

# On the Defect Physics Behind Light and Elevated Temperature-Induced Degradation (LeTID) of Multicrystalline Silicon Solar Cells

Jan Schmidt , Dennis Bredemeier, and Dominic C. Walter

**Abstract**—State-of-the-art solar cells with passivated surfaces fabricated on block-cast multicrystalline silicon (mc-Si) wafers show a pronounced degradation in efficiency under illumination at elevated temperature, as it typically occurs during operation in a solar module. This effect, frequently named ‘Light and elevated Temperature-Induced Degradation’ (LeTID), has been attributed to the activation of a specific, hitherto unrevealed bulk defect in mc-Si. Recent experimental results of several labs have indicated that hydrogen is somehow involved in the responsible defect physics, without however providing any direct evidence so far. In this article, we present experimental data unambiguously showing a direct positive correlation of the extent of LeTID with the hydrogen content introduced into the silicon bulk during firing of the silicon wafers coated with hydrogen-rich silicon nitride ( $\text{SiN}_x\text{:H}$ ) layers. Additional experiments including the pronounced impact of phosphorus gettering on the LeTID extent and the dependence of the degradation and regeneration on the wafer thickness support the involvement of a second species, with most indications pointing towards a metallic impurity. Several approaches of completely avoiding the instability in mc-Si solar cells are derived from the presented defect model, including 1) tuning of the  $\text{SiN}_x\text{:H}$  layer properties to minimize the in-diffusion of hydrogen into the wafer and 2) the thinning of the mc-Si wafer, improving the getterability of the metal impurity component toward the surfaces.

**Index Terms**—Defects, degradation, hydrogen, metallic impurity, multicrystalline silicon (mc-Si), silicon, solar cells.

## I. INTRODUCTION

IN 2012, Ramspeck *et al.* [1] reported a pronounced degradation on multicrystalline silicon (mc-Si) solar cells with an  $\text{Al}_2\text{O}_3/\text{SiN}_x$ -passivated rear surface under illumination at elevated temperature caused by a degradation of the bulk lifetime. This Light and elevated Temperature Induced Degradation (LeTID) effect has since then attracted great attention by academia and industry, because of its very detrimental impact on

module performance [2]–[7]. However, the exact root cause of the defect activation is hitherto unknown. Recently, various studies suggested that hydrogen, released from the hydrogen-rich silicon nitride ( $\text{SiN}_x\text{:H}$ ) coatings during the firing step, might play a major role in the defect activation process [3], [8]–[13]. On the other hand, there are indications that the defect activation might not be only attributed to hydrogen, but requires another, possibly metallic, species [8], [14], [15]. Within this study, we deposit a broad variety of  $\text{SiN}_x\text{:H}$  layers with different compositions, leading to different hydrogen concentrations injected into the mc-Si wafers. We observe a direct correlation of the extent of LeTID with the total hydrogen content introduced into the wafer. The tuning of the  $\text{SiN}_x\text{:H}$  properties is an easy way of reducing and even avoiding LeTID in industrially fabricated solar cells. In the second part of this contribution, we present experiments pointing toward a metal as a second component in the LeTID defect physics. We finalize the article with our current understanding of the defect physics, which allows to deduce several easy-to-implement strategies for avoiding LeTID.

## II. CORRELATION WITH HYDROGEN

We have recently demonstrated [16] that the amount of hydrogen introduced into a silicon wafer via firing a silicon nitride ( $\text{SiN}_x\text{:H}$ ) layer deposited on the wafer surface can be adjusted over a broad range by varying the composition (i.e., the Si:N ratio) of the  $\text{SiN}_x$  layer and thereby its atomic density. The atomic density of the  $\text{SiN}_x\text{:H}$  layer has been shown to be the crucial material parameter determining the fraction of hydrogen diffusing into the silicon wafer [16]. In this article, we vary the silane-to-ammonia flow ratio during the plasma-enhanced chemical vapor deposition (PECVD) of the  $\text{SiN}_x\text{:H}$  layers deposited onto both wafer surfaces, leading to silicon nitride layers with largely differing silicon-to-nitrogen ratios and hence atomic densities. The refractive index (measured by ellipsometry at a wavelength of 633 nm) of the resulting  $\text{SiN}_x$  layers varies between 1.96 and 2.68. The  $\text{SiN}_x$  layer thickness is kept constant in our experiment at 130 nm. After receiving a complete RCA clean,  $\text{SiN}_x$  layers are deposited on both wafer surfaces. The wafers are subsequently fired at a set-peak temperature of 900 °C at a belt-speed of 6.8 m/min in an industrial conveyor-belt furnace (DO-FF-8.600–300, Centrotherm International AG). The hydrogen content introduced by the firing treatment is determined on high-purity float-zone

