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Influence of Temperature on Light Induced Phenomena in Multicrystalline Silicon

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Abstract. The changes in effective lifetime for mc-Si under the influence of elevated temperatures ranging from 160°C to 400°C and illumination of 2 suns were investigated. It is shown that Light and elevated Temperature Induced Degradation (LeTID) and its subsequent curing can be observed up to a temperature of ~280°C, but vanishes above. Furthermore, it is shown that lifetimes exceed the initial value during prolonged illumination which is interpreted as advanced hydrogenation. However, even though lifetimes exceed the initial value due to advanced hydrogenation at temperatures >280°C, these lifetimes prove to be at least partially instable at low temperatures under illumination suggesting LeTID is not or at least not completely cured. It is concluded that LeTID and advanced hydrogenation are related to different defect systems. In addition, it is shown that both LeTID and advanced hydrogenation only occur above a peak set firing temperature of 720°C thus indicating that lower peak firing temperatures can successfully suppress LeTID, however, only at the price of losing the benefit from advanced hydrogenation as well. Furthermore, it is shown that increasing illumination intensity speeds up the dynamics of LeTID and advanced hydrogenation, respectively.

INTRODUCTION

Multicrystalline (mc) silicon is the most commonly used material in mass production of solar cells and modules [1] due to its superior cost-benefit structure. A key aspect for mc-Si, despite improvements to the crystallization process, is the passivation of extended structural and point-like defects by hydrogen originating from dielectric layers such as SiN_x:H. It has been shown that this passivation may be improved by advanced hydrogenation induced by illumination (excess charge carrier injection) at high temperatures (»200°C) [2].

However, with the introduction of the passivated emitter and rear cell (PERC) architecture on both mc-Si as well as Cz-Si, a devastating Light and elevated Temperature Induced Degradation (LeTID) effect has shown up not only affecting mc-Si [3,4,5], but probably Cz-Si [6,7] and even FZ-Si [8] as well. Already in the first publications it was also shown that LeTID seems to be curable by illumination or biasing (both injecting excess charge carriers) as well, but curing times (below 95°C) were ridiculously long in the range of hundreds of hours – obviously not suitable for integration into mass production [5]. Various publications have shown that curing may be accelerated by increasing temperature [5,9,10], which might bring down curing times far enough for reasonable industrial application, however, it was also shown that the curing effect appears to fail increasingly for temperatures >200°C [10].

On the one hand. it remains unclear whether the benefit from advanced hydrogenation is more or less neutralized by losses due to LeTID, especially because it is speculated that hydrogen might be the driving force behind LeTID [11]. On the other hand, the conditions leading to curing of LeTID and advanced hydrogenation (illumination and elevated temperatures) are pretty much the same, and it remains unclear whether advanced hydrogenation simply passivates other defects and simultaneously cures LeTID as well.

Within this contribution, the response of boron-doped mc-Si samples with SiN_x:H passivation layers with respect to varying peak firing temperature, varying illumination intensity and varying temperature during illuminated annealing is investigated. Furthermore, the effect of temperature switching during illuminated annealing is studied.

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EXPERIMENTAL SETUP

Lifetime samples of size 5 cm × 5 cm were made from boron-doped mc-Si (1.5 Ωcm) and FZ-Si (1.0 Ωcm) material. A $POCl_3$ based diffusion was applied in order to improve material quality by phosphorous gettering. The resulting n^+-layer was wet chemically removed and the surface was cleaned in a Piranha solution (H_2O_2:H_2SO_4 1:3, ~80°C). Both-sided SiN_x:H layers (~75 nm, $n_{633\,nm} \sim 2$) deposited by direct PECVD were applied as surface passivation. Except for the experiment with varying set peak firing temperatures, the ~170 µm thick samples were fired in a belt furnace at a set temperature of 800°C. During illuminated annealing, samples were placed on a hotplate (temperature defined in the respective experiments/graphs) and illuminated with halogen incandescent lamps with 2 suns halogen lamp illumination (j_{sc} equivalent [12]). Effective lifetime is monitored by repeated photoconductance decay (PCD) measurements at 30°C [13]. It is worth noting that this method yields a laterally averaged lifetime value only [14,15].

