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Low-Temperature Saw Damage Gettering to Improve Minority Carrier Lifetime in Multicrystalline Silicon

*M. Al-Amin, N. E. Grant, and J. D. Murphy**

The minority carrier lifetime in multicrystalline silicon – a material used in the majority of today's manufactured solar cells – is limited by defects within the material, including metallic impurities which are relatively mobile at low temperatures (≤700 °C). Addition of an optimised thermal process which can facilitate impurity diffusion to the saw damage at the wafer surfaces can result in permanent removal of the impurities when the saw damage is etched away. We demonstrate that this saw damage gettering is effective at 500 to 700 °C and, when combined with subsequent low-temperature processing, lifetimes are improved by a factor of more than four relative to the as-grown state. The simple method has the potential to be a low thermal budget process for the improvement of low-lifetime "red zone" wafers.

The majority of solar cells produced at present use multicrystalline silicon (mc-Si) wafers which are sawn from ingots grown by directional solidification. The wafer cutting process leaves saw damage on both faces of the wafer. The mechanically-damaged regions are likely to contain dislocation networks and cracks[1] and the first stage in most cell processes is a chemical etch to remove damage to avoid a detrimental impact on electrical properties later on. It is however well established that highly defective regions getter impurities in silicon (see Ref. [2] for a review). It is therefore possible, in principle, to introduce an additional thermal process to use the saw damage to getter impurities prior to its removal, thus permanently removing impurities from the wafer. This may become a relatively low-cost way of improving poor mc-Si wafers from the extrema of the ingot whose minority carrier lifetime (henceforth just "lifetime") is too short for viable cells.

This approach, called saw damage gettering (SDG), has been recently studied at high temperatures (≥800 °C) by a group at the University of Oxford, who have demonstrated an improvement in lifetime,[3–5] with the best results achieved at 850 °C followed by a relatively slow cool.[5] However, adding another high-temperature process step may be commercially unattractive in the context of cell production. As well as minimising the thermal budget, a lower temperature process could be more effective because the higher impurity supersaturation could facilitate enhanced precipitation in the damaged region.

In this letter, we demonstrate the efficacy of SDG at low temperatures (≤700 °C). We consider the low-temperature gettering effects which occur in mc-Si annealed without saw damage,[6–9] thus all of our experimental results for SDG are compared to sister samples with near-identical microstructures which have undergone an equivalent control anneal (CA). Furthermore, we use a temporary room temperature liquid surface passivation approach instead of a dielectric, since this avoids ambiguities associated with gettering by the dielectric[10,11] and potential bulk passivation by hydrogen.[12] As well as studying the SDG process itself, we evaluate the effect of an additional low-temperature (300 °C) post-SDG gettering anneal, as this simple process alone has been shown to improve lifetime previously.[7,8]

Experimental Methods: Sister wafers were sourced from the top of a *p*-type conventionally-grown (i.e., not high performance) mc-Si ingot. The manufacturer had used a diamond saw to cut the ingot into ~200 μm thick wafers. Samples measuring $39 \times 39\,\text{mm}^2$ with a ~0.7 Ω cm resistivity were studied.

A planar chemical etch comprising HF (50%), HNO_3 (69%) and CH_3COOH (100%) in the ratio of 24:58:18 was used to remove saw damage from half of the as-sawn samples. To ensure all the damage was removed, at least ~30 μm was removed from each side. Annealing of pairs of identically RCA-cleaned sister samples (one with saw damage; one without) was performed from 300 to 700 °C in nitrogen ambient, followed by a rapid cool (room temperature in <10 s). Annealing is referred to as saw damage gettering (SDG) when saw damage was present or a control anneal (CA) when saw damage had been removed. Annealing times were increased with decreasing temperature guided by the simulation of interstitial iron (a key impurity in mc-Si[13]) to both surfaces from Ref. [14] for which the results are shown in **Figure 1**(a). Experimental annealing times were 80 h at 300 °C, 12 h at 400 °C, 3 h at 500 °C, 1 h at 600 °C, and 0.5 h at 700 °C. These times are sufficient for interstitial iron to reach the solubility for pre-annealed samples from Ref. [14] or to be below our best-case detection limit. After annealing, saw damage was removed from the other half of the sample set.

