Impact of iron and molybdenum in mono and multicrystalline float-zone silicon solar cells

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Abstract. This paper investigates the impact of iron (Fe) and molybdenum (Mo) when they are introduced in the feedstock for Float-Zone (FZ) silicon (Si) growth. Neutron Activation Analysis shows that the segregation coefficient is in agreement with literature values. Lifetime maps on monocrystalline wafers show a uniform lifetime which decreases with the increase of contamination levels. Multicrystalline wafers show low lifetime areas, corresponding to grain boundaries and highly dislocated areas, which are independent from the contamination levels. Intra grain areas have a higher lifetime which changes with the contamination levels. In multicrystalline wafers the lowest level of Fe introduced (10^{12} atm/cm^3) has hardly any influence, whereas in the Mo-contaminated samples the impact is visible from the first level (10^{11} atm/cm^3). In monocrystalline wafers the diffusion length is reduced already at the first contamination level of Fe. However this is barely visible in the monocrystalline cell performance because the diffusion length is higher than the solar cell thickness.

Introduction

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. 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 parameters are affected by and cell processes can be best adapted to less pure material, which is one of the topics of our present investigation.

In this work we study the role of iron and molybdenum when intentionally introduced in a silicon melt before the crystallisation of FZ ingots. The reason for the choice for these impurities is given in the next section. The impact of the contaminants during industrial solar cells processing will be shown and analysed.

The research performed in the 1980's by Westinghouse Corp [1] is still used as reference for the effect of impurities on solar cell performance. However, those results were obtained with cell processing technology of the 1980's, and mostly on monocrystalline material. Our paper shows additional and essential information from the comparison between multicrystalline and monocrystalline Si wafers. Our paper also shows differences in sensitivity of the monocrystalline wafers to impurities, compared to the Westinghouse studies.

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.

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. It has to be taken into account that the crystal structure and the temperature history are not necessarily comparable to industrial Directionally Solidified (DS) multicrystalline silicon (mc-Si).

Unintentional contamination is most unlikely in the FZ growth technique, in contrast to small scale directional solidification. 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 grain boundaries.

Choice of the impurities

The impurities investigated in this work are iron and molybdenum. Fe is a dominant metal impurity in silicon wafers [2,5]. It is a relatively fast diffusing impurity ($D = 2.6 \times 10^{-6}$ cm^2/s @ 1000 °C), thus it can be gettered. 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 [2]. The diffusivity of Mo was investigated by Hamaguchi [3] who found a very small value ($D = 2 \times 10^{-10}$ cm^2/s @ 1000 °C) comparable, for example, to Ti. Therefore precipitation and gettering are expected to be significantly different from Fe, and it can be considered as a model impurity for other slow diffusing impurities.

Material

Fourteen boron-doped ingots (target resistivity 1 Ω·cm) were grown with pedestal growth technique [4] (see Fig. 1) at Institut für Kristallzucht (IKZ) Berlin. Three levels of impurities of each element were introduced in both mono- and multi-crystalline ingots (see Tab. 1). The target levels in the solid were chosen taking into consideration both typical level in silicon wafer (see [1] and [5]) and minimum level in order to see an effect on the minority carrier recombination [6]. Two reference ingots (mono- and multicrystalline) were grown without added impurities.

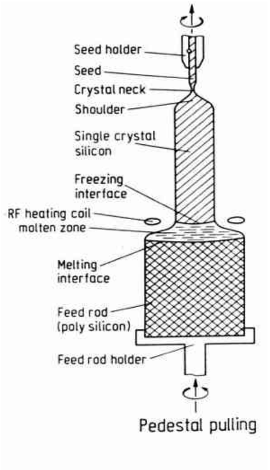


Figure 1 Schematical depiction of pedestral FZ-Si ingot growth technique [4].

Table 1 Impurity concentration introduced in the silicon melt during the growing process.

Impurity / Cont. level	Mo	Fe
	ppma	
1	**25** mc-	**2.6** mono mc-
2	**240** mc-	**54** mono mc-
3	**2800** mono mc-	**860** mono mc-
Westinghouse	**8-1900 c-Si** **~1000 mc-**	**53-5300 c-Si** **1900 mc-, partly analysed**

In the last row the impurity concentration analysed in the Westinghouse study [1] is reported for comparison.