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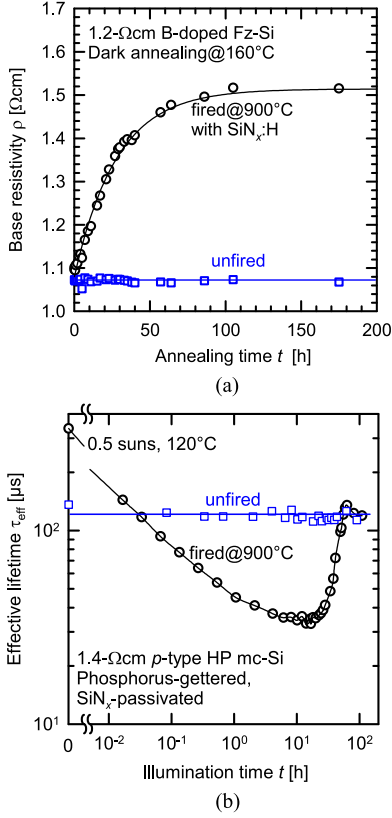


Fig. 1. (a) Increase in the base resistivity  $\rho$  upon annealing at 160 °C due to the formation of B–H pairs, measured on a 1.1  $\Omega\text{cm}$  boron-doped Fz-Si wafer after fast-firing at a set-peak temperature of 900 °C (black circles) and constant base resistivity of a nonfired reference sample (blue squares). Both samples feature the same  $\text{SiN}_x\text{:H}$  coatings. (b) Measured evolution of the effective carrier lifetime  $\tau_{\text{eff}}$  at a fixed injection density of  $\Delta n = 10^{15} \text{ cm}^{-3}$  of two HP mc-Si neighboring wafers, one of them fired (black circles), one unfired (blue squares), during illumination at 0.5 suns at a temperature of 120 °C. Only the fired wafer degrades and regenerates afterward, whereas the neighboring wafer which was not fired, does not change in lifetime.

silicon (Fz-Si) wafers by measuring the evolution of the wafer resistivity during dark-annealing at 160 °C using contactless eddy-current measurements.

Fig. 1(a) shows an exemplary measurement performed on a boron-doped Fz-Si wafer coated with PECVD- $\text{SiN}_x\text{:H}$  on both surfaces after fast-firing at 900 °C (black circles) and for comparison without firing (blue squares). In defect-lean silicon material with no other sinks to hydrogen than boron and hydrogen itself, the hydrogen is initially present in the form of hydrogen dimers  $\text{H}_2$  [17]. During annealing at 160 °C, the  $\text{H}_2$  dimers dissociate and the free hydrogen atoms passivate the boron dopant atoms, forming boron-hydrogen (B–H) pairs. By measuring the resulting increase in the wafer resistivity  $\rho$ , measured using the eddy-current method with the WCT120 bridge (Sinton Instruments), during annealing at 160 °C [see black circles in Fig. 1(a)], the absolute concentration of B–H pairs can be directly deduced. In a recent contribution [18], we have shown that the saturated B–H concentration can be identified with the total hydrogen content  $[\text{H}]_{\text{tot}}$  in the wafer, which is valid for doping concentrations greater and around  $10^{16} \text{ cm}^{-3}$ , as used in this article. Hence, in this article, we use the saturated B–H

