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High performance multicrystalline silicon: Grain structure and iron precipitation

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A study of the spatial occurrence of iron precipitation in a high performance multicrystalline silicon (HPMC-Si) sample is presented. The separated effects of grain-boundaries, sparse intra-granular dislocations, and dislocation clusters are investigated by combining the Fe_i imaging method with glow discharge mass spectroscopy, electron backscatter diffraction, and two iron precipitation models. While the area-averaged precipitation at grain boundaries is relatively minor, almost the whole iron precipitation occurs within the grains, despite the very low intra-granular dislocation density. The fraction of non-precipitated iron in the studied HPMC-Si material was found to be one to two orders of magnitude higher than that reported previously for standard materials.

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I. INTRODUCTION

Multicrystalline silicon is, together with monocrystalline silicon, the most widely used material in the photovoltaic industry. It contains a high density of extended defects, i.e., grain boundaries and dislocations, and a wide range of impurities, affecting the output solar cell performance. Iron has been identified as one of the most detrimental impurities in multicrystalline silicon^{1,2} and is found in relatively high concentrations in ingots, originating from the crucible, its coating, and silicon feedstock.^{3–7} Iron is present in silicon in the interstitial state or in the form of metal silicide nanoprecipitates, mainly identified as FeSi₂.⁸ Previous studies have shown that a large majority of iron present in as-grown multicrystalline materials is precipitated.^{2,9,10} Iron precipitation has a positive impact on the as-grown wafer quality, as the recombination activity of a precipitate per iron atom is generally considered being lower than the recombination activity of an isolated interstitial iron atom.² Iron precipitation at extended defects is, however, a strong limitation to the phosphorous gettering efficacy,¹¹ as only the mobile dissolved iron atoms have the ability to segregate towards the emitter.

Due to its relatively high solid diffusivity, iron precipitates mostly at extended defects.⁸ Those defects present favorable precipitation sites and act as internal gettering sites during the ingot cooling. Recent improvements in the silicon growth technology have led to the solidification of multicrystalline silicon ingots of higher quality, i.e., with lower densities of dislocation clusters.^{12,13} This newly developed material is commonly referred to as high performance multicrystalline silicon (HPMC-Si) and presents a smaller grain size and a higher proportion of random angle grain boundaries compared

to conventional multicrystalline silicon.¹⁴ The precipitation behavior of iron is affected by the structure evolution of multicrystalline silicon, and it is of major interest to evaluate and predict the influence of each type of extended defects.

This study presents an examination of the spatial occurrence of iron precipitation during the cooling of an HPMC-Si ingot and aims at investigating the separated effects of grain-boundaries, sparse intra-granular dislocations, and dislocation clusters.

II. EXPERIMENTAL DETAILS

The material investigated in this study has been grown in a pilot-scale Crystalox DS 250 furnace. The ingot was solidified in a fused silica crucible coated with silicon nitride. Polysilicon chips were used as feedstock, and the ingot was multi-seeded by melting only partially the feedstock. A more random structure—commonly referred to as high-performance multicrystalline silicon (HPMC-Si)—is obtained. A boron-rich master-alloy was added to the silicon feedstock in order to reach a resistivity of 1 Ω·cm in the middle of the ingot. The temperature profile resembles those typically used in industrial settings. The feedstock partial-melting was performed at a susceptor plateau-temperature of 1808 K, maintained for 170 min. The cooling rate, CR, used later for the calculations, was -2.73×10^{-2} K/s. The final ingot was cut into nine 50 × 50 × 105 mm blocks. The central one was wafered, and the sample investigated in this study was taken at ~80% ingot height. Due to its high position in the ingot, the studied material contains more iron than typical wafers sampled in the middle of the ingot. This material selection is mainly justified by the detection limit of the chemical analysis method used for this study (glow discharge mass spectroscopy), and the influence of the total iron concentration is discussed at the end of Sec. IV B.

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The selected wafers were first prepared using the standard damage-etching and cleaning process. These steps occur at low temperatures. The grain structure was characterized by electron backscatter diffraction (EBSD), and a sister-wafer was used to evaluate the intra-granular dislocation densities. It was polished, Soporietched,¹⁵ and examined with light microscopy. The evaluation of the intra-granular dislocation density across the wafer was performed by averaging dislocation densities measured within 20 different grains, where the examined regions were located at least 0.1 cm away from the grain boundaries.

The wafers were passivated prior to the interstitial iron concentration measurements, by depositing an a-Si:H layer on both sides. This process lasted approximately 10 min, and the material was heated up to a maximum temperature of 230 °C. The samples were then annealed in a belt furnace at 450 °C within 1 min. The influence of these two steps on the distribution of iron can be neglected with regard to the temperature history of the solidification process. Iron in its interstitial form, Fe_i, was quantitatively imaged on wafers by using an indirect technique based on carrier lifetime measurements,^{16,17} performed by PL-imaging.^{18,19} The sample was first placed on a hot plate at 80 °C for 15 min to form FeB pairs. The charge carrier lifetime in the FeB state was then measured using a 790 nm diode laser at the low injection level (0.1 suns). The sample was subsequently illuminated at maximum intensity for 4 min to split the FeB pairs, and the Fe_i dominated lifetime image was acquired at the low injection level. Fe_i was then calculated according to the procedure suggested by Macdonald.¹⁶

The total iron content C₀ in the wafer was measured on a sister wafer by glow discharge mass spectroscopy (GDMS). The GDMS instrument used for this study has a detection limit for iron in silicon of 0.5 ppba—i.e., 2.5 × 10¹³ cm⁻³.²⁰

III. IRON PRECIPITATION MODELS

In order to discuss the relative impact of the different defects on iron precipitation, two types of precipitation models have been used

- An area-averaged model.
- A 1D model accounting for both intra-granular and grain boundary precipitation.

