B (experiment II).

To investigate the applied measurement method, a pre-experiment was performed (experiment I).

Experiment III was carried out to learn more about the underlying mechanism of the phenomenon observed in experiment II.

### A. Experiment I: Surface passivation for [$Fe_i$] measurement—Quinhydrone-methanol (QM) compared to $SiN_x$:H

To detect [$Fe_i$], the bulk lifetime has to be measured twice (Eq. (1)). For those measurements, the surfaces need to be passivated. Most of the common surface passivation methods are realized by depositing passivation layers that contain H. During the temperature steps, necessary to deposit those layers, an in-diffusion of H into the wafer bulk is possible. This possibility is documented for various passivation layers, like for PECVD $SiN_x$:H layers,[24] for $Al_2O_3$ layers deposited by atomic layer deposition,[30] or layers of amorphous Si.[31] Both temperature and H could influence the [$Fe_i$] and have to be avoided in the present analysis. For these reasons, surface passivation of the samples before measuring [$Fe_i$] was achieved by applying a wet chemical QM solution.[32–35] This method delivers a stable surface passivation lasting a couple of hours.[32] The passivation quality is much less affected by light than similar wet chemical methods such as passivating the surfaces by iodine-ethanol are.[36] This is important when dissociating FeB pairs by optical activation for [$Fe_i$] measurement. To verify the applicability of QM as surface passivation for $Fe_i$ measurements in the described way, a pre-experiment was carried out.

Fig. 2 shows all processing steps of experiment I. Six B doped mc-Si wafers (resistivity 1.5 Ω cm, thickness 170 μm) were cut into $50 \times 50\ mm^2$ sized pieces resulting in six samples from different ingot heights. After etching off 10 μm of each surface by chemical polishing, 80 nm thick $SiN_x$:H layers were deposited by PECVD on both surfaces of all samples. These layers served as surface passivation for the following measurements of the spatial average [$Fe_i$] by QSSPC at an injection level of $\Delta n = 2 \cdot 10^{15}\ cm^{-3}$. Before the second lifetime measurement was performed (compare Eq. (1)), the FeB complexes were dissociated by optical activation (above 1 sun, at least 3 min, or until saturation was reached). The [$Fe_i$] measurements were repeated another two times. Between all measurements, the samples were kept in darkness for a couple of days, what is much longer than the time to complete the rebonding of all FeB pairs.[15]

PECVD $SiN_x$:H layers are the standard surface passivation for [$Fe_i$] measurements based on lifetime measurements.[15,21] For the comparison of this standard method with QM as surface passivation, it is important to start with depositing the PECVD $SiN_x$:H layers because the [$Fe_i$] can

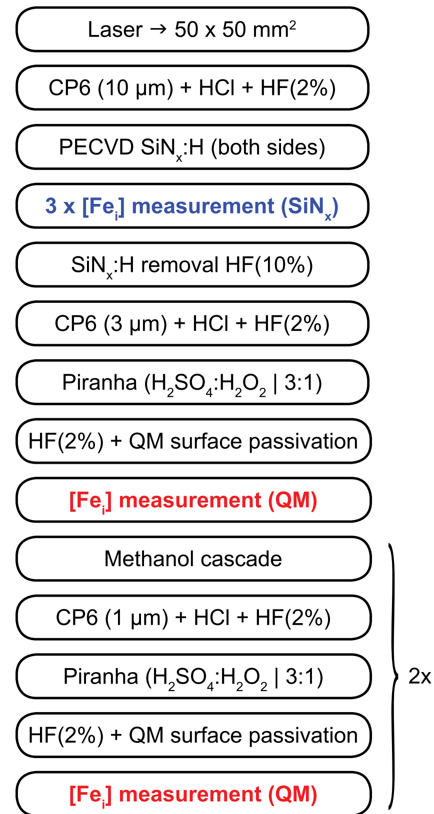


FIG. 2. Sample processing experiment I.

be influenced by the applied temperatures[21] during deposition and by a possible H in-diffusion.[24]

After the first three measurements, the $SiN_x$:H layers were etched off by hydrofluoric acid (HF) (10%) and 3 μm of the surfaces were removed by chemical polishing. After piranha clean[37] and HF dip (2%), the surfaces were passivated with QM. The [$Fe_i$] was measured again. To remove the quinhydrone residues, the samples were rinsed in methanol, in deionized water, and again two more times in methanol (methanol cascade, compare Refs. 32 and 38). 1 μm of the surfaces was removed by chemical polishing, and the measurements with QM surface passivation were repeated twice in the described way.

### B. Experiment II: Influence of H on [$Fe_i$]

The combination of MIRHP and QM as surface passivation enables an unambiguously separate examination of the contributions of H and temperature effects on the change in [$Fe_i$] after processes in the MIRHP reactor. The pure effect of temperature can be analyzed by exposing neighboring samples to the same temperature-time-profile in the same reactor, but without the injection of H.

