IMPACT OF IRON CONTAMINATION ON CZ-SILICON SOLAR CELLS

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ABSTRACT: We have systematically investigated the influence of iron on the performance of industrial Czochralski mono-

crystalline silicon solar cells. The study focused on the behavior of interstitial iron as a recombination center at three stages

of the industrial solar cell fabrication sequence: (i) on as-cut wafer level, (ii) after phosphorous diffusion and (iii) after

completed solar cell process. The investigated wafer groups were carefully chosen to represent different ingots with various

electronic properties (lifetime and purity levels). The electronic properties of the wafers were investigated by minority carrier

time measurements in order to determine the effective lifetime and the interstitial iron content. In one of the ingots,

neutron activation analysis was used to determine the total impurity concentration of the silicon raw material, revealing many

different contaminants. In this ingot, iron was found to have the highest impurity concentration. Combining the results of

both methods, we found that 0.2 % of the total iron atoms present in the sample are in interstitial form. Complete solar cells

were made from all wafer groups and analyzed by means of current-voltage characteristics. The surprising finding is that, in

spite of high iron contamination, very high solar cell conversion efficiencies could be achieved. Considerable amounts of

interstitial iron were detected not only in as cut wafers but also after phosphorous diffusion and even in the readily processed

solar cells, revealing the gettering steps to be not as efficient as expected.

Keywords: Feedstock, interstitial iron, Impurities, crystalline silicon solar cells, CZ silicon, gettering

1 INTRODUCTION

Because of the undeniable difficulties the photovoltaic (PV) industry is currently facing in securing silicon feedstock to support its expansion strategy and to meet the rapid growth of the solar cell market, sources for a wide variety of solar grade (SoG) lower-cost silicon (Si) is necessary. This is possible by exploiting sources of off-grade silicon feedstock from the microelectronic industry or reducing the silicon production process steps and/or time such as increasing the pulling speed of the CZ Si or lowering the degree of cleanliness and control in the crystal-growth process. Since the crystal growth conditions play a primary role in determining the density of precipitation sites for impurities, the above mentioned steps result in attenuating the reduction of impurities in the products. Metallic impurities are prevalent contaminants in Si and can severely degrade the performance of the final devices either by forming metal silicides or/and by acting as recombination centers. In addition to the impurity amount introduced during crystal growth, commonly reported sources of impurity contamination include high temperature process tools (annealing oven, RTP furnaces or diffusion tools), contaminated chemical solutions, and wafer handling tools. Iron is one of the primary metal impurities in Si with remarkable properties such as the decoration of defects and the formation of precipitates as well as the pairing with doping acceptors such as substitutional boron (B) in p-type silicon. Unprecipitated iron remains as the interstitial deep level impurity Fei or as Fei–B pairs in p-type silicon. It can dramatically change the injection level dependence (ILD) of the minority carrier lifetime, resulting in the modification (usually degradation) of the device performance.

Numerous studies are dedicated to the behavior of iron impurities in multicrystalline silicon (mc-Si) in its different forms such as ribbon or the Edge-defined Film-fed Growth (EFG). In general, it is known that mc-Si shows very good response to phosphorous (P-) diffusion gettering and Aluminum-silicon (Al-Si) alloying induced gettering of metallic impurities such as Fe. Ribbon Si, in contrast, respond more favorably to SiN-induced Hydrogen (H-) passivation of defects. Unfortunately very little is known about these effects in CZ Si, which is also a leading substrate for industrial solar cells. To our knowledge, the rare studies which dealt with this subject focused mainly on intentionally contaminated silicon, for instance by means of ion implantation and in most cases on small samples.

The goal of this contribution is to determine, whether a correlation exists between impurity distribution, lifetime and the performance of CZ Si solar cells.

2 EXPERIMENTAL

The investigations were carried out on different groups of p-type CZ Si wafers from several ingots provided by ersol solar energy AG. All ingots were manufactured for research purposes under various conditions, which differ from those used for the standard production. The wafers are of standard proportions with thicknesses below 200 μm and an area of 156·156 mm². The resistivity ranges between 3 and 10 Ωcm (corresponding to a doping level from 1.3 to 4.7·10^{15} cm^{-3}). The wafer groups are coded A, B, E, F, G and I, respectively. The groups A and B are assigned to two ingots, which are manufactured using the same puller but under different growth conditions, resulting in very
different lifetime ranges. The groups E, F, G were extracted from three locations along the growth direction (bottom, middle, and top) of an ingot. Group I is an additional ingot with a very low lifetime.