These models are time dependent and aim at simulating iron precipitation during the ingot cooling.

The set of assumptions and equations used for the models are based on Ham's law,²¹ where all the precipitates are modeled as spheres, and the density of precipitation sites does not vary over time. It is initially assumed that precipitation starts right when the solubility limit is overcome, but as presented later, an adjustment has been made to account for the required supersaturation. The input parameters of the models are the densities of precipitation sites. A distinction is made between the intra-granular density of precipitation sites N_p^{IG} (cm⁻³), the surficial density of precipitation sites at a grain boundary N_p^{GB} (cm⁻²), and the area-averaged density of precipitation sites \overline{N}_p (cm⁻³).

A. Area-averaged precipitation

The area-averaged evolution of the dissolved iron concentration across the wafer \overline{C}_i is calculated from Eq. (1)

$$\frac{\partial \overline{C}_i}{\partial t} = -\frac{\partial \overline{C}_p}{\partial t} = 4\pi r_p D \overline{N}_p (C_{\text{sol}} - \overline{C}_i), \quad (1)$$

where \overline{C}_p is the area-averaged concentration of precipitated iron, r_p is the average precipitate radius, \overline{N}_p is the area-averaged density of precipitation sites, D is the diffusivity of iron in solid silicon, and C_{sol} is the solubility of iron in solid silicon. The average precipitate radius varies over time and is

$$r_p = \left(\frac{3}{4\pi \overline{N}_p C_{\text{Fe/FeSi}_2}} \overline{C}_p \right)^{1/3}, \quad (2)$$

with C_{Fe/FeSi₂} being the iron concentration in a FeSi₂ precipitate.

B. Grain boundary and intra-granular precipitation

The 1D model is solved numerically and the transport of iron is calculated using the 1D diffusion equation, adjusted for the case of diffusion-limited precipitation

$$\frac{\partial C_i}{\partial t} = D \frac{\partial^2 C_i}{\partial x^2} - \frac{\partial C_p}{\partial t}, \quad (3)$$

where C_i is the concentration of dissolved iron and C_p is the concentration of precipitated iron. Intra-granular precipitation of iron is assumed to be homogenous and is accounted for by the following equation:

$$\frac{\partial C_p}{\partial t} = 4\pi r_p^{\text{IG}} D N_p^{\text{IG}} (C_i - C_{\text{sol}}), \quad (4)$$

where r_p^{IG} is the average precipitate radius in the intra-granular region and is expressed here

$$r_p^{\text{IG}} = \left(\frac{3}{4\pi N_p^{\text{IG}} C_{\text{Fe/FeSi}_2}} C_p \right)^{1/3}. \quad (5)$$

Two boundary conditions are imposed, on each side of the domain representing the grain

- On one side, a symmetry condition is set—i.e., no flux

$$\frac{\partial C_i}{\partial x} = 0. \quad (6)$$

- Iron precipitation at the grain boundary is accounted for on the other side of the grain, by introducing the following flux J (cm⁻² s⁻¹)

$$J = \frac{1}{2} \frac{\partial C_S^{\text{GB}}}{\partial t}, \quad (7)$$

where C_S^{GB} is the iron surficial concentration at the grain boundary interface. The “1/2” factor comes from the fact that only one side of the grain boundary is considered in the model. The number of iron atoms flowing to a single precipitate per unit of time Φ (s⁻¹) is introduced. In the case where the distance between the precipitate is much larger than the precipitate radius, Φ is expressed as follows:²²

$$\Phi = 4\pi r_p^{GB} D (C_i^* - C_{sol}), \quad (8)$$

where C_i^* is, in the present case, the dissolved iron concentration at the grain boundary vicinity, and r_p^{GB} is the average precipitate radius at the grain boundary. The time evolution of the surficial concentration of iron at the grain boundary interface is then

$$\frac{\partial C_S^{GB}}{\partial t} = N_p^{GB} \Phi = 4\pi r_p^{GB} N_p^{GB} D (C_i^* - C_{sol}). \quad (9)$$

The average precipitate radius at the boundary is deduced from the following equation:

$$C_S^{GB} = N_p^{GB} C_{Fe/FeSi_2} \frac{4\pi}{3} (r_p^{GB})^3. \quad (10)$$

The set of parameters used for the simulations is listed in Table I.

IV. RESULTS AND DISCUSSION

A. Precipitation at grain boundaries

The total iron concentration in the wafer Fe_{tot} was measured by GDMS to be $C_0 = 3.9 \times 10^{13} \text{ cm}^{-3}$ which is an order of magnitude above the detection limit of the instrument.²⁰ Figure 1(a) shows the map of dissolved iron of the studied wafer, as calculated using the FeB pair dissociation method. Two scales are added, one corresponding to the interstitial iron concentration Fe_i and one to the ratio Fe_i/Fe_{tot} . This ratio corresponds to the part of dissolved iron over the total iron concentration and is referred later as “dissolved iron ratio.” The average ratio value over the wafer is 0.10 and is shown in red on the Fe_i/Fe_{tot} scale, in Fig. 1(a). A sister wafer was selected for characterizing the grain structure using EBSD and is shown in Fig. 1(b).