The detailed process flow of experiment II can be seen in Fig. 3. After cutting standard industrial mc-Si wafers (B doped, resistivity 2 Ω cm, $100 \times 100\ mm^2$, thickness 330 μm) into $50 \times 50\ mm^2$ sized pieces, all samples received a chemical polishing etch removing 20 μm from each surface. The B concentration [B], that is required for the calculation of the $Fe_i$ concentration and the QSSPC measurement, was determined by measuring the resistivity and thickness of all samples. After

the samples underwent a piranha clean and a HF dip, chemical surface passivation was achieved by a QM solution. The data for the determination of [$Fe_i$] were acquired from lifetime measurements with QSSPC (at $\Delta n = 2 \cdot 10^{15}$ $cm^{-3}$) and PLI before and after dissociating the FeB complexes by optical activation (above 1 sun, at least 3 min, or until saturation was reached) as described in Sec. II A.

To avoid in-diffusion of QM residues from the sample surfaces during temperature processes in the MIRHP reactor, those residues were removed by a methanol cascade and a chemical polishing associated with a surface removal of approximately 1 μm.

All samples were grouped in sets of four directly neighboring samples with similar grain structures. The four neighboring samples from all groups were treated with processes in the MIRHP reactor, differing in temperature-time-profile and/or hydrogenation:

1. With H plasma, with cool down.
2. With H plasma, without cool down.
3. No H plasma, with cool down.
4. No H plasma, without cool down.

Samples treated with processes 3 and 4 served as references and show the influence of temperature alone ($N_2$ ambient, same pressure: 1 mbar). The temperature-time-profiles of all processes are shown in Fig. 4. All samples were annealed at 400 °C in the MIRHP reactor for different lengths of time. Cool down means that the samples were cooled down to 150 °C in the MIRHP reactor (with H plasma still on, if a hydrogenation was applied) before removing them. These cool down steps lasted 210 min. All samples of one set remained in the MIRHP reactor for the same total amount of time, but underwent different temperature-time-profiles. The total processing times (including cool down, if applied) were 250, 330, 510, and 810 min. Different in-diffusion times were chosen, to analyze their effect on the hydrogenation of $Fe_i$ and to vary the possible reduction of [$Fe_i$] due to temperature alone (compare Ref. 21). Three sets of four neighboring samples were treated equally (same total processing time) for statistical reasons.

After the processes in the MIRHP reactor, the samples were kept at least one day in darkness at room temperature to assure that the rebonding of all FeB pairs was completed.[38] Then lifetime measurements for the determination of [$Fe_i$] of all samples were performed as before, and the samples received a short chemical polishing in order to remove QM residues. At the end, the doping concentration of all samples was determined again, to check if the B concentration was affected by H in-diffusion and/or temperature processes.

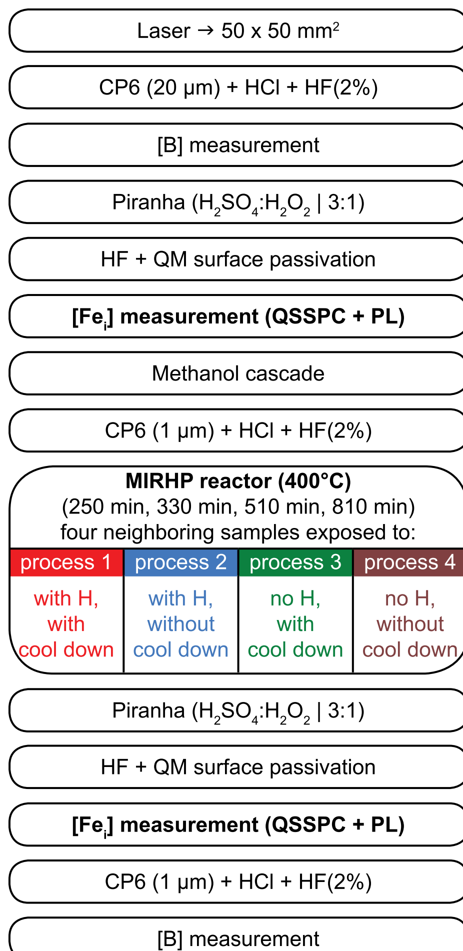


FIG. 3. Sample processing experiment II.

### C. Experiment III: Formation of H-$Fe_i$ complexes

The results of the experiment described in Sec. III B showed a reduction of [$Fe_i$] due to temperature and an even stronger reduction due to the combination of temperature and H (see Sec. IV B). Possible explanations for this stronger reduction for processes with H could be

1. Formation of H-$Fe_i$ complexes associated with passivation of electrical activity of $Fe_i$.
2. Enhanced diffusion of $Fe_i$ by H associated with enhanced gettering/formation of precipitates.

