Studying precipitation and dissolution of iron in multicrystalline silicon wafers during annealing

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ABSTRACT
In this paper we study the changes in iron concentrations and distributions in multicrystalline silicon (mc-Si) wafers after annealing in the temperature range of 600-900°C. The dissolved Fe distributions across mc-Si wafers are obtained by photoluminescence imaging taken before and after dissociation of FeB pairs. The results show that the precipitation of dissolved Fe, both near the grain boundaries and at the in-grain precipitation sites, requires a high level of supersaturation. Dissolution of precipitated Fe in the close vicinity of the grain boundaries is observed for wafers annealed at high temperatures where the solubility limit exceeds the concentration of dissolved Fe already present in the mc-Si wafer.

1. INTRODUCTION
Iron is one of the most common and harmful metallic defects in multicrystalline silicon (mc-Si) for solar cells. The majority of Fe in mc-Si is in the form of precipitates clustered mostly at the structural defects of mc-Si [1]. The remaining dissolved Fe atoms, in the form of interstitials, are more detrimental for solar cell efficiency due to the more distributed nature. During cell processing, the concentration and the distribution of Fe change as a result of dissolution or precipitation at higher temperatures. In this study we experimentally investigate the dissolution and precipitation of Fe in mc-Si in the temperature range of 600-900°C for a mc-Si wafer with an as-cut interstitial Fe concentration, [Fe_i], of around $9 \times 10^{12}$ cm$^{-3}$. The distribution of the dissolved Fe concentrations is obtained via photoluminescence imaging [2],[3].

2. EXPERIMENTS
The multicrystalline silicon wafer used in this study was from a commercial boron-doped directionally-solidified mc-Si ingot, nominally 1.4Ω cm in resistivity, and 330µm thick. The wafer is 12.5×12.5 cm$^2$ in size, and was diced into 16 smaller pieces for different processing conditions. The wafer is from near the bottom of the ingot, with an average interstitial Fe concentration of $9 \times 10^{12} \pm 10^{12}$ cm$^{-3}$.

The wafers were chemically polished in HF:HNO$_3$ solution. One of the wafers was left in the as-cut state, while some of the others underwent different temperature annealing, as outlined in Table 1. For the wafer which was loaded and unloaded at a lower than annealing temperature, the ramp rate was 10°C/minute. In order to avoid bulk contamination from the furnace during high temperature processes, the wafers were annealed in the oxygen ambient, as a thin oxidised layer can act as an effective diffusion barrier. The oxide layer was later etched off in diluted HF solution. To allow sensitive bulk lifetime measurements, the wafers were passivated with silicon nitride by
plasma-enhanced chemical vapour deposition (PECVD).

<table>
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<th>Table 1. Annealing conditions</th>
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<td>Annealing temperature °C</td>
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The images of interstitial Fe concentrations $[\text{Fe}_i]$ were obtained by photoluminescence images $[^2]$ taken before and after the dissociation of FeB pairs in silicon via strong illumination $[^3]$. In this work we used an LIS-R1 PL imager from BTImaging with an illumination laser of a wavelength of 808 nm. A zoom lens with a resulting pixel size of $\sim23\,\mu m$ was used. A point spread function $[^5]$ was applied to deconvolute image smearing caused by lateral photon scattering within the Si-CCD camera. For wafers with larger carrier diffusion length and hence stronger PL signals, a short-pass filter with a cut-off at 1050nm was also used in order to reduce the effect of lateral photon scattering within the wafers $[^6]$. Line scans of $[\text{Fe}_i]$ across straight grain boundaries (GBs) were averaged along the lengths of the GBs to reduce experimental noise.

3. RESULTS AND DISCUSSIONS

Figure 1 to Figure 3 show the $\text{Fe}_i$ images of wafers in the as-cut and annealed states. Comparison of the linescans across GBs is shown in Figure 4, with the normalised scale shown in Figure 5. In this study the linescans are taken from GBs which appear recombination active and with denuded zones. Linescans of several such GBs of the same wafer are shown to be within a reasonable uncertainty range. Therefore the effect of GB type on the behaviour of Fe is not investigated in this paper.

