

Iron gettering in CZ silicon during the industrial solar cell process

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ABSTRACT. We investigated the impact of using low quality feedstock such as recycled silicon and simplified pulling condition on the performance of CZ silicon solar cells. Groups of wafers carefully chosen from different ingots were analyzed after different solar cell process steps by minority carrier lifetime measurements, by measurements of the interstitial iron content and by measurements of the total impurity content using NAA. Our results show that the main electronic properties of the ingots, namely the carrier lifetime, interstitial iron content and base resistivity are strongly affected by feedstock quality. Surprisingly, high solar cell efficiencies were achieved using highly contaminated silicon. These positive results are due to the beneficial effect of impurity segregation gettering by phosphorous diffusion and aluminum alloying. Post-diffusion gettering by an additional annealing step was demonstrated to enhance the charge carrier lifetime.

Introduction

Czochralski (CZ) single crystalline silicon accounts for about 40 % of the photovoltaic market [1]. Hence it has a leading position as base material for industrial solar cells. To make it economically more attractive, the production costs have to be reduced. This can be achieved by using less pure feedstock material or by modifying the pulling condition towards low-cost production. However, this approach results in a high contamination level by impurities requiring the solar cell fabrication process to be adapted to a maximum tolerable impurity concentration. Numerous studies are dedicated to the behavior of impurities, especially iron in multicrystalline [2, 3 and references therein] but very little is known about these effects in CZ grown silicon. Here we perform a quantitative analysis of the electronic properties of unintentionally contaminated CZ silicon wafer from different ingots. The goal of this contribution is to determine, whether a correlation exists between contamination level, minority charge carrier lifetime, process process variation and the performance of CZ silicon solar cells.

Experimental

Our investigations were carried out on different boron doped *p*-type CZ Silicon ingots manufactured by ersol Solar Energy AG for research purposes under various conditions. The as-received wafers have a thickness below 200 μm before removing a saw-damaged layer of 12 μm and an area of 156×156 mm^2 . The wafer groups are coded A, B, E, F, G and I, respectively. The groups A, B and I correspond to three different ingots, each cut from a single crystal, while the groups E, F and G are assigned to three ingots, which were extracted from three locations (bottom, middle, and top) of a single crystal. Ingot I was made of recycled silicon. As lifetime investigation tools, we used the microwave detected photoconductance decay (μW -PCD) and the quasi-steady-state photoconductance (QSSPC) methods to determine the spatially resolved lifetime (2D maps), the injection level dependent lifetime as well as to evaluate the content of

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interstitial iron $[Fe_i]$ after various process steps. Surface passivation was made by amorphous Si nitride ($a\text{-SiN}_x\text{:H}$). In Ingot I, the total concentration of many contaminants was assessed by Neutron Activation Analysis (NAA) at the Research reactor of the Helmholtz-Zentrum Berlin. The specific resistivity (averaged over several wafers from each ingot) was measured by means the four-point-probe method after annealing the sample at 600 °C to eventually destroy the thermal donors.

Results and discussions

1. Measurements of the basic properties of the investigated ingots

Fig 1(a) shows the charge carrier lifetime obtained from the μW -PCD measurements by averaging over the whole surface of a single wafer then over the number of measured wafers. As shown in the figure, ingot A has a tight lifetime around 180 μs over the whole wafer area, while ingot B has in average high lifetimes in the ms range with a strong spatial inhomogeneity. As to the ingots E, F and G, a relatively low and gradually decreasing effective lifetime from top (~40

