

Evidence for the role of hydrogen in the stabilization of minority carrier lifetime in boron-doped Czochralski silicon

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This study demonstrates that the presence of a hydrogen source during fast-firing is critical to the regeneration of B-O defects and that it is not a pure thermally based mechanism or due to plasma exposure. Boron-doped p-type wafers were fired with and without hydrogen-rich silicon nitride ($\text{SiN}_x\text{:H}$) films present during the fast-firing process. After an initial light-induced degradation step, only wafers fired with the $\text{SiN}_x\text{:H}$ films present were found to undergo permanent and complete recovery of lifetime during subsequent illuminated annealing. In comparison, wafers fired bare, i.e., without $\text{SiN}_x\text{:H}$ films present during firing, were found to demonstrate no permanent recovery in lifetime. Further, prior exposure to hydrogen-rich plasma processing was found to have no impact on permanent lifetime recovery in bare-fired wafers. This lends weight to a hydrogen-based model for B-O defect passivation and casts doubt on the role of non-hydrogen species in the permanent passivation of B-O defects in commercial-grade p-type Czochralski silicon wafers. © 2015 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4919385>]

Boron-doped Czochralski (Cz) silicon, a common material used to make crystalline-silicon solar cells, is known to undergo degradation in carrier lifetime during carrier injection, particularly when oxygen-rich.¹ The commonly accepted cause for this degradation is the formation of recombination-active boron-oxygen (B-O) defects in the wafer bulk during carrier injection.² Thermal annealing in the dark at temperatures greater than 200 °C is known to cause electrical deactivation of the B-O defect and lead to a subsequent recovery of the carrier lifetimes. This is thought to be due to the defect being in an electrically inactive “annealed” state,³ owing to thermal dissociation of the B-O complex.⁴ However, defect deactivation through this method has been shown to be temporary, with lifetimes known to degrade again after subsequent illumination or carrier injection even at room temperature.

In 2006, Herguth *et al.* reported a new approach to prevent lifetime degradation through the use of an illuminated annealing process⁵ in which the B-O defect was “permanently” deactivated. It was suggested that this deactivation occurs due to the B-O defect being in a third, electrically inactive “regenerated” state. Achieving this state appears to require a fast thermal process (peak temperature over 600 °C) with a high cooling rate followed by a lower temperature illuminated anneal process (generally $T < 230$ °C). However, the exact mechanism of the regeneration process continues to be debated in literature.^{6–11}

One major point of contention is the role of hydrogen, which is present in the silicon nitride (SiN_x) films that are usually used as surface passivation dielectrics in silicon solar cells. The plasma enhanced chemical vapour deposition (PECVD) process typically used to deposit these films is known to result in hydrogen-rich silicon nitride films

($\text{SiN}_x\text{:H}$) through the incorporation of hydrogen into these films from precursor gases of ammonia (NH_3) and silane (SiH_4).^{12,13}

The importance of hydrogen-rich dielectric layers for B-O regeneration has been studied by varying the composition^{10,14} as well as type^{9,15} of dielectric films. It was also hypothesized that the charge state of hydrogen could play a key role in the passivation process for B-O defects.^{6,7,16} This understanding is based on experimental evidence that the fractional charge states of hydrogen in silicon can be manipulated through controlling temperature and carrier injection.¹⁷ Moreover, the ability of hydrogen to passivate various defects in silicon by bonding to and/or neutralizing the electrically active sites of the defects is well-known.^{18–20} All these suggest a very likely link between hydrogen and B-O passivation.

However, in most cases, where the use of hydrogen-containing dielectric films has led to B-O regeneration, the films were deposited using plasma-enhanced processes, making it difficult to distinguish between the effect of hydrogen-containing dielectrics and plasma processing. Hydrogen-free films deposited by low-pressure CVD (LPCVD)⁹—a non-plasma process—and reactive sputtering¹⁰ were found not to result in regeneration, whereas hydrogen-containing films deposited by remote-PECVD (where wafers are not directly exposed to plasma) were found to result in some B-O regeneration, although this process is significantly slower and less effective.¹⁵ While this suggests hydrogen and plasma exposure both impact B-O regeneration, the specific role of plasma processing remains unclear.

