Low temperature internal gettering of bulk defects in silicon photovoltaic materials

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Abstract. Multicrystalline silicon (mc-Si) substrates are widely used for photovoltaic cells. The minority carrier lifetime in mc-Si is affected by recombination associated with metallic impurities in many forms, such as point-like defects, precipitates and bound to or precipitated at structural defects such as dislocations. We have studied the effect of low temperature annealing on the lifetime and bulk iron concentration in as-received mc-Si wafers from different locations within a block. Lifetime measurements are made using a temporary iodine-ethanol surface passivation technique to minimize the occurrence of bulk hydrogenation which often occurs from dielectric films. In good wafers from the middle of the block the lifetime is reduced by annealing at 400 °C and 500 °C in a way which does not correlate with changes in bulk iron concentration. Lifetime improvements occur in relatively poor samples from the top and bottom of the block annealed at 300 °C, and also in samples from the bottom annealed at 400 °C. The improvement in bottom wafers correlates with iron loss from the bulk. Our work shows that under some conditions the lifetime in relatively poor as-grown wafers can be improved by low temperature internal gettering.

Introduction

Directionally-solidified multi-crystalline silicon (mc-Si) is used in around half of photovoltaic solar cells. Cells produced from mc-Si wafers are less efficient than those produced from monocrystalline silicon (mono-Si) wafers, but lower production costs for mc-Si mean that both technologies are viable. Wafers of mc-Si contain high concentrations of impurities and structural defects such as dislocations. Impurities, particularly transition metals, exist in various forms including as point-like defects, in precipitates or bound to dislocations. Defects often provide recombination pathways which reduce the minority carrier lifetime (hereafter referred to as just “lifetime”) and hence the conversion efficiency of a solar cell.

The material quality of mc-Si wafers, as measured by the lifetime, varies with position in the cast ingot. In general, the as-grown lifetime is highest in wafers in the middle of the ingot, and is lowest at the top and bottom \cite{1}, although the lifetime is also lower at the ingot edges \cite{2}. The as-grown lifetime is improved by impurity gettering (which redistributes impurities to locations in which they are less problematic overall) and passivation (which eliminates the effects of defects without physically removing them), but even after these processes the lifetime in the wafers from the very top and bottom of the ingots is sometimes too low for the wafers to be viable for use in photovoltaic cells. At best these make relatively inefficient cells; at worst these are discarded. Finding ways to improve the material quality at the extrema of ingots is therefore of technological importance.

External gettering processes, such as those based on phosphorus diffusion or aluminium deposition, are effective in mc-Si to an extent (\textit{e.g.} \cite{3}) and remove impurities from the bulk region of the photovoltaic device. Another approach is to use intentional \textit{internal} gettering to tie up impurities in localized regions within the bulk of the material, since it is well known that metals interact with extended defects in silicon \cite{4-7}. Effective internal gettering could result in an overall lifetime increase by redistributing the impurities into forms in which the net recombination due to a given impurity concentration is reduced. Whilst internal gettering is in principle possible at high
temperatures, adding further high temperature steps is potentially costly and care needs to be taken to avoid contamination. This study is into low temperature (≤ 500 °C) internal gettering. Although this potentially requires longer annealing times, the advantage is that the solubility of many impurities is low and so in principle the processing can be performed under non-cleanroom conditions. We note that long low temperature annealing has been demonstrated to improve lifetime in mono-Si [8, 9]. For mono-Si the gettering probably occurs externally at surfaces [8, 10], whereas in mc-Si it is likely that long low temperature annealing will result in internal gettering.

Post growth low temperature annealing has been performed on mc-Si before [11-15]. Krain et al. report a reduction in bulk iron concentration in samples annealed at 300 °C to 500 °C, consistent with iron diffusion to crystallographic defects [11]. They do not however report bulk lifetime data, nor do they investigate different parts of the ingot in detail. In their study silicon nitride surface passivation was used, and this is likely to have caused bulk hydrogenation (and hence bulk passivation). Recent studies have also questioned whether hydrogen affects the behaviour of interstitial iron itself [16, 17] and it is important to note iron is not the only impurity found in mc-Si. Another study into internal gettering in mc-Si was performed by Liu and Macdonald who studied the kinetics of iron precipitation at 400 °C to 700 °C [14]. They found a systematic decay in bulk iron concentration with annealing time dependent on the initial bulk iron supersaturation. They report limited lifetime data, which perhaps indicate a small improvement upon annealing at 400 °C. Surface passivation was achieved by an oxide layer formed at 1000 °C, which the authors state is unlikely to cause bulk hydrogenation. The high temperature will however have redistributed impurities from their as-grown states. Potential extra variables introduced by surface passivation processing make interpretation of internal gettering effects in mc-Si challenging.

