

IMPACT OF IRON AND MOLYBDENUM IN MONO AND MULTICRYSTALLINE FLOAT-ZONE SILICON SOLAR CELLS

G.Coletti¹, L.J.Geerligs¹, P.Manshanden¹, C.Swanson², H.Habenicht³, W.Warta³, J.Arumugan⁴, R.Kopecek⁵
Tel.: +31 224 564382 email: coletti@ecn.nl

¹Solar Energy, ECN, NL 1755 LE Petten, the Netherlands

²Eastman Kodak Research Laboratories, Rochester, NY, 14650, USA

³Fraunhofer Institute for Solar Energy Systems (ISE), Heidenhofstr. 2, 79110 Freiburg, Germany

⁴University of Konstanz, Faculty of Sciences, Department of Physics, 78464 Konstanz, Germany

⁵now at: International Solar Energy Research Center ISC, Rudolf-Diesel-Strasse 15, 78467 Konstanz, Germany

ABSTRACT: This paper investigates the impact of iron (Fe) and molybdenum (Mo) when they are introduced in the feedstock for mono- and multicrystalline Float-Zone (FZ) silicon (Si) growth. Neutron Activation Analysis shows that the solid impurity concentrations are found to be proportional to the liquid concentrations and that the segregation coefficient is in agreement with literature values. The solar cells show a reduced diffusion length in multicrystalline uncontaminated cells compare to the monocrystalline uncontaminated. In multicrystalline cells the lowest level of Fe introduced (10^{12} atm/cm³) has hardly any influence, whereas in the Mo-contaminated cells the impact is visible from the lowest level (10^{11} atm/cm³). In monocrystalline cells the diffusion length is reduced already at the lowest contamination level of Fe. Multicrystalline cells show no clear difference in recombination activity of the crystal defects for different impurity concentration. Intra grain areas have a lower bulk recombination which has an opposite correlation with the impurity level except for the first of Fe. This means that the gettering of Fe is not complete for the highest concentration levels.

Keywords: crystalline silicon, iron, molybdenum, neutron activation analysis, impurities, feedstock

1 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, as first elements in our overall work, 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.

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.

Clean material can be most conveniently obtained by producing FZ ingots. FZ ingots can be grown from a mono- or multicrystalline seed, resulting in a mono- or multicrystalline ingot. This permits to study the incorporation and impact of impurities when present together with grain boundaries. 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.

2.1 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 ($D = 2.6 \times 10^{-6}$ cm²/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 ($D = 2 \times 10^{-10}$ cm²/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.

2.2 Material

Fourteen boron-doped ingots (target resistivity 1Ω·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 considering 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

adding impurities.

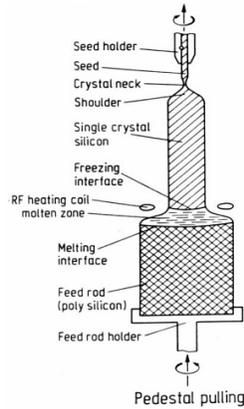


Figure 1: Schematic depiction of pedestal FZ-Si ingot growth technique [4].

Table 1: Impurity concentration introduced in the silicon melt during the growing process. In the last row the impurity concentration analysed in the Westinghouse study [1] is reported for comparison.

Impurity	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

The very low segregation coefficient of Fe and especially Mo together with the high base doping result in a high concentration of impurities in the silicon melt, which causes 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 3 h with a slow cool down. The contamination due to annealing furnace 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 – Photo Conductance (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].

3 RESULTS AND DISCUSSION

3.1 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 [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 2.5×10^{12} n/cm²/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. The lowest Fe and Mo concentrations detected in the silicon matrix were 10^{13} atm/cm³ and 5×10^{11} atm/cm³ respectively.

In Fig. 2 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. Deviation is found for the lowest Fe concentration.

The slope of the straight line through the points is a measurement of the effective segregation coefficient. The effective segregation coefficient (k_{eff}), thus found for both Mo and Fe, is in agreement with the value of the equilibrium segregation coefficient (k_{eq}) reported in literature [1, 9].