One difference between the two explanations is that the first one is based on a reversible process. If the first explanation is true, the H-$Fe_i$ complexes in a hydrogenated sample should dissociate during an annealing step under $N_2$ ambient (without H) and H should diffuse out of the sample. After all

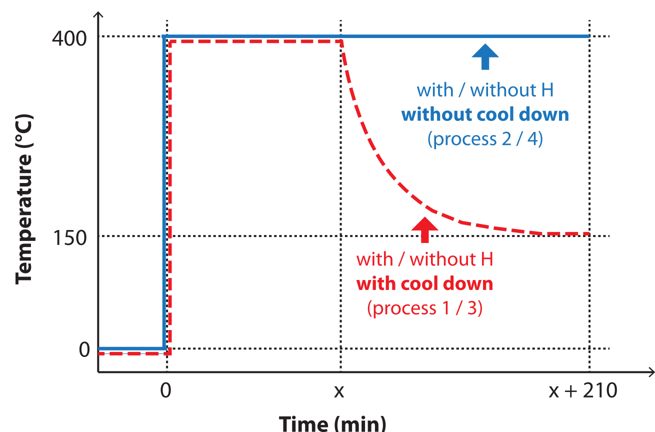


FIG. 4. Schematic temperature-time-profiles of different processes in the MIRHP reactor. x varies between 40 min and 600 min.

H is effused, [$Fe_i$] of the formerly hydrogenated sample should be the same as the one of a neighboring sample that was treated equally but without H. This is not expected if the second suggestion is true.

To investigate whether the underlying mechanism of the observed stronger reduction of [$Fe_i$] after annealing steps with H is the formation of H-$Fe_i$ complexes or not, mc-Si samples with initial [$Fe_i$] of $1 \cdot 10^{12}\,cm^{-3}$ (higher than in Sec. III B) were analyzed. The stronger reduction of [$Fe_i$] in processes with H compared to those without H is more pronounced for higher starting values, and longer subsequent effusion anneals are possible–[$Fe_i$] in mc-Si decreases during temperature treatments at 400 °C (Ref. 21) and the detection limit of [$Fe_i$] measurements is around $1 \cdot 10^{10}\,cm^{-3}$.[15] Additionally, the thickness of the new samples was smaller (170 μm) and in the range of the diffusion length L of H in mc-Si at 400 °C during t = 2 h ($L = (Dt)^{1/2}$ is between 115 μm and 480 μm according to the H diffusion coefficients D that can be found in Refs. 1 and 29). Therefore, the probability for an effusion of H originating from a possibly existing H-$Fe_i$ complex out of the sample is high and a repassivation of $Fe_i$ by dissociated H unlikely.

Sets of two directly neighboring samples were treated as shown in the first part of Fig. 3 before the processes in the MIRHP reactor. Then, instead of four different processes, only processes 2 and 4 (with and without H, annealing temperature constantly at 400 °C and no cool down) were applied to the neighboring samples for 2 h. After the processes in the MIRHP reactor, the samples were again treated as described in Fig. 3.

In place of the [B] measurement, all samples were exposed to a second temperature treatment at 400 °C for 2 h in the MIRHP reactor, but this time only under $N_2$ atmosphere (no H). Note that samples with and without H were annealed under equal conditions but in separate processes in order to avoid that effused H influences samples that were treated with temperature only. [$Fe_i$] was measured as described afore. The samples were annealed a third and a fourth time another 3 h and 2 h at 400 °C (again $N_2$ atmosphere), and [$Fe_i$] was measured again after each annealing step.

## IV. RESULTS

### A. Experiment I: Surface passivation for [$Fe_i$] measurement—QM compared to $SiN_x$:H

Fig. 5 shows the results of six repeated measurements of [$Fe_i$] of six different samples. The first three measurements were carried out with a surface passivation by PECVD $SiN_x$:H layers on both sides. After etching off the $SiN_x$:H layers, [$Fe_i$] was determined by measurements with QM surface passivation. The averaged spatial average values and the corresponding standard deviations for all measurements can be seen in Table I.

Both the [$Fe_i$] results from measurements with $SiN_x$:H as surface passivation and from those with QM as surface passivation show a very good reproducibility when values from one passivation type are compared to each other. This is documented by the small standard deviations in Table I.

The relative difference between the two surface passivation methods concerning the determination of [$Fe_i$] is below 15%.

