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The distribution of interstitial iron at dislocation clusters at elevated temperature

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Abstract

Differences of the iron-boron (FeB) concentration at dislocation clusters could be observed using a microwave detected photoconductivity (MDP) and a surface photovoltage measurement (SPV) system, respectively. This could be explained by reduced minority carrier mobility in these areas. The FeB concentration was correlated with the dislocation density after annealing at 800°C and 750°C, which show no clear trend but a tendency between higher FeB concentration and high dislocation density.

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1. Introduction

Iron is one of the most observed impurities in crystalline silicon and has a detrimental influence on the performance of solar cells. By diffusion from the crucible into the melt during the crystallization process an iron concentration of more than $10^{14}$ cm$^{-3}$ can be observed. [1] Most of this iron does not occur in the interstitial form. Especially dislocations and grain boundaries are preferred sites for iron to precipitate. [2] This can lead to a gettering effect in the surrounding areas.

However, after phosphorus gettering during the solar cell process both the recombination activity of the dislocation clusters and the dissolved iron concentration is high in these areas, too. [3] To understand
the distribution of iron at dislocation clusters it is necessary to know how interstitial iron interacts with
dislocations and how these interactions influence the lifetime in areas with high dislocation density.

2. Measuring the interstitial iron concentration in silicon at dislocation clusters

The measurement of iron-boron (FeB) concentration was done with a commercial microwave photo
conduction system (MDP) and a surface photo voltage setup (SPV). Both systems are well established for
the measurement of the FeB concentration. The FeB concentration was determined from the lifetime
before and after optical dissociation of iron-boron-pairs. [1], [2]

\[
[Fe] = A\left(\frac{1}{L_2^2} - \frac{1}{L_1^2}\right) = C\left(\frac{1}{\tau_2} - \frac{1}{\tau_1}\right)
\]  

(1)

In order to determine the correct FeB concentration it is necessary to use a correct prefactor \( A \) or \( C \).
The prefactors are a function of the recombination properties of interstitial iron and iron-boron. So for a
given temperature, doping level and excess carrier density the correct value of \( A \) or \( C \) can be set. The
measurements both with MDP and SPV work in different injection levels: with \( 10^{11} \) \( \text{cm}^{-3} \) excess carriers
for the SPV and \( 10^{17} \) \( \text{cm}^{-3} \) for MDP system, nonetheless the iron concentration should come out equal for
both systems.

In figure 1 and 2 the FeB maps measured with MDP and with SPV are pictured. The concentrations of
FeB in the most areas range from \( 4 \times 10^{12} \) \( \text{cm}^{-3} \) till \( 1.1 \times 10^{13} \) \( \text{cm}^{-3} \). In these areas differences between SPV
and MDP in FeB concentration are lower than \( 4 \times 10^{12} \) \( \text{cm}^{-3} \). Strong differences in the FeB concentration
between both measurements occur in the lower right area and in the upper left area. In the lower right area
the FeB concentration from the MDP system is around \( 1.2 \times 10^{13} \) \( \text{cm}^{-3} \) and for the SPV system around
\( 6 \times 10^{13} \) \( \text{cm}^{-3} \). For the upper left area a FeB concentration of \( 7 \times 10^{12} \) \( \text{cm}^{-3} \) for MDP system and
\( 1.5 \times 10^{13} \) \( \text{cm}^{-3} \) for SPV was measured.

![Fig. 1. FeB concentration measured with a MDP system.](image1)

![Fig. 2. FeB concentration measured with SPV system.](image2)

To understand this difference these areas were further analyzed by regarding the dislocation density.
The sample were polished, etched and the etch pit density was measured, see fig. 3. In the dislocation
density map the two areas, where differences in the FeB concentration appear, show a high dislocation
density with values of $10^6$ to $10^7$ cm$^{-2}$. This means, that in the presence of dislocations, different FeB concentrations were determined from MDP and SPV measurements.

