Hydrogenation effect on low temperature internal gettering in multicrystalline silicon

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***Abstract* — We have performed a comprehensive study into low temperature (≤ 500 °C) internal gettering in multicrystalline silicon (mc-Si). Two groups of as-grown mc-Si wafers from different ingot height positions were subjected to the same thermal treatments with surface passivation by either silicon nitride (SiN_x:H) or a temporary iodine-ethanol (I-E) chemical solution . With either passivation scheme, lifetime in the relatively low lifetime samples from the bottom of the ingot improves substantially. There are however key passivation-dependent differences in behavior in other parts of the ingot. Lifetime in relatively good wafers from the middle of the ingot is improved significantly with silicon nitride passivation but not with iodine-ethanol, for which substantial reductions in lifetime initially occur. There are also key differences in the internal gettering behavior of bulk iron. We suggest the differences arise because silicon nitride introduces hydrogen into the bulk, whereas the iodine-ethanol does not.**

***Index Terms* — multicrystalline, silicon, hydrogenation, lifetime, passivation.**

I. Introduction

Multicrystalline silicon (mc-Si) wafers contain a large number of structural crystallographic defects, such grain boundaries, dislocations and precipitates of light elements such as oxygen. They also contain a high concentration of metallic impurities, with can exist as point-like defects, in precipitates or bound to structural defects. The details of how impurities are distributed within the material govern the material's performance. For instance, the electrical activity of dislocations or oxide precipitates is governed by the degree to which they are decorated by metallic impurities [1, 2] and concentrating a fixed impurity concentration into a lower density of larger metallic precipitates can lower overall recombination activity [3]. Among the various metallic impurities present in mc-Si material, iron is one of the most detrimental to the minority carrier lifetime (henceforth referred to as just "lifetime") [4, 5]. Although most of iron is present in the form of precipitates [6], substantial recombination activity still arises from bulk iron, in the form of interstitial iron (Fe_i) or FeB pairs.

Gettering processes are often used to extract metallic impurities from the bulk or to redistribute them with the intention of increasing lifetime. Extensive research has been performed into *external* gettering using phosphorus, boron, or aluminium to remove metallic impurities from the bulk [7-9]. A number of studies have also been performed into low temperature *internal* gettering in which metallic impurities are redistributed within the material in configurations in which they are less detrimental to average lifetime [10-15].

Rinio *et al*. performed low temperature annealing (300 °C to 800 °C) on mc-Si solar cells and reported a maximum efficiency improvement at 575 °C [10]. As the processing was performed on completed cells it is difficult to distinguish between internal and external gettering. Krain *et al*. studied internal gettering at 300 °C to 500 °C in silicon nitride passivated mc-Si substrates and found a systematic reduction in the interstitial iron concentration with reductions of more than one order of magnitude achieved [12]. They did not however report the effect on bulk lifetime in detail. Furthermore, it is possible that Krain *et al.*'s results were influenced by the hydrogenation effect due to silicon nitride passivation as reported in recent studies by Karzel *et al*. and Liu *et al*. [16, 17]. In order to minimize a possible hydrogenation effect, we have recently performed a comprehensive study into low temperature internal gettering using a room temperature iodine-ethanol passivation scheme for samples from different height position of a commercially grown mc-Si ingot [14, 15]. In bottom samples annealed at 400 °C, our results show lifetime can be improved by a factor of 7 and the interstitial iron concentration is decreased by 1.7 order of magnitude. However, in general our results do not show the systematic decay in bulk iron concentration with annealing time and temperature observed by Krain *et al*. [12]. This is surprising because at the temperatures used the interstitial iron is massively supersaturated [18, 19], which provides a driving force for precipitation. The reason for the discrepancy with Krain *et al.*'s work is not clearly understood, and this study aims to start to address this.

Hydrogenation is well known to improve the bulk of silicon materials [20-24]. Silicon nitride dielectric layers deposited by plasma-enhanced chemical vapour deposition (PECVD) are commonly used to passivate wafer surfaces in silicon solar cell production [25, 26]. These films have a high hydrogen concentration [27, 28]. Several studies have found that hydrogen atoms diffuse into the bulk during thermal annealing process [21, 27] and the kinetics of iron-hydrogen complex formation has recently been studied [29]. Liu *et al*. performed a hydrogenation study after a high temperature (1000 °C) oxidation process. They suggest that hydrogenation enhances the diffusivity of the bulk iron [17]. A similar finding is

reported by Karzel *et al*. [16]. However, a study was not performed on samples from different height positions in an ingot, which is important as the microstructures (particularly dislocation densities) vary significantly [15]. Additionally, a recent deep level transient spectroscopy (DLTS) study by Leonard *et al*. suggested that hydrogen atoms can form complexes with bulk iron under certain conditions, but dissociate in an annealing at 125 °C for 30 min [30].