concentration obtained from the measured saturation value of  $\rho$  (black circles) and the resistivity  $\rho_0$  measured before annealing to determine the total hydrogen concentration  $[\text{H}]_{\text{tot}}$ , which equals the change in the hole concentration  $p_0$ . Note that it is necessary to use Fz-Si material in these experiments, as in mc-Si wafers too many defects other than boron exist, which act as additional trapping centers to hydrogen, making the methodology unreliable. Hence, we use two different kinds of materials in our study, one is Fz-Si for measuring the H content introduced into the wafer and the other is mc-Si to examine the LeTID extent. Fz and mc-Si wafers are thereby always processed in parallel. Fig. 1(b) shows the evolution in the measured effective carrier lifetime of a high-performance (HP) mc-Si wafer coated with  $\text{SiN}_x$  during illumination at 0.5 suns (halogen lamp) at a temperature of 120 °C. The measurements have been performed using photoconductance-based lifetime measurements (WCT120TS, Sinton Instruments) and are reported at a fixed injection density of  $\Delta n = 10^{15} \text{ cm}^{-3}$  in this article if not otherwise stated. The mc-Si wafer, which was fired under the same conditions as the Fz-Si wafer represented by the black circles of Fig. 1(a), shows a pronounced degradation from an initial lifetime of  $\tau_0 = 340 \mu\text{s}$  to a minimum lifetime of  $\tau_{\text{min}} = 33 \mu\text{s}$  [black circles in Fig. 1(b)]. This corresponds to a maximum effective defect concentration  $N_{\text{max}}^* = 1/\tau_{\text{min}} - 1/\tau_0$  of  $27 \text{ ms}^{-1}$  in this sample. Continuing the annealing and illumination leads to a subsequent increase in lifetime (frequently labeled “regeneration”). Note that in this experiment, the regeneration seems to be incomplete, as the final lifetime reached is smaller than  $\tau_0$ . We attribute this to the degradation of the  $\text{SiN}_x$  surface passivation during illumination at 120 °C, which is in agreement with observations of Sperber *et al.* [19]. Note that if we apply  $\text{Al}_2\text{O}_3/\text{SiN}_x$  stacks (see e.g., Fig. 3), which are considerably more stable than  $\text{SiN}_x$  single-layers, the initial lifetime  $\tau_0$  is approximately reached after complete regeneration (see Fig. 3). For the identically processed mc-Si sister wafer, which did not receive the firing step, no degradation/regeneration cycle is observed [blue squares in Fig. 1(b)], verifying that indeed the firing step is necessary to trigger the LeTID/regeneration cycle, in agreement with reports in the literature [3], [4], [20].

Fig. 2 shows the maximum effective defect concentrations  $N_{\text{max}}^*$  measured on neighboring HP mc-Si sister wafers, which were coated on both surfaces with  $\text{SiN}_x\text{:H}$  films of different Si:N ratios.  $N_{\text{max}}^*$  is plotted versus the total hydrogen content  $[\text{H}]_{\text{tot}}$  measured on boron-doped Fz-Si wafers, which were processed in parallel to the mc-Si wafers. Lower hydrogen contents are introduced into the wafer for  $\text{SiN}_x$  layers close to stoichiometry (high atomic density), whereas silicon-rich  $\text{SiN}_x$  layers of reduced atomic density introduce higher hydrogen contents. Fig. 2 clearly demonstrates that the LeTID defect concentration increases with increasing hydrogen content introduced during the firing step. Although the total hydrogen contents were extracted on defect-lean Fz-Si wafers, the hydrogen contents introduced into the mc-Si wafers are expected to show a positive correlation with the hydrogen concentration measured in the Fz-Si wafers. The dependence of  $N_{\text{max}}^*$  on  $[\text{H}]_{\text{tot}}$  depicted in Fig. 2 shows a weaker slope at lower hydrogen contents ( $< 2 \times 10^{15} \text{ cm}^{-3}$ ) and a steeper slope at larger hydrogen concentrations.

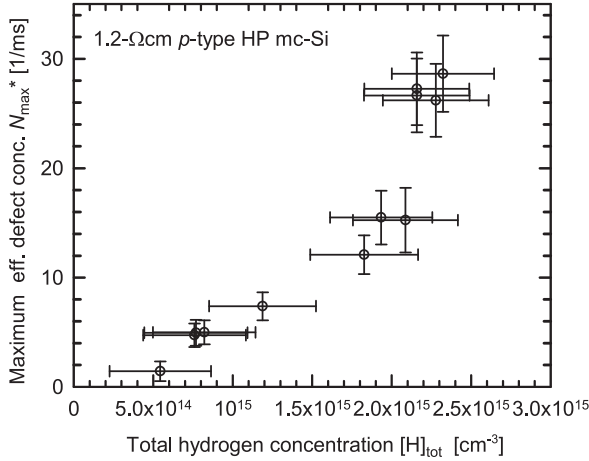


Fig. 2. Maximum effective defect concentrations  $N_{\max}^*$  measured on neighboring HP mc-Si sister wafers, which were coated on both surfaces with  $\text{SiN}_x\text{:H}$  films of different Si:N ratios and fired at 900 °C.  $N_{\max}^*$  is plotted versus the total hydrogen content  $[\text{H}]_{\text{tot}}$  measured on boron-doped Fz-Si wafers, which were processed in parallel to the mc-Si wafers (data partly taken from [16]).

