

Towards the tailoring of P diffusion gettering to as-grown silicon material properties

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Abstract. The evolution of Fe-related defects is simulated for different P diffusion gettering (PDG) processes which are applied during silicon solar cell processing. It is shown that the introduction of an *extended* PDG is beneficial for some as-grown Si materials but not essential for all of them. For mc-Si wafers with an as-grown Fe concentration $\leq 10^{14} \text{ cm}^{-3}$, a good reduction of the Fe_i concentration and increase of the electron lifetime is achieved during standard PDG. For mc-Si wafers with a higher as-grown Fe concentration the introduction of defect engineering tools into the solar cell process seems to be advantageous. From comparison of standard PDG with extended PDG it is concluded that the latter leads to a stronger reduction of highly recombination active Fe_i atoms due to an enhanced segregation gettering effect. For an as-grown Fe concentration between 10^{14} cm^{-3} and 10^{15} cm^{-3} , this enhanced Fe_i reduction results in an appreciable increase in the electron lifetime. However, for an as-grown Fe concentration $> 10^{15} \text{ cm}^{-3}$, the PDG process needs to be optimized in order to reduce the *total* Fe concentration within the wafer as the electron lifetime after extended PDG keeps being limited by recombination at precipitated Fe.

Introduction

More than 50 % of multi-crystalline silicon (mc-Si) wafers originate from the corner, edge and top regions of the ingot, containing higher amounts of impurities. Furthermore, in the course of reducing the cost of photovoltaic solar energy, cheaper solar grade Si materials of lower purity, e. g. UMG materials, are being developed. Consequently, in most mc-Si materials total as-grown Fe concentrations as high as $10^{14} - 10^{16} \text{ cm}^{-3}$ are usually found and interstitial iron, Fe_i , is usually the lifetime-limiting defect [1, 2, 3]. In accordance with an experiment by Sopori *et al.* in the nineties [2] we measured as-grown electron lifetimes on ~ 150 p-type mc-Si wafers from different providers and plotted them as a function of the as-grown Fe_i concentration [4]. The measured data together with the theoretical curve of SRH recombination at Fe-B pairs are shown in Fig.1(a). Good agreement between the theoretical curve and the experimental data points confirm that Fe_i keeps being the lifetime-limiting defect in most as-grown p-type mc-Si wafers nowadays. P diffusion gettering (PDG) during solar cell fabrication usually reduces the concentration of Fe and other metal impurities and leads to increased charge carrier lifetimes. However, the response to PDG seems to depend strongly on the Si material quality and even material degradation rather than an improvement during PDG is occasionally observed. It was shown by Coletti *et al.* [5] that the post-processed Fe_i concentration along an intentionally Fe-contaminated mc-Si ingot strongly varies with the total as-grown Fe concentration. In the first part of this work, with the help of the *Impurity-to-Efficiency (I2E)* simulation tool [6], we will systematically study the efficacy of standard PDG as a function of as-grown Fe concentration and distribution in p-type Si materials.

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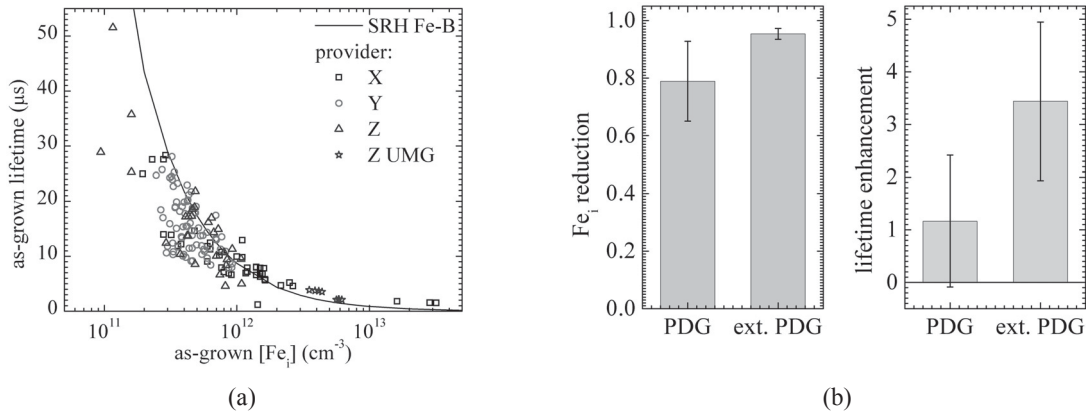


