

INFLUENCE OF HYDROGEN ON INTERSTITIAL IRON CONCENTRATION IN MULTICRYSTALLINE SILICON

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ABSTRACT: The purpose of this work is to investigate the influence of in-diffusing atomic H into a multicrystalline silicon (mc-Si) wafer on the concentration of interstitial iron (Fe_i). Vertically adjacent wafers were annealed with and without in-diffusing H. In-diffusion was realized by exposing the samples to a microwave induced remote hydrogen plasma (MIRHP). $[Fe_i]$ was detected based on lifetime measurements before and after dissociating the FeB complex. Surface passivation was achieved by a quinhydrone-methanol solution to avoid further temperature steps and in-diffusion of H during 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 experiments where $SiN_x:H$ layers were used as surface passivation for $[Fe_i]$ measurements after low temperature anneals (300°C – 500°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. This additional reduction is proportional to the $[Fe_i]$ after the annealing step alone.

Keywords: Hydrogen, Iron, mc-Si, Gettering

1 INTRODUCTION

Hydrogenation is known to significantly improve the average effective bulk minority charge carrier lifetime of mc-Si wafers [1]. This improvement is explained by the passivation of defects by atomic H. There are on-going discussions not only about the exact mechanism [2,3] but also about which defects and impurities can be passivated. One of the most detrimental impurities to wafer quality is Fe_i . The presented analysis is dedicated to the question of whether or not Fe_i in standard industrial mc-Si can be passivated by H. Previous experiments have come to different conclusions [3-6]. All analyses report a decrease of $[Fe_i]$ after the hydrogenation process, but while some explain it with the temperature driven formation of iron precipitates alone [6], others assume mainly hydrogenation of Fe_i associated with the formation of H- Fe_i complexes to be responsible for this effect [3-5]. Another investigation states that Fe_i can build a complex with H but that the recombination rate of this complex is even higher than the one of Fe_i alone [7]. This is supported by theoretical calculations [8].

The main challenge of investigations concerning hydrogenation of Fe_i is the separation between the influence of H and the influence of temperature. Depending on the initial $[Fe_i]$, as well as the applied temperature and the annealing time, the $[Fe_i]$ in p-doped mc-Si can decrease drastically [9,10]. To have good control of diffusion temperature and time, and to realize a constant H flux, this analysis uses a MIRHP to introduce atomic H into the silicon crystal [11].

2 Fe_i MEASUREMENT AND HYDROGENATION

2.1 Measuring $[Fe_i]$

The average $[Fe_i]$ of p-doped mc-Si wafers can be determined from two minority charge carrier lifetime measurements taken with the quasi steady state photoconductance (QSSPC) method [12]. Spatially resolved $[Fe_i]$ mappings are gained from two lifetime calibrated photoluminescence imaging (PLI) pictures [13-15]. These methods are based on the fact that the Fe_i content of a B doped p-type Si wafer can be deliberately cycled between being mostly present as either Fe_i or as

FeB pairs [12]. Because of the different recombination properties of these two forms of Fe in silicon 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 [12]:

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

τ_d refers to the lifetime in the dissociated state and τ_a to the lifetime in the associated state of the FeB complex. The conversion factor C depends on the excess minority charge carrier density Δn and the doping density N_A . C is determined by the capture cross sections of the Fe_i and the FeB state. Those values were taken from [16].

2.2 Effusion of H after hydrogenation

Hydrogenation 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 during a shorter anneal should enhance defect passivation in mc-Si because it can compete more effectively with the dehydrogenation process [17]. If the H supply is interrupted and the temperature is still high enough to break off H-defect-pairs, a dehydrogenation takes place.

The suggested binding energy between Fe_i and H is, at 1.5 eV, rather small [3]. A first-order reaction kinetics model for dissociation leads to the following relationship [3,19]:

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

where N_0 and N are the densities of passivated defects before and after an annealing step, t is the annealing time, ν is the attempt frequency, E_D is the binding energy, T is the annealing temperature and k_B is 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 T-ramps taken into account), under the assumption that all Fe_i was passivated by H at the beginning of the temperature treatment. This graph clarifies that all H- Fe_i -complexes can be split off 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. The diffusion coefficients of H in mc-Si are not known completely. The diffusion length at 400°C for 2 minutes (this is roughly the time to remove samples from the reactor) should be between 15 μm and 170 μm [2,20]. For that reason, after in-diffusing H, there is a possibility that it does not remain in the samples while removing them from the reactor at temperatures around 400°C.