This finding should, however, not be overrated as it could just be an artifact of the applied methodology. At lower hydrogen contents, the hydrogen might not only be available for the LeTID-specific defect, but also to other defects abundant in mc-Si in contrast to Fz-Si. At higher hydrogen contents, these defects might be saturated and hence more hydrogen might become available for the LeTID-specific defect. Two important conclusions can be drawn from the positive correlation shown in Fig. 2: 1) the extent of LeTID correlates directly with the amount of hydrogen introduced into the mc-Si wafers during firing, which points toward a direct involvement of hydrogen; 2) choosing the PECVD deposition conditions in a way that  $\text{SiN}_x\text{:H}$  films are deposited which introduce only very low hydrogen concentration into the wafer during firing (namely,  $\text{SiN}_x$  films close to stoichiometry), the LeTID extent can be minimized. Note that these conclusions are in good agreement with recent results reported by Vargas *et al.* [12], who found that there is a certain correlation between the hydrogen fraction released during the firing and the extent of LeTID, which they interpreted as a hint for the involvement of hydrogen in the LeTID defect. Fig. 2 now clearly substantiates this conjecture.

### III. INDICATIONS FOR THE INVOLVEMENT OF METALS

Fig. 3 shows the lifetime evolution of two 1.4 Ωcm mc-Si sister wafers with  $\text{Al}_2\text{O}_3/\text{SiN}_x$ -stack passivation after firing at 900 °C. Prior to surface passivation and firing, one sample received a phosphorus ( $\text{POCl}_3$ ) diffusion at 850 °C, known to effectively getter metallic impurities from the silicon bulk. The  $n^+$ -diffused regions were removed by etching prior to surface passivation. Both mc-Si wafers show a pronounced degradation in their lifetime during illumination at 0.5 suns at 120 °C. However, the absolute lifetime values are very different. The initial lifetimes  $\tau_0$  before degradation differ between  $\tau_{0,\text{gett}} = 480 \mu\text{s}$  for the gettered wafer and  $\tau_{0,\text{ungett}} = 27 \mu\text{s}$  for the ungettered one, which can be attributed to an effective gettering

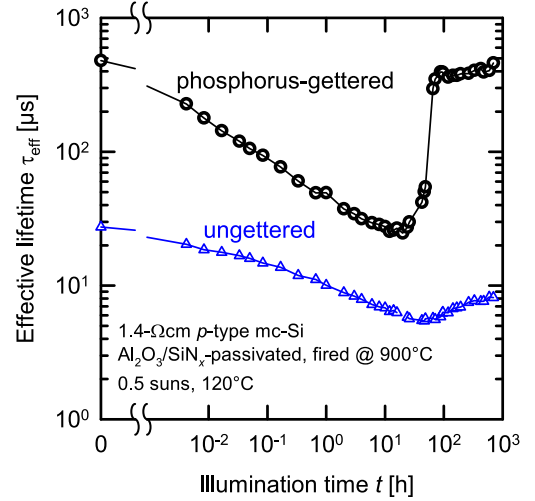


Fig. 3. Evolution of the effective lifetime  $\tau_{\text{eff}}$  at  $\Delta n = 10^{15} \text{ cm}^{-3}$  of two 1.4 Ωcm mc-Si sister wafers with  $\text{Al}_2\text{O}_3/\text{SiN}_x$ -stack passivation after firing at 900 °C during illumination at 0.5 suns at 120 °C. One wafer received a phosphorus gettering diffusion (black circles), whereas the other one is ungettered (blue triangles).

of a broad variety of metallic impurities typically present in mc-Si. Comparing the minimum lifetimes  $\tau_{\min}$  after complete LeTID, both wafers also strongly differ. Whereas after gettering  $\tau_{\min,\text{gett}} = 25 \mu\text{s}$ , without gettering only  $\tau_{\min,\text{ungett}} = 5.5 \mu\text{s}$  are reached after degradation. We can now extract the LeTID-related effective defect concentration given by  $N_{\max}^* = 1/\tau_{\min} - 1/\tau_0$  and find that the gettering reduces  $N_{\max}^*$  from 182  $\text{ms}^{-1}$  for the ungettered wafer to only 40  $\text{ms}^{-1}$ , that is by a factor of 4.6. As phosphorus diffusion gettering is well known to effectively remove metallic impurities from the silicon wafer, the fact that phosphorus diffusion gettering significantly reduces the extent of LeTID is consistent with the assumption that a metal impurity is somehow involved in the LeTID defect physics. Of course, this is not a proof, but just one of several indications discussed below that metals might be involved. Our result concerning the impact of phosphorus gettering on LeTID is in good agreement with previously published results from Zuschlag *et al.* [21], who also reported that that phosphorus gettering significantly decreases the LeTID extent.