In addition, some studies have reported a lack of regeneration when wafers are fired bare (i.e., without any hydrogen-containing films) prior to the illuminated annealing process;^{9–11} however, direct comparison between bare-fired wafers and those fired with hydrogen-containing dielectrics has been difficult due to the differing levels of surface

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passivation and the consequent impact on lifetime and open-circuit voltage, casting uncertainty on whether regeneration is truly possible without the presence of hydrogen during firing.

In fact, in a recent Letter, Walter *et al.* proposed that hydrogen is not required for B-O regeneration⁸ and is attributed solely to boron nano-precipitates,²¹ which are assumed to trap all of the interstitial boron thought to be released during the dissociation of the recombination-active B-O defect under illuminated annealing, thereby preventing B-O defects from re-forming and resulting in stable improved lifetimes. This hypothesis is based on the evidence that annealing and degradation of B-O defects are impacted by firing conditions even in the absence of hydrogen sources during firing. However, the details of the proposed hydrogen-free mechanism for B-O regeneration are developed based on data from wafers fired with PECVD SiN_x:H layers (which therefore contain hydrogen).

This study aims to conclusively determine if the presence of a hydrogen source during firing is critical to the regeneration process. Specifically, the impact of (a) the presence of PECVD SiN_x:H during the firing process and (b) plasma exposure, on the permanently improved carrier lifetimes on commercial grade Cz wafers is investigated.

Symmetrical lifetime test structures were prepared using commercial grade 156 mm × 156 mm pseudo-square boron-doped Cz wafers (1.6 Ω cm) by alkaline texturing followed by acidic neutralisation. Wafers were subjected to a RCA clean and HF dip, then diffused at 795 °C for 25 min in a POCl₃ tube furnace followed by a drive-in diffusion at 885 °C for 30 min to achieve an emitter sheet resistance of 70 Ω/sq—a process known to be effective at gettering.^{22,23} The phosphosilicate glass (PSG) and emitter thus formed were removed by etching ~2 μm from both surfaces, resulting in a wafer thickness of approximately 180 μm. This was done to ensure minimal concentrations of impurities other than B-O within the wafer bulk. The wafers were RCA cleaned and followed by a second, light POCl₃ diffusion at 780 °C for 30 min and a 20 min drive-in diffusion to achieve a sheet resistance of ~200 Ω/sq to aid in surface passivation. The resulting PSG was removed in dilute HF and wafers were divided into three groups for further processing:

- (A) The first wafer underwent rapid thermal processing (firing) bare (with no prior exposure to SiN_x:H deposition), i.e., no hydrogen source was present on the wafer during firing.
- (B) The second wafer had initial layers of SiN_x:H deposited on both sides (SiN_x:H deposition 1); however, the SiN_x:H layer was removed in HF prior to firing.
- (C) The third wafer had initial layers of SiN_x:H deposited on both sides (SiN_x:H deposition 1), which remained on the wafer during firing.

The initial SiN_x:H layers in group C were etched after firing (5% HF for 10 min). A second SiN_x:H deposition was then performed for all wafers (SiN_x:H deposition 2) to eliminate differences in surface passivation that could result from firing wafers with and without the initial SiN_x:H films. All SiN_x:H layers, deposited onto both wafer surfaces using a

Roth & Rau MAiA PECVD system, were 80 nm thick and had a refractive index of 2.08 at 633 nm. Identical SiN_x:H layers were used before (in the case of groups B and C) and after firing (for all groups).

Firing was performed in a SierraTherm infra-red fast-firing furnace. Thermal profiling performed using a Datapaq Q18 profiler confirmed that samples with and without the SiN_x:H films underwent the same thermal process. A peak temperature of 600 °C was achieved and a belt speed of 5.0 m/min was used, resulting in a rapid cooling rate of 50 ± 1 °C/s between 600 °C and 550 °C.