RESULTS

Variation of Peak Firing Temperature

In a first experiment, the set peak firing temperature was varied in the range from 600°C to 860°C. Samples were subjected to illuminated annealing at 220°C and 2 suns intensity. Figure 1 depicts the observed evolution of effective lifetime. As effective lifetimes differ significantly due to the different degree of activation of passivation quality by the firing step, lifetimes are shown relative to the initial lifetime. As can be seen, a deterioration due to LeTID and its recovery are observable for high firing temperatures. For lower firing temperatures, this effect reduces in extent and finally vanishes (600°C). This is in good agreement with the findings in [16,17]. For longer times exceeding 1 h, an increase of lifetime well beyond its initial value is observed which is interpreted as advanced hydrogenation [1]. The observable gain in lifetime depends strongly on the firing temperature. While the lowest firing temperature yields a net loss for times longer than 1 h, this loss turns into a gain for temperatures exceeding 720°C and the maximum gain is observed for the highest investigated firing temperature. Thus it can be concluded that the firing step seems to be of vital importance not only for the occurrence of LeTID, but also for the occurrence of advanced hydrogenation. This would –at least qualitatively– fit well with the speculations that hydrogen is a key component of both phenomena as hydrogen release from the hydrogen-rich SiN_x:H layers intensifies with rising firing temperature.

Even though it seems a viable way to avoid the negative impact of LeTID by reducing the firing temperature, this also would mean to sacrifice possible gains by advanced hydrogenation. Besides the technical difficulty of developing screen-printing pastes usable at lower firing temperatures, it is therefore questionable whether this way would be the best overall choice.

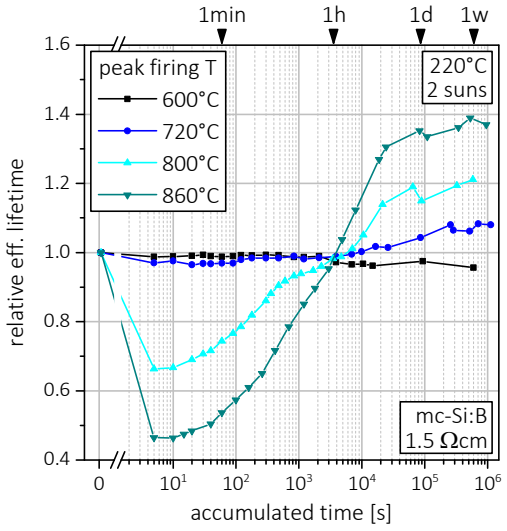

FIGURE 1. Evolution of effective lifetime (relative to their initial lifetime) of mc-Si samples with SiN_x:H passivation fired at different temperatures during illuminated annealing at 220°C and 2 suns intensity.

Variation of Illumination Intensity

In a second experiment, the effect of increasing illumination intensity on LeTID and advanced hydrogenation during illuminated annealing was investigated. The samples were held at a temperature of 220°C or 310°C, respectively. Figure 2 shows the evolution of effective lifetimes in this experiment. As can be seen in Fig. 2a, not only do the reactions at work speed up with increasing intensity, the extent of LeTID also changes (~1 min). In this investigation, LeTID seems not to be inducible in darkness in contrast to the findings in [7]. However, this might be a misinterpretation if the minimum in darkness simply shifts to ~1 h which cannot be excluded from the data taken in this experiment. For non-vanishing intensities, the curve exhibits a double minimum or at least a shoulder which, for 0.1 suns, merge into a broad minimum. The second minimum (~1 h) is most probably related to a degradation and recovery of surface passivation quality (surface related degradation, SRD) as described in [18]. FZ-Si references show this effect as well. Figure 2a also demonstrates that advanced hydrogenation can not only occur during deliberate excess carrier injection, but also in darkness, even though the reaction is slow.