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 [3]). 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.

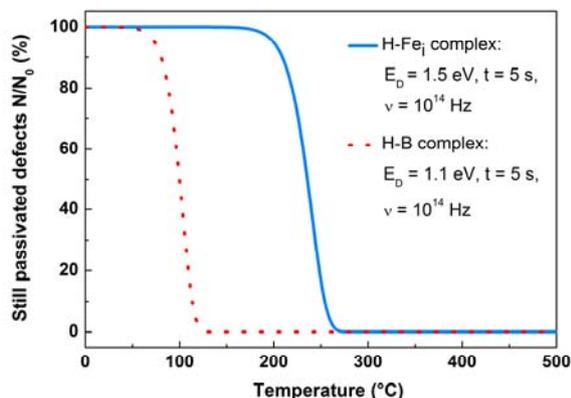


Figure 1: Fraction of Fe_i and B which are still H passivated after 5 s long temperature steps simulated with equation 2.

3 EXPERIMENT

The basic idea of the present analysis is to measure $[Fe_i]$ before and after a H in-diffusion step at a certain temperature and to compare these two results with neighboring samples that were treated with the same thermal budget but without in-diffusion of 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, like for example depositing $SiN_x:H$ layers by PECVD (plasma enhanced chemical vapor deposition) or layers of amorphous Si, involve annealing steps and possible in-diffusion of H into the wafer bulk [21]. Both, temperature and H, could influence $[Fe_i]$ and has to be avoided in the present analysis. For these reasons, surface passivation of the samples before measuring $[Fe_i]$ was achieved by applying a quinhydrone-methanol (QM) solution [18]. This method delivers a stable surface passivation lasting a couple of hours. The passivation quality is not affected by light as similar wet chemical methods such as passivating the surface by iodine-ethanol [22] are. This is important when splitting off FeB pairs by optical activation for $[Fe_i]$ measurement.

In-diffusion of H into mc-Si wafers can be achieved

by various methods. This analysis focuses on atomic H produced by a MIRHP and in-diffused at a certain temperature. 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 processing in the MIRHP reactor. The pure effect of temperature can be analyzed by exposing neighboring samples to the same temperature profile, in the same reactor, but without the injection of H.

Standard industrial mc-Si wafers (p-type, 2 Ωcm, 100x100 mm², 330 μm) were cut into samples of 50x50 mm². Sets of four vertically directly adjacent samples with similar grain structures were treated with four MIRHP processes differing in temperature profile and 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). The temperature profiles of all processes are shown in Fig. 2. 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 minutes. All samples of one set remained in the MIRHP reactor for the same total amount of time, but underwent different temperature profiles. The total processing times were 250, 330, 510 and 810 minutes. Different in-diffusion times were chosen to analyze their effect on the hydrogenation of Fe_i and to vary the reduction of $[Fe_i]$ due to temperature alone. Three sets of four adjacent samples were treated equally for statistical reasons. For each annealing time the three sets of directly adjacent samples were exposed to the four processes described above. Two further samples received no treatment in the MIRHP reactor and served only as references. In total 50 mc-Si samples were analyzed.

At the beginning all cut samples received a chemical polishing etch removing 20 μm from each surface. The resistivity of all samples was measured. After cleaning the samples, chemical surface passivation was achieved by a QM solution [18]. The data for the determination of the Fe_i concentration was acquired from lifetime measurements with QSSPC (at $\Delta n = 2 \cdot 10^{15} \text{ cm}^{-3}$) and PLI [12-15] before and after dissociating the FeB complexes

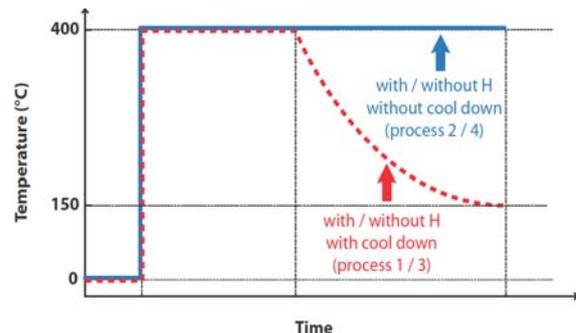


Figure 2: Temperature profiles of different processes.

by optical activation (above 1 sun, at least 3 minutes or until saturation was reached) as described above.