Wafers in all groups were then subjected to an initial light-induced degradation (LID-1) process under a halogen lamp with a light intensity of 78 ± 1 mW/cm² at a temperature of 40 ± 3 °C for a total of 48 h, comparable to the temperature and illumination conditions reported previously in literature.^{24,25} An illuminated annealing step was then performed for 2 h at 172 ± 3 °C under a halogen lamp with a light intensity of 65 ± 2 mW/cm². A second and final degradation step (LID-2) was then performed under the same conditions as LID-1. In all cases, the duration of the LID process was found to be sufficient to completely degrade sample lifetimes.

To characterize the impact of B-O defects, the bulk lifetime (τ_{bulk}) of each sample was measured after each of the processing steps. This was done by measuring the effective minority carrier lifetime (τ_{eff}) as a function of excess minority carrier density (Δn) using a WCT-120 (Sinton Instruments) photoconductance lifetime tester with nine points sampled per wafer.²⁶ The measured data were analysed using the generalised method²⁷ and corrected for Auger recombination²⁸ to obtain the inverse Auger-corrected effective lifetime ($1/\tau_{\text{eff}} - 1/\tau_{\text{Auger}}$). To enable a comparison between the different groups and remove the impact of variations in surface recombination, a value for τ_{bulk} was extracted at a carrier concentration of $2 \times 10^{14} \text{ cm}^{-3}$.²⁹ This was done by assuming that the surfaces were well modelled by the dark saturation current density (J_{0d}) values, which were extracted from the slope of the original lifetime curve³⁰ at $\Delta n = 1 \times 10^{16} \text{ cm}^{-3}$ directly after the second SiN_x:H deposition, hence prior to the introduction of Shockley-Read-Hall (SRH) recombination³¹ during LID-1. Note that τ_{bulk} measured after subsequent process steps includes the contribution of SRH defect recombination. For samples significantly affected by bulk asymmetric SRH recombination (for steps LID-1, illuminated annealing and LID-2), the extraction of J_{0d} resulted in values that were slightly underestimated, causing a slight overestimation of τ_{bulk} . These errors, however, are small and do not affect the trends or conclusions of this work.

As shown in Fig. 1, the average τ_{bulk} of all three groups improved or degraded to various extents at different stages of processing. For all groups, τ_{bulk} was observed to degrade from an average of ~590–630 μs to ~140–190 μs after LID-1 and then subsequently increase after the following illuminated annealing step. However, the τ_{bulk} improvement for group C (from ~140 μs to ~680 μs) was six-fold more than that seen in groups A and B (from ~190 μs to ~270 μs). Moreover, only in the case of group C was the improvement in τ_{bulk} largely retained even after 48 h of light soaking

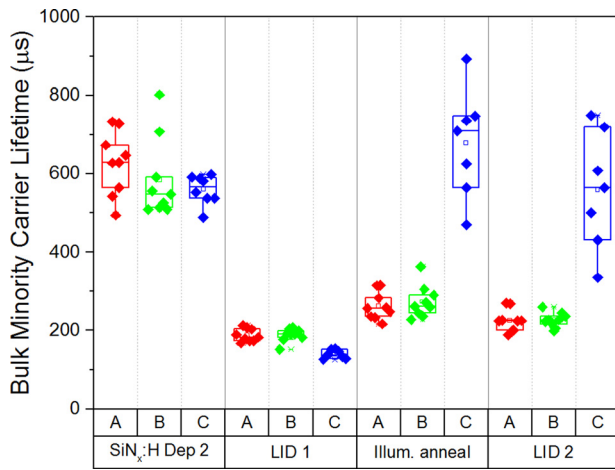


FIG. 1. Boxplot showing bulk minority carrier lifetime (τ_{bulk}) at $\Delta n = 2 \times 10^{14} \text{ cm}^{-3}$ at each successive stage of processing for wafers with: (A, red) no $\text{SiN}_x\text{:H}$ deposited before firing, (B, green) $\text{SiN}_x\text{:H}$ layers deposited then removed before firing, and (C, blue) $\text{SiN}_x\text{:H}$ present during firing.