This paper present a systematic study of low temperature internal gettering for samples sourced from different height positions of a commercially grown mc-Si ingot. Samples are passivated with PECVD silicon nitride and are annealed for long durations at 300 °C to 500 °C. Lifetime and interstitial iron concentrations are measured on average and with spatial resolution at every annealing step. New results are compared with our previous work on low temperature internal gettering using a temporary iodine-ethanol passivation scheme in which samples were sourced from the same height positions and subjected to the same thermal treatment [14, 15]. Possible differences between the cases are discussed.

II. Experimental Methods

Sister mc-Si wafers from four different height positions of an edge block from a commercially-grown boron doped ingot were used. The heights are denoted by top (T), top middle (MT), bottom middle (MB) and bottom (B). The wafers were initially 156 mm × 156 mm × 200 µm with resistivities in the range 4.75 Ωcm to 11.5 Ωcm. Wafers were laser cut into 39 mm × 39 mm samples. Two groups of adjacent samples were selected from every height position. To remove saw damage from the surface, all samples were chemically polished with a planar etch solution comprising HF (50%), HNO_3 (69%), and CH_3COOH (100%) in the ratio of 24:58:18. This was followed by RCA cleaning prior to surface passivation. Set I samples were passivated with ~70 nm silicon nitride grown on both sides by remote plasma enhanced chemical vapour deposition (PECVD) at ~375 °C at ISFH. Set II samples were passivated with a temporary 0.1 M of iodine-ethanol (I-E) chemical solution at room temperature. More details of the I-E passivation process have been reported previously [14, 15]

The lifetime was measured using quasi-steady-state photoconductance (QSS-PC) with a Sinton WCT-120 tool. Lifetimes in this paper are the effective lifetime with bulk iron in the Fe_i state at an injection level of 1×10^{15} cm^{-3}, and are denoted by τ_{Fei}. The interstitial iron concentration (denoted by $[Fe_i]$) was measured at an injection level of $\Delta n = 1 \times 10^{15}$ cm^{-3} based on the carrier lifetime changes before and after the photodissociation of the FeB complexes using a method published previously [31]. The spatial distribution of carrier lifetime was measured using a BT Imaging LIS-L1 photoluminescence (PL) imaging tool with a spatial resolution of ~160 µm.

Sister samples from each height position from both sets were annealed at 300 °C, 400 °C or 500°C in a tube furnace in nitrogen ambient, followed by rapid cooling to room temperature. Samples from the Set I were annealed with silicon nitride passivation in place, whereas Set II samples were thoroughly cleaned prior to thermal annealing. The characterization process described above was performed after every annealing step.

III. Results

Figure 1 shows the lifetime in Set I samples with silicon nitride passivation annealed at 300 °C, 400 °C and 500 °C as a function of cumulative annealing time period. The lifetime in as-grown samples (represented by the dotted lines) varies significantly with the ingot height position. The average lifetime is lowest in samples from the extrema of the block (T and B) and highest in the middle part (MB and MT). This is consistent with other studies (e.g. Ref. [32]).

Figure 1 shows that low temperature annealing affects lifetime, with both increases and decreases observed. Annealing Set I samples from any height position at 300 °C does not result in a significant lifetime improvement, and in the case of relatively high lifetime MB samples results in a slight decrease. The most significant improvement is observed when the bottom and bottom middle samples are annealed at 400 °C. Lifetime is improved from 19.5 µs to 30.9 µs in the bottom case, and 142.9 µs to 183.7 µs in the bottom middle case. For samples annealed at 500 °C, lifetime improves from 15.3 µs to 39.1 µs in samples from the bottom of the ingot whereas samples from other parts of the ingot exhibit a lifetime reductions.

Figure 2 shows the evolution of $[Fe_i]$ with annealing for the Set I (silicon nitride passivated) samples. $[Fe_i]$ ultimately reduces significantly for the top and bottom samples at all three temperatures. In the bottom middle and top middle samples, $[Fe_i]$ decreases substantially at 300 °C and 400 °C whereas it surprisingly increases upon annealing at 500 °C, returning approximately to the initial value after the longest annealing time of 47 h.

Figure 3 shows representative spatially-resolved PL lifetime images of two samples from Set I (silicon nitride passivated) measured with bulk iron in Fe_i state. The bottom and bottom middle samples in Figure 3(a) and 3(b) respectively show that lifetime is increased substantially in the intra-grain regions upon annealing at 400 °C.