Fig. 1: (a) Measured as-grown electron lifetime as a function of the as-grown Fe_i concentration on p-type mc-Si wafers from different providers and SRH lifetime calculated as a function of the Fe-B pair concentration (b) Fe_i reduction, $\Delta[\text{Fe}_i]/[\text{Fe}_i]$, and lifetime enhancement, $\Delta\tau/\tau$, after standard PDG and after extended PDG, respectively

Different research groups observed that an extended PDG, consisting of P diffusion followed by slow cooling or by low temperature annealing [7, 8, 9, 10, 11, 12], is able to further reduce Fe_i point defects and improve charge carrier lifetimes and solar cell performance in comparison to a standard PDG. As an example, Fig. 1(b) shows corresponding experimental results that were published in [11]. It is observed that a stronger reduction of the mean Fe_i concentration, $\Delta[\text{Fe}_i]/[\text{Fe}_i]$, and a stronger increase of the mean electron lifetime, $\Delta\tau/\tau$, is achieved when a slow cool down is added to the high temperature step. Therefore, in the second part of this work, we will systematically study the efficacy of an extended PDG as a function of as-grown Fe concentration and distribution in p-type Si materials.

Simulation results

Standard P diffusion gettering A standard PDG step during 20 min at 850°C followed by a fast linear cool down to room temperature (RT) within 5 min is simulated with the help of the *I2E* model. The as-grown Fe concentration is varied between $5 \cdot 10^{13}$ and 10^{16} cm^{-3} and as-grown precipitate radius is varied between 15 and 50 nm, covering a wide range of concentrations and precipitate sizes that have been found in different mc-Si materials [13, 14, 15, 16]. The corresponding precipitate densities are shown in Fig. 2(a). They reach from 10^6 cm^{-3} for low as-grown Fe concentrations and large precipitates up to 10^{10} cm^{-3} for high as-grown Fe concentrations and small precipitates. An as-grown Fe_i concentration of 10^{12} cm^{-3} is assumed for all distributions. The corresponding as-grown electron lifetime is also calculated (Fig. 2(b)) assuming recombination at Fe_i atoms and at $\beta\text{-FeSi}_2$ precipitates as detailed in [6]. The calculated as-grown electron lifetime varies between 1 and 8 μs , values that are typically measured on as-grown mc-Si wafers with similar Fe_i concentrations (see Fig. 1(a)).

The contour plot of the post-processed Fe_i concentration after standard PDG is shown in Fig. 3(a) and the corresponding plot of the electron lifetime is shown in Fig. 3(b). The electron lifetime was calculated for recombination at Fe-B pairs and $\beta\text{-FeSi}_2$ precipitates. A strong dependence on both, the total as-grown Fe concentration and the as-grown precipitate radius, is observed so that the post-processed Fe_i concentration varies between about 10^{10} and $2 \cdot 10^{12} \text{ cm}^{-3}$ and the electron lifetime varies between 1 and 120 μs . Three different regions can be distinguished within contour plot (a) which can be ascribed to three different material types:

(1) For as-grown Fe concentrations $\lesssim 10^{14} \text{ cm}^{-3}$ the post-processed Fe_i concentration is decreased below its assumed as-grown value and it decreases with decreasing as-grown Fe content. This is due to

