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MULTICRYSTALLINE FLOAT ZONE SILICON WITH FE AND MO IMPURITIES: SOLAR CELL PROCESS AND LIFETIME STUDIES

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ABSTRACT: The aim of this work is to provide an updated reference of the incorporation and the impact of impurities on solar cells performance in the current process technology for monocrystalline and multicrystalline silicon (Si) wafers. Molybdenum (Mo) and iron (Fe) are introduced in the Si melt from which Float Zone (FZ) ingots are crystallised. The impurity concentration in the feedstock ranges from 2.6 to 900 ppma for Fe and from 25 to 2800 ppma for Mo. A major drop in Voc and IQE is visible for samples with the highest Mo level. Fe results in different behaviour in mono and multicrystalline FZ Si wafers. In monocrystalline wafers the solar cell process is able to largely remove the Fe from the Si-bulk for concentrations up to 54 ppma. In multicrystalline Si, for all the Fe-impurity levels investigated, the results are equivalent and comparable to the worst results obtained for industrial directionally solidified mc-Si reference wafers.

Keywords: iron, impurities, feedstock

1 INTRODUCTION

At the moment, the PhotoVoltaic (PV) industry is facing a shortage in silicon feedstock. This has led to a steady introduction of less pure silicon. Also, it is expected that Solar Grade silicon (SoG-Si) made through the direct- or metallurgical purification route will become available on the market soon. Therefore, the PV industry should address the question how cell processes can be best adapted to less pure material, one of the topics of this study.

In this work we study the role of iron and molybdenum when intentionally introduced in a silicon melt before the crystallisation. The choice for these two elements is based on their known importance as a contaminant in wafers [1], and the fact that their physical properties are quite different [2]. The impact of the contaminants during industrial solar cells processing will be shown and analysed.

Some of this work is similar to the research performed in the 1980's by Westinghouse Corp [3]. Those results are still used as reference for the effect of impurities on the solar cell performance. However, those results were obtained with cell processing technology of the 1980's, and mostly on monocrystalline material. We expect additional and essential information from the comparison between multicrystalline and monocrystalline Si wafers.

The aim of this work is to provide an updated reference for the role of particular impurities in the current cell process technology for multicrystalline and monocrystalline silicon wafers.

2 APPROACH

The best way to investigate the impact of specific metal contaminants is to intentionally contaminate the material with a well-defined impurity concentration. At the same time the concentrations of other impurities should be kept as low as possible. In this experiment interactions with carbon and oxygen will not be considered since it complicates analysis of results.

Clean material can be most conveniently obtained by producing FZ ingots. FZ ingots can be grown from a multicrystalline seed, resulting in a multicrystalline ingot with a

range of crystal sizes. The crystal structure and the temperature history are not necessarily comparable to industrial directionally solidified (DS) multicrystalline silicon (mc-Si). However, varying the thermal history of FZ silicon and understanding its effects, will also improve the knowledge of the industrial mc-Si.

Unintentional contamination is most unlikely in the FZ growth technique, in contrast to small scale DS-Si. This is a big advantage, which was decisive in our choice for the method.

The other advantage of the FZ approach is the possibility for comparison between monocrystalline and multicrystalline material. This permits to study the incorporation and impact of impurities when present together with crystal defects.

2.1 Choice of the impurities

The impurities used for investigation in this work are iron and molybdenum. Fe is a dominant metal impurity in silicon wafers. It is a relatively fast diffusing impurity, thus it can be gettered. The diffusivity of Mo is not exactly known, but it is not a fast diffusing impurity [2]. Therefore precipitation and gettering are expected to be significantly different. Mo is not present in similar levels as Fe in silicon wafers but it is very detrimental for the lifetime. It has been detected in cast mc-Si by neutron activation analysis [1].

2.2 Material

Fourteen FZ ingots were grown, introducing three different concentrations of Mo and Fe and growing both monocrystalline and multicrystalline structures. Two reference ingots were grown without added impurities.