The interstitial iron image shown in Fig. 1(a) displays lines of dark contrast, corresponding to the active grain boundaries, i.e., the grain boundaries having the ability to precipitate iron. Thus, when performing a linescan on the interstitial iron map across an active grain boundary, a clear decrease in the interstitial iron concentration is observed close to the boundary.^{24,25} These regions of lower concentrations are commonly referred to as “depleted regions” or “denuded zones” and indicate that iron has precipitated at the grain boundary during ingot cooling. An example of the concentration profile, corresponding to the red box in Fig. 1(a), is given

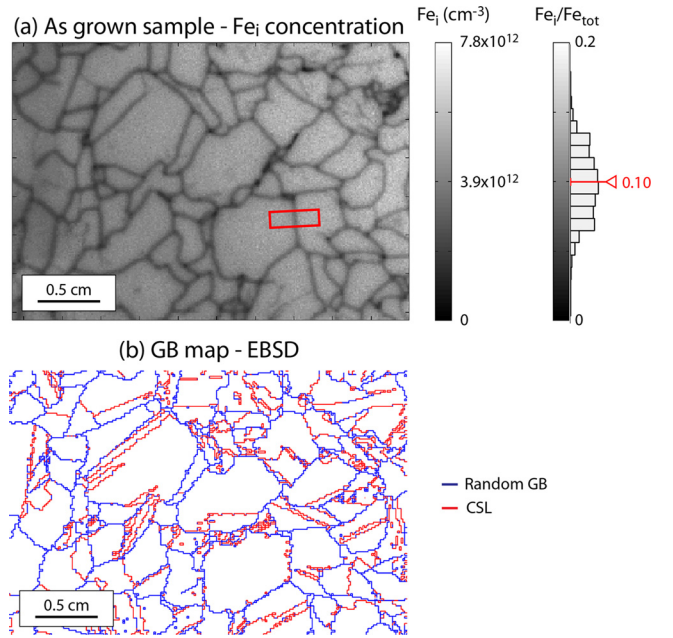


FIG. 1. (a) Fe_i map obtained by PL-imaging using the FeB pair dissociation method. Two scales are added, one corresponding to the Fe_i concentration and the other to the part of dissolved Fe, relatively to the total iron concentration Fe_{tot} , as measured by GDMS. The distribution and the average Fe_i/Fe_{tot} ratio are added on the second scale. The red box corresponds to the concentration profile plotted in Fig. 4. (b) EBSD grain boundary map of the same wafer. A distinction is made between random grain boundaries (in blue) and coincidence site lattice (CSL) grain boundaries (in red).

in Fig. 4. The interstitial iron concentrations were averaged over the vertical distance of the box.

When comparing Figs. 1(a) and 1(b), a clear correlation can be drawn between active grain boundaries and random angle grain boundaries. This comparison between grain boundary character and activity resembles the one previously made for steel, where active grain boundaries precipitate chromium, leaving denuded zones behind and causing intergranular corrosion. The identification of active grain boundaries in such materials has been the subject of many studies, and different criteria have been proposed to separate random grain boundaries from coincidence site lattice (CSL) grain boundaries.^{26–28} These criteria define allowable angular deviations $\Delta\theta$ from the perfect coincidence site lattice angle, as a function of the inverse density of coincident sites Σ . The more restrictive Palumbo’s criterion was identified in steel to be the one separating best active grain boundaries—i.e.,

TABLE I. Set of parameters used for the calculations. The iron supersaturation ratio k and the intra-granular density of precipitation sites N_p^{IG} values used for the evaluation of the average density of precipitation sites at grain boundary N_p^{GB} are added.

Parameter	Symbol	Value/Expression	References
Fe diffusivity in Si(s)	D	$1.0 \times 10^{-3} \exp(-0.67 \text{ eV/kT}) \text{ cm}^2 \text{ s}^{-1}$	23
Fe solubility in Si(s)	C_{sol}	$1.8 \times 10^{26} \exp(-2.94 \text{ eV/kT}) \text{ cm}^{-3}$	23
Fe atomic radius	r_{at}	$4.4 \times 10^{-8} \text{ cm}$	22
Fe concentration in $FeSi_2$	$C_{Fe/FeSi_2}$	$2.5 \times 10^{22} \text{ cm}^{-3}$	22
Total iron concentration	C_0	$3.9 \times 10^{13} \text{ cm}^{-3}$	GDMS
Ingot cooling rate	CR	$-2.73 \times 10^{-2} \text{ K/s}$	
Iron supersaturation ratio	k	6300	Section IV A
Intra-granular density of precipitation site	N_p^{IG}	$3.7 \times 10^8 \text{ cm}^{-3}$	Section IV A

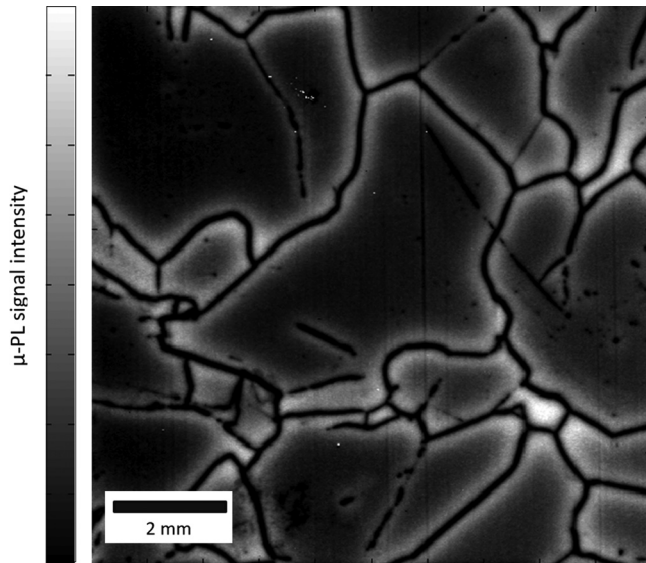


FIG. 2. Micro-Photoluminescence (μ PL) image of the sample. Depleted regions are visible at the active grain boundaries.