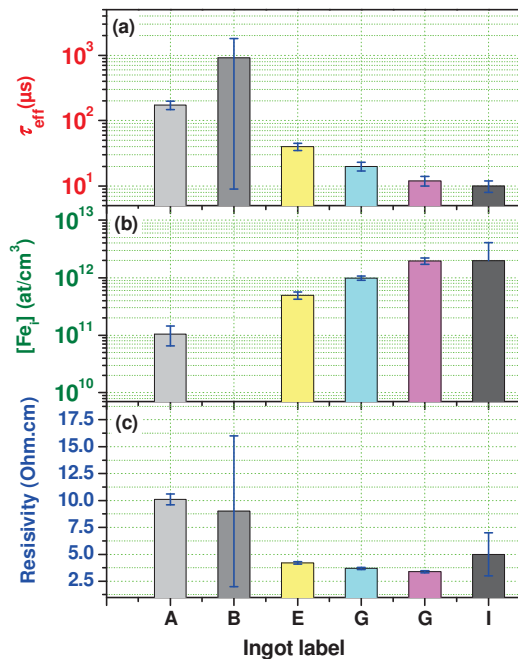


Fig. 1: (a) Effective minority carrier lifetime obtained from averaging the 2D μW -PCD maps over a large number of wafers, (b) interstitial iron content and (c) resistivity in the different ingots as well their distribution in as cut wafers from three columns (E, F and G) along a single crystal.

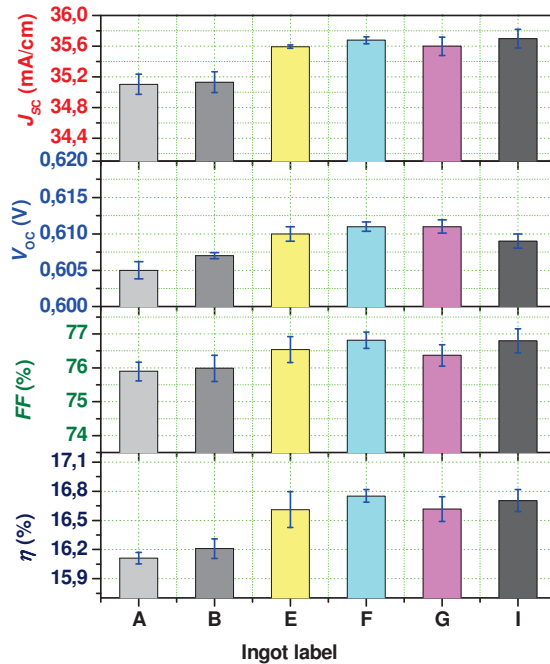


Fig. 2: Solar cell parameters as deduced from IV-measurement of the industrially processed solar cells.

μs) to bottom (~10 μs) is found. 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 .

According to the iron detection approach based on the QSSPC lifetime measurements in the dark and after light-soaking, the wafers from the ingot A contain interstitial iron amounting to 10¹¹ cm⁻³ (Fig. 1b). In the wafers from the ingot B, no iron could be detected by this procedure (detection limit ~ 10¹⁰ cm⁻³). The Ingot I, E, F and G feature high interstitial iron contents in the

range $5 \cdot 10^{11} \text{ cm}^{-3}$ to $2 \cdot 10^{12} \text{ cm}^{-3}$ and a dependence of this on the ingot position (see Fig 1(b)). In large part, a clear correlation between the minority carrier lifetime and $[\text{Fe}_i]$ can be seen. The higher $[\text{Fe}_i]$, the lower is the lifetime. This is in particular true for the wafer groups E, F and G emanating from the same crystal, in which the lifetime is strongly related to the distribution of $[\text{Fe}_i]$ along the ingots. The increasing iron content towards the bottom can be explained by segregation of iron in the melt during ingot growth. These findings demonstrate that $[\text{Fe}_i]$ impacts the carrier lifetime in as-cut wafers but it does not mean, that it is the dominant impurity. The results of resistivity measurements are plotted in Fig. 1(c). The ingots E, F, G and I have resistivities in the very narrow range of $3,5 - 5 \text{ } \Omega\text{cm}$. The averaging over several measurements revealed, that the resistivity is very homogeneously distributed over the whole wafer area and between the samples for these four ingots as well as for ingot A. However, the latter has relatively higher resistivity of about $10 \text{ } \Omega\text{cm}$. A striking exception is noted for ingot B, which features strong inhomogeneities in the resistivity distribution across the wafer surfaces. For the ingots E, F and G, a slight decrease from the top to bottom along crystal is visible, which can be attributed to the segregation coefficient (0.8) of boron in silicon [4].