During illuminated annealing at 310°C (Fig. 2b), no drop due to LeTID is observed which will be discussed in more detail in the subsequent section. For advanced hydrogenation, increasing intensity speeds up the reactions at work bringing down treatment times by approximately one order of magnitude for an increase in light intensity of one order of magnitude. Therefore, it seems reasonable to speculate on a linear dependence of the reaction rates on light intensity (or maybe injection level). For the measurement with 25 suns intensity, temperature might have noticeably exceeded the intended treatment temperature of 310°C.

Besides the gain by advanced hydrogenation, Fig. 2 shows also another decrease in lifetime for extremely long times enforcing a maximal gain by advanced hydrogenation before renewed degradation sets in. It is unclear where this phenomenon originates from. From the comparison of Figs. 2a and 2b, it can be concluded that it speeds up with increasing temperature. While it takes a few days of continuous illuminated annealing to reach that maximum at 220°C, it is already reached after a few hours at 310°C. The achievable maximal gain by advanced hydrogenation seems to depend on the temperature during illuminated annealing as well.

Figure 2 demonstrates that increasing illumination intensity is a viable way of bringing down treatment duration needed to at least cure LeTID and probably benefit from advanced hydrogenation as well. However, it is unclear from Fig. 2b whether LeTID was cured as it is not observed at all. This question is addressed in the two subsequent experiments.

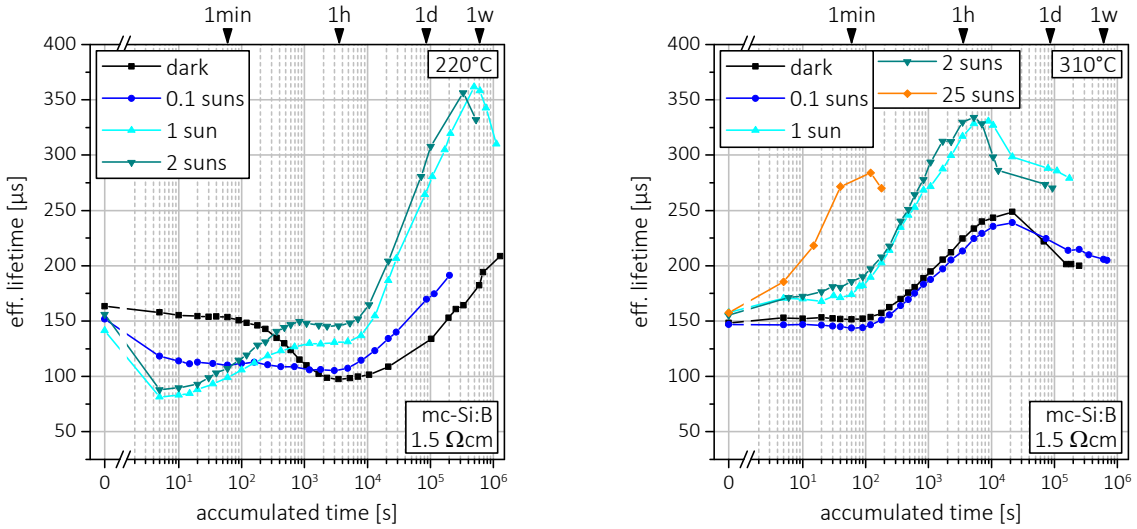

FIGURE 2. Evolution of effective lifetime of mc-Si samples with SiN_x:H passivation during illuminated annealing using variable intensity at 220°C (a) and 310°C (b), respectively.