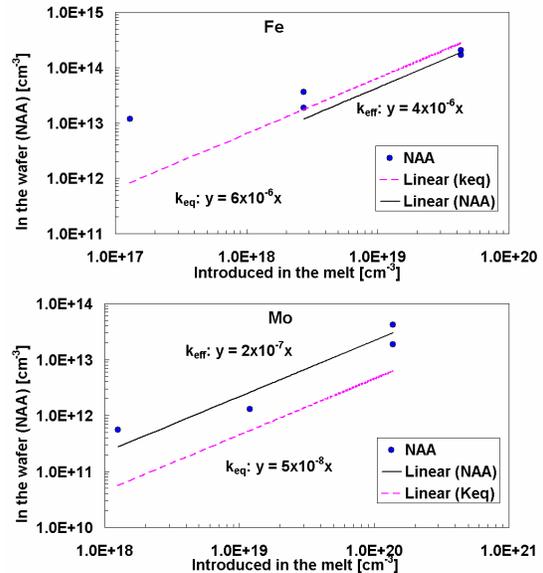


Figure 2: Iron (top) and molybdenum (bottom) concentrations in the solid versus their concentrations introduced in the Si melt. The solid line is a linear fit of the data points. The dashed lines show the equilibrium segregation coefficients reported in literature [1, 9].

3.2 Solar cell results

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 phosphorus 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 cm² by a dicing saw. The solar cell efficiency on reference directionally solidified mc-Si was about 14.5% on polish etched wafers (15% on alkaline etched wafers).

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

The V_{oc} 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 Figs. 3, 4. 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, even at high concentration levels, the emitter recombination and surface passivation properties are not influenced by the impurities.

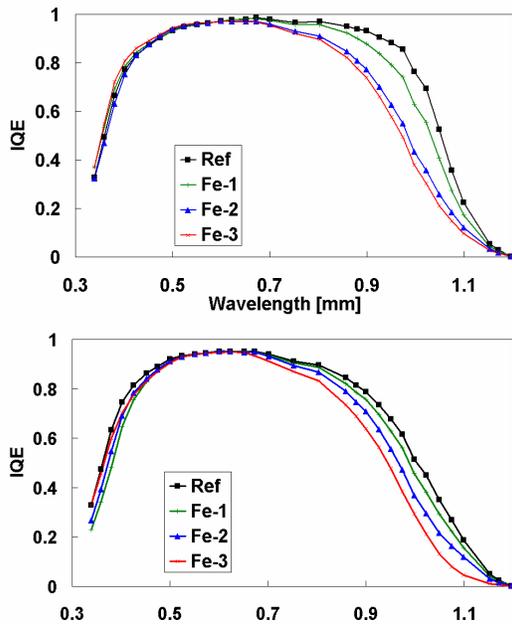


Figure 3: Internal Quantum Efficiency for different concentration of Fe (see Tab.1). Top: Fe-contaminated and reference mono-Si solar cells. Bottom: Fe-contaminated and reference mc-Si solar cells. The level of Fe are The quantum efficiency is strongly reduced at long wavelength with the increase of impurity level.

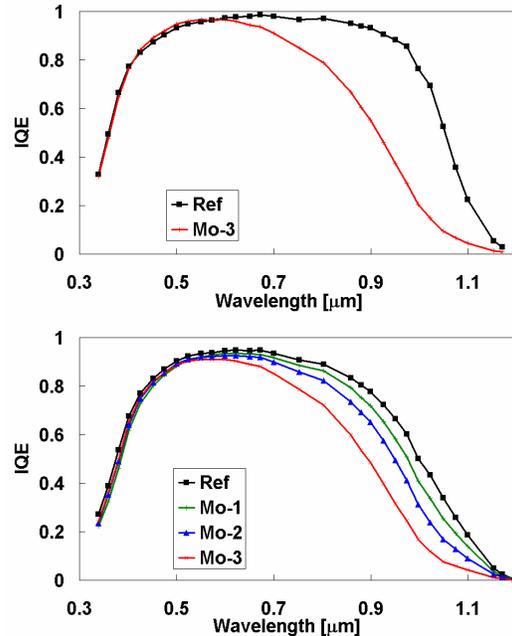


Figure 4: Internal Quantum Efficiency for different concentration of Mo (see Tab.1). Top: Mo-contaminated and reference mono-Si solar cells. Bottom: Mo-contaminated and reference mc-Si solar cells. The quantum efficiency is strongly reduced at long wavelength with the increase of impurity level.