On the wafer level, lifetime investigation tools such as the microwave detected photoconductance decay (µW-PCD) and the quasi-steady-state photoconductance (QSSPC) methods were used to determine the spatially resolved lifetime, the ILD lifetime as well as to evaluate the content of interstitial iron [Fe] \(^\text{\varepsilon}\). To allow meaningful lifetime measurements, the surfaces were passivated by means of the plasma-enhanced chemical-vapor deposition (PECVD) of Si-rich hydrogenated amorphous Si nitride (\(a\)-Si\(_3\)N\(_x\) :H) films on both wafer surfaces in an AK 1000 PECVD reactor. Prior to deposition, the wafers were subjected to KOH-etch to remove the saw-damage followed by a standard RCA cleaning procedure. Besides other impurities the total iron content in ingot I was determined by means of Neutron Activation Analysis (NAA) \(^\text{\varepsilon}\) at the Research reactor of the Helmholtz-Zentrum für Energie und Materialien Berlin GmbH. The technique is based on the irradiation of the sample with neutrons in a nuclear reactor and the analysis of the residual radioactivity (γ-ray) of the excited state of the compound nucleus resulting from the interaction of the neutron with the target nucleus. The solar cell fabrication was performed in a standard industrial in-line process including damage etching/ texturization, phosphorous diffusion, \(a\)-Si\(_3\)N\(_x\) :H antireflection coating (ARC) and screen printing followed by co-firing. Solar cell analysis were performed by means of conventional current-voltage measurements under standard conditions (AM 1.5, 1000 W/m\(^2\), 25 °C) using a calibrated tool. To investigate the properties after P-diffusion, some samples were subjected to a HF-dip and a KOH etching step to strip the P-silicate glass and the diffused layer, respectively, followed by surface passivation with \(a\)-Si\(_3\)N\(_x\) :H. Some of the solar cells were etched back and subsequently passivated to allow carrier lifetime measurements.

3 RESULTS

3.1 NAA Analysis

Carefully prepared samples from ingot I are subjected to neutron activation for more than 2 weeks and subsequently, the γ-ray spectrum is measured yielding trace levels of impurities in the samples.

![Fig. 1: Elemental distributions of metal impurities in a wafer from ingot I detected by NAA in ingot I](image)

As shown in Fig. 1, the impurity detection by NAA reveals the presence of a large number of impurities and that iron is the most abundant contaminant, at least in this ingot.

3.2 Lifetime measurements

As a first step, we measured the lifetime of numerous wafers from different ingots and analyzed the interstitial iron content.

Fig. 2 gives an overview of the lifetime distribution of representative wafers from each group (please note the different scales because of the very different lifetime ranges).

![Fig. 2: Lifetime distribution over the area of representative samples from the investigated ingots. The letters refer to the wafer groups.](image)

Looking at the two dimensional (2D) lifetime images of ingot A and B, which were grown in the same puller, it is obvious to see how the growth conditions of the feedstock strongly govern the magnitude and the distributions of charge carrier lifetime. Ingot A has a tight lifetime around 180 µs over the whole wafer area, while ingot B shows a strong inhomogeneity of the lifetime distribution with regions reaching relatively higher lifetime in the ms range as well as regions with lifetimes below 10 µs. These degraded regions which dominate the 2D lifetime maps are distributed all over the area in the form of stripes likely due to sawing induced damage of the wafer bulk or extending over a relatively wide circular region at the contour of the wafer. As to the ingot E/F/G, a gradually decreasing effective lifetime from top to bottom is visible. The lifetime images reveal that this decrease is attributed to the increasing area of a region with lower lifetime in the center of the ingot as clearly seen in the lifetime images corresponding to groups E, F and G. The 2D maps of the wafers from ingot I show homogeneously distributed lifetime with an average around 10 µs. The lifetime values averaged over the area of each wafer as well as over a high number of measured wafers are plotted in Fig 3a.

In average, ingot B has the highest lifetime around 900 µs, followed by ingot A (150-180 µs), while the ingots E/F/G and I feature the lowest averaged lifetimes, respectively, with a clear dependence on the ingot
position. In addition, he results obtained by means of 
µW-PCD correlate very good with those from QSSPC 
around the excess carrier density of $10^{15}$ cm$^{-3}$ (not 
shown).

