ON ACCURATE AND QUANTITATIVE MEASUREMENTS OF IRON-CONCENTRATION IN MULTICRYSTALLINE SILICON BY IRON-BORON PAIR DISSOCIATION.

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ABSTRACT: This paper presents practical experimental aspects for determining the concentration of Fe_i in mc-Si by carrier lifetime measurements and $(Fe_i^+)(B_s^-)$-pair-dissociation. The information presented is useful to perform *quantitatively* correct measurements and understand the limitations of this measurement method. We focus on two aspects. First, we show the effect of performing measurements on areas with inhomogeneous lifetime. This can result in a significant error. At least in some cases this error is accompanied by a significant shift of the so-called crossover point of the Fe_i and FeB lifetime spectra, the fingerprint of Fe_i in silicon. Second, we demonstrate and quantify the effect of insufficient pair dissociation. The equations we provide can be used to estimate when pair dissociation is insufficient. This could happen, for example, when performing measurements on a silicon sample without surface passivation or with a relatively high Fe_i-concentration.
Keywords: silicon, recombination, iron

1 INTRODUCTION

Iron is one of the major contaminants in mc-Si. Measurements of Fe_i are very useful for monitoring changes in ingot crystallisation procedures, wafer quality, process contamination and gettering. This paper treats two important aspects for quantitative (reliable, reproducible) measurement of the Fe_i concentration by $(Fe_i^+)(B_s^-)$-dissociation, not just for monocrystalline but especially for mc-Si. First, the paper provides a model for the effect of lifetime inhomogeneities in samples. In some cases a practical assessment procedure via the cross-over point is possible. Second, the paper provides formulas and constants for the dissociation rate. Both these aspects are relevant to determine the accuracy of a measurement in mc-Si.
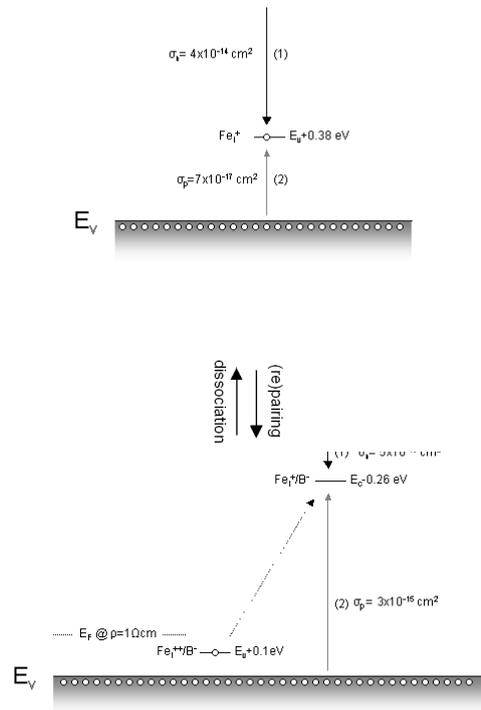
2 THE Fe_i and FeB DEFECTS

The Fe_i^+ interstitial point defect in thermal equilibrium at room temperature forms pairs with ionised boron acceptors B_s^-. It can be dissociated by heating or by carrier injection, e.g. by illumination. The energy levels and carrier capture cross sections for both defects have been discussed in several studies, with some variation of results. Some of the most recent results are discussed in [1-4]. Values of the defect parameters based on DLTS and carrier lifetime spectroscopy of Fe-implanted monocrystalline samples are given in Table I and Figure 1.

Table I: Fe_i and FeB defect parameters, most likely values according to recent studies. E_t is the defect energy level, σ_p the capture cross section for holes, and σ_n that for electrons.

	E_t eV	σ_p cm^2	σ_n cm^2
Fei	$E_v+0.38$	7.2×10^{-17}	4×10^{-14}
$Fe_i^+B_s^-$	$E_c-0.26$	3×10^{-15}	5×10^{-15}

These values at the moment appear to be good, based on a number of experiments and model fits, but it should be noted that in the future they might be further refined or revised. Anyway, the precise values of the parameters will not change the essential points of this paper.