The very low segregation coefficient of Fe and especially Mo together with the high base doping result in high concentration of impurities in the silicon melt which cause dislocations in the crystal lattice. The presence of dislocations in the crystals causes residual stress at room temperature which can cause ingot breakage especially during wafering. The maximum ingot diameter to avoid breakage during the cool down phase is 40 mm. In order to release the remaining residual stress the ingots were annealed at 1000 °C for 2 h with a slow cool down. The contamination due to annealing was tested and its impact is considered negligible.

To study the change in the electrical activity of the material after annealing, due to e.g. the formation or the dissolution of precipitates, part of the ingots were cut into wafers and characterised before annealing despite the residual stress. The Quasi Steady State - PhotoConductance (QSS-PC) lifetime measurements reveal hardly a significant change in the electrical activity due to the thermal treatment. Only one monocrystalline Mo-doped ingot could, so far, be processed because the other ingots were too fragile before annealing.

In the remainder of this paper, all the characterisation and solar cell process results are obtained on material after annealing if not differently specified. The wafer and solar cell characterisation before annealing was reported in [7].

Neutron Activation Analysis

Neutron Activation Analysis (NAA) is a technique successfully applied to silicon for the detection of impurity elements at very low concentration levels. Fe and Mo can be detected at concentrations as low as 3x10^{12} atm/cm^3 and 5x10^{10} atm/cm^3 respectively in the silicon matrix [8]. NAA provides the total number of the elements present, regardless of their electrical activity. The concentration level reported, assumes a homogenous distribution of the impurity in the sample. This assumption is largely confirmed as revealed by the lifetime map of spatial homogeneity (see next section).

Wafers with a thickness of about 3 mm were cut from each ingot for NAA. After a chemical etch the samples were irradiated at the Missouri State University with a thermal neutron flux of 2.5x10^{12} n/cm^3/s for 75 h. The samples were then counted for gamma emission at the Kodak Eastman research lab in order to obtain concentration levels of several elements (see Fig. 2).

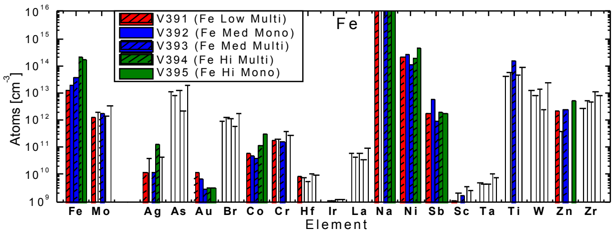
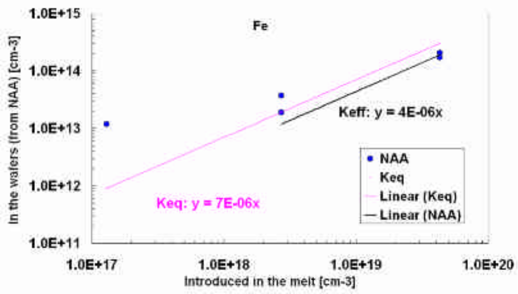


Figure 2. Measurement of impurities in Fe contaminated ingots. Error bars indicate that the element concentration is below the detection limit.

In Fig. 3 and Fig. 4 the levels of iron and molybdenum detected with NAA are reported versus the known amounts of impurity introduced in the melt. The solid concentrations are found to be proportional to the liquid concentrations for both Mo and Fe ingots. Deviations are found for the lowest concentrations.

The slope of the straight line through the points is a measurement of the effective segregation coefficient. The effective segregation coefficient we find is in agreement with the value of the equilibrium segregation coefficient found in literature [1].



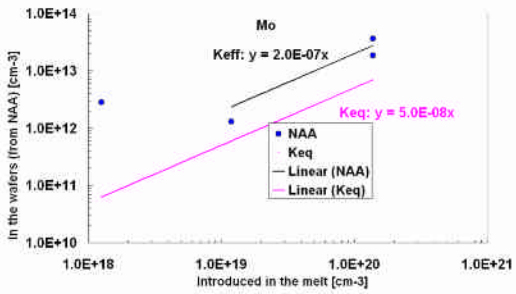


Figure 3. Fe concentration in the solid versus Fe concentration introduced in the Si melt.

Figure 4. Mo concentration in the solid versus Mo concentration introduced in the Si melt.