Impurity Cont. level	Mo		Fe	
	Mono	Multi	Mono	Multi
1		25		2.6
2		240		54
3		2800		860

Table I: Impurities added in the silicon melt in ppma.

The amount of impurity introduced is reported in Table I. Those ranges have been estimated targeting typical value of Mo and Fe in mc-Si [1]. The crystal solidification velocity varied between 1 and 2 mm/min.

The ingots were boron doped with a base resistivity of ~0.8

$\Omega\text{-cm}$ for the Fe-contaminated ingots and $\sim 1.7 \Omega\text{-cm}$ for the Mo ones. The ingot diameter was 40 mm. All ingots were grown with pedestal growth technique at IKZ Berlin.

After crystallisation the ingots suffer from residual stress. Thus it was not possible to wafer some of them before relaxing the stress by a thermal annealing. Monocrystalline Mo-doped samples could, so far, not be processed because the ingots were too fragile before annealing. In the case of Iron samples of both monocrystalline and multicrystalline wafers were characterised and processed.

In this work we present first results, from non-annealed ingots only. The reference FZ ingots have not been processed yet. So far, industrial DS mc-Si was used as reference.

2.3 Cell process

The solar cell process was a standard industrial firing through SiN_x process. The wafers received an alkaline saw-damage etch, a phosphorous diffusion in a belt furnace, and a remote plasma-enhanced CVD of SiN_x at ECN. The SiN_x is optimised for multicrystalline Si wafers in order to obtain a good anti-reflective coating as well as bulk- and surface-passivation properties at the same time. The screen-printed metallisation and co-firing was carried out at the University of Konstanz. The solar cells were then cut to $2 \times 2 \text{ cm}^2$. The solar cell efficiency on reference DS mc-Si was about 15%. The solar cell results are summarised in section 4.

3 LIFETIME MEASUREMENTS AND INTERPRETATION

The as-grown wafers received chemical polishing and a PECVD SiN_x deposition to passivate the surface in order to measure the bulk recombination lifetime.

	Mo [μs]		Fe [μs]	
	Mono	Multi	Mono	Multi
1	n/a	3.6	5.3	2.7
2	n/a	2.3	0.7	n/a
3	n/a	0.5	n/a	0.3

Table II: QSS-PC lifetime @ $\Delta n = 1 \times 10^{15} \text{ cm}^{-3}$. n/a means ingot could not be sawn before anneal due to stress.

In Table II the lifetime as measured with the QSS-PC is shown. The lifetime is quite low for all the wafers, and decreases with increase of both Mo and Fe concentrations, indicating the dominant impact of the impurities.

The lifetime of the monocrystalline sample is higher than that of the multicrystalline sample with the same melt doping.

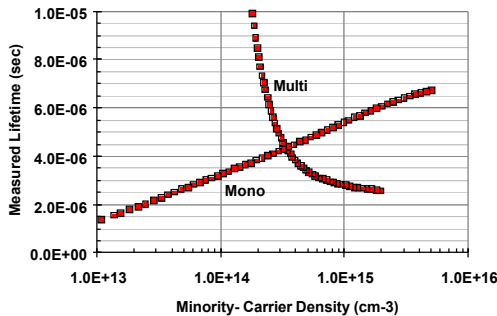


Figure 1: Effective lifetime as a function of minority carrier concentration for mono and multicrystalline samples with the lowest level of Fe.

The QSS-PC lifetime consistently shows trapping [4] for both the iron and molybdenum-doped mc-Si. In Fig. 1, as an example, the τ_{eff} versus Δn is reported of the samples with the lowest amount of Fe. A higher apparent lifetime is visible for the mc-Si sample at low injection level. It is otherwise clearly visible that no trapping is present in the case of monocrystalline samples.

Therefore, the trapping seems to be directly related to the grain boundaries or decoration thereof, rather than to just the presence of either Fe or Mo.

3.1 Modelling

To interpret the lifetime variation shown in Table II a simple model is adopted. The aim is to analyse the relationship between the impurities intentionally introduced and the lifetime obtained.