random grain boundaries—from inactive ones—i.e., CSL grain boundaries.²⁸ The allowable angular deviation defined by Palumbo *et al.* is

$$\Delta\theta = \frac{15}{(\Sigma)^{5/6}}. \quad (11)$$

Similar conclusions are drawn in this work for the precipitation of iron in multicrystalline silicon. The Fe_i map shown in Figure 1(a) was compared with its associated grain boundary map, as given by EBSD, using in turn Brandon's, Déchamps', and Palumbo's criteria. As for chromium in steel, the best separation was obtained for the Palumbo's criterion, where 90% of the random grain boundaries and 10% of CSL grain boundaries were identified as being active.

Concentration profiles were extracted from Fig. 1(a) across 32 active grain boundaries. Interstitial iron concentrations evaluated close to grain boundaries are likely to be influenced by lateral carrier diffusion occurring during PL imaging. This problem is discussed by Liu *et al.* in Ref. 24. In order to obtain a better evaluation of the concentration at the grain boundary interface, the profiles were fitted with an error-function. An example is given in Fig. 4. The average minority charge carrier lifetime over the studied wafer is 0.44 μs , corresponding to an approximate diffusion length of 40 μm . Lateral carrier diffusion impacts the calculated Fe_i concentrations close to grain boundaries over a distance of the same order of magnitude: Fig. 4 shows that the deviation of the Fe_i data from the fit curve is the highest in the 100 μm the closest to the grain boundary. In the current study, only the interstitial iron concentrations evaluated further from the grain boundary are trusted.

Lateral photon scattering occurring during PL measurements can also affect the Fe_i image calculated from the PL images taken before and after FeB pairs splitting. In order to assess the impact of this phenomenon on the Fe_i concentration profiles across the active grain boundaries, the studied sample was characterized using Micro-Photoluminescence

TABLE II. Average widths of the denuded zones shown in the μ PL and the Fe_i images.

	μ PL image	Fe_i image
Average width (μm)	408 (± 80)	404 (± 44)

(μ PL). This method is not influenced by lateral photon scattering, as the PL signal is measured “pixel-by-pixel.”²⁹ The measured PL intensity map, which directly correlates with the minority charge carrier lifetime, is shown in Fig. 2. Bright areas with higher contrast can be observed close to the grain boundaries. These correspond to the depleted regions of lower Fe_i concentrations described previously and visible in Fig. 1(a).³⁰ The widths of the denuded zones are evaluated in the μ PL image and the Fe_i image by fitting line-scans across active boundaries with an exponential decay function. The results are summarized in Table II.

The average widths of the denuded zones in the Fe_i image and in the μ PL image are very similar. The effect of lateral photon scattering on the Fe_i concentration profiles across active grain boundaries is therefore negligible, and the extrapolation given by the error function is believed to provide a good evaluation of the Fe_i concentration at the boundary interface.

From the error-function fit, a “depletion-ratio” R_D was evaluated for each boundary, where

$$R_D = \frac{C_{\text{int}}}{C_{\infty}} \quad (12)$$

with C_{int} being the Fe_i concentration at the vicinity of the grain boundary and C_{∞} the Fe_i concentration far from the grain boundary—i.e., bulk concentration. The results are summarized in Fig. 3(b). A relatively homogeneous distribution of the depletion-ratio values is observed around an average of 0.63. This preliminary investigation suggests that, when a grain boundary precipitates iron, it does it with a remarkable homogeneous intensity.

Preliminary calculations have been performed using the *no-supersaturation assumption*—i.e., iron precipitation starts exactly when the temperature is low enough for the solubility limit to be overcome. An example is given in Fig. 4, where both data and calculated profiles are added for a selected grain boundary (see red box in Fig. 1(a)). A good estimation of the depletion ratio—i.e., the depth of the depleted region—is obtained for a surficial density of precipitation site $N_p^{\text{GB}} = 4.1 \times 10^5 \text{ cm}^{-2}$, but a deviation is observed between the data and the model, as the calculated profile exhibits a wider depleted region. This decay is the result of the *no-supersaturation assumption*, implying that precipitation starts too early during the cooling process, leaving more time for iron to precipitate and diffuse towards the boundary. It has been, however, shown in several studies that the onset of iron precipitation in silicon requires high supersaturation.^{31,32} In order to account for supersaturation, the “triggering temperature” was adjusted, so that the calculated depleted region width would fit to the measured one. The adjusted triggering temperature ($T_t = 900 \text{ K}$) introduces a decay of 270 K from the supersaturation temperature