In preparation for processes in the MIRHP reactor, QM residues at the sample surfaces were removed by a methanol cascade and a chemical polishing associated with a surface removal of approximately 1 μm . Then all samples were exposed for four different lengths of time to the different processes (1–4) in the MIRHP reactor.

After the processes in the MIRHP reactor, lifetime measurements for the determination of $[\text{Fe}_i]$ 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 that is required for the calculation of the Fe_i concentration was determined by measuring the resistivity and thickness of all samples.

4 RESULTS

As can be seen in Fig. 3, all four previously described processes for different annealing times at 400°C reduce $[\text{Fe}_i]$ in p-doped mc-Si wafers significantly. A stronger decrease is observed for the hydrogenation processes. For the shorter annealing times (250 minutes and 330 minutes) the two processes involving H (process 1 and 2) show a reduction of $[\text{Fe}_i]$ that is a factor of 2 higher than for the processes without H (processes 3 and 4). For longer annealing times (510 minutes, 810 minutes) the difference is still existent but smaller. Longer annealing times during hydrogenation only lead to a small further decrease in total $[\text{Fe}_i]$. But the influence of temperature becomes more dominant as can be concluded from comparing the absolute decreases due to hydrogenation and temperature with the ones in samples that were treated with temperature alone. This is illustrated even more clearly in Fig. 4 that shows the relative average decrease of $[\text{Fe}_i]$ due to the four different annealing steps. Note that the absolute initial

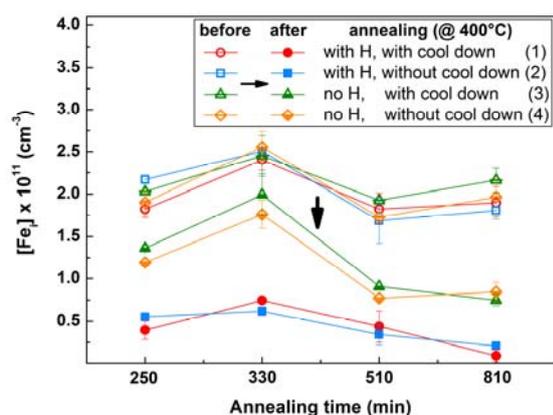


Figure 3: $[\text{Fe}_i]$ of p-doped mc-Si samples before and after annealing steps at 400°C for different lengths of time and different cool down processes (1–4, description in the text above). The different processes for each length of time were applied to three sets of four adjacent samples with similar grain structure. The error bars give the standard deviation from averaging the results of three samples out of the three sets. The solid lines are just guides to the eye.

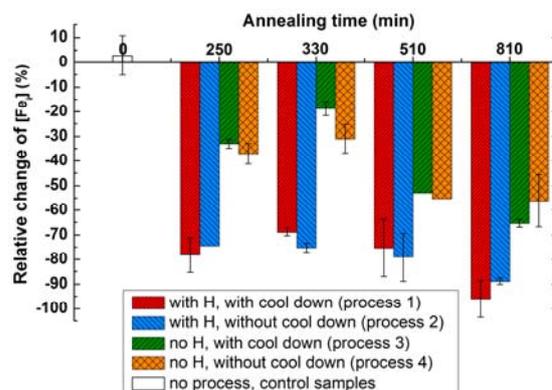


Figure 4: Relative change of $[\text{Fe}_i]$ calculated with the values depicted in Fig. 3. See Fig. 3 for further details.

concentrations of Fe_i vary for the different annealing times and for the different samples. Low-temperature induced internal gettering obeys an exponential decay law ([9], Fig. 6) and the absolute decrease in $[\text{Fe}_i]$ strongly depends on the starting $[\text{Fe}_i]$, which also influences the relative decrease.