The effective lifetime can be modelled using Shockley-Read-Hall theory:

$$\frac{1}{\tau_{\text{eff}}} = \frac{1}{\tau_{\text{other}}} + \frac{1}{\tau_{\text{SRH}}} = a + b \cdot N_t \quad (1)$$

$1/\tau_{\text{SRH}}$ is the recombination due to defects created by the contamination with impurity (Fe or Mo). $1/\tau_{\text{SRH}}$ is proportional to the density of such defects (N_t). $1/\tau_{\text{other}}$ is the recombination not linearly related to the concentration of the added impurity. $1/\tau_{\text{other}}$ may still be related to the presence of the impurities but it is not a function of their concentration.

We hypothesize that N_t is proportional to the amount of impurity introduced (Conc.) in the melt

$$\frac{1}{\tau_{\text{eff}}} = a + b \cdot k \cdot \text{Conc} \quad (2)$$

N_t could e.g. be related to point defects or small homogeneously nucleated precipitates.

In Fig. 2 the inverse effective lifetime is shown as a function of Mo concentration (open squares). The figure shows a striking linearity between the inverse effective lifetime and the Mo concentration. The concentration of the defects N_t and the Mo concentration are proportional. There is not yet enough data to verify whether this holds for Fe, too.

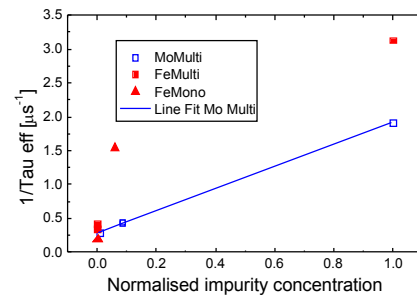


Figure 2: Inverse effective lifetime as function of impurity concentration. The impurity concentration is normalised to the highest introduced (see table I).

Concentrations of interstitial iron (Fe_i) were calculated from lifetime measurements [5] and are shown in Table III. These measurements are hard to do accurately for high iron concentrations, and the level in sample 3 is very uncertain.

Fe in melt	$\text{Fe}_i [\text{cm}^{-3}]$
---------------------	--------------------------------

	[cm ⁻³]	Mono	Multi
1	5×10^{17}	6×10^{12}	7×10^{12}
2	1×10^{19}	4×10^{13}	
3	2×10^{20}		$\sim 5 \times 10^{13}$

Table III: Fe_i calculated from lifetime measurements.

Chemical analysis is in progress in order to determine the total Fe concentration, and therefore the actual amount of Fe segregated in the solid silicon. It will then be possible to know, besides the effective segregation coefficient of Mo and Fe in silicon (for the mono and multi-crystalline structure), also the percentage of Fe present in form of interstitial impurity. In addition DLTS measurements are being performed, and when successful, will give similar information for Mo.

4 SOLAR CELL RESULTS

The solar cell process was carried out on three neighbouring wafers for each impurity concentration, of the available ingots shown in table I.

A set of four wafers of the same size as the contaminated ones was cut from a conventional multicrystalline wafer. This reference mc-Si wafer originated from a central brick of a good-quality industrial DS ingot. The Voc obtained ranges from 580 to 600 mV. This variation is due to the variation of the material quality inside this single wafer.

4.1 Molybdenum in solar cells

The Voc of the solar cells are shown in Fig. 3.

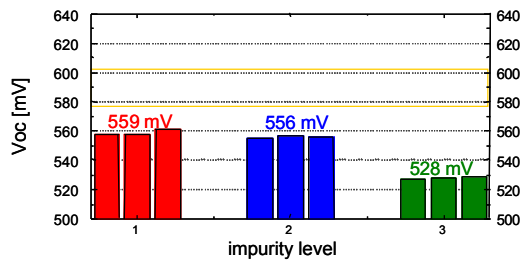


Figure 3: Voc of the solar cells contaminated with three different concentrations of Mo. Reference cast mc-Si range in dark.