The values determined by measurements with QM are always higher. The surface passivation by QM and by PECVD $SiN_x$:H layers differ in quality,[32] but for a [$Fe_i$] measurement, two lifetime measurements are necessary and the contribution of recombination processes at the surface should cancel out[15] according to Eq. (1). A condition for this is that the surface recombination contributions are the same for the lifetime measurement in the associated and in the dissociated state. A change of the QM surface passivation quality during illumination for the optical dissociation of FeB between the two lifetime measurements might explain why [$Fe_i$] measured with QM surface passivation is higher. The lifetime measurements were performed at $\Delta n = 2 \cdot 10^{15}$ $cm^{-3}$, which is at higher excess charge carrier density than at the position of the cross over point.[19] This means that the lifetime values after dissociation are expected to be higher than the ones before dissociation because of the different recombination properties of FeB and $Fe_i$ for charge carriers. If the measured lifetimes are even higher due to an improved surface passivation (compared to the first lifetime measurement before dissociation), the determined [$Fe_i$] is overestimated (compare Eq. (1)).

Nevertheless, QM films can be used for [$Fe_i$] measurements of the planned experiment because the method shows a very good reproducibility and the overestimation of [$Fe_i$] should be in the same range for samples treated with H and for those treated without H.

### B. Experiment II: Influence of H on [$Fe_i$]

As can be seen in Fig. 6, all four previously described processes for different annealing times at 400 °C reduce [$Fe_i$] (spatial average measured by QSSPC) in B doped mc-Si wafers significantly.

A stronger decrease is observed for the hydrogenation processes. For the shorter annealing times (250 min and

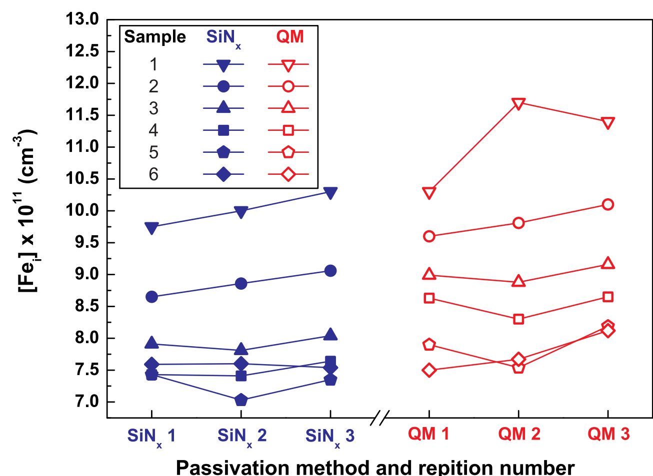


FIG. 5. [$Fe_i$] of six mc-Si samples from different ingot heights. Full symbols show results of three repeated measurements with PECVD $SiN_x$:H surface passivation. After etching off the $SiN_x$:H layers, [$Fe_i$] measurement was repeated three times with QM surface passivation (open symbols). The solid lines are just guides to the eye.

TABLE I. Spatial average [$Fe_i$] averaged over three measurements from Fig. 5 at $\Delta n = 2 \cdot 10^{15}\,cm^{-3}$ with $SiN_x$:H layers and over three measurements with QM as surface passivation, and the relative differences between the two methods.

| Sample | Average [$Fe_i$] with $SiN_x$:H ($10^{11}\,cm^{-3}$) | Average [$Fe_i$] with QM ($10^{11}\,cm^{-3}$) | Relative difference (%) |
|---|---|---|---|
| 1 | $10.00 \pm 0.30$ | $11.10 \pm 0.77$ | 10.86 |
| 2 | $8.86 \pm 0.21$ | $9.84 \pm 0.26$ | 11.12 |
| 3 | $7.92 \pm 0.11$ | $9.01 \pm 0.20$ | 13.75 |
| 4 | $7.50 \pm 0.12$ | $8.52 \pm 0.20$ | 13.73 |
| 5 | $7.27 \pm 0.21$ | $7.88 \pm 0.32$ | 8.34 |
| 6 | $7.58 \pm 0.03$ | $7.76 \pm 0.32$ | 2.44 |

330 min), the two processes involving H (processes 1 and 2) show a reduction of [$Fe_i$] that is a factor of two higher than for the processes without H (processes 3 and 4). For longer annealing times (510 min, 810 min), the difference is still existent, but smaller. Longer annealing times during hydrogenation only lead to a small further decrease in total [$Fe_i$].

If a clear separation of the contributions of temperature and H to the reduction of [$Fe_i$] was possible, it could be stated that the contribution of temperature becomes more dominant for longer annealing times. This can be concluded from comparing the absolute decreases due to hydrogenation and temperature with the ones in samples that were treated with temperature alone. Note that the absolute initial concentrations of $Fe_i$ vary for the different annealing times and for the different samples. Low-temperature induced internal gettering obeys an exponential law (compare Ref. 21, Fig. 7, and Eq. (3)), and the absolute decrease in [$Fe_i$] strongly depends on the starting [$Fe_i$].