Variation of Treatment Temperature

In a third experiment, temperature during illuminated annealing at 2 suns intensity was varied ranging from 160°C to 400°C. The evolution of effective lifetime is shown separately for temperatures below and above 280°C in Figs. 3a and 3b, respectively. As can be seen in Fig. 3a, the observable extent of LeTID reduces with increasing treatment temperature (blue to cyan) and finally vanishes in the 280°C measurement (red). Concurrently, the position of the LeTID related minimum shifts to shorter times before it vanishes. The same holds for the second surface related minimum as well. These results are in good agreement with [10].

Above 280°C (Fig. 3b), lifetimes are found to steadily increase right from the beginning until the final decrease of unknown origin –already mentioned in the previous section– sets in and enforces a maximum. The maximal gain by advanced hydrogenation and the duration after which it is reached both depend on the treatment temperature thus meaning that there is a trade-off between the gain and the required time to reach it.

As in the context of Fig. 2, it is unclear, whether LeTID is cured at temperatures exceeding 280°C as it is not observable anymore and if the gain by advanced hydrogenation proves sustainable. To clarify these questions, the subsequently described experiment was performed.

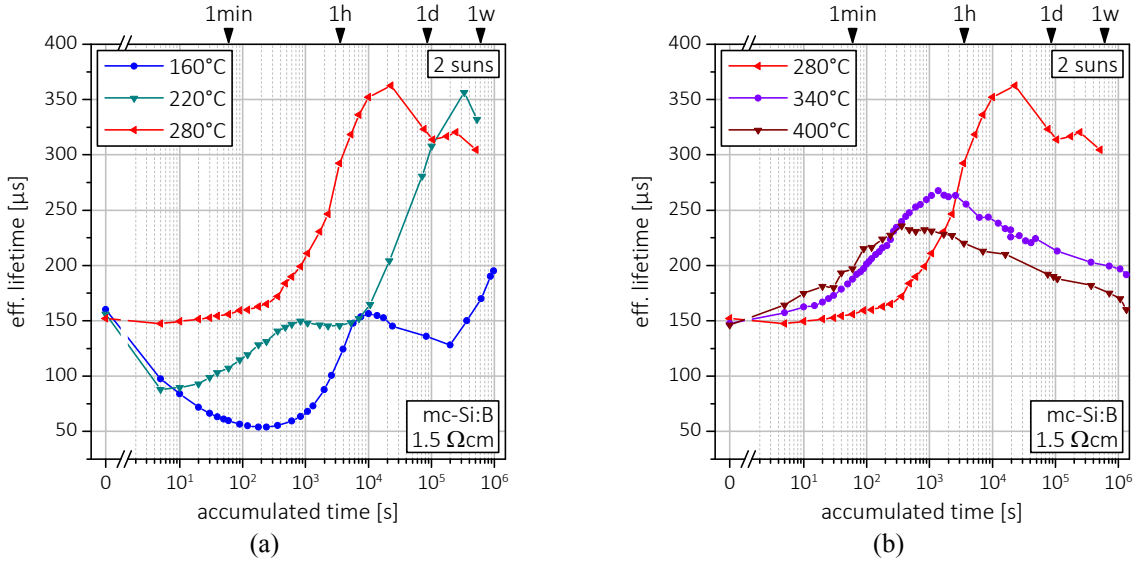

FIGURE 3. Evolution of effective lifetime of mc-Si samples with SiN_x:H passivation during illuminated annealing using 2 suns intensity and variable temperatures. Below 280°C (a), LeTID is still observable, whereas it vanishes above 280°C (b).

Switching of Treatment Temperatures

In this experiment, treatment temperature during illuminated annealing with 2 suns intensity is switched between 310°C and 160°C (different hotplates). As can be seen from Figs. 2b and 3b, LeTID is not observable at 310°C, but advanced hydrogenation occurs at the time scale of hundreds of seconds. In contrast, it can be seen from Fig. 3a that LeTID is clearly observable at 160°C, but advanced hydrogenation occurs only on the time scale of millions of seconds (weeks). The fundamental questions behind this experiment are (I) whether a treatment at 310°C does cure LeTID even though it is not observable in the experiment and (II) whether the observed gain in lifetime is stable under conditions leading otherwise to degradation.