Boulfrad et al. apply low temperature internal gettering (550 °C) after higher temperature annealing (≥ 950 °C) [15]. They report an improvement in carrier lifetime in “red zone” wafers from the bottom of ingots, and explain this in terms of impurity segregation to oxide precipitates nucleated in the high temperature step. Other studies were performed by Pickett and Buonassisi [12] and Rinio et al. [13] who applied low temperature annealing during or after the solar cell fabrication process, respectively. Rinio et al. found the cell efficiency is dependent on the annealing temperature, increasing slowly with temperature until a peak at ~575 °C. At higher temperatures the efficiency decreases fairly sharply with cells annealed at 650 °C exhibiting lower efficiency than cells which had not been annealed. Pickett and Buonassisi’s work showed increased cell efficiencies as a result of an additional 500 °C anneal after phosphorus diffusion. These studies show long low temperature annealing can have tangible benefits for PV cells. The effect of low temperature annealing on mc-Si is far from being fully understood however.

In this paper we report the preliminary results of a systematic study of internal gettering in as-grown mc-Si. Our methodology should provide more information than some previous studies for several reasons. Firstly, we take into account the vertical location of the wafers within the block to distinguish between initially-good and initially-poor wafers. Secondly, we have attempted to minimize hydrogenation of the sample by using a room temperature temporary liquid surface passivation scheme based on iodine-ethanol (IE) for all lifetime measurements. Consequently we are able to report bulk lifetime values (as well as bulk iron concentrations) on samples which are not annealed at high temperatures during passivation. Thirdly, we are able to correlate changes in recombination rate with changes in bulk iron concentration to establish the role of bulk iron in any lifetime change which occurs. Our long-term aim is to establish the conditions under which a single low temperature internal gettering step can improve relatively poor quality mc-Si wafers.

**Experimental methods**

**Samples.** Wafers were sourced from four different height positions (top (T), top of the middle (MT), bottom of the middle (MB), and bottom (B)) of an edge block from a commercially-grown boron doped mc-Si ingot. The wafers were 156 × 156 mm² in size with an initial thickness of ~200
µm. Resistivities were in the range 7.5 Ωcm to 11.5 Ωcm, Neighbouring “sister” samples measuring 39 × 39 mm² were cut from each wafer. To remove saw damage samples were chemically treated with a planar etch solution comprising HF (40%), HNO₃ (69%), and CH₃COOH (100%) in the ratio of 24:58:18.

**Surface passivation.** Samples were first RCA cleaned then dipped into a 10% HF solution for 1 minute to remove the native oxide. Samples were then immediately placed in optically-transparent plastic seal bags. A thin uniform layer of 0.1M iodine-ethanol (I-E) solution was formed on the surfaces and excess solution and air bubbles were squeezed out. Lifetime measurements were made within a few minutes, as soon after this time the surface passivation quality degrades substantially.

**Lifetime measurement.** Bulk lifetimes were measured by quasi-steady-state photoconductance (QSS-PC) [18] using a Sinton WCT-120 lifetime tester. Bulk iron concentrations were determined using a method based on photodissociation of FeB pairs described in Ref. [19], with the first measurement made with the bulk iron in the form of FeB pairs which were then dissociated by intense illumination followed by the second measurement made immediately afterwards with the iron in the interstitial (Feᵢ) state. Spatially-resolved PL images on I-E passivated samples were also acquired at each processing stage using a BT Imaging LIS-L1 system which uses 650nm excitation and a silicon charge-coupled device (CCD) camera. These were cross-calibrated using the QSS-PC data to give calibrated lifetime images, with a spatial resolution of ~160 µm.

**Thermal processing.** After each lifetime measurement stage samples were cleaned in methanol and subjected to an RCA clean to remove residues of the I-E solution. Samples were annealed in nitrogen at 300 °C, 400 °C or 500 °C in a tube furnace followed by a rapid cool to room temperature. After annealing samples were again RCA cleaned and then were stored in the dark for at least 36 hours. This is known to be sufficient time for re-association of FeB pairs [19, 20]. Samples were then subjected to the same surface passivation treatment and lifetime measurement procedure described above, then the process was repeated many times for each sample.

**Results**

**Average bulk lifetime measurements.** Lifetime measurements are reported as a function of annealing time at different temperatures in Fig. 1 and Fig. 2. Lifetime is reported at an excess minority carrier density of 1 × 10¹⁵ cm⁻³ with bulk iron in the interstitial state and so is denoted by \( \tau_{Fe_i} \). As the starting lifetimes in the samples at the extrema of the block (T and B) are lower than those in the middle (MT and MB) the data are presented on separate graphs with different scales in Fig. 1 and Fig. 2 respectively. Lifetime values are assumed to be accurate to ± 8% [21].