Comparing the influence of the different temperature-time-profiles (Fig. 4) and the different processes (1–4) on [$Fe_i$], it can be stated that the expected effect of a smaller reduction of [$Fe_i$] due to a possible effusion of H during the removal of the samples from the reactor is not observed. Considering the statistical error bars and the error in measurement, the differences in Fig. 6 between processes 1 (with H, with cool down) and 2 (with H, without cool down) are negligible.

To have a possibility to compare the data gained by in-diffusion of H by MIRHP to processes where H was in-diffused by annealing PECVD $SiN_x$:H layers, the results were plotted again, in a different way. Fig. 7 shows part of the results already presented in Fig. 6. In this plot, only the data of samples treated with processes 2 and 4, which were annealed constantly at 400 °C and not cooled down, is included. The open symbols again give the average initial $Fe_i$ concentrations before the annealing steps. They are fitted into data from Krain *et al.*[21] (black crosses), showing $Fe_i$ concentrations of mc-Si wafers that were coated with PECVD $SiN_x$:H layers on both sides (as surface passivation) and annealed at 400 °C several times.

As the initial $Fe_i$ concentrations of our data vary and differ from that of Krain *et al.*, they had to be placed at different

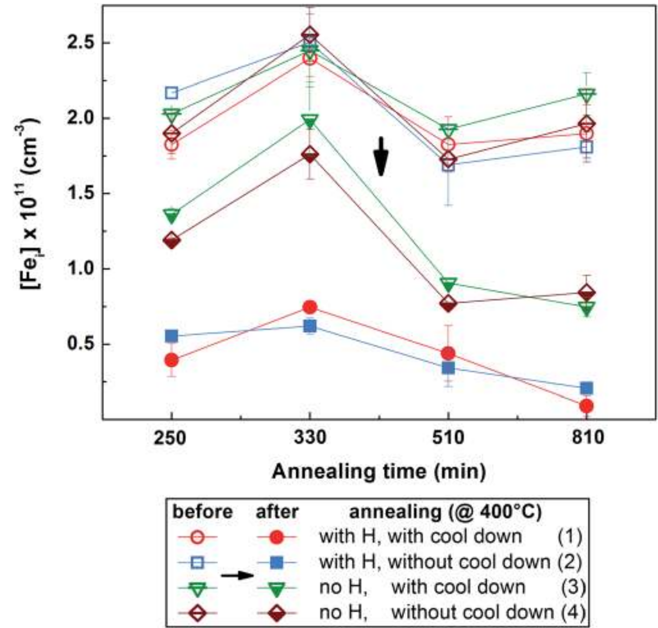


FIG. 6. Spatial average [$Fe_i$] (measured by QSSPC) of B doped mc-Si samples before and after annealing steps at 400 °C for different lengths of time and processes with/without H and with/without cool down (processes 1–4). The values are averaged over three samples with similar initial [$Fe_i$] (cut out of one wafer). The error bars give the standard deviation from averaging the results of three samples. The different processes for each length of time were applied to four neighboring samples with similar grain structure. The solid lines are just guides to the eye.

time values in the graph of Krain *et al*. The time difference between corresponding (same shape and color) open and filled/semi-filled (with H/without H) symbols equals the annealing time at 400 °C (compare Fig. 6). The data acquired by processes involving H fit very well into the data of Krain *et al.*, while the ones from processes with temperature only (no H) did not reduce the [$Fe_i$] in the same way (as described previously). We can therefore conclude that the influence of H on the decrease of [$Fe_i$] in mc-Si at 400 °C is not affected by the different methods used for in-diffusion of hydrogen. Furthermore we can state that the reduction of [$Fe_i$] observed by Krain *et al.* is not a pure temperature effect. This could explain why the activation energy for temperature induced gettering of $Fe_i$ reported in Ref. 21 is lower than the migration energy of $Fe_i$ found in Ref. 4. These energies were expected to be the same in Ref. 21, what would mean that the migration of $Fe_i$ to gettering sites within the mc-Si sample is the limiting factor in the reduction process of [$Fe_i$]. The PECVD $SiN_x$:H layers in Ref. 21 served not only as surface passivation, but also unintentionally as source of H that affected the reduction of [$Fe_i$] and the activation energy of $Fe_i$.

Fig. 8 shows mappings of [$Fe_i$] of two neighboring B doped mc-Si samples before and after annealing steps with and without H at 400 °C (processes 2 and 4) for 330 min. The initial local [$Fe_i$] before annealing is very similar for both samples. This shows that a comparison of different annealing steps with and without H on neighboring wafers can be trusted. The discussion of the spatially resolved data is basically the same as for the average values. When comparing processes with and without cool down, some small local differences can be observed.