2. Processing and analysis 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. 2. Ingots 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 on one hand, a decrease of the open-circuit voltage by about 3 mV and a slight degradation of the conversion efficiency (η) of the solar cell from ingot A by 0.2 % compared to the ingot B can be clearly seen. As to the ingots E, F and G on the other hand, clearly higher solar cell parameters are obtained with respect to A and B. The values of the open-circuit voltage (V_{OC}) exceeding 610 mV for the whole single crystal are on a sufficient level for the measured resistivity range ($3,5 - 4,2 \text{ } \Omega\text{cm}$). Even the fill factor (FF) above 76.5%, which is known to become severely degraded by the injection level dependence of the lifetime (e.g., because of $[\text{Fe}_i]$ deep levels) does not show any distinguishable degradation. However, no monotonous trend was found for the electrical parameters, if going from top via center toward bottom of the crystal, as were observed for $[\text{Fe}_i]$ and carrier lifetime (Fig. 1). Even ingot I made from low quality recycled feedstock results in high performance. Comparing the conversion efficiency between 16.7 and 16.8 % (in average) of the two best ingots 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 ingots.

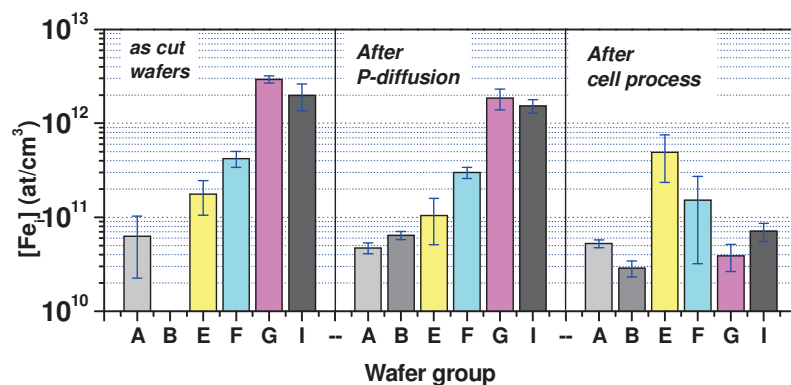


Fig. 3: Interstitial iron content determined at different stages of the process chain.

to achieve a low surface recombination. The results are plotted in Fig. 3. The surprising observation is that considerable amounts of interstitial iron remain in the silicon after the P-diffusion step as well as in the completed solar cells. Hence, there is no perceivable response of $[\text{Fe}_i]$ to the P-diffusion gettering, since the iron distribution remains nearly unchanged or minor

To check whether any relation exists between the presence of iron and the solar cell parameters, $[\text{Fe}_i]$ was determined at the main stages of the solar cell fabrication process, namely in as-received wafers, after phosphorous (P-) diffusion as well as after the completed solar cell process. Therefore, wafers were completely etched and passivated with $a\text{-SiN}_x\text{:H}$

after this step for all ingots. This can be explained either by an inefficient P-gettering or by the compensation of the gettering effect through re-dissolution of the iron precipitates acting as an inexhaustible source for interstitial iron. Furthermore, even in group B interstitial iron is found found not intentionally but after processing. That 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. 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 [5]. Even in ingot B which was not contaminated at the beginning of the process, $[Fe_i]$ amounts to nearly $3 \cdot 10^{10} \text{ cm}^{-3}$.

Focusing furthermore on the behavior of the ingots E, F and G, we see that the iron content at the end of the process exhibits precisely the opposite trend along the crystal 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 crystal.

3. NAA Analysis

To check the existence of other impurity elements, carefully prepared samples from ingot I were

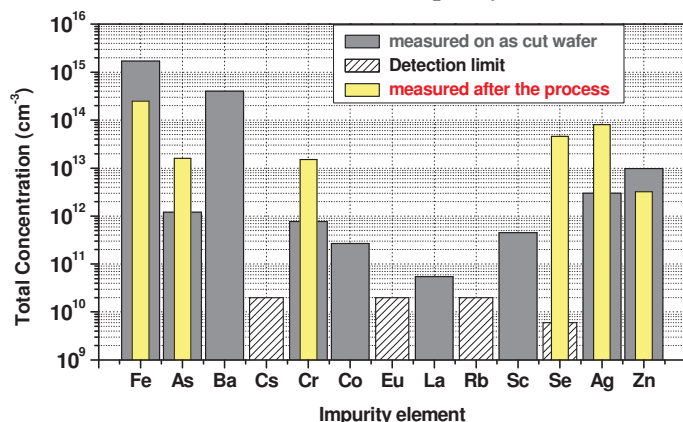


Fig. 4: Elemental distributions of metal impurities in a wafer from ingot I detected by NAA in ingot I