(LID-2) (final stabilized $\tau_{\text{bulk}} = \sim 560 \mu\text{s}$), whereas τ_{bulk} for groups A and B degraded again after LID-2, with final stabilized τ_{bulk} for both groups being $\sim 230 \mu\text{s}$ —comparable to the lifetime after LID-1. Hence, group C saw no net reduction in lifetime (relative to the value after the second $\text{SiN}_x\text{:H}$ deposition), whereas groups A and B underwent a 60% net reduction in τ_{bulk} . Further, improvement in groups A and B after illuminated annealing were found to be temporary. This result implies that a source of hydrogen was required during firing for subsequent permanent passivation of a SRH defect during the illuminated annealing step.

One concern with this result could be the impact of processing wafers through a metal firing furnace with no protective nitride coating. This bare firing may result in differences in surface passivation and τ_{bulk} between the sample groups immediately after a subsequent deposition of $\text{SiN}_x\text{:H}$. However, the effect on surface passivation was minimized in our case by stripping the $\text{SiN}_x\text{:H}$ layers in group C after firing and deposition of new $\text{SiN}_x\text{:H}$ layers for all groups. This resulted in comparable J_{od} values for all groups after $\text{SiN}_x\text{:H}$ deposition 2 ($J_{\text{od}} = 73, 74, \text{ and } 90 \text{ fA/cm}^2$ for groups A, B, and C, respectively). More importantly, as seen in Fig. 1, all three groups were found to have similar τ_{bulk} after $\text{SiN}_x\text{:H}$ deposition 2 regardless of whether they were fired with or without $\text{SiN}_x\text{:H}$ films (625, 585, and $560 \mu\text{s}$, respectively, for groups A, B, and C). Thus, bare firing (with or without plasma-exposure) was found to have no significant impact on τ_{bulk} .

To further clarify the impact of the illuminated annealing process on bulk passivation, curves of excess minority carrier concentration versus Auger-corrected effective lifetime ($1/\tau_{\text{eff}} - 1/\tau_{\text{Auger}}$) curves were studied, which are plotted in Fig. 2 for all three groups at different stages of processing.

After $\text{SiN}_x\text{:H}$ deposition 2 (black squares), all three samples had lifetimes which were effectively independent of excess minority carrier density for $\Delta n < 10^{15} \text{ cm}^{-3}$, indicating the absence of SRH recombination. Light soaking the samples after firing (LID-1) resulted in a reduction in effective lifetime for all three groups (red circles). In contrast to the starting lifetimes, these degraded lifetime curves display a