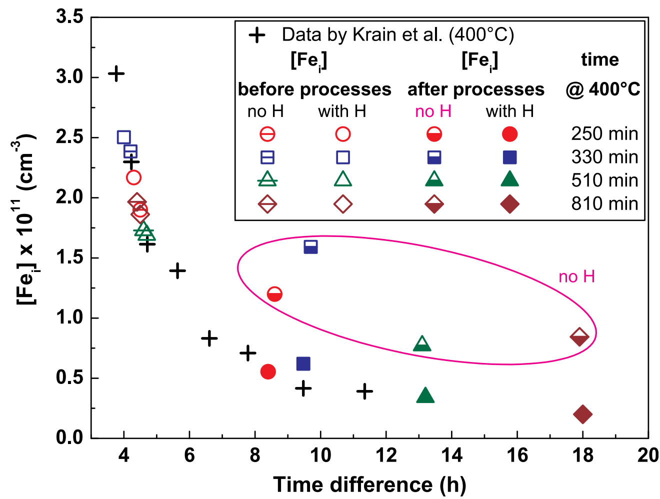


FIG. 7. Decrease of spatial average [$Fe_i$] of B doped mc-Si after annealing steps at 400 °C for different lengths of time. Black crosses show data from PECVD $SiN_x$:H coated wafers taken from Ref. 21. Initial [$Fe_i$] (open symbols) of data from Fig. 6 (processes 2 and 4) was fitted into data from Krain et al. The time differences between corresponding symbols before and after processes equal the annealing times.

A significant passivation of B by H can be excluded, because all samples showed equal resistivity values before and after the different processes in the MIRHP reactor.

### C. Experiment III: Formation of H-$Fe_i$ complexes

For a better overview, Fig. 9 shows the results of one set of samples only. The other sets basically behave similar. The decrease of [$Fe_i$] due to temperature in dependence of time t is described by an exponential law[21]

$$[Fe_i] = [Fe_i]\,(t = 0)\exp\left(-\frac{t}{\tau}\right), \qquad (3)$$

where $\tau$ is the time constant of the exponential decrease. The behavior of sample 1 in Fig. 9 is described by this equation. A neighboring sample (sample 2) with very similar initial [$Fe_i$] but—in contrast to sample 1—annealed in H instead of $N_2$ atmosphere for the first 2 h, behaves as expected from the results of experiment II (full symbols in Fig. 9). As already discussed in Sec. III C, the stronger decrease in [$Fe_i$] in sample 2 can be explained either by a formation of H-$Fe_i$ complexes (1) or by an enhancement of $Fe_i$ diffusion by H associated with enhanced gettering and/or enhanced formation of precipitates (2). A mechanism based on the first explanation should be fully reversible because the H-$Fe_i$ complexes can be dissociated. A dissociation of eventually formed H-$Fe_i$ complexes at 400 °C depends on the binding energy of the two complex partners and the annealing time. According to Eq. (2), an anneal step for 7 h at 400 °C should lead to a dissociation of