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. One sample was prepared from as-cut wafers and two other samples were obtained by etching the metallization scheme and the diffused region of solar cells. As shown in Fig. 4, in addition to several transition metals with high concentrations such as Cr, Co, Sc, Ag and Zn, other active metals from the second group such as Ba

or from the semimetals such as Se were detected in this material. The major contaminants with concentration above 10^{13} cm^{-3} are Fe, Ba, Cr, Se, Ag and Zn with Fe as the most abundant contaminant in this ingot with a concentration exceeding 10^{15} cm^{-3} . Comparison of the data for as-cut samples and for solar cells indicates, that the concentration of some detected impurities experienced a reduction (Fe, Zn) or even a drop below the detection limit (Ba, Co, Sc or La) after the final solar cell process step which could be explained by a gettering efficiency. In contrast, As, Cr, Se and Ag were found to be more abundant after the final solar cell process, suggesting that the contamination was introduced or enhanced by the process itself. Comparing the total concentration of 10^{15} cm^{-3} to the interstitial iron amount of $2 \cdot 10^{12} \text{ cm}^{-3}$ assessed by QSSPC in the as-cut wafers, we conclude that about two parts per thousand ($\sim 0.2 \%$) atoms of iron is in interstitial form.

4. Effect of different high temperature process steps on the charge carrier lifetime.

To check how the material responds to the different high temperature (HT) processes encountered in the solar cell manufacturing chain, we measured the lifetime of adjacent wafers from ingot I after exposing them to various individual HT steps. The recombination lifetimes measured by the QSSPC procedure are depicted in Fig. 5. On one hand, departing from as-cut wafers and applying a standard P-Diffusion (POCl_3 source), an increase of the carrier lifetime by

nearly an order of magnitude can be seen.

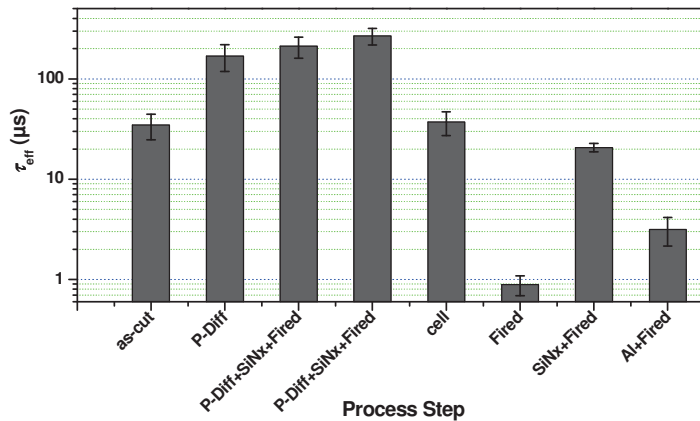


Fig. 5: Impact of various HT process steps on the minority carrier lifetime. “Cell” refers to wafers obtained by etching the metal contacts, *a*-SiN_x:H antireflection coating and the P-diffused layer.

a-SiN_x:H coating alone acts as barrier for firing-induced degradation of the lifetime, but results in a severe degradation as well with respect to the as-cut wafer. Also an Al coating on one side has an overall degradation effect. These findings are evidence, that the investigated material responds well to the segregation gettering provided by P-diffusion and Al-alloying. The increase of carrier lifetime in ingot I after P-diffusion without any reduction of [Fe_i] (compare with Fig. 3) suggests that iron is not the sole contaminant governing the carrier lifetime. The additional improvements due to Al-alloying shows, that the combination of Al and P-gettering are responsible for the drop of [Fe_i] in the final solar cell process. However, adding the screen printed silver grid prior to firing to complete the solar cell results in no significant change in the carrier lifetime. Similarly, a decrease of the iron content in the solar cell with respect to as-cut wafers is not necessarily accompanied by a remarkable increase of the carrier lifetime. This in turn could mean, that in spite of gettering iron away from the bulk silicon, other contaminants could have impacted the lifetime, e.g., by increasing their content. Calculating the lifetime in the absence of interstitial iron shows that other potential impurities could also be getterred, suggesting that gettering efficiency in the test wafers can not be solely attributed to the decrease in [Fe_i].