![Fig. 3](image)

**Fig. 3:** Lifetime obtained from averaging the 2D µW-
PCD maps over a large number of wafers, interstitial iron 
content and resistivity in the different ingots as well their 
distribution in as cut wafers in columns along the ingot 
E/F/G. The data refer to as received, damage etched, 
cleaned and passivated wafers.

According to the iron detection approach based on 
the QSSPC-lifetime measurements $^2$ in the dark and after 
light-soaking, the wafers from the ingot A contain interstitial iron 
amounting to $10^{15}$ cm$^{-3}$ (Fig. 3b). In the wafers from the ingot B, no iron could be detected by this 
procedure (detection limit ~ $10^{10}$ cm$^{-3}$). Ingot I and EFG 
feature high iron contents surpassing $5 \cdot 10^{11}$ cm$^{-3}$ to 
$2 \cdot 10^{12}$ cm$^{-3}$ and a dependence of this on the ingot 
position. Comparing the interstitial iron amount of 
$2 \cdot 10^{12}$ cm$^{-3}$ to the total concentration of $10^{15}$ cm$^{-3}$ detected 
by the NAA, we conclude that two parts per thousand 
(0.2 %) atoms of iron is in interstitial form.

In large part, a clear correlation between the minority 
carrier lifetime and [Fe] can be seen. The higher [Fe], 
the lower is the lifetime. This is also true for the wafer 
groups E, F and G emanating from the same ingot, in 
which the lifetime is strongly related to the distribution of 
$[Fe]$ along the ingots. The increasing iron content 
towards the bottom can be explained by segregation of 
iron in the melt during ingot growth.

The resistivity of the different groups as averaged 
over several wafers was measured by means the four-
point-probe method after annealing the sample at 600 °C 
to eventually destroy the thermal donors. For this 
purpose, other wafers than those used for lifetime 
analysis were dedicated to exclude any effect of the 
annealing on the lifetime, since the latter can degrade 
under the influence of high temperatures. The results are 
plotted in Fig. 3c. In general, the resistivity is very 
homogeneously distributed over the whole wafer area and 
between the samples with a striking exception for ingot 
B, but differs for the wafer groups. In all wafers from 
ingot B, the regions which were found to show strongly 
degraded lifetime (contour) are highly resistive with 
doping levels below $6.5 \cdot 10^{15}$ cm$^{-3}$, while over the 
remaining of the area the highest doping level around 
$7 \cdot 10^{15}$ cm$^{-3}$ has been found. Particularly, an increase from 
the top to bottom is visible in the ingot EFG, which 
correlates well with the segregation coefficient (0.8) of 
boron in silicon$^8$.

3.3 Processing of industrial solar cells

The results of the IV-characterization of solar cells as 
processed from these wafers by the industrial process are 
plotted in Fig. 4. The wafers are processed to solar cells 
in two runs. Run one consists of groups A and B and run 
two of groups E/F/G and I. Ingot A and B features the 
lowest solar cell performance, in spite of the highest 
lifetimes and the lowest iron content compared to the 
other ingots. Comparing the iron contaminated ingot A 
with ingot B, a decrease of the open-circuit voltage by 
about 3 mV and a slight degradation of the conversion 
efficiency ($\eta$) of the solar cell from ingot A by 0.2 % 
compared to the ingot B can be clearly seen.

As to the three wafer groups of the ingot E/F/G, 
clearly higher solar cell parameters are obtained. The 
values of the open-circuit voltage ($V_{OC}$) exceeding 
610 mV for the whole ingot are quite high for the 
measured resistivity range (doping level ~ 3 to 
$4.5 \cdot 10^{15}$ cm$^{-3}$). Also the short-circuit current ($J_{SC}$) above 
$35.6$ mA/cm$^2$ shows no sign of drop which could 
the result of iron induced recombination centers.

![Fig. 4](image)

**Fig. 4:** Solar cell parameters as deduced from IV-
measurement of the industrially processed solar cells.

Even the fill factor (FF) above 76.5%, which is known to 
become severely degraded by the injection level 
dependence (ILD) of the lifetime as $[Fe]$ increases$^5$, does 
not show any distinguishable degradation.
However, no monotonous trends were found for the electrical parameters, if going from top via center toward bottom of the ingot, as were observed for [Fe]i and lifetime. More striking among these findings is that the solar cells from the center (F) of the ingot E/F/G exhibit the highest performance followed by ingot I in spite of the highest iron content and the lowest lifetime.