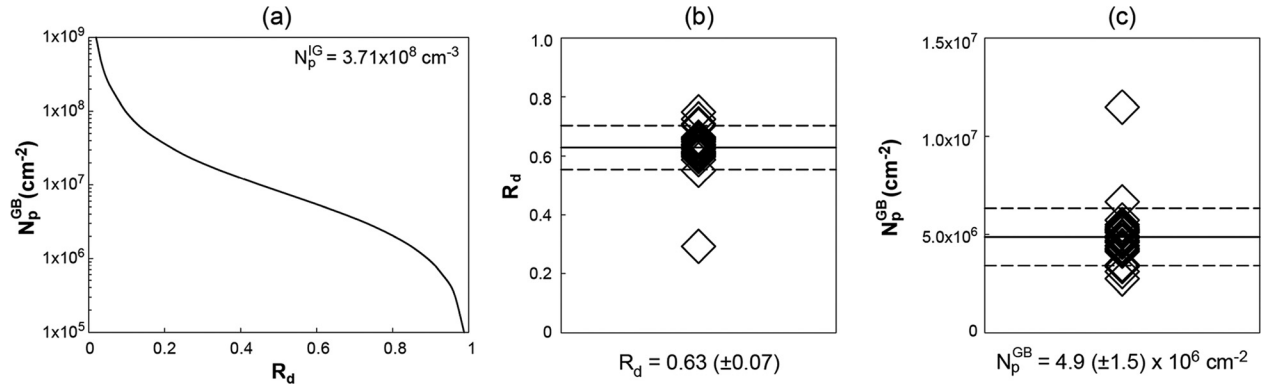


FIG. 3. (a) Surficial density of precipitation sites at the boundary N_p^{GB} as a function of the final depletion-ratio R_d , as calculated by the 1D model, for the parameters listed in Table I. (b) Depletion ratios R_d , as evaluated by extracting 32 concentration profiles across grain boundaries in Fig. 1(a). An average value and the standard deviation are indicated. (c) Evaluated densities of precipitation sites at active grain boundaries. An average value and the standard deviation are indicated.

($T_s = 1170$ K), corresponding to a supersaturation ratio of $k \sim 6300$, where

$$k = \frac{C_0}{C_{sol}(T_1)}. \quad (13)$$

This matter has been previously discussed by Liu *et al.*,²⁴ where the authors estimated for their material an iron supersaturation ratio of 55. The much higher ratio evaluated in the present study is consistent with the much lower average dislocation densities present in HPMC-Si, relatively to standard multicrystalline silicon, resulting in lower densities of available precipitation sites. Higher supersaturation levels are therefore expected in HPMC-Si material to trigger iron precipitation.

By using the 1D precipitation model presented before, an average surficial density of precipitation sites at active grain boundaries N_p^{GB} was evaluated. The intra-granular Fe_i concentration of each grain is directly measured on the iron interstitial map. An average intra-granular concentration of $5.5 (\pm 0.7) \times 10^{12} \text{ cm}^{-3}$ is evaluated. From this value and by using Eq. (8), an intra-granular density of precipitation sites

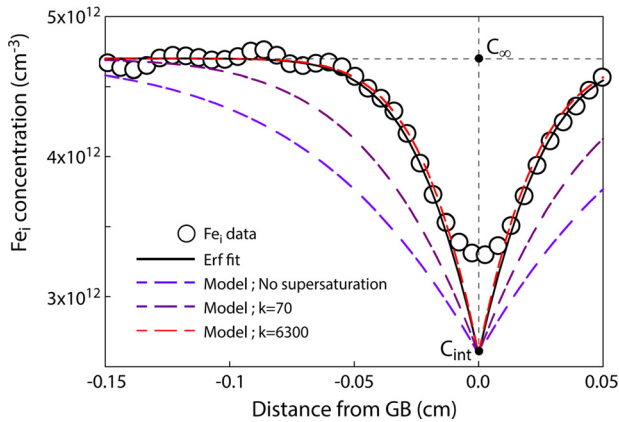


FIG. 4. Example of the Fe_i profile, as measured across a grain boundary in Fig. 1(a). The data are fitted with an error function (Erf fit) in order to evaluate the interstitial iron concentration at the grain boundary interface (C_{int}). The 1D model simulates the concentration profile, using the no-supersaturation assumption. A good estimation of the depletion ratio is obtained by adjusting the surficial density of precipitation site N_p^{GB} , but a deviation is observed between the data and the model, as the calculated profile exhibits a wider depleted region. A good fit is obtained between the model and the Fe_i data when introducing a supersaturation ratio $k = 6300$.

N_p^{IG} of approximately $3.7 \times 10^8 \text{ cm}^{-3}$ is determined. This value is used for the 1D calculations.

An example of dissolved iron concentration profile time-evolution during the ingot cooling is displayed in Fig. 5. The initial concentration level corresponds to the total iron concentration, as measured by GDMS. As the temperature decreases, iron precipitates, the dissolved intra-granular concentration decreases, and a depleted region forms close to the boundary interface. Diffusivity strongly limits iron precipitation at low temperatures, and almost no iron precipitates are found below 650 K. By adjusting the surficial density of precipitation sites at the boundary, a good fit is obtained between the final calculated concentration profile and the linescan performed on the iron interstitial image.