Compared to the as-cut state, the overall $[\text{Fe}_i]$ of the wafer annealed at 600°C for 2 hours and 40 minutes (Figure 2) is reduced by more than 30% (shown in Figure 4), and the width of the GB denuded zone is evidently widened (Figure 5). This indicates precipitation of the dissolved Fe in the close vicinity of the GBs during annealing, as the
reduction in [Fe\textsubscript{i}] close to the GBs drives the diffusion of Fe\textsubscript{i} towards the GBs, thus creating a wider denuded zone. This is as expected, since the solubility of Fe at 600\degree C (see Table 1) is more than 2 orders of magnitude lower than the [Fe\textsubscript{i}] present in the wafer.

The concentration of Fe\textsubscript{i} within the grains far from the denuded zones, as shown in Figure 2 and Figure 4, is also reduced and the profile is quite flat. The diffusion length of Fe atoms during the annealing, calculated from Fe diffusivity\textsuperscript{[7]}, is 360\textmu m, much smaller than the mm-sized grains. Therefore the reduction in [Fe\textsubscript{i}] within the grains cannot be explained by Fe precipitation in the vicinity of the GBs. One possible explanation is the presence of uniform in-grain precipitation sites within the mc-Si.

The wafer annealed at 800\degree C, however, demonstrates negligible change in the overall [Fe\textsubscript{i}] or its distribution within the uncertainty range (Figure 4 and Figure 5). The diffusion length of Fe atoms during the 800\degree C annealing is in fact greater than that of the 600\degree C annealing. This indicates that the precipitation of Fe\textsubscript{i} near GBs was hindered during the 800\degree C anneal. The Fe solubility at 800\degree C (Table 1) is about half of the [Fe\textsubscript{i}] already present in the wafer, as opposed to the 2 orders of magnitude difference at 600\degree C. The comparison therefore clearly shows that the precipitation of Fe\textsubscript{i}, both at the lattice distorted regions near the GBs and at the in-grain precipitation sites, requires a high level of supersaturation. This is consistent with previous studies\textsuperscript{[8],[9]}.

At 900\degree C, the solubility of Fe (Table 1) is higher than the [Fe\textsubscript{i}] in the as-cut state, therefore dissolution of precipitated Fe
near GBs is expected. An increase in [Fe\textsubscript{i}] in the vicinity of the GB can be observed in Figure 3 and Figure 4. However, we note that all of the Fe\textsubscript{i} images presented in this and previous works consistently show a slight apparent increase in [Fe\textsubscript{i}] close by the GBs. This has been shown in ref\textsuperscript{[6]} to be a measurement artefact caused by the photon scattering within the wafer and the Si-CCD camera, and the electrical carrier smearing effects. Hence it is unclear whether or not the observed increase is solely due to the measurement artefact for wafers with uniform [Fe\textsubscript{i}]. To clarify this point, Figure 6 shows the simulation of Fe\textsubscript{i} diffusion during the 900°C annealing, assuming a constant in-grain [Fe\textsubscript{i}], as little difference is observed in the experimental data (Figure 4). The simulation reveals that the diffusion mechanism alone cannot homogenise the distribution of [Fe\textsubscript{i}] across the GBs. Therefore dissolution of precipitated Fe in the vicinity of GBs does indeed seem to occur at 900°C.

4. CONCLUSION

In this paper we have examined the impact of temperature on the precipitation and dissolution of Fe in multicrystalline silicon wafers. The results show that the difference between the solubility limit and the [Fe\textsubscript{i}] present in the wafer determines the behaviour of Fe. The precipitation of dissolved Fe, both near the grain boundaries and at the in-grain precipitation sites, requires a high level of supersaturation. When the solubility limit exceeds the [Fe\textsubscript{i}] in a wafer, dissolution of precipitated Fe is observed in the close vicinity of the grain boundaries.

REFERENCES