Figure 4 shows a comparison in lifetime (with iron in Fe_i state) and $[Fe_i]$ for samples from the Set I (silicon nitride passivated) and Set II (iodine-ethanol passivated) annealed at 400 °C. The lifetimes and $[Fe_i]$ values in Figure 4 are normalized to the starting values for that Set so that the data can be compared directly. The behavior in Set I and Set II samples from the top and bottom of the block is qualitatively similar. The $[Fe_i]$ decay rate in the bottom samples is almost

identical. In the middle part of the ingot (MB and MT) there are however significant differences in behavior. Lifetime in these samples reduces substantially with iodine-ethanol (Set II) but increases slightly with silicon nitride (Set I). [Fe_i] in these samples surprisingly increases with iodine-ethanol (Set I) but decreases with silicon nitride (Set II).

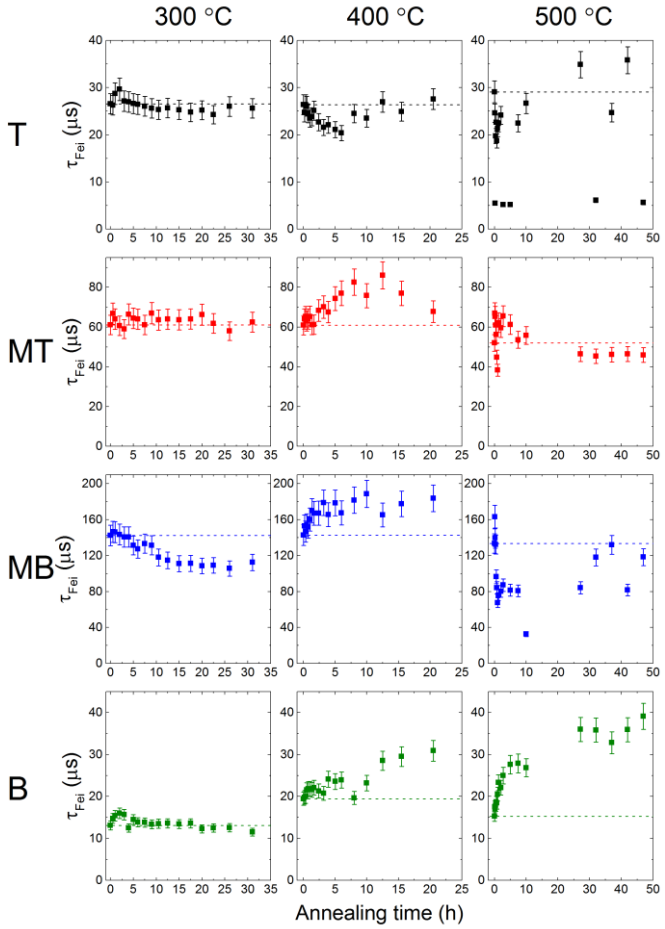

Fig. 1. Effective lifetime with bulk iron in the interstitial state (τ_{Fei}) in the Set I (silicon nitride passivated) samples annealed at 300 °C, 400 °C and 500 °C for the cumulative time period shown. Dotted lines represent the as-grown values.

IV. Discussion

New results are presented on the effect of low temperature annealing on silicon nitride passivated mc-Si samples from different ingot height positions. In general, the results do not show a systematic relationship with the annealing time and temperature. Low temperature annealing gives rise to both decreases and increases in the bulk lifetime. Annealing silicon nitride passivated samples at 300 °C gives rise to no improvement, and in some cases a slight worsening, of lifetime (Figure 1). The most significant improvement in lifetime is observed after annealing at 400 °C in samples from all height positions. Lifetime improvement in the bottom sample is from 19.5 μs to 30.9 μs and in the middle bottom samples from 142.9 μs to 183.7 μs. The largest improvement in bottom samples is from 15.3 μs to 39 μs in annealing at 500 °C for 47 h of cumulative time period. The spatially resolved lifetime maps follow the same trend of bulk changes. Lifetime significantly improves in the intra-grain regions, indicative of gettering of impurities to extended crystallographic defects within the material.