The calculations are repeated for a wide range of surficial density of precipitation site values. A power curve is

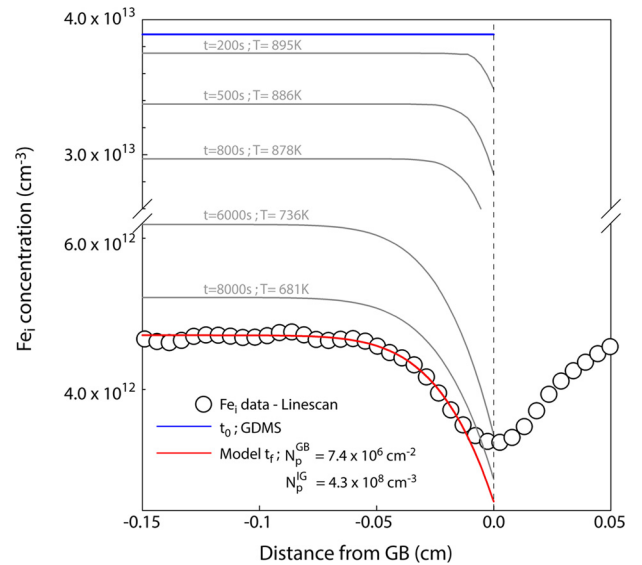


FIG. 5. Example of the evolution of the dissolved iron concentration profile close to an active grain boundary, during the ingot cooling. The initial concentration corresponds to the total iron concentration, as measured by GDMS. Iron precipitation is triggered for a supersaturation ratio $k = 6300$, and intra-granular precipitation occurs as the bulk level of dissolved iron decreases. Grain boundary precipitation involves the development of a depleted region, close to the boundary interface. Fe_i data are added, corresponding to the red box in Fig. 1(a). For a surficial density of precipitation site $N_p^{GB} = 7.4 \times 10^6 \text{ cm}^{-2}$, these data are well fitted by the model.

obtained, giving the final depletion-ratio R_d as a function of the surficial density of precipitation sites at the boundary N_p^{GB} [see Fig. 3(a)]. It is important to note here that these calculations correspond to a specific set of parameters listed in Table I. From this curve and the previously measured depletion-ratios [Fig. 3(b)], a set of surficial densities of precipitation site is evaluated [see Fig. 3(c)]. These values are homogeneously stacked around an average density of $4.9 (\pm 1.5) \times 10^6 \text{ cm}^{-2}$. The density of iron silicide precipitates at a random grain boundary was evaluated experimentally by Fenning *et al.* using X-ray fluorescence microscopy.^{33,34} The material studied by these authors contained a total iron concentration of $\sim 1 \times 10^{14} \text{ cm}^{-3}$. A precipitate density of $1.5 \times 10^7 \text{ cm}^{-2}$ was measured at the boundary in the as-cut material, where only precipitates with more than 3×10^4 iron atoms were considered. This value is consistent with our evaluation.

It is assumed in the 1D model that iron precipitates homogeneously in the intra-granular region. The density of dislocations can however be expected to vary from one grain to another and within a single grain. A sensitivity study has therefore been performed to evaluate the dependence of the evaluated average density of precipitation sites at grain boundaries, N_p^{GB} , to the input intra-granular density of precipitation sites, N_p^{IG} . Figure 6(a) shows the surficial density of precipitation sites at the boundary, N_p^{GB} , plotted as a function of the calculated depletion-ratio R_d , for three different intra-granular densities of precipitation sites N_p^{IG} . The standard case presented in Fig. 3(a)—i.e., $N_p^{IG} = 3.7 \times 10^8 \text{ cm}^{-3}$, is shown in Fig. 6(a), and two other cases are added, $N_p^{IG} = 3.7 \times 10^7 \text{ cm}^{-3}$ and $N_p^{IG} = 3.7 \times 10^9 \text{ cm}^{-3}$. The average density of precipitation site at grain boundaries, N_p^{GB} , is evaluated for $R_d = 0.63$ as a function of the intra-granular density of precipitation sites, N_p^{IG} . The results are plotted in Fig. 6(b).

An estimated N_p^{GB} approximately two times higher than the one evaluated for $N_p^{IG} = 3.7 \times 10^8 \text{ cm}^{-3}$ is obtained when considering an average N_p^{IG} an order of magnitude

higher. Similarly, considering an average intra-granular density of precipitation site N_p^{IG} an order of magnitude lower results in an estimated N_p^{GB} only 1.4 times lower. A linear relationship between dislocation density and intra-granular density of precipitation site N_p^{IG} is commonly assumed.^{33,34} It is therefore believed that local variations of dislocation densities within a grain can safely be treated in the model by using the *homogeneous intra-granular precipitation assumption*, without affecting greatly the evaluation of N_p^{GB} .

A homogeneous intra-granular dislocation density of $4.8 (\pm 1.5) \times 10^3 \text{ cm}^{-2}$ was evaluated across the wafer. A variation of intra-granular density of precipitation sites of $\pm 30\%$ is consequently expected from one grain to another across the wafer. This variation corresponds to an evaluated N_p^{GB} ranging from $4.4 \times 10^6 \text{ cm}^{-2}$ to $5.1 \times 10^6 \text{ cm}^{-2}$ [Fig. 6(b)]. These values are very close to the N_p^{GB} evaluated for $N_p^{IG} = 3.7 \times 10^8 \text{ cm}^{-3}$, supporting once again the validity of the *homogeneous intra-granular precipitation assumption*.

