Simulated Co-Optimization of Crystalline Silicon Solar Cell Throughput and Efficiency Using Continuously Ramping Phosphorus Diffusion Profiles

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Abstract — **Defect engineering is essential for the production of high-performance silicon photovoltaic (PV) devices with cost-effective solar-grade Si input materials. Phosphorus diffusion gettering (PDG) can mitigate the detrimental effect of metal impurities on PV device performance. Using the Impurity-to-Efficiency (I2E) simulator, we investigate the effect of gettering temperature on minority carrier lifetime while maintaining an approximately constant sheet resistance. We simulate a typical constant temperature plateau profile and an alternative "volcano" profile that consists of a ramp up to a peak temperature above the typical plateau temperature followed by a ramp down with no hold time. Our simulations show that for a given PDG process time, the "volcano" produces an increase in minority carrier lifetime compared to the standard plateau profile for as-grown iron distributions that are typical for multi-crystalline silicon. For an initial total iron concentration of 5×10^{13} cm^{-3}, we simulate a 30% increase in minority carrier lifetime for a fixed PDG process time and a 43% reduction in PDG process cost for a given effective minority carrier lifetime while achieving a constant sheet resistance of 100 Ω/ .**

Index Terms — **iron, gettering, minority carrier lifetime, phosphorus, photovoltaic, sheet resistance, silicon**

I. INTRODUCTION

While high as-grown iron concentrations can severely limit minority carrier lifetimes of crystalline silicon solar cell materials, the negative effect of iron contaminants can be mitigated by phosphorus diffusion gettering (PDG) [1]. Thus, tailoring annealing profiles during solar cell manufacturing to the specific concentration and distribution of impurities in as-grown wafers could reduce manufacturing costs by enabling significant performance improvements and potentially relaxing tolerances on input material purity [2].

A typical time-temperature profile of PDG consists of a ramp up to a high temperature, a hold at that high temperature (T_{hold}) during which phosphorus is thermally diffused from a surface boundary layer, followed by some cooling profile [3]. There have been a number of alternatives to this standard process with modeling and experimental support. Multiple authors [4,5] have investigated rapid-thermal annealing from spin-on dopant sources, achieving cell efficiencies as high as 17.5% for high-purity Czochralski silicon. However, a reduction in cell performance was observed for materials with higher iron concentrations [6]. Plekhanov [7] attempted to simulate enhanced gettering profiles for materials with higher iron concentrations, exploring higher temperatures to promote precipitate dissolution. In subsequent years, Manshanden [8]

compared a single-step plateau profile to a two-step plateau profile and found that the two-step process is more effective at gettering iron point defects; the physics of the process was clarified by subsequent work by Pickett [9] and Rinio [10] and related to the time-temperature transformation diagram of Fe interstitials in silicon [11]. Schön explored a profile consisting of a ramping high-temperature pre-anneal followed by a plateau [12] similar to Plekhanov [7], and Ossiniy [13] explored similar multi-plateau profiles designed to enhance precipitate dissolution and point-defect gettering, resulting in minority carrier lifetime enhancements as compared with standard processes.

In this contribution, we propose a POCl$_3$ diffusion profile that incorporates many of the benefits of these previous approaches with the goal of optimizing both throughput (process time) and electrical performance. We analyze the additional limitation of iron-silicide precipitates and how process time and temperature affect lifetime for a constant sheet resistance. As an alternative to a standard plateau profile, we hypothesize that ramping up to a peak temperature above the typical process hold temperature and then immediately ramping down with no holding time (a "volcano" profile) could accelerate impurity gettering. We hypothesize that the "volcano" process increases minority carrier lifetime, while also shortening overall processing time for a range of initial iron concentrations because of the exponential dependence of the diffusivity of iron in silicon on temperature.

II. METHOD

We simulated the effect of POCl$_3$ diffusion on final minority carrier lifetime and iron distribution for two different classes of time-temperature profile (Fig. 1), using the Impurity-to-Efficiency (I2E) simulation tool [14,15]. We chose profiles that produce phosphorus-diffused emitters with equal sheet resistances because cell processes downstream of emitter formation are optimized for a given sheet resistance. We use Klaassen's mobility model [16] to compute the emitter sheet resistance, while neglecting the effect of band gap narrowing (an approximation leading to errors in calculated sheet resistance of less than 0.2%). Since our model does not consider surface oxide growth during diffusion, all emitter sheet resistances reported herein are approximate.

First, we simulated a standard POCl$_3$ diffusion profile consisting of a ramp up from 800°C to a constant high-temperature plateau ($T_{plateau}$) followed by an exponential cool from the high temperature plateau with an exponential time constant of 6 min, which is roughly equivalent to removing the wafer from the furnace to cool. POCl$_3$ flow starts once $T_{plateau}$ is reached. To achieve a constant emitter sheet resistance, we determined the requisite plateau time for several different values of $T_{plateau}$ and calculated the resulting interstitial and precipitated iron concentrations and effective minority carrier lifetime.