It is known that FeB determination with lifetime systems can be misleading, if there are traps in the concentration range of the excess carrier concentration. Especially in dislocation clusters a high trap density can be observed. To exclude this case the measurement were done at high injection level for the MDP system. So we expect that the FeB measuring of MDP is the correct one. [3]

To understand the differences in the measured FeB concentration it is useful to compare the prefactors $A$ and $C$. From the Shockley-Read-Hall-Statistic one get the value for $C$ from the difference recombination properties of interstitial iron and iron-boron-pairs (equation 2).

\[ C = \frac{1}{\chi_{FeB} - \chi_{Fe_i}} \]

\[ \chi = \frac{v_{th}\sigma_{n}(N_A + \Delta n)}{(N_A + p_i + \Delta n) + k(n_i + \Delta n)} \]  

(2)

The so calculated value $C$ is connected with the value $A$ by the minority carrier diffusion coefficient $D_n$ which depends on the carrier mobility via the Einstein relation.

\[ A = D_n C \]  

(3)

\[ D_n = \frac{\mu_n k_B T}{q} \]  

(4)

Hence the iron concentration determined from carrier diffusion length measurement is only correct, if the carrier mobility is known and homogenous over the sample. However, if there are dislocation clusters, this must not be the case. Regarding the dislocation clusters in the shown sample in the lower right area, one can assume that the minority carrier mobility and the diffusion coefficient is more than four times lower in this dislocation clusters because of the more than four times higher FeB concentration measured with the SPV system. In the upper left area the dislocations are not so dense. So the differences in FeB concentration...
concentrations are just a factor of two, which means that the mobility is by a factor of two smaller. The reason for a smaller mobility could be the high concentration of additional scattering centers at decorated dislocations and/or a high trap concentration. High trap concentrations are often observed at structural defects like dislocations. [4] Especially at the low injection level of the SPV system a high trap concentration in a dislocation cluster can influence the minority carriers pretty. Palais et al. [5] reported heterogeneity values in minority carrier mobility in multicrystalline silicon, which is confirmed with our study.

The differences of the iron concentrations from the MDP and the SPV measurements can be used to determine the local minority carrier mobility. In fig. 4 the mobility of this sample is plotted and shows the areas with the higher dislocation density as areas with lower mobility. Also other areas show lower values of mobility but not as decrease as in the dislocation clusters. In some parts of the sample mobility values of more than 1400 cm²V⁻¹s⁻¹ appear which is quite high for multicrystalline silicon with an acceptor concentration of 10¹⁶ cm⁻³. These higher mobility values are a consequence of typical measurement errors by the FeB measurement.

For further investigation of the FeB concentration at dislocation clusters it is meaningful to use the MDP-based FeB measurement, which is less sensitive for errors on structural defects.

![Fig. 4. Logarithmic plot of the minority carrier mobility calculated from the differences of FeB measurement from SPV and MDP.](image)

### 3. Iron-boron at dislocation clusters after annealing

For the investigation of the distribution of interstitial iron at dislocations the FeB concentration was measured in the as cut state at first. The sample above was measured with the MDP at an injection level of around 10¹⁷ cm⁻³ to make sure that there is no influence of traps on the FeB measuring. The lifetime in the as cut state vary between 30 μs to 60 μs in the areas without dislocation clusters in the not illuminated state and an interstitial iron concentration of around 1*10¹¹ cm⁻³ was measured (fig. 5 and fig. 6). In the lower right area, where the dislocation cluster is localized, lifetime is reduced with values between 2 μs until 15 μs and the highest FeB concentration with values over 5*10¹¹ cm⁻³ can be found there.
A higher concentration of FeB at dislocation clusters in the as cut state has been observed already.[6] In this state the distribution and segregation of iron are mainly influenced by the cool down process of the ingot and the precipitation during this time. For the understanding of the interaction of interstitial iron and dislocations at equilibrium conditions the sample was heated up at 800°C for several hours and after that the sample was quenched with a cooling rate of more than 80 K/s.

After this process the lifetime and the FeB concentration was measured again. Fig. 7 shows the lifetime after annealing in the not illuminated state. The lifetime is drastically reduced with values lower than 8 μs and in the dislocation cluster lower than 3 μs. Fig. 8 shows the distribution of the FeB concentration after annealing in a high resolution map. In this measurement one can also see that the highest concentration of FeB is in the region of the dislocation cluster in the lower right area. The average concentration was measured of around $6 \times 10^{12}$ cm$^{-3}$, but in the dislocation cluster FeB concentration was measured over $10^{13}$ cm$^{-3}$, which is two times higher than the concentration of the rest of the sample.