Figure 1: Fe_i and FeB defect parameters, according to the recent analysis by Macdonald et al [4].

2.1 Measurement of Fe-concentration

An example of the change in lifetime curves upon FeB pair dissociation by illumination, measured by the quasi steady state photoconductance (QSSPC) technique, is given in Fig. 2. From the change in lifetime, the concentration of FeB pairs which have dissociated can be calculated:

$$\Delta[FeB] \propto \Delta(1/\tau_{eff})$$

where the proportionality constant is given by the Shockley-Read-Hall equations and the defect parameters.

The FeB measurement technique was developed by Zoth and Bergholz for lifetime measurements at low injection levels [5]. It was extended to the injection levels typical for QSSPC measurements in ref [2].

Two aspects which are important in practical FeB measurements, and which have been rather neglected in literature up to date, are the subject of this paper:
1. The lifetime is normally assumed to be spatially homogeneous. If it's not, the calculation should be adjusted. This is of course especially relevant for mc-Si.
2. The measurement is normally meant to determine the concentration of Fe_i in the sample. In that case it must be ensured that the dissociation of the FeB is complete.
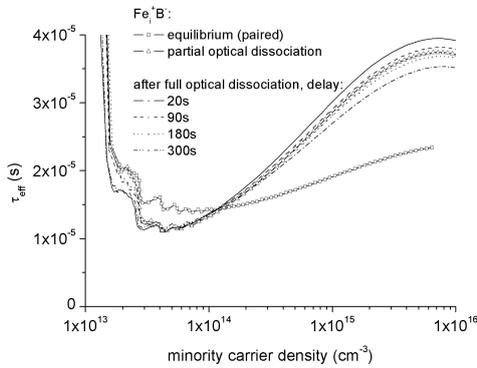
Figure 2: QSSPC lifetime measurements on a floatzone silicon wafer implanted with a known dose of Fe, subsequently annealed and surface-passivated. Effect of optical FeB dissociation and repairing are shown. Note the characteristic "cross-over point" at approx. 1.5×10^{14} cm^{-3}. The increasing lifetime at the lowest injection levels is probably due to carrier trapping.

3 INHOMOGENEOUS LIFETIME

QSSPC measurements determine the recombination lifetime from the photoconductance $\Delta\sigma$ measured by inductive coupling, $\tau_{eff} \propto \Delta\sigma$. Basically the QSSPC method determines an areal average of the effective lifetime: $\Delta\sigma \approx \iint d\sigma(x,y)$. Low lifetime areas provide only small contributions to the QSSPC signal. In typical mc-Si, therefore, τ_{eff} is underestimated compared to the lifetime in the good areas, and, because $[FeB] \propto \Delta(1/\tau_{eff})$, the Fe-concentration is overestimated. Fig. 3, for example, shows multicrystalline and monocrystalline wafers implanted with the same Fe dose. The mc-Si wafer has a significant fraction of low-lifetime area. When the QSSPC on the full area of the sample is measured the apparent lifetime is reduced and the apparent Fe-concentration increased (both by a factor ≈ 2) compared to the implanted dose. (The implanted dose is measured correctly on the FZ sample.) With the aperture on the good area of the mc-Si wafer (measurement on the bad area is difficult), the correct implanted dose of Fe_i is measured (within $\approx 20\%$ error).
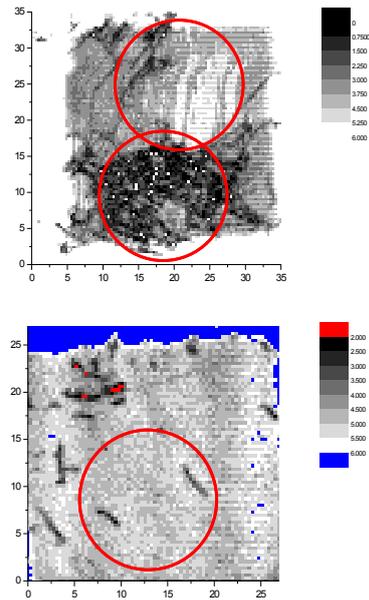
Figure 3: Example of inhomogeneity in mc-Si sample (top), versus FZ sample (bottom). Both have been homogeneously doped with Fe_i by implantation and anneal. Usual QSSPC measurement is on 40mm Ø sampling area, and is significantly incorrect for the mc-Si. QSSPC measurements on smaller homogeneous areas given by the red circles give accurate results as described in the text. Map coordinates are in mm, grey scale legend is in µs.
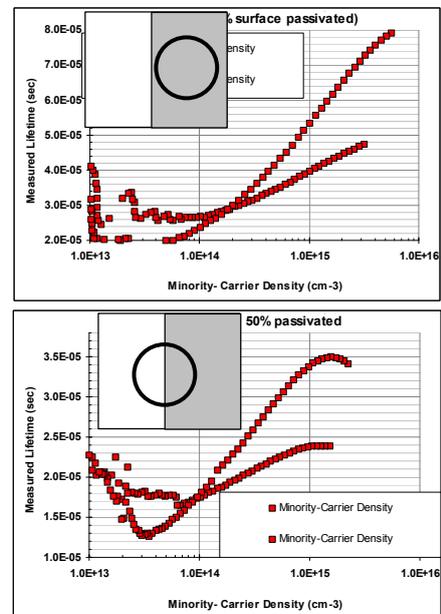
Figure 4: Model sample to study the effect of inhomogeneity of effective lifetime on measurements. Top: QSSPC measurement on homogeneous area. Bottom: measurement on inhomogeneous area. Note the change in lifetime as well as cross-over point.