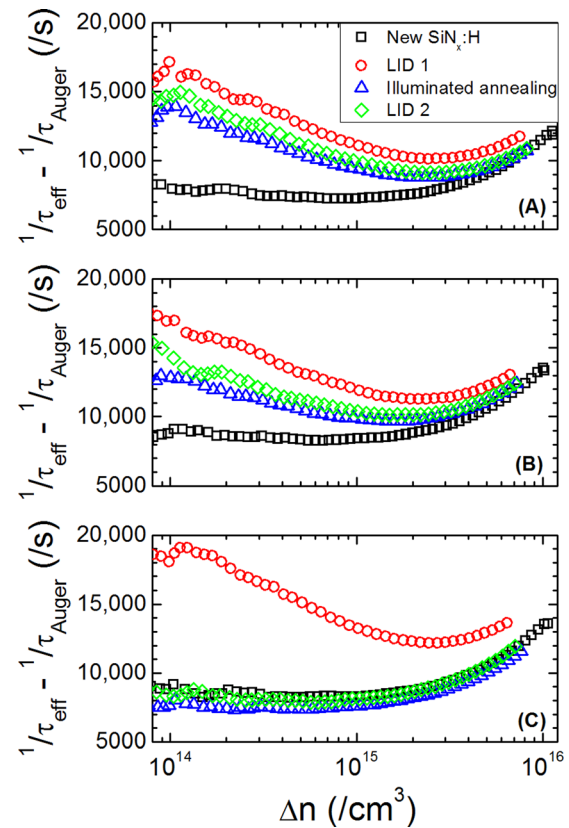


FIG. 2. Auger-corrected inverse effective lifetime ($1/\tau_{\text{eff}} - 1/\tau_{\text{Auger}}$) versus minority carrier density (Δn) plotted for wafers with $\text{SiN}_x\text{:H}$ layers (a) not deposited prior to or present during firing, (b) deposited and removed prior to and not present during firing, and (c) deposited prior to and present during firing, at four different post-firing process stages: (1) after the second, post-firing $\text{SiN}_x\text{:H}$ deposition (black squares), (2) after LID-1 (red circles), (3) after illuminated annealing (blue triangles), and (4) after LID-2 (green diamonds). Curves within each plot are from the same point on the wafer.

clear dependence on carrier concentration, indicating bulk asymmetric SRH recombination. Modelling of the curve obtained by subtracting the lifetime curves obtained after the $\text{SiN}_x\text{:H}$ deposition 2 and after LID-2 revealed that the SRH defect associated with this injection dependence has an electron-to-hole capture cross section ratio of ~ 10 . Since this value was comparable to the capture cross section ratio of 9.3 reported for the B-O defect,³² the B-O defect was confirmed to be the dominant source of SRH recombination.

Subsequent illuminated annealing (blue triangles) resulted in a complete lifetime recovery only for the sample fired with $\text{SiN}_x\text{:H}$ (group C). This result was found to be consistent with the “permanent recovery” process demonstrated by Herguth *et al.*^{3,5} In contrast, both groups fired without $\text{SiN}_x\text{:H}$ layers (groups A and B) continued to be affected by injection level dependent SRH recombination due to the B-O defect. Although there appeared to be less injection dependence after illuminated annealing in group B compared with group A, the subsequent LID-2 step (green diamonds) resulted in the both groups reverting back to the same injection-dependent lifetime behavior seen prior to illuminated annealing (i.e., after LID-1, red circles). In other words, mere exposure to the hydrogen-rich PECVD plasma during $\text{SiN}_x\text{:H}$ deposition 1 without actually firing the wafer with the dielectric on (as in group B) did not cause a

measurable increase in bulk passivation. Moreover, the negligible improvement in τ_{eff} observed in group B was clearly not permanent, suggesting that the B-O defect simply underwent annealing rather than regeneration after $\text{SiN}_x\text{:H}$ deposition.²

This is in stark contrast to group C, in which the elimination of injection dependence achieved after illuminated annealing (blue triangles) was largely retained even after the final 48-h LID-2 step (green diamonds), resulting in permanent deactivation (regeneration) of the B-O defect.

These observations suggest that (a) wafers fired with $\text{SiN}_x\text{:H}$ undergo more B-O passivation during the illuminated annealing step than wafers fired without $\text{SiN}_x\text{:H}$, and (b) permanent passivation of the B-O defect does not occur unless the $\text{SiN}_x\text{:H}$ is present on the wafer during firing.

Based on these results, it may be deduced that B-O regeneration does not occur without a hydrogen-containing dielectric present during the firing process. This corroborates the findings of other studies in which hydrogen-free dielectrics did not lead to regeneration during subsequent illuminated annealing steps,⁹ whereas even low levels of hydrogen within the dielectric were found to be sufficient to cause B-O regeneration.³³

Further, temporary passivation observed immediately after firing or after PECVD $\text{SiN}_x\text{:H}$ deposition may be because the post-firing and post-deposition cooling process subject the wafer to temperature and illumination conditions that favour the B-O defect annealing reaction (thermal dissociation). Similarly, the temporary passivation after illuminated annealing in groups A and B may also have been due to net annealing of B-O defects as these wafers likely lack a reaction pathway to cause B-O regeneration in the absence of any hydrogen incorporation into the wafer bulk.