5. Effect of Post-diffusion gettering

The previous section demonstrated the beneficial effect of phosphorous diffusion in inhibiting

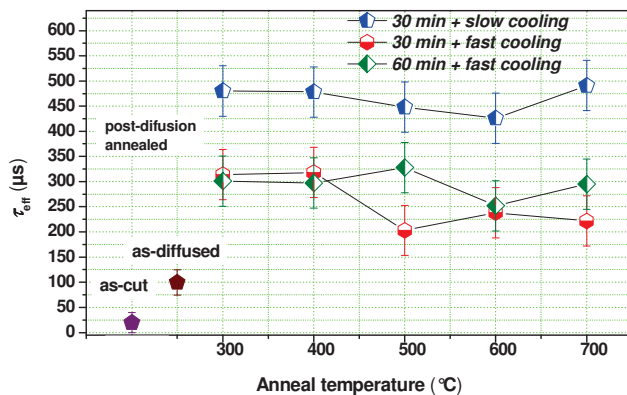


Fig. 6: Effective lifetime of as-cut wafers from ingot I, after P-diffusion as well as after different annealing regimes as indicated in the figure.

An additional coating of the diffused wafer with *a*-SiN_x:H and firing the whole structure results in a slight increase of the effective lifetime by some tens of μs. The combination of P-diffusion and Al-coating followed by firing has a more beneficial effect inducing an additional increase of the lifetime. On the other hand, firing of as-cut wafers without any diffusion, *a*-SiN_x:H or metal coating reduces dramatically the minority carrier lifetime below 1 μs. The graph also reveals, that

the degradation or even increasing the carrier lifetime of contaminated wafers. A way to make the diffusion process step more efficient is to add an annealing profile to the diffusion process. This concept is known as variable temperature gettering [6], time temperature transformation (TTT) [7] or as extended gettering [8] and was mainly applied to multicrystalline silicon with different results [7, 8, 9]. We conducted annealing tests on P-diffused wafers from the ingot I (recycled feedstock) at different

temperatures lower than the diffusion temperature. The different annealing regimes consist of plateau temperatures varying from 300 to 700 °C. The annealing times were 30 and 60 min followed by slow (~ 15 °C/min) or fast cooling (quench within 5 min. The results are given in Fig. 6. After post-diffusion anneal and fast cooling, a further twofold to threefold increase is obtained with respect to as-diffused samples. The change of the anneal duration (60 min vs 30 min) does not result in a significant additional lifetime improvement. However, a post-anneal slow cooling results in a much higher carrier lifetime. Beside the strong overall increase of the minority carrier lifetime, these annealing tests resulted in a drop of the interstitial iron content from $2 \times 10^{12} \text{ cm}^{-3}$ below the detection level of 10^{10} cm^{-3} . In particular the slow cooling turned out to enhance the gettering activity by enabling the diffusing impurity atoms to reach the gettering sites. The fast cooling, in contrast, keeps atoms in a highly recombination active state (e.g. on interstitial sites) within the silicon matrix

Conclusion

We investigated different CZ single crystalline silicon ingots, which were grown under different conditions or from low quality feedstock. These different material qualities, which were applied to reduce the costs, resulted in a large range of minority carrier lifetimes and very different iron contamination levels. In addition of iron, the presence of numerous impurities in the ingot made of recycled silicon was manifested by neutron activation analysis. We have demonstrated that silicon wafer heavily contaminated with iron and having very low carrier lifetimes can be used to fabricate high performance solar cells. This property is attributed to the beneficial effects of segregation gettering of phosphorous diffusion and aluminum alloying. Different high temperature tests conducted on a large numbers of wafers, demonstrated that low-cost highly contaminated CZ silicon responds very positively to segregation gettering. In particular post-diffusion gettering by an additional annealing step was demonstrated to enhance the minority carrier lifetime. This process has great potential to be implemented in the solar cell fabrication sequence offering the possibility to increase the solar cell conversion efficiency whilst maintaining low manufacturing costs.

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