The continuously ramping "volcano" POCl$_3$ diffusion profile consists of a ramp up from 800°C to a peak temperature (T_{peak}), then a ramp down with no hold time from T_{peak} to 785°C, and an exponential cool with a 6 min time constant. The phosphorus diffusion starts at the beginning of the profile. As T_{peak} increases, the phosphorus diffusivity increases and therefore, the required PDG process time decreases.

For all simulated time-temperature profiles, we assumed an initial interstitial iron concentration of 5×10^{11} cm^{-3} and an initial iron precipitate radius of 25 nm.

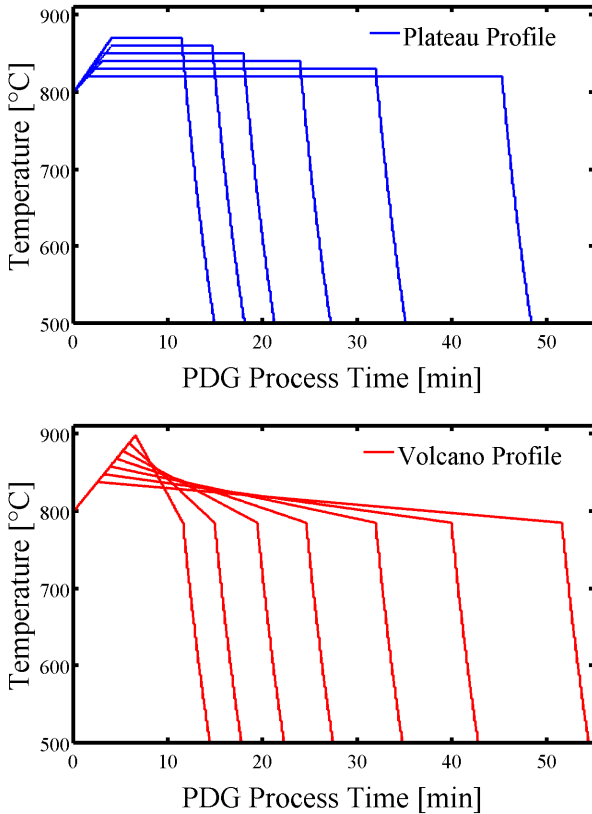Fig. 1. Simulated $T(t)$ Profiles: Standard plateau (top) and alternative continuously ramping "volcano" (bottom).

III. RESULTS: I2E SIMULATION

Our simulations of PDG for continuously ramping profiles show that minority carrier lifetime increases and that the sheet resistance decreases with increasing T_{peak} and increasing PDG process time (Figs. 2 and 3). For simulations shown in Figs. 2 and 3, the ramp time from 800°C to T_{peak} was 5 min and the ramp down time from T_{peak} to 785°C varied from 10 to 50 min. The 18 min long, 840°C profile produces the lowest lifetime, 44.8 μs, and the highest sheet resistance, 178 Ω/ , while the 58 min process with a T_{peak} of 890°C results in a 96 μs lifetime and a 53.6 Ω/ sheet resistance. For the standard plateau, the relationships between effective lifetime, sheet resistance, and process time are similar.
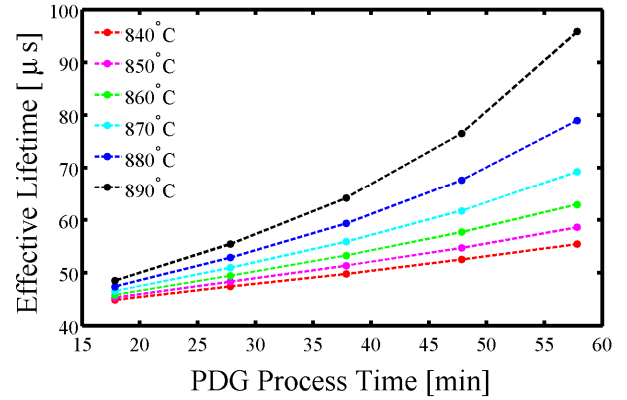

Fig. 2. For the "volcano" profile, minority carrier lifetime increases with peak temperature and process time.
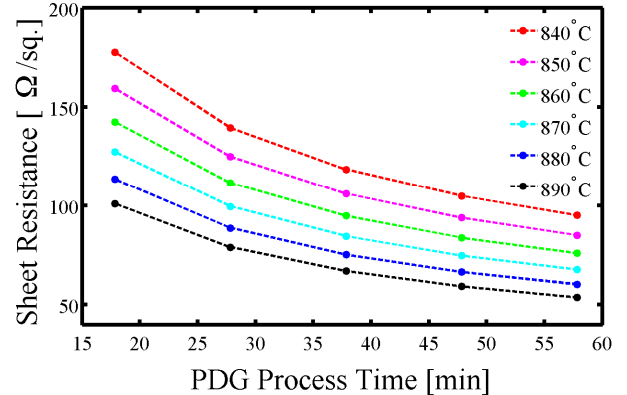

Fig. 3. For the "volcano" profile, sheet resistance decreases with increasing temperature and time spent above std. hold temperature.