A model experiment for this effect is shown in Fig. 4. Here, 50% of a sample has a low effective lifetime because of reduced surface passivation. Measurements were first performed on the passivated area (Fig. 4, top), and next on a sampling area 50% passivated/50% non-passivated. Both lifetime (and therefore calculated Fe_i-

concentration) and cross-over point change by a factor 2.

This suggests that the crossover point can be used to estimate the error due to the averaging effect. However this is not generally valid. Modelling indicates that such a correction can only be used if the ratio of lifetime in high and low lifetime areas is large.

Hence, generally, the safe approach for correct measurements is to measure on homogeneous areas (e.g. by using sufficiently small sampling area). Alternatively, if the exact amount of Fe_i is not of great interest but rather changes of Fe_i-concentration (e.g. after gettering) are to be studied, make sure that exactly the same location on the sample is measured in each measurement.

## 4 ENSURING COMPLETE FeB DISSOCIATION

4.1 Illustration of the problem

As soon as $(Fe_i^+)(B_s^-)$-pair dissociation starts, there will be a reverse process of pair formation occurring. If the dissociation rate is Γ_d, and the repairing rate Γ_r, the maximum fraction of dissociated pairs will be:

$$\frac{N_{FeB}(t \to \infty)}{N_{FeB}(0)} = \frac{\Gamma_r}{\Gamma_r + \Gamma_d}$$

If the dissociation rate is not much larger than the association rate, and this effect is neglected, the FeB-concentration will therefore be underestimated.

As the dissociation rate depends on the illumination intensity, this effect can be demonstrated by measuring dissociation with different illumination intensities, e.g., as in Figure 5.

Of practical importance is that the dissociation rate also depends on the effective lifetime of the sample, which is influenced by the surface passivation and the FeB-concentration (and of course any other recombination channels). Especially for Si without surface passivation (e.g. mc-Si blocks before wafering) or with very high FeB-concentration, it is therefore important to verify whether the illumination intensity is sufficient to dissociated all FeB. (in fact, full dissociation might be not even be feasible for realistic illumination intensities).
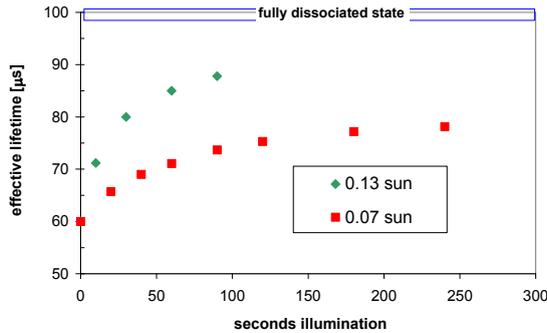
Figure 5: Effect of insufficient illumination intensity on FeB-pair dissociation.