Samples were characterised by quasi-steady-state photoconductance (QSS-PC) lifetime measurement using a Sinton WCT-120 lifetime tester and photoluminescence imaging with a BT Imaging LIS-L1 PL system with a photon flux of $1.1 \times 10^{17}\,\text{cm}^{-2}\,\text{s}^{-1}$. Prior to measurement samples were subjected to RCA cleaning and iodine-ethanol surface passivation, as described previously.[7]

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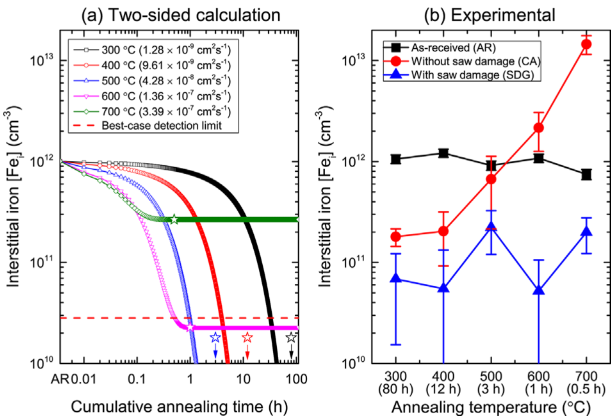

Figure 1. (a) Simulation of interstitial iron level as supersaturated interstitial iron diffuses to saw damage at both surfaces. The legend includes diffusion coefficients and the starting concentration is the mean from etched samples. Starred symbols indicate the annealing times used (well below the scale for ≤500 °C). (b) Experimental interstitial iron values in the as-received (AR) state, after saw damage gettering (SDG) and after a control anneal (CA).

Photodissociation of FeB pairs[15,16] was used to measure the interstitial iron concentration with details of parameters used given in Ref. [17]. QSS-PC lifetimes are reported at $1 \times 10^{15}\,\text{cm}^{-3}$ injection. All reported data are with bulk iron in the FeB state, measured >36 h after annealing which gives sufficient time for FeB pairs to reform.[17,18]

Results: **Figure 2** shows the spatial distribution of lifetime in mc-Si sister samples. All samples have very similar lifetime distributions in the as-received (AR) state, with QSS-PC lifetimes measured in samples with saw damage removed by etching to be 14 to 18 μs (**Figure 3**(b)). Starting interstitial iron concentrations were $\sim 10^{12}\,\text{cm}^{-3}$ (Figure 1(b)).

Figure 2 shows a clear difference between samples subjected to SDG and those which experienced a CA under the same conditions at the same time. Samples annealed with saw damage experienced a lifetime improvement, whereas those annealed without saw damage got considerably worse at 500 to 700 °C. The QSS-PC lifetimes measured at the centre of these samples are labelled SDG or CA in Figure 3. Although the starting values cannot be measured in the exact same samples because of the saw damage, the value in all cases increases compared to the mean measured in the CA sample set prior to the annealing process. Figure 1(b) shows the interstitial iron in SDG samples reduces at all temperatures, whereas in the CA samples significant reductions are achieved at 300 and 400 °C, and significant increases occur at 600 and 700 °C.

Processes were checked for contamination by using float-zone silicon control samples and no evidence of contamination was found. Even if contamination were to occur, the CA and SDG samples were annealed simultaneously, so both would be contaminated and the fact that there is a difference in some cases would still be significant. The interstitial iron concentrations measured after SDG are close to our "best-case" detection limit (Figure 1) which was calculated based on the highest lifetimes in this study. The detection limit for the samples after SDG is likely to be slightly higher than plotted in Figure 1(a), so these interstitial iron values lie at the margin of what can be reliably measured by photodisociation of FeB pairs for these samples.