The differences between the relative changes of $[\text{Fe}_i]$ after processes with H (red and blue bars in Fig. 4) and without H (green and orange bars in Fig. 4) are smaller for longer annealing times. Because of the variation of the absolute starting values (Fig. 3) this is not completely true for the absolute values. But if the values are sorted by the Fe_i concentrations $[\text{Fe}_i]_{\text{no H}}$ after the anneals without H, it can be stated, that the differences $[\text{Fe}_i]_{\text{no H}} - [\text{Fe}_i]_{\text{with H}}$ between the Fe_i concentrations after corresponding (3 and 1, 4 and 2) annealing steps without and with H are smaller for smaller $[\text{Fe}_i]_{\text{no H}}$. This is shown in Fig. 5. Assuming, that effects of temperature and H could be clearly separated, this plot gives the pure influence of H alone. This influence is higher for higher Fe_i concentrations after anneals only. This trend is confirmed by the results of experiments that will be published elsewhere. The stronger total decrease of $[\text{Fe}_i]$ has to be explained by an interaction between H and Fe_i particles. Possible interactions could be the formation of H- Fe_i complexes or, for example, an electrostatic interaction between the positively charged Fe_i atoms and the also positive atomic H. This ionic interaction could accelerate the gettering process of Fe_i and the reduction of $[\text{Fe}_i]$. 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 [23]. Future H effusion experiments will give information about which of the two suggested effects (direct passivation or increased mobility) causes the additional decrease in $[\text{Fe}_i]$ when H is in-diffused. If an effusion of H does not lead to a re-increase of $[\text{Fe}_i]$, the previous decrease of $[\text{Fe}_i]$ cannot be explained by the formation of H- Fe_i complexes and a classical passivation. First results indicate that the stronger decrease of $[\text{Fe}_i]$ when applying H and temperature together can be explained by an enhanced gettering and precipitation of Fe_i , but this finding has to be confirmed by further experiments.

Comparing the influence of the different temperature profiles (Fig. 2) and the different processes (1–4) on $[\text{Fe}_i]$, it can be stated that the expected effect of effusion of H during the removal of the samples from the reactor is not observed. Considering the statistical error bars and

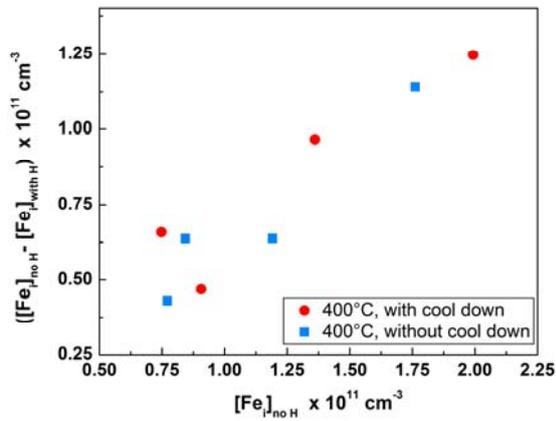


Figure 5: Influence of H alone on $[Fe_i]$ assuming that the influence of temperature and H can be clearly separated. $[Fe_i]_{no\ H}$ is the $[Fe_i]$ after an annealing step alone, while $[Fe_i]_{with\ H}$ indicates the $[Fe_i]$ on neighboring wafers after the same annealing step but with H. H was in-diffused at different temperatures. Data see Fig. 3.

the error in measurement, the differences in Fig. 3 and 4 between the processes 1 (with H, with cool down) and 2 (with H, without cool down) are negligible. This contradiction to the expected result can perhaps be explained by an overestimation of the diffusion length of H in mc-Si, by an underestimation of the activation energy of H trapped at Fe_i , or by a combination of both. If the diffusion length is shorter than assumed, H- Fe_i complexes could have been thermally dissociated but the H would not have effused out of the crystal completely and may have been trapped again by Fe_i . If the assumed activation energy is assumed too low, the temperature would not have been high enough to break off the complexes. A fourth possibility could be again that the higher decrease of $[Fe_i]$ for processes involving H is not caused by formation of H- Fe_i complexes but could be explained by an enhanced gettering of Fe_i under the influence of H. An effusion of H while removing the samples would not influence $[Fe_i]$ in this case.

