ABSTRACT: In this contribution the impact of iron-boron pairs on silicon solar cells is investigated by numerical simulations and experiments. The parameters of a typical industrial solar cell are simulated in dependence of the iron boron pair contamination level and during the iron-boron-pair dissociation. A detrimental impact of the iron-boron pairs on the solar cell efficiency is found above a contamination level of about $[\text{Fe}] = 10^{11} \, \text{cm}^{-3}$. The results of the numerical simulation are compared to open circuit voltage measurements of illuminated p-n-junctions on iron contaminated boron doped silicon samples. For the first time the effect of the iron-boron-pair dissociation on the open circuit voltage is experimentally observed. This is confirmed by the appearance of a crossover point and by comparison to quasi-steady-state photoconductance measurements. To preserve interstitial iron in the silicon while forming the p-n-junction, gettering by the high temperature phosphorous diffusion step is avoided using a laser-doping method.

Keywords: Silicon Solar Cell, Impurities

1 INTRODUCTION

Silicon which is used for solar cell production is usually contaminated with iron. A small fraction of the total iron content is solved interstitially and, in the case of boron doped silicon, forms meta-stable pairs with the boron acceptor. Both states of the iron-boron pairs reduce the lifetime of minority carriers and thus are detrimental to the efficiency of solar cells. Fortunately, the iron-boron pairs are made harmless by gettering during the phosphorous diffusion step during the industrial solar cell production. Nevertheless, the impact of the iron-boron pairs on solar cells is of fundamental interest. Furthermore, a recent investigations of heavily iron contaminated Czochralski silicon shows that considerable amounts of interstitial iron remain in the solar cell [1]. In the first part of this paper we study the impact of iron-boron pairs on the solar cell parameters by numerical simulation of a typical industrial solar cell. The second part deals with the experimental investigation of iron-boron pairs in silicon with and without p-n-junction by quasi-steady-state open circuit voltage (QSS-$V_{OC}$) and quasi-steady-state photoconductance (QSSPC) measurements, respectively.

2 SIMULATION AND THEORY

2.1 Solar cell parameters

The impact of interstitially solved iron on the solar cell parameters is simulated using the software AFORS-HET v2.2 [2]. This software is chosen, because it is able to simulate more than one defect simultaneously. As a starting point a typical industrial n+p-solar cell is simulated using the properties which are summarized in Tab. 1.

The results of the numerical simulation are plotted in Fig. 1a-d. As expected from the literature [3, 4, 5] most of the parameters decrease with increasing interstitial iron contamination level. For this specific set of solar cell properties the interstitially solved iron becomes detrimental above a density of about $[\text{Fe}] = 10^{11} \, \text{cm}^{-3}$ (see Fig. 1d). In p-type silicon interstitial iron forms meta-stable pairs with the acceptor, which is usually boron [6]. Hence several states are introduced into the band gap caused by interstitial iron and by the iron-boron pairs. Due to the strongly differing defect parameters the minority carrier lifetime varies in both states of the iron-boron pairs. This has a strong impact on the solar cell parameters and thus the simulations are made for both states. The defect parameters of interstitial iron and the iron-boron pairs used for the simulation are taken from [7] and [8] respectively. For almost all defect densities the dissociation of the iron-boron pairs degrades the four solar cell parameters. Only around $[\text{Fe}] = 10^{12} \, \text{cm}^{-3}$ the open circuit voltage increases after dissociation of the iron-boron pairs (see Fig. 1a). This is due to the strongly differing capture cross sections of electrons and holes, which cause a strong injection dependence of the minority carrier lifetime, in the interstitial-iron state [9]. The minimum of the fill factor shown in Fig. 1c is also caused by this effect.

<table>
<thead>
<tr>
<th>Cell properties</th>
<th>Values</th>
</tr>
</thead>
<tbody>
<tr>
<td>Base doping</td>
<td>$2.2 \cdot 10^{19} , \text{cm}^{-2}$ and $1 \cdot 10^{16} , \text{cm}^{-3}$</td>
</tr>
<tr>
<td>Wafer thickness</td>
<td>200 µm</td>
</tr>
<tr>
<td>Emitter doping</td>
<td>$1 \cdot 10^{19} , \text{cm}^{-3}$</td>
</tr>
<tr>
<td>Emitter depth</td>
<td>1 µm</td>
</tr>
<tr>
<td>Bulk lifetime</td>
<td>200 µs</td>
</tr>
<tr>
<td>Front SRV</td>
<td>$5 \cdot 10^{12} , \text{cm}^{-2} \cdot \text{s}^{-1}$</td>
</tr>
<tr>
<td>Back SRV</td>
<td>$5 \cdot 10^{12} , \text{cm}^{-2} \cdot \text{s}^{-1}$</td>
</tr>
</tbody>
</table>