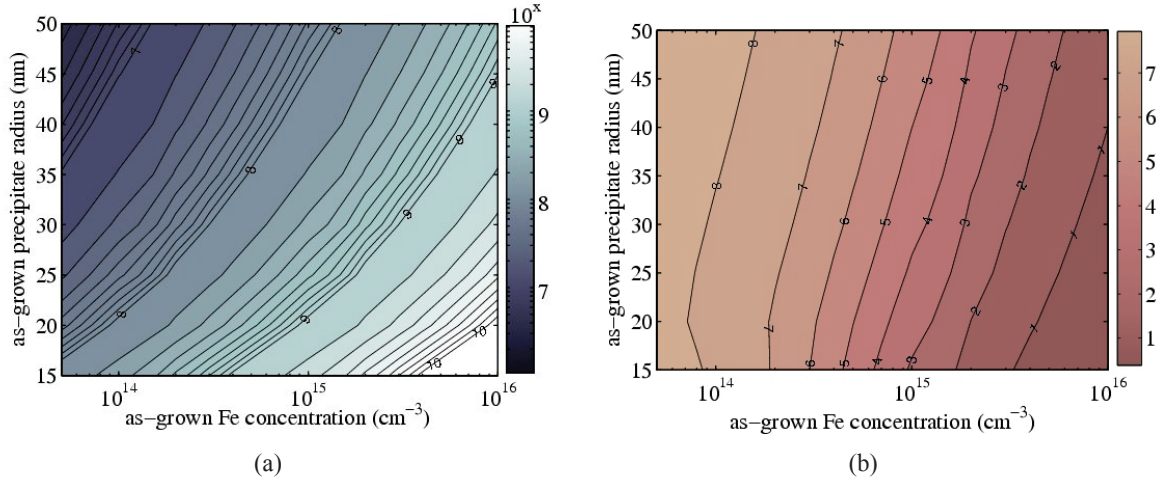


Fig. 2: As-grown (a) precipitate density and (b) electron lifetime as a function of total as-grown Fe concentration and as-grown precipitate radius; an as-grown Fe_i concentration of 10¹² cm⁻³ is assumed

a lower precipitate density which results in a smaller interface area between precipitates and Si matrix, leading to a decelerated dissolution during high temperature processing. Similarly, the interface area between precipitates and the silicon matrix decreases with increasing precipitate radius for any given as-grown Fe concentration. Therefore, the post-processed Fe_i concentration decreases with increasing precipitate radius for any given as-grown Fe concentration below 10¹⁴ cm⁻³.

(2) For an as-grown total Fe concentration between $\sim 10^{14}$ and $\sim 10^{15}$ cm⁻³ a post-processed Fe_i concentration $\geq 10^{12}$ cm⁻³ is obtained after standard PDG, i.e., it is higher than the as-grown Fe_i concentration. The increase of the Fe_i concentration is coupled to a decreased charge carrier lifetime below 5 μ s as shown in Fig. 3(b).

(3) For an as-grown Fe concentration $\gtrsim 10^{15}$ cm⁻³ a decrease of the post-processed Fe_i concentration is observed with increasing as-grown Fe concentration and with decreasing as-grown radius. With increasing as-grown Fe content, the density of precipitates increases up to 10¹⁰ cm⁻³ as shown in Fig. 2(a) so that the distance between precipitates decreases down to a few μ m. With decreasing distance between precipitates, an enhanced precipitation of Fe_i atoms takes place during cool down to RT and a lower post-processed Fe_i concentration is obtained due to an internal gettering effect. However, as observed in Fig. 3(b), no corresponding increase of the electron lifetime is achieved because it is limited by recombination at Fe precipitates.

In Fig. 4(a), the *total* post-processed Fe concentration is plotted as a function of the as-grown Fe concentration and precipitate radius. The relative post-processed Fe concentration, $[\text{Fe}]_{\text{post}}/[\text{Fe}]_{\text{as-grown}}$, is plotted in Fig. 4(b). Simulation results indicate that for any given as-grown Fe concentration, Fe extraction is more effective for smaller precipitates due to a higher interface area and faster precipitate dissolution. During 20 min PDG at 850 °C an Fe reduction of up to 60–80 % can be achieved for as-grown Fe concentrations $\lesssim 3 \cdot 10^{14}$ cm⁻³ and precipitate radii $\lesssim 20$ nm. For an increasing Fe concentration and/or precipitate radius, the Fe extraction is less efficient. For an as-grown Fe concentration $\gtrsim 3 \cdot 10^{15}$ cm⁻³ and/or precipitate radii $\gtrsim 35$ nm less than 20% of the total Fe concentration is extracted during standard PDG.

Extended P diffusion gettering

An extended PDG step consisting of 20 min P diffusion at 850 °C followed by an exponential cool down to RT with a cooling rate of $\delta = 213$ min is assumed. The contour plot of the post-processed Fe_i concentration as a function of the as-grown Fe concentration and precipitate radius is shown in Fig. 5(a). It exhibits three different regions similar to those in the corresponding plot for standard