The starting (as-grown) average bulk lifetimes vary substantially with sample location from the block. For the samples studied here, the initial lifetimes plotted are in the range 9 µs to 12 µs for the bottom (B), 60 µs to 77 µs for the bottom middle (MB), 32 µs to 38 µs for the top middle (MT), and 17 µs to 21 µs for the top (T). The starting lifetime for each sample is plotted as a horizontal line on each graph so the effects of annealing relative to the starting condition are easily visible. Low temperature annealing generally affects the lifetime, with both increases and decreases observed. General trends with location and temperature are summarized qualitatively in Table 1.

Fig. 1 and Fig. 2 also show plots of the average bulk iron concentrations (determined by photodissociation of FeB pairs) as a function of annealing time at different temperatures. The initial bulk iron concentrations (plotted horizontally) are 2.9 ± 0.7 × 10¹² cm⁻³ for the bottom (B), 1.9 ± 0.6 × 10¹¹ cm⁻³ for the bottom middle (MB), 4.0 ± 1.3 × 10¹¹ cm⁻³ for the top middle (MT), and 1.1 ± 0.3 × 10¹² cm⁻³ for the top (T). General trends are also summarized qualitatively in Table 1.

Fig. 3 shows representative spatially-resolved lifetime images for two samples measured with bulk iron in the form of FeB pairs with I-E passivation. Fig. 3 (a) shows a sample from the bottom (B) improved by annealing at 300 °C. The in-grain lifetime improves with annealing. Fig. 3 (b) shows a sample from the top middle (MT) generally worsened by annealing at 500 °C.
Figure 1. Data from mc-Si samples from the bottom (B) and top (T) of the ingot annealed for the times plotted at 300 °C, 400 °C or 500 °C. The left-hand graphs show minority carrier lifetime at an excess minority carrier density of $1 \times 10^{15}$ cm$^{-3}$ with bulk iron in the interstitial state ($\tau_{Fe}$). The right-hand graphs show interstitial iron concentration measured by photodissociation of FeB pairs. The dotted/ dashed lines are the initial values.
Figure 2. Data from mc-Si samples from the bottom middle (MB) and top middle (MT) of the ingot annealed for the times plotted at 300 °C, 400 °C or 500 °C. The left-hand graphs show minority carrier lifetime at an excess minority carrier density of $1 \times 10^{15}$ cm$^{-3}$ with bulk iron in the interstitial state ($\tau_{Fe^i}$). The right-hand graphs show interstitial iron concentration measured by photodissociation of FeB pairs. The dotted/dashed lines are the initial values.
Figure 3. Lifetime images acquired with bulk iron in the FeB state for mc-Si samples: (a) from the bottom of the block (B) annealed at 300 °C for the times indicated; and (b) from the top of the middle of the block (MT) annealed at 500 °C for the times indicated. Both samples measure 39 mm by 39 mm.

**Analysis**

We can analyse the data in Fig. 1 and Fig. 2 to determine whether interstitial iron reconfiguration gives rise to the lifetime change by considering the correlation between the normalized change in recombination rate after annealing for time $t$ with the normalized change in interstitial iron concentration. This correlation can be written as:
where $A$ is a proportionality function. Fig. 4 shows plots in accordance with Equation 1 from samples annealed at different temperatures from different parts of the mc-Si block. If $A$ takes the value 1 then there exists a 1:1 correlation between the normalized recombination rate change and the normalized bulk iron change, and this is indicated by the diagonal dashed lines on the graphs.

Fig. 4 shows a good correlation for samples from the bottom of the block annealed at 300 °C and 400 °C, and a possible correlation at 500 °C. For samples from other parts of the block there is not a 1:1 correlation between the normalized bulk iron change and the normalized recombination rate change. For the bottom of the block it is therefore likely that the improvements in lifetime found at 300 °C and 400 °C arise from an effect associated with bulk iron. The situation for bottom wafers annealed at 500 °C is less clear-cut, and more data are required. For top wafers improved by annealing at 300 °C there is not good correlation with the bulk iron changes. For the samples in which there is a substantial reduction in lifetime upon annealing there is very poor correlation, which implies that bulk iron-related effects alone cannot explain the effect observed.

**Discussion**

The aim of our work was to establish how mc-Si from different parts of a block responds to long low temperature annealing. Our liquid passivation technique was intended to minimize the introduction of bulk hydrogen into the samples, and by re-passivating the same samples after every thermal process we are able to measure bulk lifetimes. The initial results show the situation is very complicated.