The solar cells with the lowest and middle concentration (1 and 2 in Fig. 3) result in the same Voc, which is 35 mV lower than the reference cast mc-Si value of 592 mV. A drop in the Voc of about 60 mV occurs for the cell with the highest concentration of Mo.

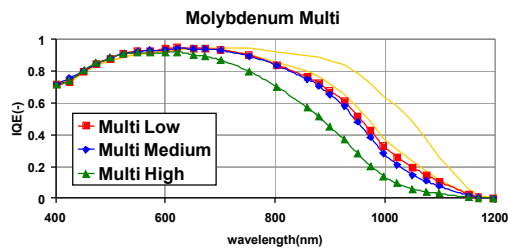


Figure 4: Internal quantum efficiency of solar cells with the three different Mo concentrations. Reference cast mc-Si range in dark.

Also in the internal quantum efficiency at 1000 nm (Fig. 4) the difference between the first two concentrations is still very

small.

4.2 Iron in solar cells

Fig. 5 depicts the results from the solar cells contaminated with Fe in case of monocrystalline (left) and multicrystalline (right) structure.

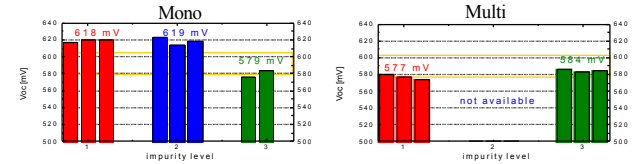


Figure 5: Voc of the solar cells contaminated with three different concentrations of Fe for mono (left) and multi (right). Reference cast mc-Si range in dark.

In the case of multicrystalline Si the Voc remains at the same level for the highest and the lowest concentration of Fe. A drop of 40 mV is instead present in the case of monocrystalline solar cells with the highest level of Fe. Still this Voc is comparable to the Voc of multicrystalline Fe-samples and to the lower value found on the reference DS mc-Si wafers.

It is surprising that such low lifetime values for mono Fe wafers result in high Voc. This will be analysed in a further work.

The Voc of the Fe contaminated samples is in all cases higher than the Mo one.

The IQEs confirms the Voc results as visible in Fig. 6.

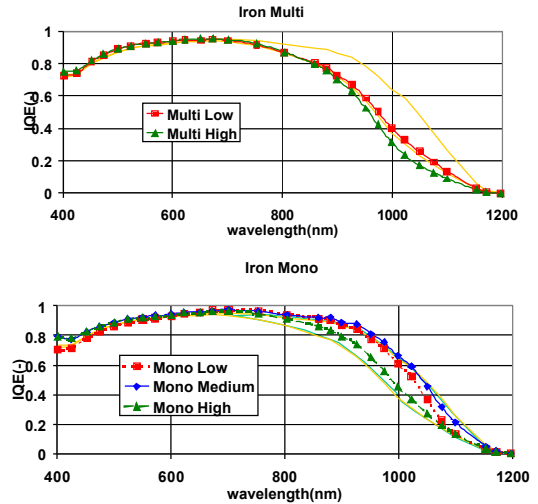


Figure 6: Internal quantum efficiency of solar cells with three different Fe concentration. Multicrystalline top, monocrystalline bottom. Reference cast mc-Si range in dark.

Furthermore from the overlapping of the IQE curves in Fig. 4 and 6 for low wavelength (<600nm) we conclude that the emitter diffusion and the SiN_x deposition were stable for all the solar cells.

5 DISCUSSION

The results for Mo, when compared with equation 1, show the presence of a high recombination activity independent of the Mo concentration (τ_{other}). This recombination is characterised by

a lifetime of 3.6 μs and is dominant in the samples with the two lowest concentrations. This is not the case for the highest amount of Mo where the defects proportional to the Mo-contamination in the melt dominate. A possible interpretation is that in all the three cases Mo is completely decorating crystal defects and only in case 3 enough dissolved Mo is available to further increase the recombination noticeably (i.e. in form of precipitates or cluster or intra-grain atomic impurity), further lowering IQE and Voc.