B. Area-averaged precipitation

The as-grown dissolved iron ratio has been calculated from Eq. (1), for a range of area-averaged densities of precipitation sites. The results are plotted in Fig. 7. As shown in Fig. 1(a), the remaining interstitial iron concentration constitutes about 10% of the total iron concentration, corresponding to an area-averaged density of precipitation sites $\bar{N}_p = 4.5 \times 10^8 \text{ cm}^{-3}$. The average intra-granular concentration was measured on the iron interstitial map to be $5.5 (\pm 0.7) \times 10^{12} \text{ cm}^{-3}$ —corresponding to a dissolved iron ratio of 0.14. It should be noted here that the homogeneity of the intra-granular interstitial iron concentration across the studied wafer is consistent with a relatively homogeneous intra-granular dislocation density of $4.8 (\pm 1.5) \times 10^3 \text{ cm}^{-2}$. Such low dislocation densities are expected to have a very limited effect on the minority carrier diffusion length.^{35,36} The present results, however, show that such low dislocation densities can still drive iron to precipitate. The intra-granular

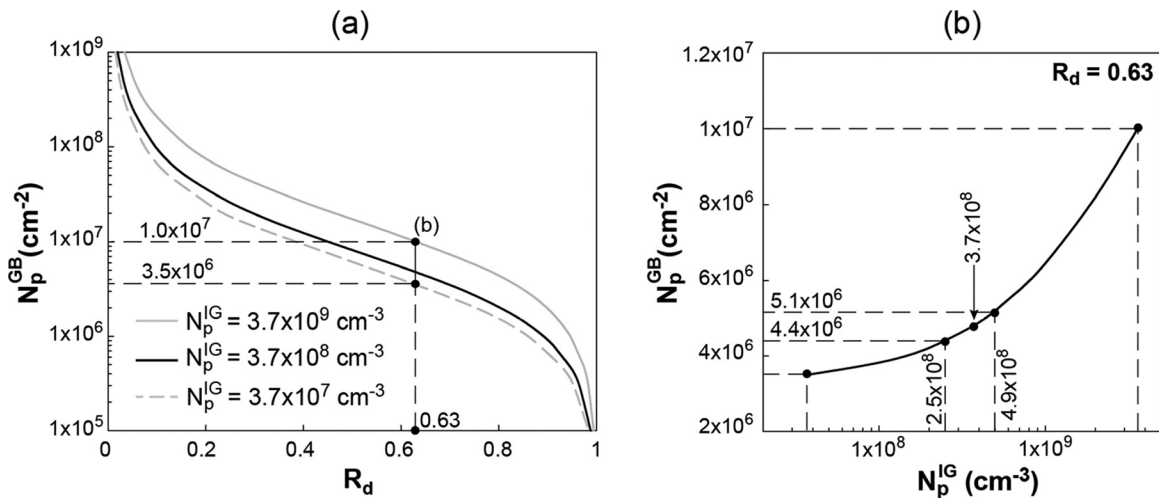


FIG. 6. (a) Surficial density of precipitation sites at the boundary N_p^{GB} plotted as a function of the final depletion-ratio R_d for three different intra-granular densities of precipitation sites N_p^{IG} , namely, $3.7 \times 10^7 \text{ cm}^{-3}$, $3.7 \times 10^8 \text{ cm}^{-3}$, and $3.7 \times 10^9 \text{ cm}^{-3}$. The evaluated average depletion-ratio $R_d = 0.63$ is indicated. (b) Sensitivity curve showing the average density of precipitation site at grain boundaries N_p^{GB} calculated for $R_d = 0.63$, as a function of the intra-granular density of precipitation site N_p^{IG} .

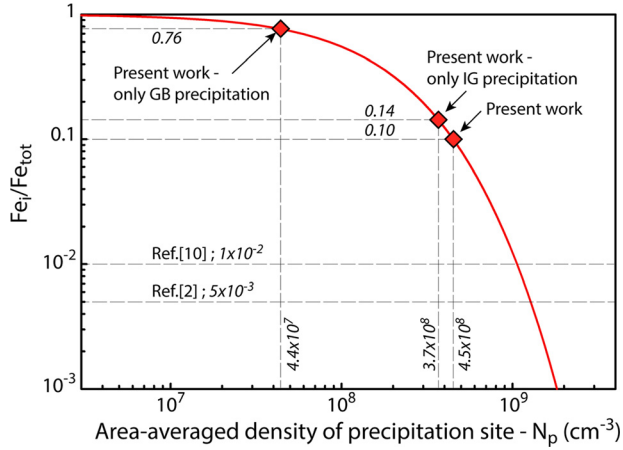


FIG. 7. Ratio of dissolved iron at the end of the solidification process, as a function of the area averaged density of precipitation sites, as calculated from Eq. (1). The dissolved iron ratio corresponding to the present work is 0.10. The isolated effect of intra-granular (IG) precipitation and grain boundary (GB) precipitation is added on the graph. Previous ratios obtained by Macdonald *et al.*¹⁰ and Istratov *et al.*² are added for qualitative comparison.

dissolved iron ratio corresponds to an intra-granular density of precipitation sites of approximately $3.7 \times 10^8 \text{ cm}^{-3}$, and therefore, a linear density of precipitation sites at dislocations of $7.7 \times 10^5 \text{ cm}^{-1}$. This latest value is consistent with the linear density of precipitation site at dislocations used in the work of Morishige *et al.*³⁷ and Schön *et al.*³⁸—i.e., $3.3 \times 10^5 \text{ cm}^{-1}$. The average intra-granular density of precipitation site— $3.7 \times 10^8 \text{ cm}^{-3}$ —is shown in Fig. 7 and corresponds to a case where iron precipitation occurs exclusively in the intra-granular regions—i.e., precipitation at grain boundaries and dislocation clusters is discarded. Even though the average density of dislocations in the present material is low, the intra-granular density of precipitation sites is close to the area-averaged density of precipitation sites in the wafer, and almost the whole iron precipitation occurs in the intra-granular regions.