In many cases, perhaps surprisingly, low temperature annealing results in a substantial deterioration in bulk lifetime. This is particularly evident in the material from the middle of the block, in which the relatively high starting lifetimes were reduced significantly by annealing at 400 °C and substantially by annealing at 500 °C. For instance the lifetime in the bottom middle sample was reduced from 77 µs to below 10 µs by annealing for just 5 minutes at 500 °C. Similar abrupt lifetime reductions were found at 500 °C for samples from the top, and top middle (but not the ingot bottom). Data in Fig. 4 demonstrate that the lifetime reductions did not generally correlate with changes in bulk iron concentration, so we attribute the lifetime change to formation of another recombination centre. The lifetime images in Fig. 3 (b) shows a worsening of lifetime in the bulk of the grains. At this stage we cannot be specific about the nature of any centres which may be forming. We do however note that annealing samples at the bottom of the ingot at 500 °C does not result in a sharp reduction in lifetime, so any explanation would need to account for this observation. A speculative explanation could be that the bulk oxygen concentration is higher at the bottom [15] and that this plays a role in stabilizing the defect at 500 °C.

Lifetime reductions from short annealing at 500 °C do not seem to have been observed by many, and this could be because of a difference between surface passivation schemes used. Silicon nitride surface passivation typically introduces hydrogen into the bulk [16] and this could passivate the centre which forms. We note that Rinio et al. find an improvement in cell efficiency and internal quantum efficiency after annealing at 500 °C [13], and a cell efficiency improvement was achieved with a 30 minute anneal at 500 °C after phosphorus diffusion by Pickett and Buonassisi [12]. These improvements could be due to either hydrogen passivation or external gettering of impurities during cell processing. We are currently performing additional experiments using silicon nitride surface passivation.
Figure 4. Normalized change in recombination rate versus normalized change in bulk interstitial iron concentration in accordance with Equation 1 for samples from the top (T), top middle (MT), bottom middle (MB) and bottom (B) of a mc-Si ingot. Dotted lines represent one-to-one correlation.

Table 1. A summary of this study of low temperature annealing of mc-Si. The general qualitative trends in lifetime and bulk iron concentrations are stated. Any correlation between the two is stated.
Our work suggests there is potential for improving a sub-set of as-grown mc-Si wafers by long low temperature annealing. We have found that samples from the top and bottom of the block can be improved by annealing at 300 °C, with 400 °C also improving bottom samples. Fig. 1 shows that lifetimes in bottom wafers have been increased to 22.9 μs from 9.7 μs at 300 °C, and to 31.7 μs from 10.8 μs at 400 °C. A smaller improvement in top wafers was measured, with the increase being from 17.1 μs to 22.9 μs. Experimental work on these samples is on-going, so further annealing may bring more improvement. Correlation with iron data (Fig. 4) shows that the improvement in bottom wafers is most likely due to redistribution of bulk iron. The lifetime images in Fig. 3 (a) demonstrate an improvement in the bulks of the grains. The destination of the bulk iron lost is the subject of further investigation. At 300 °C it is noted that the initial bulk iron level is about seven orders of magnitude above the extrapolated solid solubility [10, 20], so there could be sufficient driving force for nucleation of new iron-containing precipitates, but the annealing times are also sufficient for iron diffusion to existing precipitates (or possibly even to the surfaces [10]).

The studies of Krain* et al. [11] and Liu and Macdonald [14] found a systematic reduction in bulk iron with annealing time. Krain* et al. find the bulk iron concentration to decay in a way consistent with iron diffusion to crystallographic defects [11]. Our results are not generally consistent with those of Krain* et al.. In many samples, particularly those from the middle of the block, we do not find a systematic decay in bulk iron concentration, and it some cases it appears to increase. Our working explanation for the discrepancy would involve bulk hydrogen present in the samples of Krain* et al. but probably not in ours, but experiments to verify this are ongoing. The work of Karzel* et al. supports a hypothesis involving hydrogen [16]. We can also cautiously compare our data to those of Liu and Macdonald [14], but note that their high temperature passivation step (45 minutes at 1000 °C) will have had a substantial effect on the starting material. Liu and Macdonald suggest the hydrogenation level affects the decay rate of bulk iron, and our bulk iron decay data at 400 °C are much more similar to theirs with SiO₂ passivation (very low hydrogen) than the Al₂O₃ passivation data (moderate hydrogen) and silicon nitride data of Krain* et al. (relatively high hydrogen) they also consider.

Conclusion

The effect of low temperature annealing on the lifetime and bulk iron concentration in mc-Si has been studied with a view to understanding internal gettering. A temporary room temperature liquid iodine-ethanol passivation scheme is used to minimize the introduction of hydrogen into the bulk. Perhaps surprisingly, for wafers from the middle and top of a block it is found that annealing at 400 °C and 500 °C results in a lifetime reduction, and this cannot be explained only by the redistribution of bulk iron. Annealing at 300 °C improves the lifetime in relatively poor samples from the top and bottom of the block. Annealing at 400 °C also improves bottom samples. The improvement observed in bottom wafers correlates with the change measured in bulk iron concentration. These preliminary results show that long low temperature annealing can improve the minority carrier lifetime in some lower quality as-received mc-Si wafers.

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