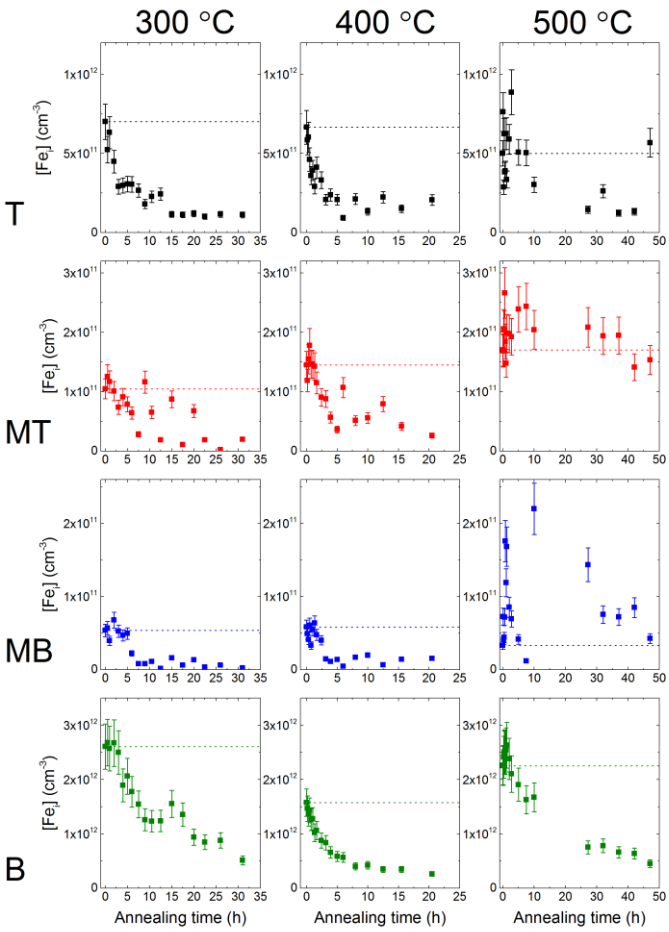

Fig. 2. The interstitial iron concentration ([Fe_i]) in the Set I (silicon nitride passivated) samples annealed at 300 °C, 400 °C and 500 °C for cumulative time period shown. The dotted lines represent the as-grown values.

The interstitial iron concentrations in samples with silicon nitride passivation show a substantial reduction in most cases (Figure 2). The bottom samples, which have a relatively high starting concentration, exhibit a reduction at all three annealing temperatures. In other samples, interstitial iron concentration is reduced by annealing at 300 °C and 400 °C. It is important to note that our silicon nitride results do not generally show a systematic decay with annealing temperature and time as presented in Krain *et al*. [12], who used a similar passivation scheme to our Set I samples. We note that for a given ingot location our samples for each Set were sisters to one another and therefore had near identical microstructures. Thus if internal gettering of interstitial iron is entirely

governed by iron diffusion one would expect a more rapid decay in bottom samples at 500 °C than at 400 °C, but this is not what our data show (Figure 2). The five samples used by Krain *et al.* were from different ingot heights. As the rate of internal gettering of interstitial iron is likely to be highly dependent on the density and distribution of possible sinks, it is possible that any correlation between temperature and interstitial iron decay in Krain *et al.*'s study was coincidental.

At 500 °C we find that the interstitial iron concentration initially increases in silicon nitride passivated samples. At all temperatures studied, the measured interstitial iron concentrations are substantially in excess of the solubility values [18, 19]. It is therefore surprising that the measured values increase upon annealing. It could be that annealing at 500 °C is sufficient to release iron from precipitates or other defects within the material, but this topic is the subject of further study.

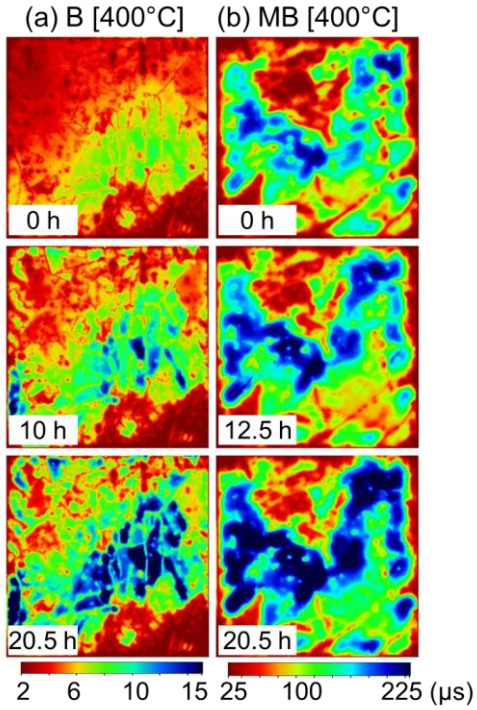

Fig. 3. Spatial distribution of lifetime with iron in the Fe_i state for the Set I (silicon nitride passivated) samples annealed at 400 °C: (a) bottom (B) samples; and (b) bottom middle (MB) samples. Different scales are used as the as-grown lifetime differs considerably.