4.2 Dissociation rate

In an earlier publication [6], we have described that dissociation of FeB pairs during illumination is a recombination-enhanced process which follows a quadratic dependence on recombination events per FeB-center:

$$\Gamma_d = K \times U_{FeB}^2 /[FeB]^2 \quad \text{with } K \approx 5 \times 10^{-15} \text{ s}^{-1}.$$

This was demonstrated for high quality samples, where nearly all recombination took place through FeB or Fe_i (rather than through other bulk defects or through surface defects). Results are given in Fig. 6. For practical application, it is important to verify whether this relation holds also in the presence of other defects. Representing such other defects by τ_{other}, the expected dependence can be found by substituting U_{FeB} by

$$U_{FeB} = \frac{\Delta n}{\tau_{FeB}} = \frac{G\tau_{other}}{\tau_{FeB} + \tau_{other}} \quad \text{which yields}$$

$$\Gamma_d = K \frac{G^2}{[FeB]^2} \times \frac{1}{\left(1 + \tau_{FeB}/\tau_{other}\right)^2}, \text{ i.e.}$$

$$\left(\frac{\Gamma_d \times [FeB]^2}{G^2 K}\right)^{1/2} = \left(1 + \tau_{FeB}/\tau_{other}\right)^{-1} \quad (1)$$

This equation is necessary for estimating the dissociation rate in samples with imperfect surface passivation, or samples with low lifetime due to other defects.

We have verified this equation on a model sample, by varying the surface passivation. The results are given in Fig. 7. The experimental values for dissociation rate versus surface passivation (the latter expressed as τ_{other}) confirm eq. (1).

In recent experiments, as in Fig. 7, we have encountered a lower prefactor K, by roughly a factor 20, than earlier. We are presently investigating whether this variation may be due to a strong temperature dependence of the recombination-enhanced dissociation process, use of the wrong defect parameters, etc.
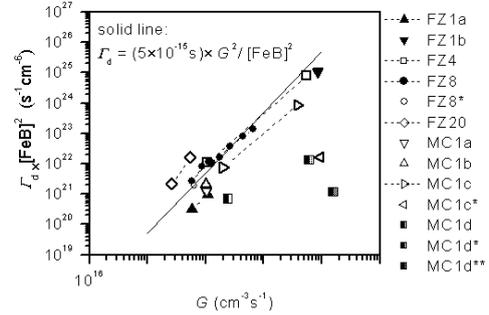
Figure 6: Dissociation rate for a variety of samples showing the dependence on generation rate G. Samples with * have non-negligible surface recombination.
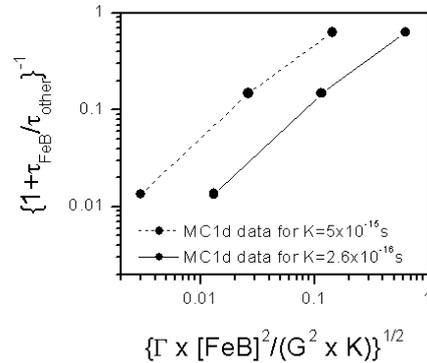
Figure 7: Example of dependence of dissociation rate on surface passivation. See text for further explanation.

5 CONCLUSIONS

In conclusion, we have presented practical experimental aspects for determining the concentration of Fe_i in mc-Si by carrier lifetime measurements and $(Fe_i^+)(B_s^-)$-dissociation. The information presented is needed to perform *quantitatively* correct measurements and understand the limitations of measurement method.

First, we have provided a model for the effect of lifetime inhomogeneities in samples. In some cases a practical assessment procedure via the cross-over point is possible, but this has to be investigated further. Second, we have provided formulas and constants for the dissociation rate. Both are relevant to determine the accuracy of a measurement in mc-Si.

6   ACKNOWLEDGEMENTS

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