We performed simulations for two different as-grown total iron concentrations of 5×10^{13} and 1×10^{14} cm^{-3}. In both cases, an interstitial iron concentration of 5×10^{11} cm^{-3} was assumed. All profiles resulted in calculated sheet resistances of 100 Ω/ . Our model predicts that both plateau and "volcano" profile shapes decrease iron concentrations and increase minority carrier lifetime as process time increases and temperature decreases (Figs. 4 and 5). Iron gettering results are summarized in Table I: All simulated profiles result in a reduction of the interstitial Fe concentration between 67 and 93%, while the precipitated iron concentration is reduced only between 25 and 38%.
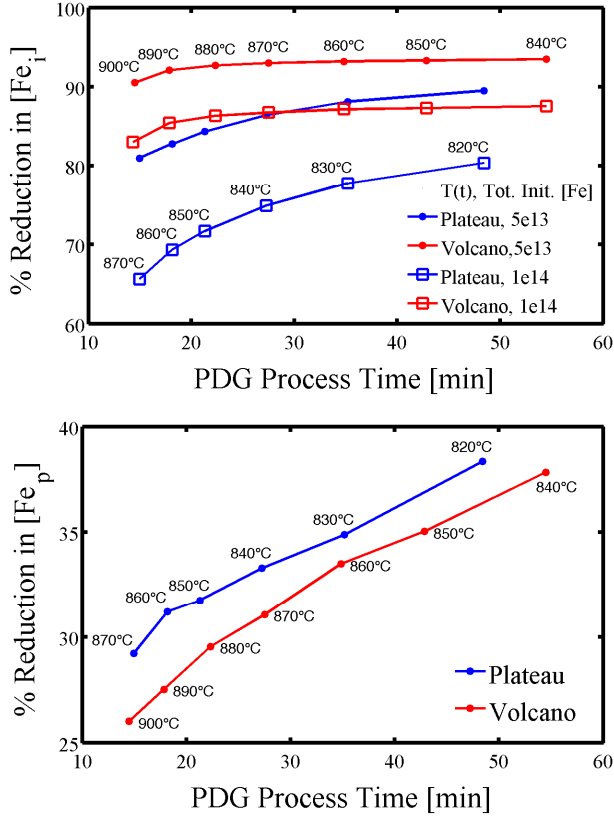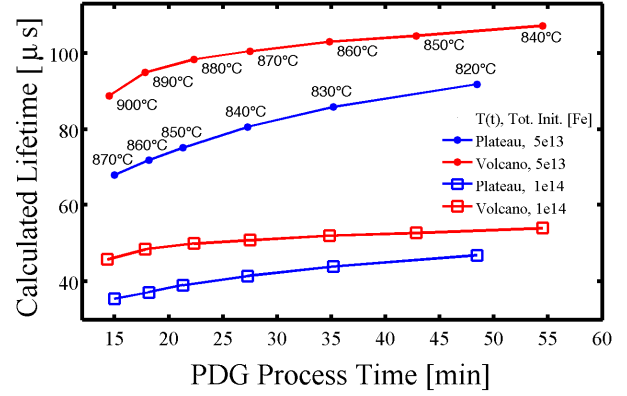
Fig. 5. Effective lifetime increases with process time. The "volcano" profile results in a higher effective minority carrier lifetime than the plateau for the same process time.

Fig. 4. The percent reduction of [Fe] (normalized to initial concentrations) increases with process time. The "volcano" profile reduces interstitial Fe more effectively and precipitated iron less effectively than the standard plateau profile for the same process time. The percent reduction in precipitated Fe is very similar for an initial total Fe concentration of 10^{14} cm^{-3} and is therefore not shown.

TABLE I
SUMMARY OF IRON GETTERING

Total Initial [Fe]	Profile Shape	Reduction Interstitial [Fe]	Reduction Precipitated [Fe]
5×10^{13}	Plateau	81-90%	29-38%
	Volcano	90-93%	26-38%
1×10^{14}	Plateau	67-80%	28-38%
	Volcano	83-87%	25-37%

IV. DISCUSSION

Standard PDG and an alternative continuously ramping "volcano" profile were simulated to evaluate the effect of PDG process time, temperature, and profile shape on iron gettering and final effective minority carrier lifetime.