Lifetime maps

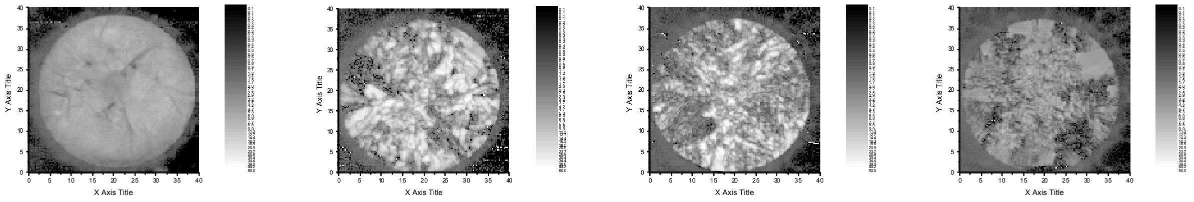
For surface passivation, the wafers were subject to a chemical polishing and a cleaning followed by a Plasma Enhanced-Chemical Vapour Deposition SiN_x deposition optimised for surface passivation. The effective lifetime measured represents the lifetime in the bulk of the wafers. Modulated Free Carrier Absorption (MFCA) [9] measurements were performed. In Fig. 5 lifetime maps are reported.

Multicrystalline wafers

The multicrystalline wafers show areas with high and low lifetime. The low lifetime areas show a pattern typical for grain boundaries and dislocated areas, similar to what is observed in directionally solidified mc-Si. There appears to be no difference in recombination activity of the crystal defects in the different wafers (see Fig. 5).

The high lifetime areas, which coincide with intra grains areas, have a lifetime which decreases with the increase of Fe and Mo level.

In Fig. 6 the lifetime distribution within each wafer is reported for each contaminant level.



Mono Ref *Multi Ref* *Multi Fe 1st level* *Multi Fe 2nd level*

Figure 5. Lifetime map (MFCA) of as-cut wafers with different level of Fe and uncontaminated.

Monocrystalline wafers

The lifetime map in monocrystalline wafers is uniform apart from a limited inhomogeneity in the centre of some wafers (see Fig. 5 mono Ref). Whether this inhomogeneity is related to crystal defects is under investigation. The lifetime decrease with the increase of Fe level.

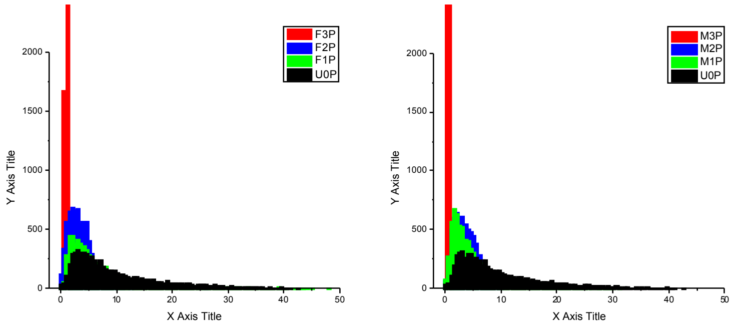


Figure 6. Lifetime histogram of Fe (left) and Mo (right) multicrystalline wafer measured by MFCA.

Solar cell process

The solar cell process was based on a standard industrial firing-through-SiN_x process. In order to apply the same process to mono- and multicrystalline wafers, the wafer surface was polished. The wafers received 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. The screen-printed metallisation and co-firing was carried out at the University of Konstanz. The solar cells were then cut to 2 x 2 cm^2 by a dicing saw. The solar cell efficiency on reference directionally solidified mc-Si was about 14.5% on polished etched wafers (15% on alkaline etched wafers).

The solar cell process was carried out on two neighbouring wafers for each impurity level.

The Voc of cells on uncontaminated substrates is 625 mV for the mono c-Si substrate and 593 mV for the mc-Si substrate. The latter is quite low. The large amount of crystal defects seems to have a significant impact on the solar cell performance.

Spectral response and reflectance measurements were carried out on all solar cells to determine the Internal Quantum Efficiency (IQE). The IQE curves are reported in Fig. 7. A decrease in the quantum efficiency at long wavelength is observed with increase of contamination level for both elements. The IQE at short wavelength is comparable for all the cells. This shows the stability of the solar cell process. In addition, at even high concentration level, the emitter recombination and surface passivation properties are not influenced by the impurities.

The diffusion length was calculated from the slope of the curve 1/IQE versus 1/α(λ) [10]. The results are reported in Table 2

Table 2 Effective diffusion length as calculated from the 1/IQE versus 1/ α(λ) curves.