The role of plasma exposure has also been clarified in our study, which shows no influence of plasma exposure on B-O regeneration unless fired with the $\text{SiN}_x\text{:H}$ present. The enhanced regeneration observed in other studies where hydrogen-containing films are deposited using direct-plasma techniques¹⁵ may be due to plasma-assisted diffusion of hydrogen into the wafer during $\text{SiN}_x\text{:H}$ deposition, as suggested by Sopori *et al.*³⁴ However, the introduced hydrogen, which may be assumed to exist largely near the surface of the wafer,³⁵ may be lost to effusion into the ambient if fired bare^{9,11} (also seen in the case of group B). In contrast, the presence of the $\text{SiN}_x\text{:H}$ film during firing may act both as an out-diffusion barrier and as an additional source of hydrogen during firing.³⁶ Hence, while plasma exposure may enhance hydrogen diffusion into the wafer, regeneration may not occur in subsequent steps unless hydrogen is retained in the wafer during firing.

The key role of hydrogen in the above analysis calls into question the recent claim made by Walter *et al.*⁸ that the increase in carrier lifetimes after firing is not due to a hydrogen-related effect. This claim was made based on an observed dependence on firing conditions of effective lifetimes of wafers fired bare (without any hydrogen source) that were either degraded or dark-annealed immediately after firing. However, the study did not consider (a) carrier lifetimes for bare-fired wafers annealed under illumination after firing or for wafers that have been degraded subsequent to

annealing, and (b) changes in surface passivation quality (J_{0d}) due to the $\text{SiN}_x\text{:H}$ being fired under varying conditions, both of which have been accounted for in this study.

Consequently, the hypothesis that boron nano-precipitates²¹ formed during the rapid cooling process after firing⁸ are largely responsible for the permanent passivation of B-O defects may not offer a complete picture of the B-O defect regeneration mechanism as such a mechanism does not take into account the role of $\text{SiN}_x\text{:H}$ layers as a hydrogen source, which has been shown in this work to be critical to B-O regeneration. However, permanent passivation of the B-O defect, enabled by a favourable hydrogen charge-state configuration^{6,7} offers a suitable alternative hypothesis.

Therefore, we expand on previously-proposed hydrogen-based mechanisms^{6,7} and offer the following explanation for permanent B-O defect passivation in p-type silicon: When hydrogen is absent or is in an unfavourable charge state (through inappropriate thermal conditions and/or carrier injection), permanent passivation is not achieved. In fact, any recovery in lifetime achieved in such conditions is temporary and is instead due to thermal dissociation of the B-O defect. However, if the introduced hydrogen is subjected to processes that result in optimal thermal conditions and carrier injection, hydrogen charge states favourable for permanent passivation may be achieved wherein the hydrogen bonds to the B-O defect. The source of hydrogen may be in the form of hydrogen-containing dielectrics (such as $\text{SiN}_x\text{:H}$, Al_2O_3 , etc) deposited through non-plasma- or plasma-based processes (the latter may be thought of as enhancing hydrogen incorporation into the wafer). Although other sources of hydrogen may also potentially be used, the lack of a barrier dielectric may be ineffective at retaining the hydrogen within the bulk during any subsequent process used to achieve hydrogen diffusion into the bulk (such as firing). In fact, firing temperatures and cooling rates may strongly affect the net diffusion and retention of hydrogen within the bulk even when barrier dielectrics are present, and are expected to be dependent on the nature of the dielectric.

Based on this model, B-O regeneration efficacy is expected to ultimately depend on (1) the solar cell structure, (2) hydrogen source(s) (such as $\text{SiN}_x\text{:H}$ or aluminium oxide layers, forming gas, hydrogen plasmas, etc.), and (3) the thermal process used, to allow sufficient diffusion of hydrogen into (and retention within) the wafer bulk for the subsequent regeneration process. Another implication of such a model is that it may be possible to perform B-O regeneration at peak firing temperatures lower than that deemed to be required by alternative B-O regeneration mechanisms such as the boron nano-precipitate theory (575 °C).⁸

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