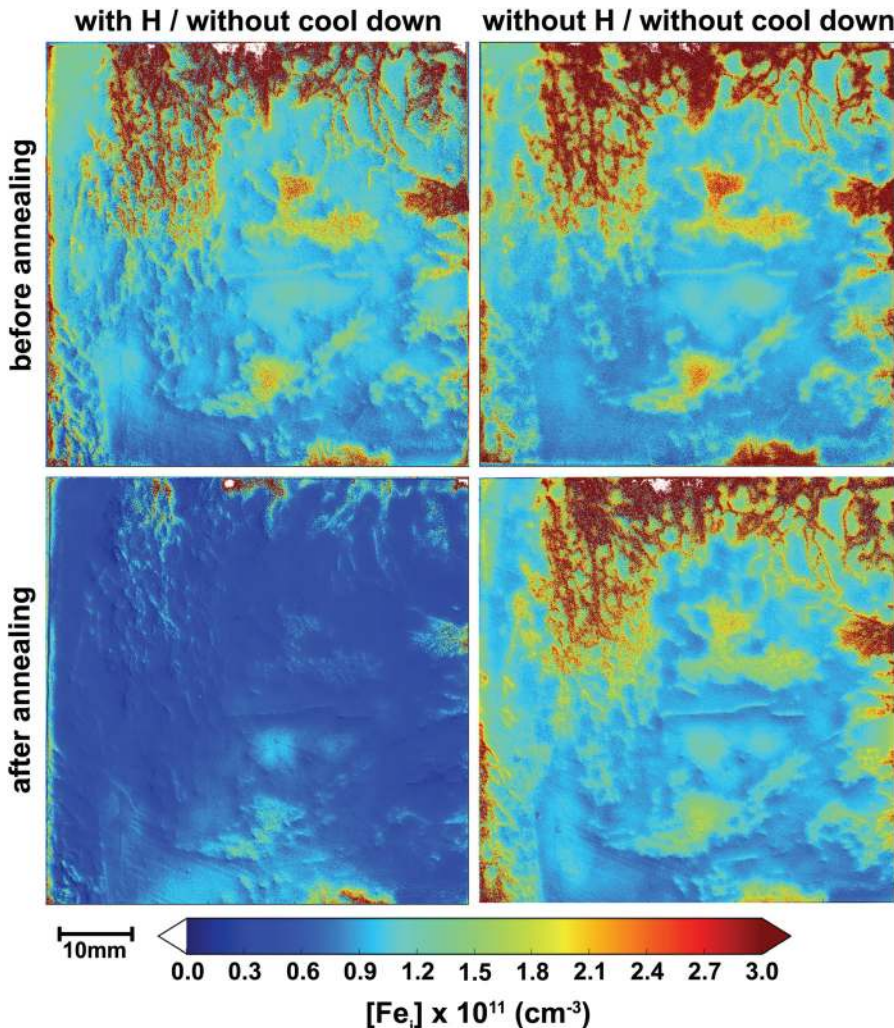


FIG. 8. [$Fe_i$] mappings of two neighboring mc-Si samples before and after annealing steps with and without H at 400 °C (processes 2 and 4) for 330 min. Mappings were produced from two lifetime calibrated PLIs.

almost all H-$Fe_i$ complexes if the binding energy is below 2.4 eV (what is a rather high value compared to binding energies of H with transition metals[3,28]).

As already mentioned in Sec. III C, the diffusion length of H for this kind of anneal should be large enough to allow H to effuse from the wafer. This should result in identical or at least very similar [$Fe_i$] in samples 1 and 2 after 9 h (or even less time) of total annealing time at 400 °C. As this is not the case (semi-full data points in Fig. 9), the first explanation is considered to be not true.

According to the second explanation the stronger decrease of [$Fe_i$] in sample 2 during hydrogenation is caused by an enhanced gettering and/or precipitation of $Fe_i$ under the influence of H. This enhancement can be described by a smaller $\tau$ in Eq. (3) and is expected to endure during a subsequent annealing step without H (under $N_2$ atmosphere) for a certain period of time, because the formerly in-diffused H still interacts with $Fe_i$ during its effusion out of the crystal. This is why the time constant $\tau$, equal to the negative inverse gradient of the data in Fig. 9, does not change significantly for sample 2 during the first $N_2$ anneal (between 2 h and 4 h shown in Fig. 9). After most H effused out of sample 2, $\tau$ is expected to be the same as in sample 1, as now the reduction of [$Fe_i$] in both samples is governed by temperature only. This expectation was confirmed by the experiment. As shown in Fig. 9 between 4 h and 9 h, the gradients of the two curves are very similar and $\tau$ is no longer influenced by diffusing H. This result is supported by the expectation described in Sec. III C that all H should have left sample 2 after 2 h of effusion at 400 °C (after 4 h of total annealing time for sample 2 in Fig. 9).

## V. DISCUSSION

An explanation of the observed results based on the idea that H-$Fe_i$ complexes are formed leads to contradictions.

In experiment II, a difference between the processes with and without cool down was expected, because it was assumed that H-$Fe_i$ pairs dissociate while removing the samples after processes without cool down. The contradiction to the expected result can perhaps be explained by one of the following suggestions:

1. Overestimation of the diffusion length of H in mc-Si: No effusion of H could lead to a repassivation of dissociated H-$Fe_i$ complexes.
2. Underestimation of the activation energy of H trapped at $Fe_i$: 400 °C would not be enough to dissociate the H-$Fe_i$ complex.
3. A combination of 1 and 2.
4. H-$Fe_i$ complexes are not formed and therefore not the reason for the stronger reduction of [$Fe_i$].

The first three suggestions were discussed in Secs. II C and IV C. All three are not supported by the results of experiment III, where no reversion of the possible passivation effect of $Fe_i$ during annealing steps of hydrogenated samples under $N_2$ ambient and therefore no dissociation of H-$Fe_i$ pairs was observed. This could be explained by the fourth suggestion that no such pairs are formed. In this case, the stronger total decrease of [$Fe_i$] for samples annealed under H atmosphere has to be explained by a different interaction between H and $Fe_i$ particles (at 400 °C, virtually all FeB pairs are dissociated and dissolved Fe in B doped mc-Si should only be present as $Fe_i$).[39]

A possible effect that leads to the stronger reduction of [$Fe_i$] when temperature application is combined with H in-diffusion could be an acceleration of the precipitation and/or gettering of $Fe_i$ by H. This could be, for example, explained by an electrostatic interaction between $Fe_i$ atoms and atomic H which are both positively charged in B doped Si.[1,3,4] This ionic interaction could increase the mobility/diffusivity of $Fe_i$ and accelerate the gettering and/or precipitation of $Fe_i$ and therefore the reduction of [$Fe_i$]. In this case, no dissociation of H-$Fe_i$ pairs would take place while removing the samples at elevated temperatures and the [$Fe_i$] would not be affected in the expected way.

