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Limitation of industrial phosphorus-diffused emitters by SRH recombination

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Abstract

It is commonly assumed in the PV community that Auger recombination is the dominant loss mechanism in heavily phosphorus-doped emitters of industrial Si solar cells. Contrary to this assumption, we show in this work that most of the losses are caused by Shockley-Read-Hall (SRH) recombination via defect states introduced by inactive phosphorus. Using numerical device simulations, we successfully reproduce all the measured \(J_0\) values of a series of profiles (with various concentrations of inactive phosphorus) with an effective SRH capture cross-section for holes, \(\sigma_p = 7.5 \times 10^{-18} \text{ cm}^2\). The composition of inactive phosphorus (e.g. in form of clusters of interstitial phosphorus, fine and rod-shaped precipitates) may vary under different fabrication conditions, hence we do not claim that this \(\sigma_p\) value is globally valid. However, because the series of profiles is representative for many emitters in mass production, our result implies generally higher SRH than Auger recombination rates and has decisive implications on the improvement of such industrial emitters: many emitters have not yet reached the Auger-limit and they may still be significantly improved by reducing their density of inactive phosphorus.

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1. Introduction

For most industrial crystalline Si solar cells, the low-cost screen-printed contacts require high phosphorus concentrations at the surface. Therefore, typical industrial diffusion processes result in profiles of electrically active phosphorus concentrations that are higher than $1 \times 10^{20} \text{ cm}^{-3}$ at the surface. Because of this high phosphorus surface concentration, it is widely accepted that Auger recombination is the dominant loss mechanism in such emitters. Based on this assumption it has been concluded that selective emitters suffer significantly less from recombination mainly because their peak dopant density is lowered.

On the other hand, it is well known that such heavily phosphorus-diffused emitters contain high amounts of electrically inactive phosphorus that may lead to precipitation phenomena [1-4]. It was already suggested in the early 80s to consider these precipitates as SRH recombination centers, that influence the excess carrier lifetime in the emitter region and reduces the open-circuit voltage [5, 6].

Although recent progress demonstrates that the reduction of inactive phosphorus atoms improves cell efficiency considerably [7-9], it is not straightforward to determine whether SRH recombination (due to inactive phosphorus) is stronger than is Auger recombination (caused by the active phosphorus atoms).

To answer conclusively this question we analyse various emitter profiles, published in Ref. [10], where the amount of active and inactive phosphorus atoms was varied. In order to account for the influence of inactive phosphorus in our device simulation, we interpret it by SRH recombination as indicated in Ref. [6]. The fact that all measured saturation current density $J_{0e}$ values of the series of profiles can be successfully reproduced strongly indicates that the SRH recombination is the dominant loss mechanism in heavily doped emitters of typical industrial Si solar cells.

2. Simulation model

The numerical device simulations are performed with the software SENTAURUS in two dimensions. We apply the most recent silicon material parameters and device models from Ref. [11] and include the recently published parameterization for Auger recombination of Richter et al. [12]. Fig. 1 shows two representative density profiles of the active phosphorus $N_{\text{don}}$, obtained from electrochemical capacitance-voltage (ECV) measurements, and of the total phosphorus $N_P$, from secondary ion mass spectroscopy (SIMS) measurements [10]. Near the surface, we correct the SIMS profiles with the dotted red line to eliminate measurement artefacts.

![Fig. 1. Two representative SIMS and ECV measurements of POCl₃ emitters from Ref. [10]. The hashed area indicates the density of inactive phosphorus.](image-url)
The difference between $N_p$ and $N_{don}$ is shown as hashed area and indicates the concentration of inactive phosphorus $N_i$. It can be either in form of interstitial P atoms, inactive P clusters, fine silicon phosphide (SiP) precipitates, or even rod-like SiP structures. Since we do not know the exact composition, we choose $N_i$ as effective density of a single type of defect, thus the SRH capture cross-section for holes, $\sigma_p$, has an effective meaning. Note that, at low POCl$_3$ flows, the amount of $N_i$ is very small, while at high POCl$_3$ flows, there is a spill-over of precipitates up to 140 nm deep, where $N_{don}$ drops down to $2 \times 10^{19}$ cm$^{-3}$. Accordingly, the high minority carrier concentration in that region results in high SRH recombination rates. The starting material of the analysed experiment consists of boron-doped float zone wafers with a specific resistivity of 200 $\Omega$ cm. To measure the saturation current density $J_{0e}$ values, the emitters on both wafer surfaces were passivated using plasma enhanced chemical vapour deposition and were fired in a conveyor belt furnace to facilitate hydrogen passivation. See Ref. [10] for a detailed description of the experiment.

3. Results and discussion

The measured $J_{0e}$ values of all profiles in Ref. [10] can be reproduced in these simulations by concurrently adjusting a single value of $\sigma_p$ for all profiles, and by keeping the SRH surface recombination velocity of minority carriers $S_p$ as a free parameter. In order to distinguish which recombination type dominates, we consider the following two scenarios: (i) the “Auger scenario” neglects SRH recombination via inactive phosphorus, thus Auger recombination dominates; (ii) the “SRH scenario” takes SRH recombination via inactive phosphorus additionally into account. In both cases, SRH surface recombination and SRH bulk recombination (via the usual defects in the wafer) as well as radiative recombination are taken into account.