The 400 °C annealing results for the Set I samples (passivated with silicon nitride) are compared with our previous work using an iodine-ethanol passivation scheme (Figure 4). Both sets of samples were subjected to the same thermal treatment, so differences in behavior can be attributed to differences arising from the surface passivation techniques used. For lower lifetime samples from the bottom and top of the block, the behavior is qualitatively the same in both cases, with interstitial iron concentration decreasing at the same approximate rate and lifetime varying in approximately the same way (although the effect on lifetime is more pronounced in bottom samples with iodine-ethanol than with silicon nitride). In the middle samples (both MB and MT), lifetime improves slightly upon annealing at 400 °C with silicon nitride passivation, whereas with iodine-ethanol passivation it initially reduces sharply. Interstitial iron concentrations fall in the case of silicon nitride but increase with iodine-ethanol. It is concluded that the passivation methodology can strongly affect the internal gettering behavior.

It is suggested that the difference in behavior arises because of hydrogenation from the silicon nitride film in the case of Set I samples which does not occur in the Set II samples. Recent studies by Liu *et al.* [17], Karzel *et al.* [16] and Leonard *et al.* [30] provide evidence for hydrogen interacting with bulk iron. Our working assumption is that the hydrogen in Set I samples stabilizes bulk lifetime upon annealing at 400 °C. Without hydrogen interstitial iron is released into the bulk from some other source within the material, but with hydrogen the as-grown interstitial iron concentration reduces by internal gettering to bulk defects.

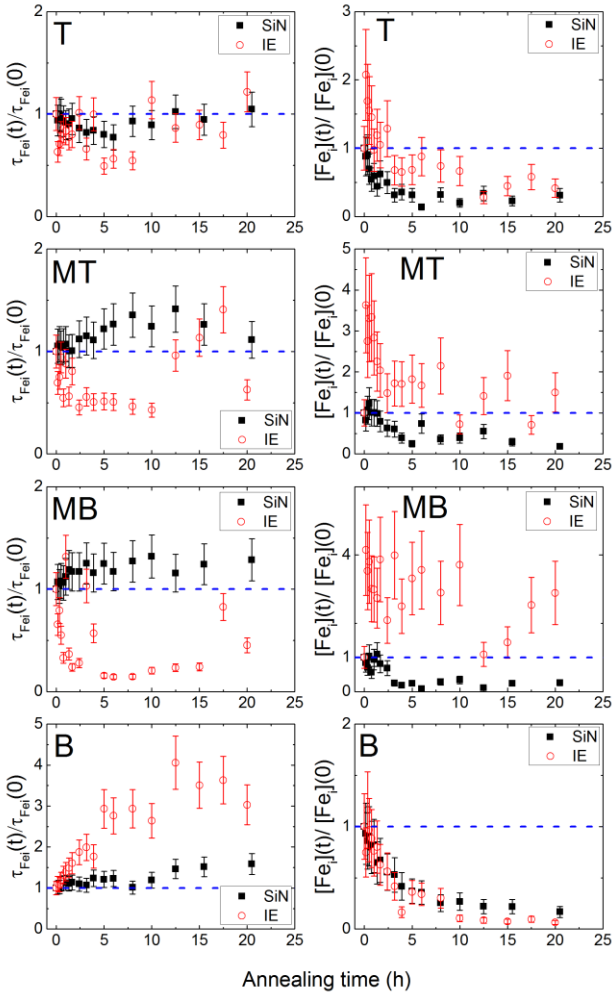

Fig. 4. Comparison in normalized lifetime with iron in the Fe_i state and $[Fe_i]$ for the Set I (silicon nitride passivated) and Set II (iodine-ethanol passivated) samples annealed at 400 °C as a function of cumulative time period. Lifetimes were measured at an injection level of 1×10^{15} cm^{-3}.

V. Conclusion

A study has been performed into the effect of low temperature annealing on as-grown mc-Si samples from different height positions in the block. New data using a silicon nitride surface passivation scheme are presented and compared with our previous data acquired with a temporary liquid iodine-ethanol passivation at room temperature. Annealing silicon nitride passivated samples at 300 °C did not result in significant lifetime improvements. Annealing at 400 °C generally had a positive effect on bulk lifetime. Annealing at 500 °C increased lifetime in relatively poor bottom samples. Using sister samples we have shown that the behavior of interstitial iron at low temperatures is a complex problem. The diffusion of interstitial iron is not the only controlling factor which has previously been implied by Krain *et al.* [12]. Comparison of the behavior of samples passivated by iodine-ethanol and silicon nitride shows clear differences, and it is suggested that hydrogenation from the silicon nitride plays a role in lifetime stabilization and the release of iron from iron-containing defects within the material.

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