Comparing the conversion efficiency between 16.7 and 16.8 % (in average) of the two best wafer groups F and I, we see that this high performance is mainly governed by \( V_{OC} \) which is some mV higher for F, while \( J_{SC} \) and FF are in the same order for both groups.

To get information about this anomalous behavior, lifetime investigations were done at different stages of the solar cell fabrication process, namely after diffusion and after the completed solar cell process. Fig. 5 shows the ILD lifetime in the dark and after the light-soaking of an as cut wafer, after diffusion and stripping off of the diffused layer as well as after solar cell fabrication. It is obvious that the lifetime after each step of the process increases after light-soaking. This is a clear sign of the presence of interstitial iron in the silicon.

![Fig. 5: Injection level dependent lifetime of a wafer from ingot I. This behavior is representative also for the other wafers.](image)

Applying this, [Fe]i after each step was determined and the results are plotted in Fig. 5. The surprising observation is that considerable amounts of interstitial iron remain in the silicon after the P-diffusion step as well as after the co-firing process. Hence, there is no perceivable response to the P-gettering, since the iron distribution remains nearly unchanged after this step for all wafer groups. This can be explained either by an inefficient P-gettering or by the compensation of the gettering effect through dissolution of the iron precipitates acting as an inexhaustible source for interstitial iron. Beyond this, even in group B interstitial iron is found, the appearance of which step might stem either from dissolution of precipitates or from contamination from the process equipment after the high temperature diffusion.

In contrast, a clearly distinguishable change is observed after the solar cell process. An overall decrease of the iron content is seen. For all ingots, [Fe]i was reduced. With the exception for the wafer groups E and F still having [Fe]i above \( 10^{11}\) cm\(^{-3}\), for all other ingots [Fe]i drops below this value, which was demonstrated by our simulations to be the maximum acceptable level below which no degradation of the device performance occurs\(^{11}\). Even in ingot B which was not contaminated at the beginning of the process, [Fe]i amounts to nearly \( 3 \times 10^{10}\) cm\(^{-3}\). In spite of high [Fe]i in the samples of ingot E and F, no impact on the solar cell parameters is observed. This can be explained by a large standard deviation in the solar cell parameters (as visualized by the error bars in Fig. 4).

![Fig. 6: Interstitial iron content determined at different stages of the process chain.](image)

Focusing furthermore on the behavior of the ingot E/F/G, we see that the iron content at the end of the process exhibits precisely the opposite trend along the ingot length compared to the as cut wafers. This was true also for the lifetime (not shown), which shows a considerable increase from the bottom towards the top of the ingot.

4 CONCLUSION

We investigated different wafers of CZ Si originating from several ingots, which were grown under different conditions. Apart from one ingot (B), which contains no detectable amount of interstitial iron before the beginning of the solar cell process and features high lifetimes in the millisecond range, all other ingots were found to be heavily contaminated by iron (e.g. interstitial iron content \( 10^{11} \) - \( 2 \times 10^{12}\) cm\(^{-3}\)). A clear correlation between interstitial iron content and lifetime was found (cp. Fig. 3 and 6). Samples from one of the ingots were investigated by NAA revealing the presence of different impurities with iron having the highest concentration exceeding \( 10^{15}\) cm\(^{-3}\). The interstitial iron as evaluated by means of lifetime measurements amounts to \( 2 \times 10^{12}\) cm\(^{-3}\), hence two among 1000 atoms are in the interstitial forms. This ratio is even lower than the reported ones for mc-Si materials\(^{11}\). This is remarkable because we assumed that mono-crystalline Si contains less heterogeneous nucleation sites for the formation of iron containing precipitates. The interstitial iron was found to influence the lifetime but does not have any detrimental effect on
the solar cell performance. Regardless of the contamination levels, the solar cell performance (including all electric parameters) was relatively high and showed no correlation to the amount of iron impurities in the as-cut wafers of the base material. After phosphorous diffusion and after the solar cell process, high concentrations of interstitial iron remain in the silicon, which means that P-gettering and Al-Si-gettering are not as effective as expected. However, it is found that high contamination levels, e.g. total iron above $1 \times 10^{15}$ cm$^{-3}$, do not affect the solar cell efficiency and hence is tolerable in the industrial CZ silicon solar cell manufacturing process.

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