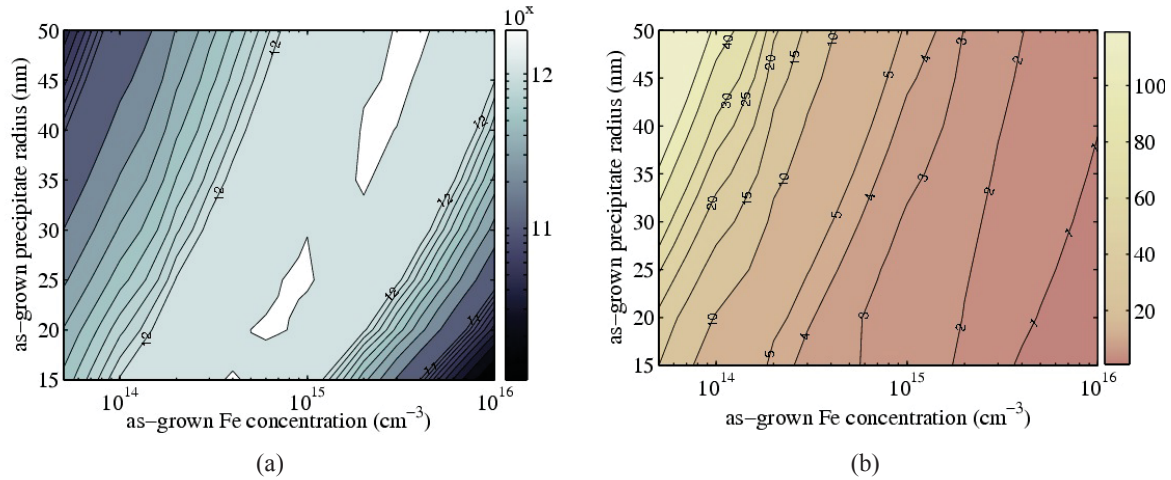


Fig. 3: Post-processed (a) Fe_i concentration and (b) electron lifetime as a function of as-grown Fe concentration and precipitate radius after 20 min PDG at 850 °C; an as-grown Fe_i concentration of 10^{12} cm^{-3} is assumed.

PDG: for a given as-grown precipitate radius, the post-processed Fe_i concentration exhibits a maximum for an as-grown Fe concentration between 10^{14} and 10^{15} cm^{-3} ; with increasing as-grown precipitate radius, this maximum shifts to higher as-grown Fe concentrations. However, the calculated post-processed Fe_i concentration lies between $2 \cdot 10^5 \text{ cm}^{-3}$ and $2 \cdot 10^8 \text{ cm}^{-3}$, being several orders of magnitude lower than after a standard PDG for all as-grown Fe concentrations and precipitate radii.

The calculated electron lifetime after extended PDG is shown in Fig. 5(b). It is observed that the enhanced Fe_i extraction leads to increased electron lifetime between 10 and up to 300 μs for an as-grown Fe concentration below 10^{15} cm^{-3} , assuming that Fe_i and $\beta\text{-FeSi}_2$ precipitates are the lifetime-limiting defect. For a higher as-grown Fe concentration, the electron lifetime remains low at values below 5 μs . This indicates that the electron lifetime, even after extended PDG, is limited by charge carrier recombination at small precipitates present in high density rather than at Fe_i atoms.

The contour plot of the total Fe concentration after extended PDG (not shown here) is almost identical to the corresponding plot for standard PDG shown in Fig. 4(a). This means that the total Fe concentration is hardly affected by a slow cool down after PDG. This is because with decreasing temperature, the solid solubility of Fe in Si decreases and no further precipitate dissolution takes place. Only the small fraction of Fe that is present in interstitial form can be further reduced during slow cooling.

Discussion

Simulations performed in this work indicate the evolution of the Fe_i concentration and electron lifetime in p-type mc-Si wafers during solar cell processing for different processing schemes. Only the interaction between interstitial Fe atoms and $\beta\text{-FeSi}_2$ precipitates and their respective impact on charge carrier lifetimes are considered in the current model. The interaction of Fe-related defects with other defects that are frequently observed in mc-Si material, e.g. other metal impurities or crystalline defects, are not taken into consideration so far. However, the current *I2E* model gives good indication for process optimization for most mc-Si materials in which Fe is the lifetime-limiting impurity. It allows to perform fast simulations and is therefore suitable for design of experiment.