In order 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 $SiN_x:H$ layers deposited by PECVD, the results can be plotted in a different way. Fig. 6 shows part of the results already presented in Fig. 3. In this plot, only the data of samples treated with processes 2 and 4, that 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. [9] (black crosses), showing Fe_i concentrations of mc-Si wafers that were coated with PECVD- $SiN_x:H$ layers on both sides 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 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. 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 did not reduce the $[Fe_i]$ in the same way (as described previously). The influence of H on the decrease

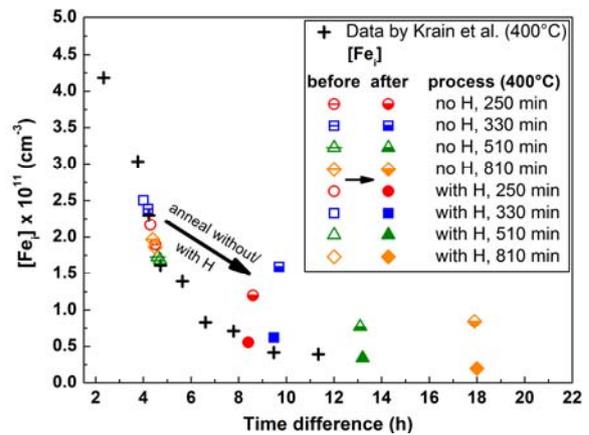


Figure 6: Decrease of $[Fe_i]$ of mc-Si after annealing steps at 400°C for different lengths of time. Black crosses show data from $SiN_x:H$ coated wafers [9]. Initial $[Fe_i]$ (open symbols) of data from Fig. 3 (processes 2 and 4) were fitted into data from Krain et al. The time difference between corresponding symbols equals annealing time.

of $[Fe_i]$ in mc-Si at 400°C is not affected by the different in-diffusion methods of hydrogen.

Fig. 7 shows mappings of $[Fe_i]$ of two neighboring mc-Si samples before and after annealing steps with and without H at 400°C (processes 2 and 4) for 330 minutes. The initial local $[Fe_i]$ before annealing is very similar for the two 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.

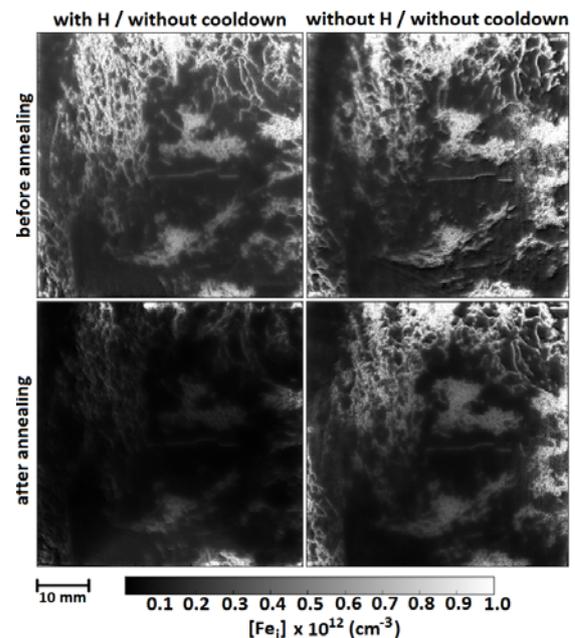


Figure 7: $[Fe_i]$ mappings of two neighboring mc-Si samples before and after annealing steps with and without H at 400°C (processes 2 and 4) for 330 minutes. Mappings were produced from two lifetime calibrated PLLs.

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.

5 SUMMARY

This investigation shows that in-diffusion of atomic H into a mc-Si p-type wafer while applying a certain temperature definitely has an additional influence on $[Fe_i]$. The decrease of $[Fe_i]$ is stronger when annealing steps are combined with H in-diffusion. The absolute additional decrease of $[Fe_i]$ is proportional to $[Fe_i]$ after a temperature step alone.

Comparisons to an experiment presented by Krain et al. [9] 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).

First results of H effusion experiments currently carried out indicate that the increased reduction of $[Fe_i]$ due to H might be explained by catalysis of Fe_i diffusion that accelerates the formation of iron precipitates. This could also explain why no differences in $[Fe_i]$ could be observed after hydrogenating neighboring samples in the MIRHP reactor with and without cooling down the samples before removing them from the H atmosphere.

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.

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