The average surficial density of precipitation sites at random grain boundaries was evaluated to be $4.9 (\pm 1.5) \times 10^6 \text{ cm}^{-2}$ [see Fig. 3(c)]. From the EBSD map shown in Fig. 1(b), the density of random grain boundaries across the studied wafer is evaluated to be approximately 9.0 cm^{-1} . The area-averaged density of precipitation site at grain boundaries across the wafer is then $\bar{N}_p = 4.4 \times 10^7 \text{ cm}^{-3}$. This value is shown in Fig. 7 and corresponds to a case where iron precipitation occurs exclusively at the grain boundaries—i.e., precipitation in the intra-granular regions and dislocation clusters is discarded. In this case, the value of the dissolved iron ratio is close to 1, and grain boundaries have a relatively limited impact on iron precipitation.

Ratios between dissolved and total iron contents have been previously reported by Macdonald *et al.*¹⁰ and Istratov *et al.*² These values are more than one order of magnitude lower than the one presented in this work and are shown in Fig. 7.

The material investigated in the present study has been obtained from a multi-seeded growth process, resulting in the solidification of a so-called high-performance multicrystalline silicon (HPMC-Si) ingot. As mentioned in the

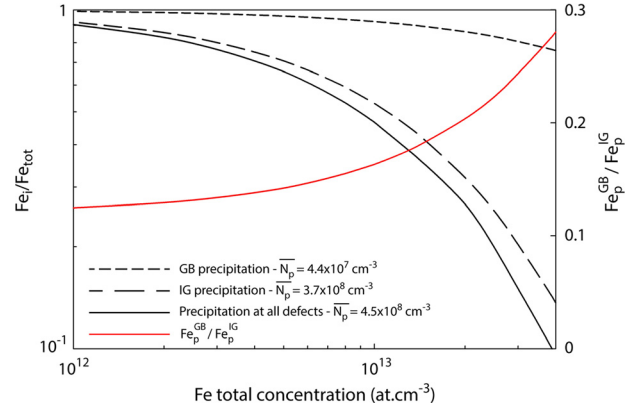


FIG. 8. Ratio of dissolved iron at the end of the solidification process, as a function of the total iron concentration. Three cases are presented, showing the separated effect of grain boundary (GB) and intra-granular (IG) precipitation, and the combined effect of all structural defects.

introduction, this technique favors the growth of a more random structure, characterized by a limited development of dislocation clusters.¹³ The lower density of dislocation clusters in HPMC-Si leads to a limited precipitation of iron, as the density of available precipitation sites is lower than in standard multicrystalline silicon. The difference between the dissolved iron ratio evaluated by Macdonald *et al.* and Istratov *et al.* and the one obtained in the present study clearly illustrates the important effect of dislocation clusters on iron precipitation.

The studied material was taken at $\sim 80\%$ ingot height. This relatively high position in the ingot was selected in order to (1) obtain clear depleted regions close to the grain boundaries on the Fe_i map and (2) measure the total iron concentration with GDMS. The iron levels in the present material are an order of magnitude higher than the iron concentration found in the center of the ingot. In order to discuss the influence of the total concentration of iron on the results presented in this work, the as-grown ratio of dissolved iron was calculated as a function of the total iron concentration. It is assumed that the grain structure does not change over height—i.e., the average precipitation site densities used for the calculations are the ones evaluated in Sec. IV A—and the same ingot-cooling rate CR was utilized. The supersaturation ratio is also assumed to not vary with the total iron concentration. The results are plotted in Fig. 8. Three separated cases are displayed, showing the sole effects of grain boundary and intra-granular precipitation, and the combined effect of all structural defects. A fourth curve is shown (in red), corresponding to the ratio between the precipitated iron at grain boundaries and intra-granular dislocations.

The limited effect of grain boundaries on iron precipitation is still valid for lower iron concentrations, and most of precipitation still occurs at intra-granular dislocations. The final dissolved iron ratios are furthermore closer to one for lower concentrations, and only $\sim 10\%$ of the iron is expected to precipitate for total concentrations in the order of 10^{12} cm^{-3} . The relatively lower ability of the HPMC-Si material to precipitate iron is then even more remarkable in the low iron concentration range.

V. SUMMARY AND CONCLUSION

A study of the spatial occurrence of iron precipitation in the HPMC-Si material has been conducted. By examining the depleted region width developing close to the grain boundaries, a supersaturation ratio $k \sim 6300$ has been estimated. This value is much higher than the previous value reported in the literature for the standard multicrystalline material. This difference is attributed to the lower density of precipitation sites available in HPMC-Si compared to standard mc-Si, due to the relatively low dislocation density. Active grain boundaries are mostly identified as random angle grain boundaries, and an examination of their depleted ratio showed that they precipitate iron with a relatively homogeneous intensity. An average surficial density of precipitation sites at active grain boundaries $N_p^{GB} = 4.9 (\pm 1.5) \times 10^6 \text{ cm}^{-2}$ has been evaluated, which is consistent with the values from the literature.

The area-averaged fraction of dissolved iron Fe_i/Fe_{tot} in the studied HPMC-Si material is more than an order of magnitude higher than ratios estimated in previous work for the standard material. This observation is associated with the relatively lower density of dislocation clusters found in HPMC-Si and indicates that grain growth control has led to a clear decrease of iron precipitation in multicrystalline materials.

However, even though dislocations are present in HPMC-Si in relatively low densities, they prove to still be active in terms of iron precipitation. The separated effect of grain-boundaries, sparse intra-granular dislocations, and dislocation clusters on iron precipitation was investigated. It is shown that almost the entire iron precipitation occurs in the intra-granular regions and that the contribution of grain boundary precipitation is surprisingly low, despite the comparably small grain sizes in HPMC-Si.

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