Figure 4a shows the evolution of effective lifetime in this experiment. As can be seen in the first 310°C phase, effective lifetime starts to increase due to occurring advanced hydrogenation just as expected from Fig. 2b. After temperature is reduced, effective lifetime is found to degrade significantly which is interpreted as LeTID still kicking in. This is observed after every temperature switch from 310°C to 160°C answering the first question: A 310°C treatment does obviously not cure LeTID to a large extent or probably not at all. This qualitatively confirms the findings described in [10].

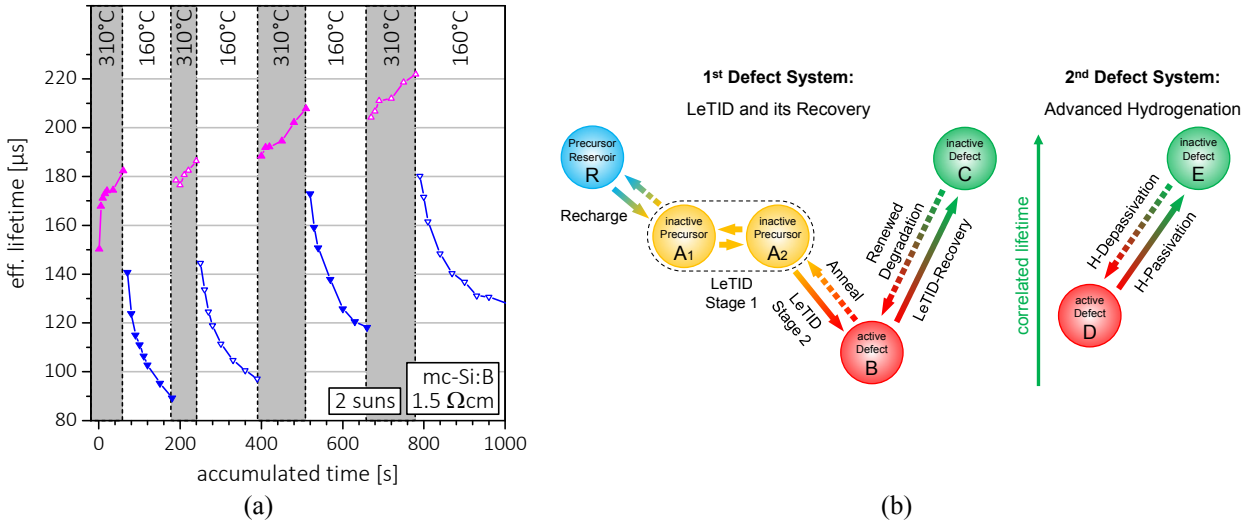

FIGURE 4. (a) Evolution of effective lifetime of mc-Si samples with SiN_x:H passivation during illuminated annealing using 2 suns intensity and switching temperatures between 310°C and 160°C. (b) Proposed model for the observations comprising two separate defect systems responsible for LeTID and advanced hydrogenation, respectively.

Interestingly, the first 10 seconds at 310°C after the 160°C phase seem to suffice to almost completely recover the LeTID losses of the prior 160°C phase. Lifetime then keeps steadily increasing, forming a monotonously rising curve just as if the 160°C phases had not existed at all. This gives a partial answer to the second question: The gain by advanced hydrogenation is obviously stable to a high degree with regard to the 160°C phase, otherwise the pink 310°C curve in Fig. 4a should exhibit the shape of a horizontal zigzag curve instead. However, the answer is not complete, because obviously lifetime is instable in the 160°C phase which is attributed to the occurrence of LeTID. It therefore has to be differentiated at this point: While the gain by advanced hydrogenation seems stable, this gain is worthless as long as LeTID keeps kicking in. Unfortunately, as it was discussed in the context of Fig. 1, the occurrence of both seem to be somehow linked even though the trigger mechanism might still be different. Therefore, it seems more than ever important to find ways to mitigate LeTID without sacrificing gains by advanced hydrogenation. Lowering the firing temperature is probably not the best choice.