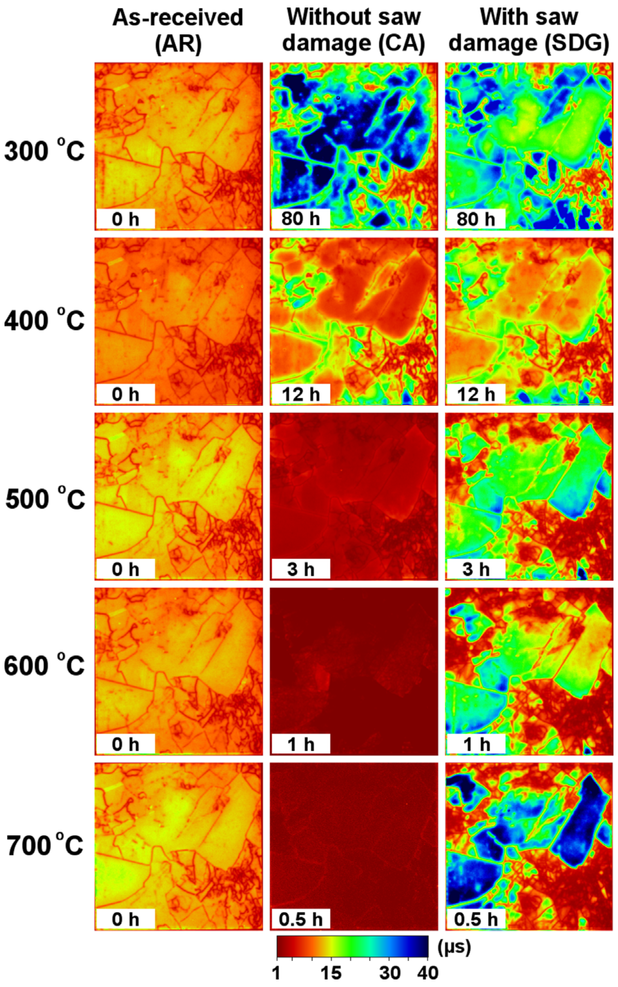

Figure 2. Spatial distribution of lifetime in mc-Si sister samples (39 × 39 mm^2) from PL imaging (5 s exposure). The left column shows the as-received samples, the central column shows the same samples in the left column subjected to a control anneal without saw damage, the right column shows sister samples annealed with saw damage present.

After the initial SDG or CA step at a range of temperatures (300 to 700 °C), all the samples were subjected to a secondary annealing process at 300 °C for 100 h in increments of 20 h. All samples (including those which had previously undergone SDG) were without surface saw damage for this stage. Figure 3 shows substantially different responses occur depending on whether samples experienced SDG or a CA step. **Figure 4** shows spatially-resolved lifetime images of these samples as-received and after 100 h of secondary annealing following either a CA or the SDG process. The lifetime in SDG samples was improved substantially by the 300 °C annealing in all cases. The best lifetimes (>60 μs) were achieved when SDG had been performed at 300, 500, or 600 °C. Similar lifetimes in CA samples subjected to a CA at 300 and 400 °C were achieved after secondary annealing at 300 °C. The samples which experienced lifetime reduction after their CA at 500 and 600 °C could be recovered to some extent by 300 °C secondary annealing. The sample which experienced a 700 °C CA could not