Sample L_{Deff} [µm]	U0	F1	F2	F3	M1	M2	M3
Mono	536	259	111	96	-	-	38
Multi	179	143	93	70	120	75	31

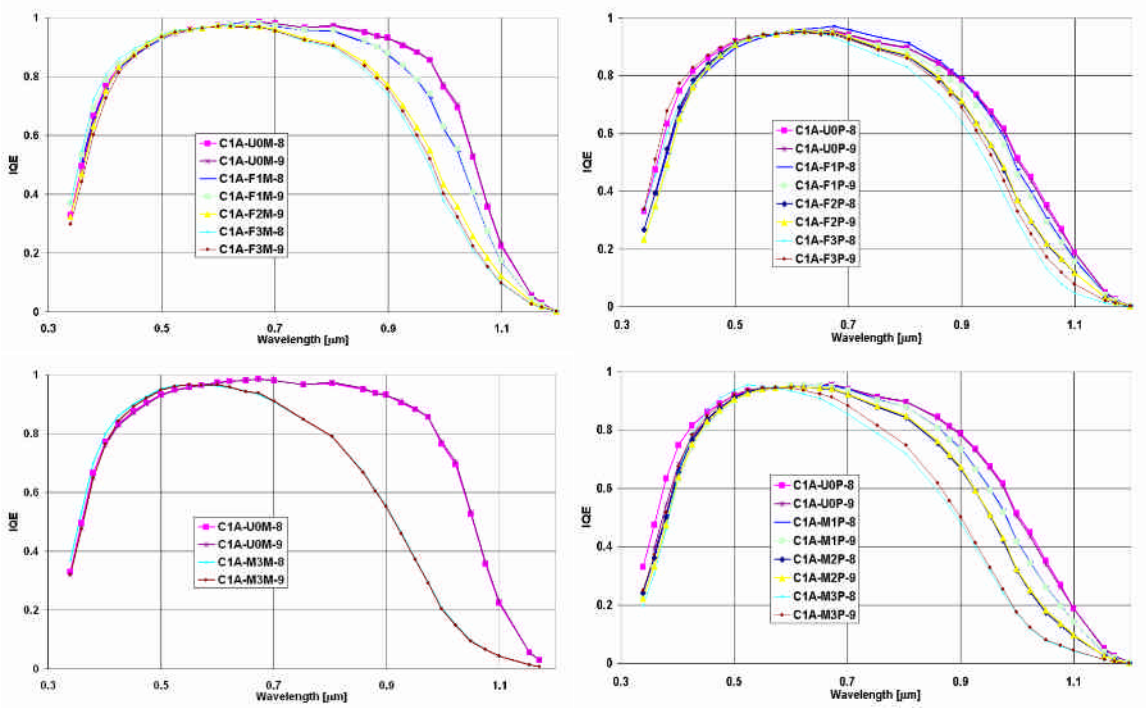


Figure 7. Top left: Fe-contaminated and reference mono-Si. Top right: Fe-contaminated and reference mc-Si. Bottom left: Mo-contaminated and reference mono-Si. Bottom right: Mo-contaminated and reference mc-Si. The quantum efficiency is strongly reduced at long wavelength with the increase of impurity level.

The IQE at long wavelength for the uncontaminated multicrystalline solar cells is much lower than in monocrystalline wafers. The reduction in the diffusion length is more than 60%. The crystal defects should be the only cause for this decrease. The first level of Fe introduced (10^{12} atm/cm^3) has hardly any influence on mc-Si cell performance. For Mo, however, an impact is visible at the first level (10^{11} atm/cm^3). In monocrystalline wafers the diffusion length is reduced already at the first contamination level of Fe. However this is barely visible in cell performance because the diffusion length is anyway higher than the solar cell thickness.

Conclusions

This paper investigates the impact of Fe and Mo in FZ ingots. NAA shows that the segregation coefficient is in agreement with literature values. Multicrystalline wafers show low lifetime areas, corresponding to grain boundaries and high dislocated areas, which are independent from the contamination levels. Intra grains areas have a higher lifetime which changes with the contamination levels. The solar cells shows a reduced diffusion length in multicrystalline uncontaminated cell than in monocrystalline one. The first level of Fe introduced (10^{12} atm/cm^3) have hardly an influence in multicrystalline. For Mo the impact is visible since the first level (10^{11} atm/cm^3). In monocrystalline the diffusion length is reduced already at the first contamination level of Fe. However this is barely visible in cell performance because the diffusion length is anyway higher than the solar cell thickness.

Another paper is in preparation in which the change in the recombination from wafers to cell and the specifications for the SOG-Si feedstock are discussed.

Acknowledgements

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