Figure 4b shows a qualitative model for the description of observations in this contribution in the style of the defect model discussed for boron-oxygen related degradation and regeneration [19,20]. From Fig. 4a it seems reasonable to assume that two different independent defect systems are responsible for the observed lifetime changes: a first system describes the occurrence of LeTID, a second system the occurrence of advanced hydrogenation. As the gain due to advanced hydrogenation seems to be stable, it appears to be –at least in the investigated temperature and intensity range– a one-way reaction D ⇨ E of recombination active defects (state D) converting to (passivated) recombination inactive (or less active) defects (state E). The dynamics in the first system seems to be more complex (especially taking the findings in other publications into account). Losses by LeTID can be described by a reaction A ⇨ B meaning a conversion of recombination inactive (or less active) defects (precursor state A) into recombination active defects (state B). Even though the data in this contribution do not imply a split precursor state A, other studies suggest it, as lifetime degradation by LeTID follows a two stage scheme [21]. Recovery of LeTID is in this model a result of the reaction B ⇨ C corresponding to the conversion of defects in state B into a (passivated) recombination inactive species (state C).

For the more or less instant recovery of LeTID losses when switching from 160°C to 310°C in Fig. 4a, two scenarios are imaginable: (I) At least the reverse reaction A ⇦ B exists and lifetime recovers at 310°C via this reaction meaning that the reaction A ⇦ B dominates over the reaction (B ⇨ C) at 310°C. In the next 160°C phase, lifetime is limited by the activation of defects via the renewed reaction A ⇨ B. The reduced amplitude in subsequent 160°C phases could then indicate that at least some defects reach state C either during the 160°C phase or during the 310°C phase via the reaction B ⇨ C even though the reaction A ⇦ B dominates. This dominance might be supported by an amplified reverse reaction B ⇦ C apparently weakening the forward reaction B ⇨ C.

In a second scenario (II) taking up the proposal of a reservoir of LeTID related defects in [22], the reaction B ⇨ C might effectively convert defects into state C and thus this reaction would be responsible for the recovery of lifetime when switching from 160°C to 310°C. Then, however, the reaction B ⇦ C would have to occur at 160°C to explain the observed degradation. But this seems to be in contradiction to the observed recovery of LeTID at 160°C (Fig. 3a). The introduction of a precursor reservoir [22] could resolve this contradiction, if the precursors are replenished from the reservoir in the 310°C phase while not converting to the degraded state B. With regard to the data presented here, both scenarios could explain the observations.

CONCLUSIONS

Multicrystalline silicon shows two phenomena during illuminated annealing: Light and elevated Temperature Induced Degradation (LeTID) and its recovery as well as gains by advanced hydrogenation. Both phenomena are found to occur only in combination with high firing temperatures meaning that the avoidance of LeTID by reducing firing temperatures seems to come at the price of sacrificing gains by advanced hydrogenation. Therefore, it seems reasonable to rather cure LeTID than to avoid it.

Increasing illumination intensity (and thus stronger excess carrier injection) is found to speed up both LeTID and its recovery as well as the advanced hydrogenation process.

Increasing temperature speeds up the reactions as well, however, only up to a treatment temperature of ~280°C using 2 suns intensity during illuminated annealing. Above 280°C, LeTID (and its recovery) is not observable and it seems to not occur at all meaning curing LeTID at high temperatures does not work. Gains by advanced hydrogenation occur nevertheless and related gains seem to be stable. However, as LeTID is not cured, it occurs during illuminated annealing at lower temperatures rendering apparently the gains by advanced hydrogenation instable.

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