In this work, the effectiveness of an extended PDG as opposed to a standard PDG is confirmed and explained. According to simulation results, three different Si materials can be classified with respect to their as-grown Fe concentration:

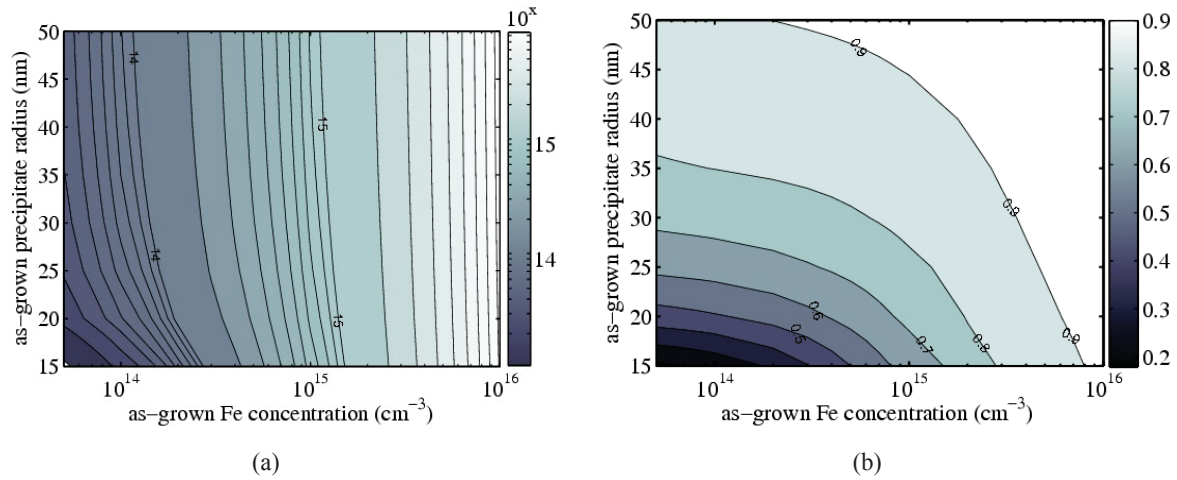


Fig. 4: (a) Total post-processed Fe concentration and (b) relative post-processed Fe concentration as a function of as-grown Fe concentration and precipitate radius after 20 min PDG at 850 °C.

(1) As-grown Fe concentrations $\leq 10^{14} \text{ cm}^{-3}$ are usually found in the center region of cast mc-Si ingots [17, 18, 19]. On such wafers, an efficient reduction of the Fe_i concentration can be achieved during standard PDG. This Fe_i reduction comes along with an increased post-processed electron lifetime of up to 120 μs , assuming that no other recombination-active defects apart from Fe_i and $\beta\text{-FeSi}_2$ precipitates are present.

(2) As-grown Fe concentrations between 10^{14} cm^{-3} and 10^{15} cm^{-3} are usually found in wafers originating from border and towards the top of cast mc-Si ingots, throughout mc-Si ingots grown from low-purity Si feedstock materials (e.g. UMG) and in Si sheet material [3, 13, 14, 18, 19]. On wafers with such a high Fe concentration, the dissolution of precipitated Fe can lead to a material degradation rather than improvement of material performance during PDG. For these materials a modification of the standard PDG step may be beneficial. Simulations show that a lower Fe_i concentration and higher charge carrier lifetimes can be achieved during extended PDG, i.e. when a slow cooling or LTA step is added to the standard PDG. Experiments indicate that the strong reduction of the Fe_i concentration during the low temperature tail are due to an enhanced external gettering effect towards the P-diffused layer [11, 20]. This result is confirmed by additional simulations of slow cooling with no external gettering layer present (not shown here).

(3) The highest as-grown Fe concentrations $> 10^{15} \text{ cm}^{-3}$ can be found in Si sheet materials like Ribbon and edge-defined film-fed grown (EFG) wafers and at the very top of mc-Si ingots [13, 18]. In these materials, smaller precipitates are usually present due to much faster cooling rates during wafer crystallization as opposed to the long cooling rates of cast mc-Si ingots [15]. According to our simulations, no lifetime improvement is achieved on these materials, neither during standard PDG nor during an extended PDG. The impact of different processing schemes on Fe precipitates in highly Fe-contaminated mc-Si has been investigated by means of X-Ray fluorescence microscopy by different researchers [16, 21]. Experimental results confirm that both, standard PDG and LTA, mainly act on the concentration of interstitially dissolved Fe but hardly affect the distribution of precipitated Fe. Therefore, in sheet materials one should aim for more efficient reduction of the *total* Fe concentration or the formation of less but bigger precipitates by means of defect engineering on the wafer level. A reduction of the total Fe concentration might be achieved through a two-step PDG as proposed by several authors [22, 23]: (A) the dissolution of all precipitates at a sufficiently high temperature at which the solid solubility limit exceeds the total as-grown Fe concentration and (B) the subsequent