Fig. 4 shows the evolution of the effective defect concentration  $N^*(t) = 1/\tau(t) - 1/\tau_0$  in sister mc-Si wafers of three different thicknesses at 1 sun illumination intensity and 75 °C. Importantly, the extent of LeTID decreases strongly with decreasing wafer thickness. In addition, the regeneration speeds up with decreasing wafer thickness. This is a characteristic property of LeTID, which can be explained by the diffusion of the recombination-active defect to the wafer surfaces. The lines in Fig. 4 show the modeled behavior if a mobile species of diffusivity  $D$  is assumed to out-diffuse to the wafer surfaces. Details of our diffusion model can be found in [22]. Note that in this model, we also need to assume that the concentration of the LeTID precursor defect (before activation via illumination) is reduced in the thinner wafers, i.e., a significant surface gettering takes already place during the firing step and not only during

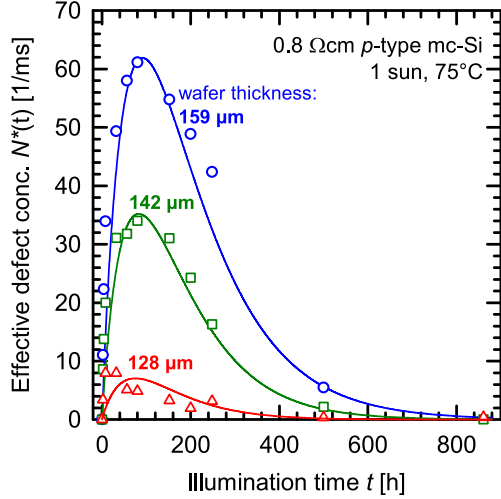


Fig. 4. Evolution of the effective defect concentration  $N^*(t) = 1/\tau(t) - 1/\tau_0$  in sister mc-Si wafers of three different thicknesses at 1 sun illumination intensity and 75 °C (data taken from [22]). The extent of LeTID decreases strongly with decreasing wafer thickness.

regeneration. This is also in excellent agreement with spatially resolved lifetime measurements, which frequently show denuded zones around grain boundaries after complete LeTID, pointing toward a gettering of most likely metallic impurities toward grain boundaries, acting in this respect in the same way as the wafer surfaces. Importantly, all curves in Fig. 4 (solid lines) have been modeled using the same diffusion coefficient of  $D = 5 \times 10^{-11} \text{ cm}^2/\text{s}$  for all sample thicknesses [22]. The diffusion coefficients of mobile impurities in crystalline silicon vary over many orders of magnitude. Regarding the metallic impurities, only cobalt and nickel are reported to have diffusion coefficients (at 75 °C) within the same order of magnitude as determined from our thickness-dependent measurements shown in Fig. 4 [22]. For hydrogen, reported diffusion coefficients in crystalline silicon vary over many orders of magnitude and the reported values would in principle also be compatible with the extracted  $D$  of  $5 \times 10^{-11} \text{ cm}^2/\text{s}$ . Based on this finding, it was proposed in the literature [23] that the regeneration might be due to the out-diffusion of hydrogen to the wafer surfaces. Due to the fact that extremely hydrogen-rich layers are present at the surfaces of our samples, we consider a diffusion of hydrogen to the surfaces as highly unlikely. Interestingly, there are well known recombination centers for cobalt and nickel in silicon. In particular, Co is known to form two recombination centers in silicon: one with an electron-to-hole capture ratio of  $k = 0.15$  and the other one with a value of  $k = 16 \pm 3$  [24]. The latter Co-related center has a  $k$  value which is in the same order of magnitude as recently published values for the LeTID defect. We will discuss this in more detail below. Ni is also known to form recombination centers in silicon, however, not much is known about capture ratios, as Ni tends to precipitate and is hence difficult to examine [25]. Nevertheless, in a most recent study, Ni was in fact directly detected at the grain boundary after LeTID in an mc-Si solar cell [26].