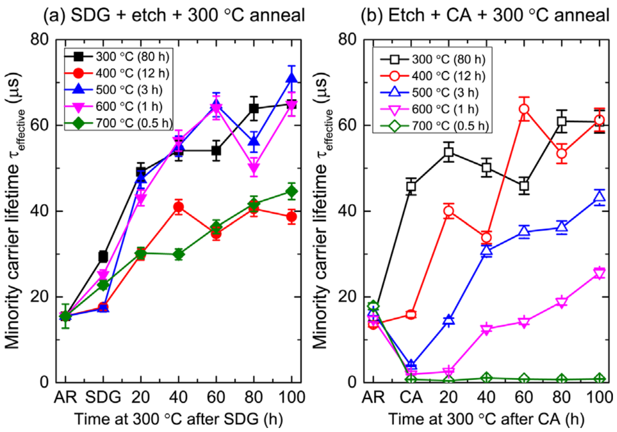

Figure 3. QSS-PC lifetime for mc-Si sister samples subjected to (a) saw damage gettering (SDG) and (b) a control anneal (CA) at the same time but with the saw damage removed. After SDG or the CA, samples were subjected to annealing at 300 °C. Accurate measurement of lifetime with saw damage still present is not possible, so the as-received (AR) lifetime in (a) is the mean of those in (b) with the error bar corresponding to the range measured.

be recovered. The sample which was subjected to SDG at 400 °C did not recover as well as might have been expected. The slightly lower than expected lifetime in this sample was a real result and not an artefact of the passivation as measurements were repeated reliably after 100 h of secondary annealing.

Discussion: Figure 2 shows a clear difference between sister samples annealed with or without saw damage. The lifetime in samples annealed without saw damage got considerably worse at 500 to 700 °C, with a substantial increase in average interstitial iron observed at 600 and 700 °C (Figure 1(b)). This is broadly consistent with our findings in mc-Si top samples published previously,[7] in which we found an abrupt lifetime reduction at 500 °C and improvements at 300 and 400 °C. Annealing at 500 to 700 °C releases interstitial iron (and probably other impurities) from sites within the mc-Si bulk and in the absence of an external gettering system (saw damage) this remains in solid solution after the extremely rapid cooling stage. In samples annealed with saw damage, the impurities released are able to leave the bulk of the material by gettering to the saw damage region. A large lifetime improvement was found in the CA sample annealed at 300 °C even without secondary annealing. We attribute this to the internal gettering of impurities to features which may include dislocations, grain boundaries and existing metallic precipitates. The addition of a 300 °C anneal after SDG or a CA results in lifetime improvements. These are also likely to be due to internal gettering of bulk impurities. Gettering of interstitial iron to the sample surfaces is also kinetically feasible, but previous work[14] has shown this to be thermodynamically unlikely in the absence of a pre-existing silicide at the surface.