To compare the FeB concentration with the dislocation density fig. 9 shows a plot of the measured FeB concentration versus the averaged dislocation density at the current point. The framed area in fig. 8 is the analyzed area in fig. 9. One can see that there is a relationship between high dislocation density and high FeB concentration. Starting at a dislocation density of $10^3$ cm$^{-2}$ till higher densities the FeB concentration reaches the highest values of this area with $1.5 \times 10^{13}$ cm$^{-3}$ FeB. Also the averaged FeB concentration
increases at higher dislocation density. However, it is difficult to find a dedicated FeB concentration for a given dislocation density because of a high scattering of the FeB concentrations in the dislocation rich area. So there are also values with high dislocation density and low FeB concentration. The scattering of FeB values can be explained if we assume that also other mechanism influence the concentration of interstitial iron at 800°C. For example, oxygen precipitates frequently appear at dislocation clusters. The presence of oxygen precipitates reduce the concentration of interstitial iron in silicon, so this is also a point which has to be taken into account. [7], [8]

![Graph showing the correlation between dislocation density and FeB concentration after annealing at 800°C.](image)

Fig. 9. Correlation between dislocation density and FeB concentration after annealing at 800°C.

However, at 800°C there are areas with high dislocation density, which have a higher concentration of interstitial iron in an equilibrium state, than to the rest of the sample. Even though the solubility in silicon at this temperature is smaller, in the dislocation cluster an interstitial iron concentration of more than $10^{13}$ cm$^{-3}$ appear in a thermodynamic equilibration. A Cottrell cloud, which is attractive for interstitial atoms around the dislocations, could explain this higher concentration of FeB pairs. [9]

![Lifetime map measured with MDP after annealing at 750°C.](image)

Fig. 10. Lifetime map measured with MDP after annealing at 750°C.

![Map of FeB concentration measured with MDP after annealing at 750°C.](image)

Fig. 11. Map of FeB concentration measured with MDP after annealing at 750°C.
After this investigation the same sample was annealed a second time for more than nine hours at 750°C. The lifetime and the FeB concentration were measured as before. The lifetime is now higher and reaches values up to 15 µs (fig. 10) and the FeB concentration is decreased with values of around $1 \times 10^{12}$ cm$^{-3}$. Just like at 800°C the highest FeB concentration appears at the dislocation cluster in the lower right area. The FeB concentration in the dislocation cluster is around four times higher, than the concentration in the areas next to (fig. 11). It can also be seen, that the region around the dislocation cluster is an area with low FeB concentration, which shows also a gettering effect of dislocation clusters of the surrounding areas.

In fig. 12 the FeB concentration is plotted against the dislocation density like in fig. 9 for 800°C. In the plot for 750°C the same trend as for 800°C can be observed. The measured FeB concentration rise at high dislocation density and also a scattering in values appear.

![Fig. 12. Correlation between dislocation density and FeB concentration after annealing at 750°C.](image)

It is also interesting to determine the influence of these FeB concentrations on the lifetime in this areas. In fig. 13 for the annealing at 800°C the lifetime versus FeB concentration is plotted and the maximum lifetime for the corresponding FeB concentration from the Shockley-Read-Hall equations is pointed. One can clearly see that the lifetime in this area is quite low but does not agree with the lifetime determined from the FeB concentration. Only for areas where the FeB concentration is high (more than $10^{13}$ cm$^{-3}$) the recombination of the FeB affected the lifetime more than 50 %. For lower FeB concentration FeB does not limit the lifetime. This means that other defects are present in these areas, which reduce and dominate the lifetime. One candidate can be oxygen precipitates in these areas, which also decrease the lifetime and reduce the solute interstitial iron concentration.
Conclusion

The FeB concentration at a dislocation cluster was measured in the as cut state and after annealing for several hours at 800°C and at 750°C. For the determination of the FeB concentration two different lifetime techniques were used. A difference in FeB concentration was found for the SPV measurements, when the minority carrier mobility changes, since this technique measures the minority carrier diffusion length and is sensitive to change in minority carrier mobility. A higher FeB concentration could be found in dislocation clusters in the as cut state and after annealing. However, there is no clear correlation between dislocation density and FeB concentration but a strong scattering at high dislocation densities and a trend to higher values. It turns out, that there have to be also other defects like oxygen precipitates, which influence the FeB concentration and also the lifetime in dislocation clusters.
References