Based on injection-dependent lifetime measurements on mc-Si wafers in the fully degraded state it has been shown in various

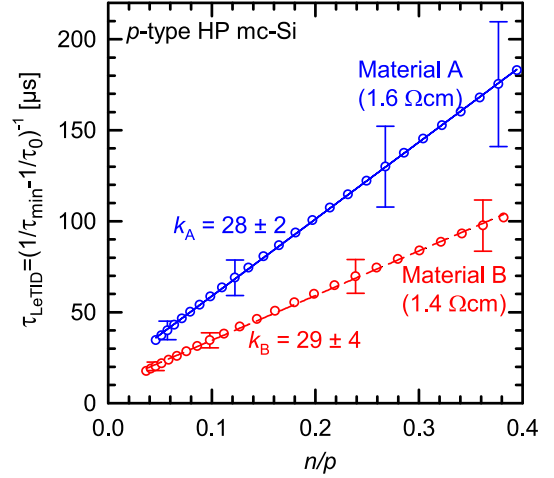


Fig. 5. Extracted lifetime of the LeTID defect  $\tau_{LeTID} = (1/\tau_{min} - 1/\tau_0)^{-1}$  as a function of the electron-to-hole concentration ratio  $n/p$  for two different HP mc-Si materials. The defect-specific electron-to-hole capture ratios  $k$  were extracted by a linear fitting routine which is weighting the data points by their uncertainties shown as error bars.

studies [4], [5], [7], [14], [15], [27] that the defect responsible for LeTID is a deep-level center with a largely asymmetric electron-to-hole capture ratio  $k = \sigma_n v_{th,n} / \sigma_p v_{th,p}$ .  $\sigma_n$  and  $\sigma_p$  are the capture cross sections and  $v_{th,n} \approx v_{th,p}$  are the thermal velocities for electrons and holes, respectively. Despite the fact that the experimentally determined values for  $k$  vary in the literature over a relatively broad range between  $\sim 20$  [5], [27] and  $\sim 36$  [14], [15], it is consensus that the  $k$  value of the LeTID defect is relatively large ( $\gg 1$ ), which would be consistent with a donor-type defect in silicon, such as, e.g., a donor-type metallic impurity [28]. In order to pin down the  $k$  value more precisely, we have performed injection-dependent lifetime measurements before degradation [resulting in  $\tau_0(\Delta n)$ ] and after complete degradation [resulting in  $\tau_{min}(\Delta n)$ ] on different HP mc-Si materials. Fig. 5 shows the extracted lifetime of the defect  $\tau_{LeTID} = (1/\tau_{min} - 1/\tau_0)^{-1}$  as a function of the electron-to-hole concentration ratio  $n/p$  for two different HP mc-Si materials. Assuming a deep-level center, the Shockley–Read–Hall equation for the lifetime has been shown [29], [30] to simplify to  $\tau_{SRH} = \tau_{n0}(1 + k \times n/p)$ , allowing to determine  $k$  from a linear fit to the measured data. In contrast to previous studies, we have now included a weighting of the measured data points accounting for their measurement uncertainties, which are larger for larger  $n/p$  values, because  $\tau_0$  and  $\tau_{min}$  approach at large  $n/p$ . For material A, our fitting result in  $k_A = 28 \pm 2$  and for material B in a comparable value of  $k_B = 29 \pm 4$ . We have also fitted the measurement data using a conventional fit without taking into account the uncertainty of the data, which resulted for both materials in a  $k$  value of 25, clearly demonstrating that the fitting routine applied has some effect on the extracted  $k$  values. This might be one reason for the broad scatter in the  $k$  values reported in the literature for LeTID. Based on our fitting routine and measurements on different mc-Si materials, we can now state that the  $k$  value of the LeTID-specific defect is in the range between 26 and 30. This  $k$  value would, e.g., be compatible with interstitial titanium ( $Ti_i$ ) and molybdenum ( $Mo_i$ ) [14], however,



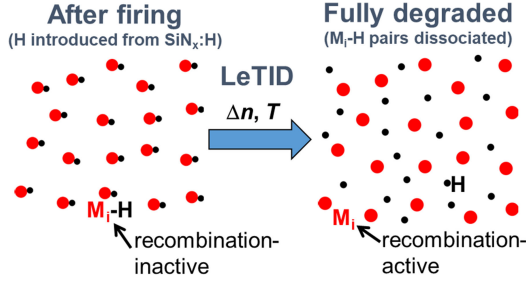


Fig. 6. Suggested LeTID model attributing the degradation to the dissociation of a metal-hydrogen ( $M_i$ -H) defect complex. The hydrogen H is introduced from the  $\text{SiN}_x\text{:H}$  layers at the wafer surfaces during firing and initially passivates the metal  $M_i$ . Only during excess carrier injection (via illumination) and increased temperature, the  $M_i$ -H complex dissociates and recombination-active  $M_i$  centers limit the lifetime. Note that it could also be envisaged that several hydrogen atoms are required to passivate the metal. Degradation would in that case still involve the detachment of hydrogen from the initial complex, but the final recombination-active center would not necessarily be an isolated  $M_i$ , but could also still include hydrogen.