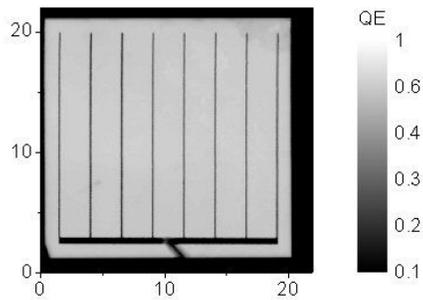
The IQE at long wavelength for the uncontaminated multicrystalline solar cells is much lower than in monocrystalline wafers. The reduction in the diffusion length is more than 60%. The crystal defects should be the only cause for this decrease. The first level of Fe introduced (10^{12} atm/cm³) has hardly any influence on mc-Si cell performance. For Mo, however, an impact is visible at the lowest level (10^{11} atm/cm³). In monocrystalline wafers the diffusion length is reduced already at the lowest contamination level of Fe. However this is barely visible on cell performance because the diffusion length is anyway higher than the solar cell thickness.

3.3 Laser Beam Induced Current scans

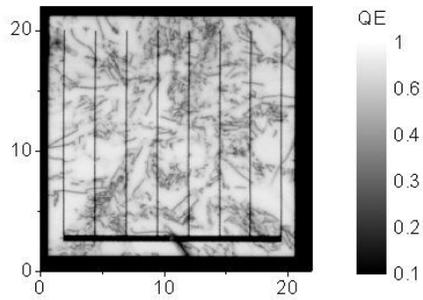
Measurements of Laser Beam Induced Current (LBIC) were carried out at Fraunhofer ISE. The laser used has a wavelength of 950 nm which give indication of the recombination in the bulk region of the solar cell. In Fig. 5 the external Quantum Efficiency scans derived from LBIC data are reported.

Multicrystalline wafers

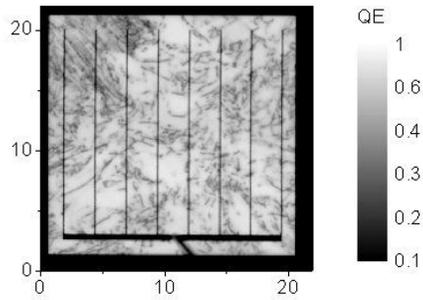
The multicrystalline cells show areas with high and low QE corresponding to low and high bulk recombination assuming the constant reflectivity of the cells. The ARC has been deposited in the same condition thus the assumption of constant reflectivity is consistent. The dark areas show a pattern typical for grain boundaries and dislocated areas, similar to what is observed in directionally solidified mc-Si. It appears to be no clear difference in recombination activity of the crystal defects in the different wafers (see Fig. 5), but this has not yet been analysed quantitatively.



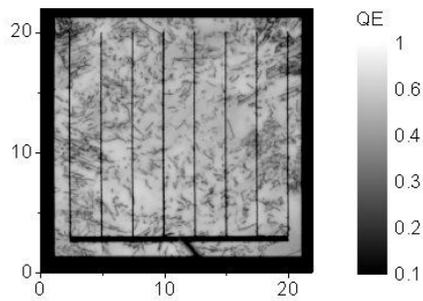
Mono Reference



Multi Reference



Multi Fe 1st level



Multi Fe 2nd level

Figure 5: QE map derived from LBIC measurements of solar cell with different level of Fe and uncontaminated.

The light areas, which coincide with intra grains areas, have a QE which have an opposite correlation with the impurity level except for the first level of Fe (see Multi reference and Multi Fe 1st level in Fig. 5). This means that the gettering of Fe is not complete for the highest concentration levels.

The change in recombination from wafer to cell and the specifications for the SoG-Si feedstock will be discussed in a forthcoming publication.

4 CONCLUSIONS

This paper investigates the impact of Fe and Mo in FZ ingots. NAA shows that the solid impurity concentrations are found to be proportional to the liquid concentrations and that the segregation coefficient is in agreement with literature values. The solar cells show a reduced diffusion length in multicrystalline uncontaminated cells compare to the monocrystalline uncontaminated. In multicrystalline cells the lowest level of Fe introduced (10^{12} atm/cm³) has hardly any influence, whereas in the Mo-contaminated cells the impact is visible from the lowest level (10^{11} atm/cm³). In monocrystalline the diffusion length is reduced already at the lowest contamination level of Fe. However this is barely visible on cell performance because the diffusion length is anyway higher than the solar cell thickness. Multicrystalline cells show no clear difference in recombination activity of the crystal defects for different impurity concentration. Intra grain areas have a lower bulk recombination which has an opposite correlation with the impurity level except for the first level of Fe. This means that the gettering of Fe is not complete for the highest concentration levels.

5 ACKNOWLEDGEMENTS

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