Tab.1: Numerical values of the solar cell properties taken for the simulation

2.2 Dissociation of the iron-boron pairs

Both states of the iron-boron pairs can be easily adjusted in the experiment (see section 3.2). To investigate the solar cell parameters during the dissociation process, the parameters are simulated for different ratios of the iron-boron pair fraction and the interstitial iron fraction. The dissociation process is described by an exponential law and the time constants of
density. The relation between the excess carrier density can be compared to measurements of the excess carrier region. Hence measurements of the open circuit voltage at the boundaries of the space-charge region. The open circuit voltage $V_{OC}$ is given by [11]

$$V_{OC}(\Delta n) = \frac{kT}{q} \ln \left( \frac{\Delta n (p_i + \Delta n)}{n_i^2} \right). \quad (1)$$

Here are $p_i$ the doping density and $n_i$ the intrinsic carrier density. Using this relationship, quasi-steady-state photoconductance (QSSPC) [12] measurements can be compared to quasi-steady-state $V_{OC}$ (QSS-$V_{OC}$) [13] measurements [9] in both states of the iron-boron pairs (see section 3.4).

![Fig. 1a-d: Simulated solar cell properties as a function of the density of the interstitially solved iron. Both states of the meta-stable iron-boron pairs are simulated.](image)

2.3 Calculation of the open circuit voltage

The open circuit voltage $V_{OC}$ measured on an illuminated p-n-junction is determined by the excess carrier density at the boundaries of the space-charge region. Hence measurements of the open circuit voltage can be compared to measurements of the excess carrier density. The relation between the excess carrier density $\Delta n$ and open circuit voltage $V_{OC}$ is given by [11]

![Fig. 2: Simulation of the open circuit voltage and the efficiency during dissociation of the iron-boron pairs for different iron-boron-pair contamination levels](image)

3 EXPERIMENTAL

3.1 Sample preparation

Adjacent wafers are taken from a boron doped Czochralski silicon ingot ($p_i = 2.2 \times 10^{15} \text{ cm}^{-3}$), which is contaminated with iron. A small fraction of the total iron content is interstitially solved [14] in the silicon giving the base for our investigations. All wafers are etched with an alkaline solution to remove the saw damage. One wafer referred to as A is coated with a silicon nitride layer, which minimizes the recombination of excess carriers at the surface [15], allowing measurements of the bulk minority carrier lifetime of the silicon. Two wafers (B and C) are diffused with phosphorus by different diffusion methods. First, the standard industrial POCl$_3$-diffusion step is applied to form the n-emitter (sample B) and second, a laser diffusion step, developed to dope thin silicon films on low temperature substrates [16], is used (sample C). In contrast to the first diffusion process, where the interstitial iron is gettered by the phosphorous doped region during the high temperature step, the second diffusion process preserves the interstitial iron in the silicon while forming the p-n-junction. Applying the laser diffusion step only a very thin surface layer covered by a phosphorous containing spin on glass is heated up

<table>
<thead>
<tr>
<th>Sample</th>
<th>Preparation</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>Raw wafer, silicon nitride passivated</td>
</tr>
<tr>
<td>B</td>
<td>POCl$_3$-diffused, rear metalized</td>
</tr>
<tr>
<td>C</td>
<td>Laser-diffused, rear metalized</td>
</tr>
<tr>
<td>D</td>
<td>Complete industrial solar cell</td>
</tr>
</tbody>
</table>

![Tab.2: Sample overview](image)
by an excimer laser pulse for a short period of time. Both diffused samples are contacted at the rear side by bringing up an industrial aluminum paste and sintering subsequently. The fourth wafer referred to as D is used to produce a complete solar cell by applying the standard industrial solar cell process (POCl$_3$-diffusion, SiN$_x$-coating, metallization and sintering). An overview of the samples used for this experiment is given in Tab. 2.