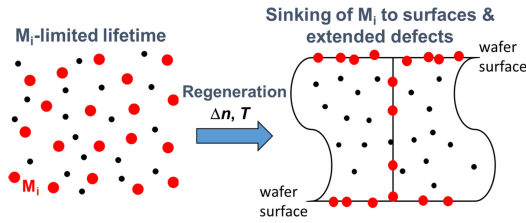


Fig. 7. Lifetime regeneration is attributed to a sinking/gettering of the interstitial metal impurity  $M_i$  to the wafer surfaces and also crystallographic defects. This explains the pronounced dependence of the regeneration on the wafer thickness. This graphic representation is for illustrative purposes only.

both are extremely slow diffusers in silicon and are not compatible with the results of the thickness-dependent experiments and would also not result in any denuded zones around grain boundaries. The  $k$  value reported for Co, on the other hand, is a bit lower ( $16 \pm 3$ ) than what we extracted for the LeTID defect. However, it should be kept in mind that there is only one study available [24], where the  $k$  value has been extracted for Co in intentionally contaminated monocrystalline silicon and it has not been determined using the linear fitting routine discussed above, which might lead to a significant deviation in the  $k$  values from that determined by linear fitting. In addition, Co might exist in other configurations in mc-Si wafers, which have not been examined so far. We therefore think that Co in Si needs a re-evaluation concerning its  $k$  value and its existing configurations in mc-Si. Hence, Co can still be considered a strong candidate for the involvement in LeTID. The next most likely candidate seems to be Ni. For isolated Ni, however, no  $k$  values have been reported in the literature so far, because it is very difficult to prepare isolated Ni centers in silicon, since Ni tends to form precipitates, exactly the property we need in our defect model, which is described in more detail in the following.

#### IV. SUGGESTED DEFECT MODEL

Figs. 6 and 7 summarize our current understanding of the defect physics. During the fast firing, hydrogen diffuses from the  $\text{SiN}_x\text{:H}$  layers on the wafer surfaces into the silicon bulk,

where it passivates metal impurities  $M_i$  (likely interstitials). The  $M_i$  might stem from metal precipitates dissolved during the fast firing step and are immediately passivated by hydrogen. If no hydrogen is present, the  $M_i$  immediately attach to precipitates again (and no LeTID is observed). If hydrogen is present, it prevents the metal atoms (partly) from rejoining, by forming  $M_i$ -H complexes. The resulting  $M_i$ -H complexes are no strong recombination centers or might even be completely recombination-inactive. During injection of minority carriers via illumination at enhanced temperature, the  $M_i$ -H complex dissociates and the isolated  $M_i$ , which is assumed to be highly recombination active, reduces the bulk lifetime (the H attaches either to B, forms  $\text{H}_2$  dimers, or attaches to other defects abundant in mc-Si). This model (sketched in Fig. 6) explains the LeTID effect and is consistent with the experimental observations. Nevertheless, this might not be the only possible kind of defect reaction being consistent with the experimental data, of course. It could also be envisaged that the metal is initially passivated with several hydrogen atoms and that after detachment of some of the hydrogen atoms (by carrier injection at increased temperature), the remaining recombination-active center is not an isolated  $M_i$ , but is in fact a metal-hydrogen complex possessing an energy level within the silicon bandgap. Fig. 7 shows the proposed model for the regeneration. The pronounced wafer thickness dependence of the regeneration can be explained by a gettering of the interstitial metal impurity  $M_i$  toward the wafer surfaces and to crystallographic defects within the wafer. Note that a significant amount of  $M_i$  is already gettering to the surfaces and the crystallographic defects during the firing step.