Newman *et al.* observed a similar effect for O in crystalline Si: O diffusion jumps in Si can be significantly catalyzed by collisions with diffusing H atoms.[40]

The observed results of experiment III during annealing steps of hydrogenated samples under $N_2$ ambient can also be explained by the assumption that H enhances the diffusion of $Fe_i$. During this further temperature treatment without H (under $N_2$ atmosphere), the formerly in-diffused H could effuse out of the crystal. On its way out of the sample, H could enhance the precipitation of $Fe_i$ in the same way as during the in-diffusion and could lead to a continued stronger reduction of [$Fe_i$]. After all H has left the sample, the reduction rate of [$Fe_i$] during further anneals is lower because it is only influenced by temperature and not—as before—by a combination of temperature and H.

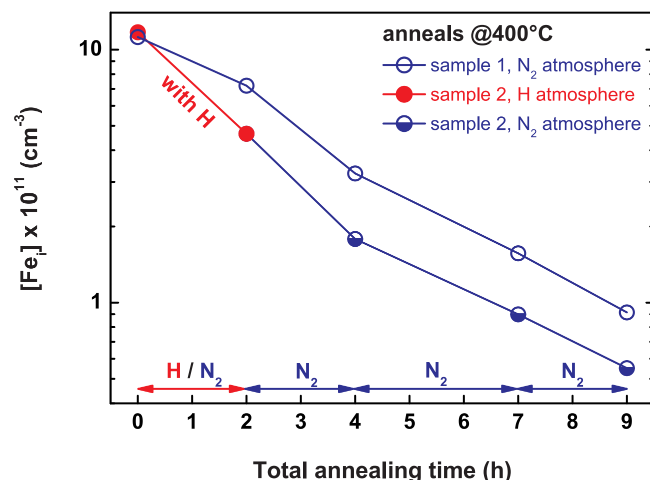


FIG. 9. [$Fe_i$] of B doped mc-Si samples before and after annealing steps at 400 °C for different lengths of time. Sample 2 was treated with H during the first 2 h long annealing. Sample 1 was treated equally but in $N_2$ atmosphere. The subsequent temperature treatments at 400 °C were carried out without H for 2 h and for 3 h. The solid lines are just guides to the eye.

## VI. SUMMARY

The pre-experiment for this investigation (experiment I) reveals that the applied surface passivation with QM is suited for measuring [$Fe_i$] with lifetime measurements and avoids

changes in [$Fe_i$] due to temperature and H during surface passivation.

The main result of this investigation is that in-diffusion of atomic H into a mc-Si B doped wafer while applying a certain temperature definitely has an additional influence on the reduction of the [$Fe_i$] apart from the pure temperature effect. The decrease of [$Fe_i$] is significantly stronger when annealing steps are combined with H in-diffusion.

Comparisons with an experiment presented by Krain *et al.* in Ref. 21 show that there is no dependence on the method of H in-diffusion at 400 °C (annealing $SiN_x$:H layers or exposing to MIRHP). Based on the knowledge of the heavy influence of H and temperature on [$Fe_i$], it can be strongly recommended not to use $SiN_x$:H layers deposited by the PECVD method as surface passivation for measurements of interstitial iron concentrations. Especially, when temperature effects are investigated, H diffusing out of the $SiN_x$:H layers can significantly influence [$Fe_i$].

H effusion experiments strongly indicate that the increased reduction of [$Fe_i$] due to H might be explained by an enhanced diffusion of $Fe_i$ that accelerates the formation of iron precipitates and speeds up gettering of $Fe_i$. Based on these experiments, a formation of H-$Fe_i$ complexes associated with a passivation of the electrical activity of $Fe_i$ can be excluded as explanation for the stronger decrease of [$Fe_i$] when annealing steps are combined with in-diffusion of H.

This also explains why no differences in [$Fe_i$] could be observed after hydrogenating neighboring samples at 400 °C in the MIRHP reactor with and without cooling down the samples before removing them from the H atmosphere. As the formation of H-$Fe_i$ complexes is not the reason for the differences in [$Fe_i$] after processes with and without H, no depassivation of such complexes at 400 °C can be observed.

## ACKNOWLEDGMENTS

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