### 3.2 QSSPC lifetime measurements

The minority carrier lifetime of sample A is measured using the quasi-steady-state photoconductance (QSSPC) [12] method, which determines the photoconductance during illumination with a flash lamp. If the generation rate is known and steady state conditions can be assumed, the lifetime is extracted as a function of the excess carrier density. Fig. 3 shows the lifetime measurements of sample A after illumination with 30 flashes of the QSSPC flash lamp (red squares) and after storing the wafer in darkness for 24 h (black dots). This adjusts both states of the iron-boron pairs. Sample A was previously illuminated for 20 h at 1 sun to activate the boron-oxygen complex [17], which will otherwise disturb the iron-boron-pair dissociation routine. The interstitial iron content can now be determined by the difference of the lifetime in both states of the iron-boron pairs using the methodology developed in Ref. [18]. An interstitial iron content of [Fe$_i$] = 2.7·10$^{12}$ cm$^{-3}$ is obtained, which is representative for all other samples in the initial state, because adjacent wafers are investigated. The QSSPC measurements can be compared to measurements of the open circuit voltage revealing the impact of different preparation steps applied to the samples.

#### 3.3 QSS-V$_{OC}$ measurements

The quasi-steady-state open circuit (QSS-V$_{OC}$) measurement method [13] determines the open circuit voltage of a p-n-junction at different illumination levels. The sample is illuminated by a flash lamp assuming quasi-steady-state conditions. As shown in Eq. (1) the open circuit voltage depends on the excess carrier density, which itself is determined under steady-state condition by the minority carrier lifetime. Hence, changes in the lifetime due to defect reactions in the silicon will be detectable by measurements of the open circuit voltage.

Sample D is used to investigate the effect of the iron-boron-pair dissociation on the open circuit voltage of an industrial solar cell. Both states of the iron boron pairs are adjusted as described in section 3.2. The black and the red curve of sample D in Fig. 4 represent the iron-boron-pair and the interstitial-iron state, respectively. A slight decrease of 3 mV in the open circuit voltage at 1 sun after the dissociation is observed. The simulation predicts an increase of about 3 mV. Hence, the observed change in the open circuit voltage is not caused by the iron-boron pairs.

![Fig. 3: QSSPC lifetime measurements in both states of the iron-boron pairs of sample A.](image)

![Fig. 4: QSS-V$_{OC}$ measurement of the samples B and D before and after different illumination steps (see section 3.3).](image)
change in the measured signal is indeed caused by the iron-boron-pair dissociation [18]. The minority carrier lifetime as a function of the excess carrier density in the iron-boron-pair state crosses the lifetime curve in the interstitial-iron state (see Fig. 3).

3.4 Comparison of QSSPC and QSS-V\textsubscript{OC} measurement

The excess carrier density obtained by QSSPC measurements of sample A (see Fig. 3) can be transformed via Eq. (1) into open circuit voltage assuming a p-n-junction. For a direct comparison of QSSPC and QSS-V\textsubscript{OC} measurements the illumination intensity of the flash lamp is plotted in Fig. 6 as a function of the open circuit voltage. Due to the lower lifetime caused by the missing surface passivation of sample C, the curves of the QSS-V\textsubscript{OC} measurement are shifted to higher illumination densities. The crossover point is clearly visible in both types of measurement and occurs at the same V\textsubscript{OC} value confirming the defect reaction, which is observed by the QSS-V\textsubscript{OC} measurement, to be caused by the iron-boron-pair dissociation.

![Fig. 5: QSS-V\textsubscript{OC} measurement of the laser doped sample C. The measurements are taken after 30 flashes (red line) and after storing the sample in darkness for 24 h (black line).](image)

![Fig. 6: Comparison of QSS-V\textsubscript{OC} and QSSPC measurement of sample C and A respectively. The excess carrier density is transformed to open circuit voltage using Eq. (1).](image)

4 CONCLUSION

It is of fundamental interest to understand the impact of iron-boron pairs on the solar cell parameters. Simulations of a typical industrial solar cell reveal, if the iron is not gettered, a detrimental contamination level of interstitially solved iron of about [Fe\textsubscript{i}] = 10\textsuperscript{11} cm\textsuperscript{-3}. To avoid gettering by high temperature diffusion steps, p-n-junctions are prepared on iron contaminated silicon samples by applying a laser-doping process. The effect of the iron-boron-pair dissociation is observed for the first time by quasi-steady-state open circuit voltage (QSS-V\textsubscript{OC}) measurements. A crossover point of the open circuit voltage measurements proves the effect to be caused by iron-boron pairs. The QSS-V\textsubscript{OC} measurements are compared to quasi-steady-state photocconductance measurements.

ACKNOWLEDGEMENT

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REFERENCES