The fact that the results for Voc and IQE in the case of Mo concentration 1 and 2 are so similar is indicative that the solar cell process is not able to clean the wafers and lower the recombination (in the crystal defects, according to our hypothesis). This is not unexpected considering that Mo is not a fast diffusing impurity.

In the case of iron the linearity of $1/\tau_{\text{eff}}$ versus Fe concentration could not be verified due to lack, so far, of sufficient wafers with different concentrations. However assuming the same model holds, it results in a τ_{other} of 2.7 μs for the multicrystalline sample. This value is in rough agreement with the value found for Mo. The slightly lower value might be related to the lower resistivity of the Fe contaminated wafers.

The high "other" recombination activity in the mc-Si samples can have several origins: for example, i) the crystal defects are highly recombination-active as soon as they are decorated by even a small amount of Mo or Fe, or ii) there is unexpected contamination from other impurities or iii) the crystal defects are intrinsically active. This will be analysed using the uncontaminated samples, grown with the same technique. The first hypothesis should be the most plausible considering the cleanliness of the FZ technique.

The lifetime of the monocrystalline (Fe-doped) samples is lower than one would expect (i.e., τ_{other} is not very high). This can again have several origins, e.g. i) not defect-free crystals (i.e. dislocations) as also this ingot revealed the presence of residual stress and inhomogeneous lifetime maps, and/or ii) bulk nucleation of Fe precipitates, or iii) unexpected contamination from other impurities. This will be further clarified with investigations on annealed crystals.

The high levels of Voc and IQE @1000 nm obtained in the case of monocrystalline Fe samples with the low and middle concentration level, suggests that the specific solar cell process applied is tolerant to Fe up to a concentration of about 54 ppma in the silicon feedstock. This can be explained by the gettering effect of the phosphorous diffusion carried out for the emitter preparation. In the case of the highest level of Fe the large amount of iron or the presence of precipitates result in a less effective gettering. This results in the lower Voc shown, and the suppressed IQE.

For the multicrystalline Fe case, the cell results are suppressed, similarly to the case of Mo. The process seems not be able to improve the wafer quality even in the case of the lower amount of Fe. However the results are comparable to the worst results obtained for the reference DS mc-Si wafers. The question is why the cell properties are so much worse than in the monocrystalline wafers. The formation of precipitates is maybe enhanced at the grain boundaries of the multicrystalline samples, or gettering is hindered in multicrystalline silicon, for example by trapping at crystal defects or because precipitates are more stable when formed at crystal defects. This means that

grain boundaries do not lower the impact of the impurities but prevent them from being gettered. It is alternatively possible that impurities segregate more in the grain boundaries. Thus the total Fe in the wafers would be higher than in the monocrystalline wafers.

6 CONCLUSIONS

FZ growth has been used in order to investigate the incorporation and the impact of Mo and Fe on monocrystalline and multicrystalline Si solar cells. The different concentration of impurities, introduced in the silicon melt, result in corresponding lifetime variation. This indicates that the impurity concentrations have a dominant impact on the wafer quality, thus the material can be used for the investigation aims.

By means of a simple model it is possible to demonstrate the proportionality between the number of SRH defects (N_t) and the amount of the introduced impurities.

Trapping is visible only in multicrystalline samples, revealing its relationship with the grain boundaries.

The cell process is not able to clean the wafers contaminated with Mo. A drop with respect to standard cast mc-Si between 35 and 60 mV is visible. In the case of multicrystalline cells contaminated with Fe, no variation between different concentrations can be observed. In the case of low Fe (2.6 ppma) the Voc values are comparable to the worst results obtained for the reference DS mc-Si wafers.

For monocrystalline cells Voc is high (30 mV higher than for the mc-Si reference) for the lower and middle Fe concentration. It is possible to conclude that the solar cell process is able to tolerate Fe contamination up to a concentration of about 54 ppma in the silicon feedstock.

These first results are very promising in order to quantify the impact of the impurities on solar cell level.

7 ACKNOWLEDGEMENTS

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