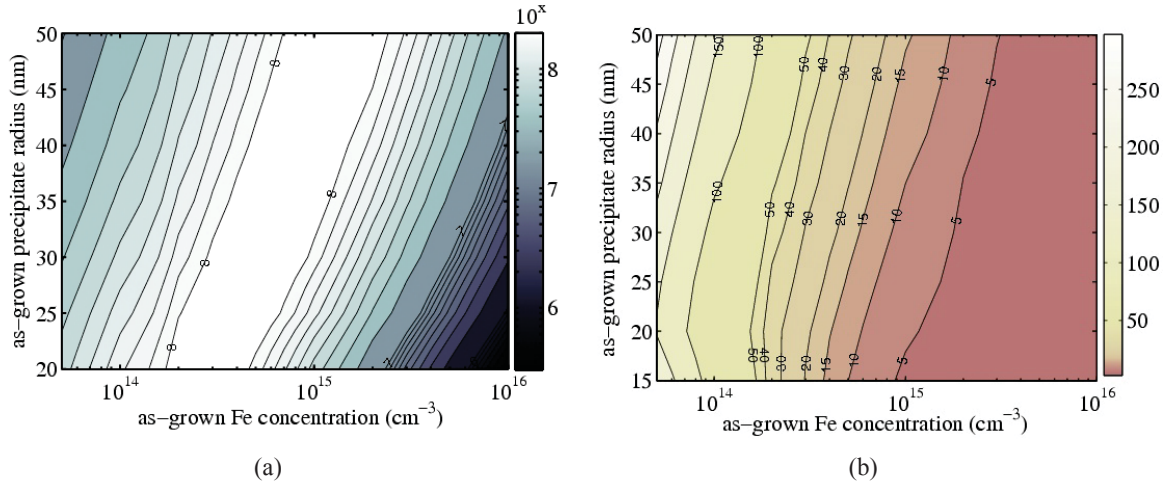


Fig. 5: Post-processed (a) Fe_i concentration and (b) electron lifetime as a function of as-grown Fe concentration and precipitate radius after 20 min PDG at 850 °C followed by a slow exponential cool down to RT with $\delta = 213$ min.

extraction of dissolved metal impurities at lower temperatures. With the help of the *I2E* simulation tool such two-step PDG can be easily designed and optimized.

Besides the tailoring of processing steps to different material types, the *I2E* simulator is suitable to optimize solar cell processing schemes under the constraint of short processing time for industrial applications. Very recently, a "short-tail" extended PDG was designed that consists of a standard PDG followed by a short LTA at an optimum temperature [4, 24]. An appreciable solar cell efficiency enhancement of 0.4% absolute has been found experimentally by Rinio *et al.* [12] when introducing a 90 min LTA around 550°C into the solar cell fabrication process. According to *I2E* simulations and indicated by first experimental results, an equally enhanced efficiency can be obtained for a much shorter 15 min LTA at temperatures between 600 and 700°C.

Finally, for integral process optimization, the last high-temperature step during industrial solar cell processing, the contact co-firing step, has also to be taken into account. Much effort has been made so far to optimize PDG in order to achieve lower post-processed metal concentrations and higher charge carrier lifetimes [7, 8, 11, 9, 10, 12]. However, it has been observed experimentally and by simulation [25, 26] that the Fe_i concentration can significantly increase during rapid thermal annealing (RTA) even during a few seconds at 800°C. Therefore, the optimization of the time-temperature profile of the contact co-firing step is essential when a low Fe_i concentration and a high electron lifetime is achieved during the previously optimized PDG. Very recently, a modified RTA step has been designed and optimized with the help of the *I2E* simulation tool and its effectiveness has been demonstrated experimentally [26].

Conclusions

Predictive *I2E* simulations allow one to study the effectiveness of different P diffusion gettering schemes on the improvement of p-type mc-Si wafers of varying as-grown Fe concentrations and distributions. Consequently, processing schemes can be tailored and optimized for different parts of the mc-Si ingot and, more generally, for different Si materials. Lastly, the *I2E* simulator is suitable for integral process optimization under the constraint of short processing times for industrial solar cell fabrication.

Acknowledgments

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