Fig. 2(a) compares the measured with the simulated $J_{0e}$ values in dependence of the POCl$_3$-flow maintained during deposition of the phosphorus silicate glass (PSG) layer. Because the SRH surface recombination velocity of minority carriers $S_p$ is a free parameter, it is plotted in Fig. 2(b) in dependence of the total phosphorus concentration $N_p$ at the surface, $N_{P,surf}$. The measured $J_{0e}$ values (crosses) can be reproduced with the Auger scenario (circles) only for very low POCl$_3$ flows, even if setting $S_p$ to its physical limit, the thermal velocity $v_{th}$. By contrast, the SRH scenario reproduces all measured $J_{0e}$ values (open rectangles) if using $\sigma_p = 7.5 \times 10^{-18}$ cm$^2$. Additionally, we observed in the SRH scenario that (i) for $\sigma_p < 7.5 \times 10^{-18}$ cm$^2$, the simulation cannot reproduce all of the measured $J_{0e}$ values, even when setting $S_p = v_{th}$; (ii) for $\sigma_p > 9 \times 10^{-18}$ cm$^2$, the simulation overestimates $J_{0e}$ of some samples in Ref. [10];
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(iii) even by using $\sigma_p = 8 \times 10^{-18} \text{ cm}^2$, the resulting $S_p$ values (diamonds) decrease towards high $N_{P,\text{surf}}$ in Fig. 2(b), which does not make physically sense. Hence, only a very narrow range near $\sigma_p = 7.5 \times 10^{-18} \text{ cm}^2$ eliminates any inconsistency between simulations and these experiments.

One possible empirical parameterisation of $S_p$, shown as line in Fig. 2(b), is:

$$S_p = 1091 \frac{\text{cm}}{\text{s}} \cdot \left( \frac{N_{P,\text{surf}}}{10^{19} \text{ cm}^3} \right)^{3.37} + 0.6 \frac{\text{cm}}{\text{s}} \cdot \left( \frac{N_{P,\text{surf}}}{10^{20} \text{ cm}^3} \right)^{3.84}$$

for $N_{P,\text{surf}}$ up to $8.4 \times 10^{20} \text{ cm}^{-3}$ for fired SiNx layers.

Alternative to this explanation, Yan and Cuevas [14] recently fabricated a series of emitters and reproduced their measured $J_{0e}$ values by empirically adjusting band gap narrowing (BGN). Indeed, they obtained a consistent BGN model, which yields a significantly stronger gap-shrinkage than Schenk’s quantum-mechanical model [15], which is used in our simulations. We therefore tried to reproduce the $J_{0e}$ values of Fig. 2(a) by using Yan and Cuevas’ BGN model. While such simulations (open triangles) reproduce $J_{0e}$ significantly better than with our Auger scenario, the model is unable to reproduce $J_{0e}$ at the POCl$_3$ flows of 500 and 750 sccm, even if setting $S_p = v_{th}$. With the BGN model of Yan and Cuevas, we simulated other emitters from industry, but failed in many cases. Our simulations of ion-implanted emitters, where no precipitates are present, significantly overestimate $J_{0e}$ when using that BGN model.

At high dopant densities, however, the Schenk’s BGN model may underestimate the gap-shrinkage, since the model does not account the increase of electron masses shown in Fig. 3(a). In order to clarify this uncertainty, we revised the Schenk’s BGN model by considering the increase of electron masses. Therefore, we perform an empirical parameterization of measured data in Fig. 3(a), we then use this parameterization as multiplication factor for the reduced effective mass in Schenk’s Padé approximation by assuming that the hole masses stay constant as observed in Ref. [16, 17]. As result, we found only a slight increase in BGN is derived compared to Schenk’s original BGN as shown as red dashed line in Fig. 3(b). We found currently no other physical reason why BGN should be as strong as proposed by Yan and Cuevas.

Fig. 3. Left: electron conduction mass in n-type silicon, measured by reflection [18-21] and by transmission [19]. Right: comparison of different BGN models
4. Implication

These findings have very useful implications to the fabrication of typical industrial emitters: A) their recombination losses are still dominated by SRH recombination and not Auger recombination; B) because inactive phosphorus may exist in various forms in various proportions of phosphorus clusters and precipitates, there will be no universal emitter model available for optimisation, but must be tuned to fabrication conditions. C) The good news is that this gives manipulation opportunities to significantly improve emitters by reducing the density of inactive phosphorus, e.g. by tuning the POCl₃-flow, by solid-state diffusion, or epitaxy. This finding is also predicted by process and device simulations using SENTAURUS shown in Fig. 4 and described in details in a forthcoming paper – while Yan and Cuevas imply that there is no perspective for improvement except by reducing \( N_{\text{dop}} \).

![Graph](image.png)

Fig. 4. Process and device simulations of industrial-type PERC cells predict that avoiding inactive phosphorus in the homogeneous emitter may increase cell efficiency by about 0.5% absolute.

5. Conclusion

In this paper, we show that the SRH recombination caused by inactive phosphorus dominates the recombination process in a typical series of heavily doped emitters of industrial Si solar cells. For modelling the influence of inactive phosphorus, we suggest to interpret it by SRH recombination with capture cross section for holes around \( 7.5 \times 10^{-18} \text{ cm}^2 \).

As alternative to our suggestion, the empirical BGN model of Yan and Cuevas can be applied for modelling heavily doped emitters. However, this model may not be suitable to describe carrier recombination in samples with high amount of inactive phosphorus atoms, if the SRH recombination due to inactive phosphorus is not accounted.

These results imply opportunities for significant improvement of cell efficiency by reducing the density of inactive phosphorus atoms, as demonstrated in Ref. [7-9].

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