For a given process time and sheet resistance, the "volcano" profile is calculated to reduce interstitial iron more effectively and precipitated iron less effectively than the plateau profile as shown in Fig. 4. The "volcano" and the plateau both reduce interstitial iron more effectively for lower as-grown (initial) iron concentrations than for higher as-grown concentrations. While interstitial iron concentration reduction is decreased for higher as-grown iron concentration, the "volcano" getters interstitial iron significantly better than the plateau. On the other hand, our calculations indicate that the reduction of precipitated iron does not depend on the as-grown precipitated iron concentration for this range of concentrations and sheet resistance (Fig. 4).

The final concentrations of both interstitial and precipitated iron determine the final effective minority carrier lifetime. Although the "volcano" profile getters precipitated iron less effectively than the standard plateau profile, it getters interstitial iron more effectively, resulting in a higher effective minority carrier lifetime for the bulk iron concentrations explored herein (Fig. 5), which are typical of mc-Si [17]. The ramp down to lower temperature before the exponential cool takes advantage of the increasing segregation coefficient in the P-diffused layer with decreasing temperature [7], resulting in a larger driving force for interstitially dissolved iron to be gettered. For example, for an initial total iron concentration of 5×10^{13} cm^{-3} and a constant emitter sheet resistance of 100 Ω/ , a continuously ramping profile with a 900°C T_{peak} and a PDG process time of 14.3 min results in a simulated lifetime of 88 μs, while a plateau profile with 820°C $T_{plateau}$ and 48.4 min process time results in a comparable lifetime of 92 μs. According to our calculations, the 900°C "volcano" process achieves 95.6% of the lifetime produced by the 820°C plateau

process in less than 30% of total PDG process time. Similarly, the 900°C "volcano" process results in a 30% increase in the lifetime over that of the 870°C plateau process for the same total PDG process time. Applying the "volcano" process rather than a standard plateau can mitigate the tradeoff between process throughput and effective minority carrier lifetime for a constant sheet resistance.

However, at high total as-grown iron concentration, the difference in the calculated effective lifetimes due to the two different profiles decreases (Fig. 5). This trend occurs because as the as-grown total iron increases, precipitated iron becomes more important, and the ability of the standard plateau to more effectively getter precipitated iron shrinks the gap between the two processes.

We evaluated the economic impact of the alternative process was with a bottom-up cost model for the PDG process [18] with inputs from [19,20]. The 14.5 min volcano process with 900°C T_{peak} results in a 43% cost savings (PDG only) over a 42 min plateau process with 825°C $T_{plateau}$ while both processes result in the same effective minority carrier lifetime. The cost savings is due to an increase in throughput for the alternative process, which is slightly offset by an increase in electricity use from the elevated process temperature.

The one-dimensional I2E model used for the simulations in this study has been shown to match trends observed in experimental data [15,21]. It accounts for two significant effects that determine post-processed material performance, which are the dissolution of iron precipitates and external gettering of interstitial iron. However, the I2E model assumes homogeneous precipitate distribution and it excludes the effect of crystal defects, oxygen-related defects, and phosphorus silicate glass formation on the wafer surface during annealing. Nevertheless, it has been shown to provide valuable guidance for the majority of Si materials in which iron complexes are the performance–limiting defects.

In ongoing work, simulation results obtained in this contribution are being tested experimentally. One obstacle to overcome is that current POCl₃ diffusion furnace technology is designed well for the standard plateau profiles. Experimentally testing the fast ramping rates we simulate for the "volcano" profile is limited by the rates at which the furnace can change temperature. We are able to achieve fairly uniform emitters for continuously ramping processes that are at least ~35 min long. Furnaces designed to change temperature and deposit phosphorus uniformly but more rapidly would be required to test shorter processes.

V. Conclusions

We simulated several standard and continuously ramping "volcano" PDG time-temperature profiles. Minority carrier lifetime is predicted to increase with peak temperature and time spent above the typical hold temperature, while sheet resistance decreases. By using a continuously-ramping "volcano" time-temperature PDG profile, our simulations indicate that it is possible to improve minority carrier lifetime and shorten process time. For a given total process time, using a continuously-ramping profile can improve lifetime after gettering compared to that achieved by a traditional time-temperature profile. Our simulations enable emitter process optimization and indicate that for an initial iron concentration of 5×10^{13} cm⁻³, a potential exists to increase minority carrier lifetime by 30% for a given PDG process time and reduce PDG process cost by 43% for a given effective lifetime while achieving a constant sheet resistance. Alternative high-temperature cell processing may improve gettering kinetics while shortening total manufacturing time, thereby making silicon solar cell devices more cost-effective.

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