#### V. DISCUSSION

In this section, we are discussing a few of the most important LeTID results published recently in the literature within the context of the described  $M_i$ -H defect model. Dark annealing experiments (at 150–200 °C) of degraded mc-Si solar cells published by Luka *et al.* [31] showed a recovery in efficiency during dark annealing. Applying LeTID conditions after dark annealing, the solar cells showed a pronounced renewed degradation. In later studies, Fung *et al.* [32], [33] performed subsequent degradation/dark annealing cycles. In these experiments, the LeTID conditions were applied for such a long period that the lifetimes of the examined mc-Si samples fully regenerated. A subsequent dark annealing step triggered, however, a renewed degradation under LeTID conditions. Performing such cycles again and again led, interestingly, to a successive decrease in the maximum observed LeTID defect concentration, which Fung *et al.* explained by assuming a reservoir state releasing hydrogen during the dark annealing (hydrogen was assumed to be a central part of the LeTID defect in that study) [33]. The assumption of such a depletable reservoir state was able to explain the observed lifetime changes consistently [33]. With respect to the  $M_i$ -H model described in the previous section, such a depletable reservoir could either release hydrogen during the dark annealing step or, alternatively, it could release metal atoms  $M_i$  from successively shrinking metal precipitates. In the second case,

it could be conceivable that during dark annealing, a part of the  $M_i$  is already sinking to the wafer surfaces, in particular at increased dark annealing temperatures. This could also explain the reduced degradation amplitudes reported by Chan *et al.* [34] for dark annealing temperatures  $\geq 250$  °C. Note that also prolonged dark annealing at temperatures around 175 °C was shown by Chen *et al.* [9] to activate the LeTID defect without any illumination or electrical injection of excess carriers. This effect can be attributed to a purely thermal dissociation of the  $M_i$ -H complexes.

Another important experimental result was recently reported by Jensen *et al.* [35], demonstrating that LeTID can also be triggered without high-temperature firing by injecting hydrogen into the mc-Si wafer from a hydrogen plasma source at relatively low temperature (350–375 °C), clearly confirming the involvement of hydrogen. Note that the mc-Si wafers examined in the study of Jensen *et al.* [35] were previously phosphorus gettered, which could have dissolved some of the metal precipitates. Also, the relatively long ( $\geq 10$  min) anneal at 350–375 °C might have dissolved an additional relevant fraction of the metal precipitates, which after hydrogenation might have led to the formation of  $M_i$ -H complexes, the precursors of the LeTID defect in the  $M_i$ -H model. Interestingly, Jensen *et al.* [35] found that mc-Si samples, which were fired before hydrogenation, showed only very small degradation amplitudes. In the framework of the  $M_i$ -H model, this could be explainable by a reattachment of the  $M_i$ 's to the metal precipitates during the cooling ramp after the firing, as no hydrogen is present for preventing the  $M_i$ 's to reattach to its precipitates.

## VI. SUMMARY

In this article, we demonstrated that the LeTID defect concentration shows a direct increase with increasing hydrogen concentration introduced via firing of  $\text{SiN}_x\text{:H}$  layers deposited on the wafer surface. We consolidated thereby recent conjectures of the involvement of hydrogen in the LeTID effect. Importantly, tuning the  $\text{SiN}_x\text{:H}$  layer composition can be used as an easy-to-apply method to reduce the hydrogen incorporation into the silicon wafer and thereby the LeTID extent. Nearly stoichiometric  $\text{SiN}_x\text{:H}$  layers introduce minimal hydrogen, leading to minimal degradation. Further experimental results suggest that, in addition to hydrogen, another component is involved in the detailed defect physics. The following findings point thereby to the involvement of an interstitial metallic impurity.

- 1) Phosphorus gettering drastically reduces LeTID (as it is well known for fast diffusing metals in silicon).
- 2) Reducing the wafer thickness reduces LeTID and accelerates the regeneration (well compatible with the assumption of a metal such as Co and Ni diffusing to the wafer surfaces).
- 3) The LeTID defect is characterized by a deep-level center with a strongly asymmetric  $k$  value between 26 and 30 (typical for donor-like interstitial metal impurities).

In our suggested defect model, during the fast firing, hydrogen diffuses from the  $\text{SiN}_x\text{:H}$  layers on the wafer surfaces into the

silicon bulk. In parallel, during the high-temperature firing step, metal precipitates dissolve and the resulting isolated interstitial metal atoms  $M_i$  are subsequently passivated by hydrogen, forming  $M_i$ -H complexes. If no hydrogen is present, the  $M_i$  reattach/form precipitates again. Hence, the hydrogen prevents a fraction of the metal atoms from rejoining. The resulting  $M_i$ -H complexes are no strong recombination centers or might even be completely recombination-inactive. During the injection of minority carriers via illumination at enhanced temperature, the  $M_i$ -H complex first reconfigures (fast degradation component) and then dissociates (slow LeTID component) and the isolated  $M_i$ , which is assumed to be highly recombination active, reduces the bulk lifetime. The pronounced wafer thickness dependence of LeTID is explained in this model by a gettering of the interstitial metal impurity  $M_i$  toward the wafer surfaces.

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