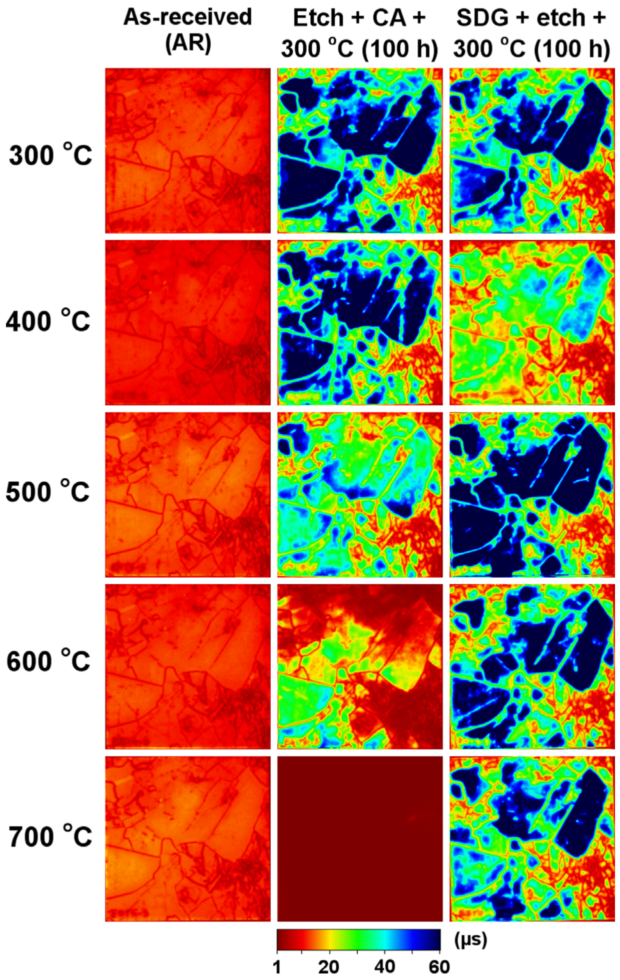

Figure 4. Spatial distribution of lifetime in mc-Si sister samples (39 × 39 mm^2). The left column represents the as-received samples (5 s exposure). The central and right columns (both 1 s exposure) show CA and SDG samples subjected to 100 h at 300 °C.

Interstitial iron is not the only mobile impurity present in mc-Si. Whilst the behaviour of interstitial iron is indicative of the effectiveness of the gettering process, changes in interstitial iron alone cannot explain our lifetime results. This is particularly evident in the CA case at 500 °C, where the interstitial iron concentration reduces slightly (Figure 1(b)) but the lifetime reduces substantially (Figure 3(b)). Thus whilst monitoring interstitial iron provides some insight into the gettering process, the behaviour of other lifetime-reducing impurities is also important. The 400 °C results in Figure 2 show a surprising lack of lifetime improvement and this is further evidence for the complexity of the mc-Si materials system. Bottom samples subjected to the equivalent of the CA process at 400 °C show a clear lifetime improvement.[7] We tentatively suggest the difference might be related to the higher dislocation density in top samples (as used here), noting that the in-grain lifetime in the lifetime images includes contributions from dislocations which are probably decorated with impurities. The interaction between metallic impurities and dislocations at these low temperatures remains an important topic for future study.

The presence of saw damage clearly makes a positive difference at 500 to 700 °C (Figure 2), but it is unclear whether it has a beneficial effect at 300 to 400 °C. Controls at these lower temperatures result in similar (or better at 400 °C) lifetimes than in SDG samples (Figure 3). The reason for this is not known. The fact that SDG is more effective at the higher temperatures is positive from the perspective of cell processing, as the processing times required at these higher temperatures are much shorter (≤3 h). It is noted that sophisticated diffusion furnaces are not required for SDG processes, so these processes could be implemented with little capital cost.

It is not straightforward to compare our results to high temperature SDG experiments[3–5] due to the different material types, different surface passivation schemes, and because the high temperature SDG studies used a relatively slow cool from the peak processing temperature during which impurity gettering occurs. The "standard performance bottom red zone" used in Ref. [5] is probably the most similar to our material, although it is likely to have a lower dislocation density than our top material. For this material, average lifetime improved from ~10 to 37 μs by SDG at 850 °C.[5] Considering just the samples annealed at ≥500 °C for reasons discussed above, our best lifetime after SDG was 25.2 μs at 600 °C which is an improvement of 63% relative to the average as-received lifetime in sister samples (15.5 μs). It is however noted that our subsequent 300 °C annealing can improve the lifetime to 64.9 μs, which is a factor of 4.2 relative to the average starting value. The sample subjected to a CA rather than SDG but the same thermal process (including the 100 h 300 °C anneal) had a final lifetime of just 25.6 μs. In summary, it appears that low-temperature SDG and subsequent annealing gives similar, if not slightly better, results than high-temperature SDG.

Conclusions: SDG is a simple procedure which could potentially be added to a mc-Si solar cell manufacturing process and only requires a basic furnace. In this letter we have demonstrated that SDG at 500 to 700 °C can be used as part of a low-temperature processing strategy to improve lifetime in as-grown mc-Si for solar cells. Lifetime improvements by a factor of 4.2 have been demonstrated by combining SDG with subsequent low-temperature internal gettering, with no process exceeding 600 °C. Future work should focus on combining SDG with subsequent solar cell processes, such as phosphorus diffusion gettering.

Acknowledgments

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Conflict of Interest

The authors declare no conflict of interest.

Keywords

gettering, minority carrier lifetime, silicon, solar cells

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