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Observation of an Injection Dependent Lifetime Effect in Highly Hydrogenated Boron Doped Wafers

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Abstract. The correlation between hydrogen content and boron-oxygen related degradation is under debate. In this study surface passivated boron doped silicon wafers with different hydrogen content were illuminated at room temperature with three different light intensities. Their lifetime degradation was monitored with quasi-steady state photoconductance. A characteristic degradation that is separated into a fast and a slow decay characteristic for all light intensities is expected for such wafers. However, with increasing hydrogen content, we observe that the initial lifetime prior to illumination decreases, reducing the fast decay part of the degradation curves. For low intensity illumination the samples with reduced initial lifetimes follow the predicted degradation curve and show only the slow decay. For higher light intensities the degradation curves differ considerably; there is first a temporary lifetime increase before the decay sets in.

Keywords: Crystalline Silicon, Degradation, Hydrogen, Solar Cell

1. Introduction

The minority charge carrier lifetime in Czochralski (Cz) silicon wafers containing boron dopants as well as oxygen may degrade to about 10% of the initial value due to boron-oxygen (BO) related light induced degradation (LID) under illumination or other charge injection [1], [2], [3]. An initial fast decay occurs during the first few minutes of illumination, while a second slow decay proceeds over hours and days [1], [3], [4]. This, so called, fast and slow decay is considered characteristic of the degradation process. It is widely accepted that above a very low threshold the degradation rate is independent of the minority carrier injection, and thus the illumination for a large range of light intensities [4], [5], [6], [7]. The BO defect responsible for the degradation can be permanently regenerated through carrier injection at elevated temperatures [8], [9], [10]. Only recently has the formation of recombination active BO-complexes been associated to the presence of hydrogen [11]. Both Münzer, and Nampalli et al. have, however, reported that hydrogen is required for the corresponding regeneration process [12], [13]. Partial recovery of the initial lifetime in wafers without intentionally introduced hydrogen has also been demonstrated indicating a link between the fast degradation mechanism and hydrogen [11]. It has also been shown that hydrogen affects the rates of lifetime regeneration upon illuminated annealing [11], [12], [13], [14], [15], [16]. Different regeneration mechanisms for the fast and slow decay have been proposed based on the different timescales of the degradation as well as their different capture cross-section ratios, $k = \sigma_n/\sigma_p$ [17]. Reported values for k are in the range of 65-86 for the fast recombination centre (FRC) and 10-14 for the slow recombination centre (SRC) [18], [19], [20], [21]. However, a considerable range of k-values that differs from these has also been reported, e.g. Hallam et al. reported a much lower value of $k_{FRC} = 18$ [22].

Light and elevated temperature induced degradation (LeTID) affecting both p-type and n-type silicon wafers and solar cells is strongly linked to the presence of hydrogen [23], [24], [25], [26], [27]. Both light soaking at elevated temperatures as well as dark annealing can cause lifetime degradation and a subsequent regeneration that has been attributed to LeTID [28], [29]. In addition, a temporary recovery of the lifetime in degraded gallium doped wafers has been reported for high injection conditions at RT [30], [31]. An equilibrium between degradation and temporary recovery has been proposed to explain the seemingly stable behavior of such wafers under certain conditions [32]. Winter et al. have demonstrated a temporary recovery effect at RT also in boron doped float-zone wafers that have been degraded at an elevated temperature [32].

During contact firing with a hydrogen rich dielectric film (e.g. $SiN_X{:}H$) present hydrogen diffuses into the bulk where it is present predominantly as H_2 molecules [33], [34], [35], [36], [37], with a non-negligible concentration of hydrogen-acceptor pairs [38], [39]. During dark annealing at temperatures between 140°C and 180°C the H_2 molecules may dissociate by capturing a hole (h^+) [33], [35], [40] where the resulting H^+ can neutralize a B^- and form a hydrogen-boron (HB) pair. The corresponding resistivity change from this hydrogen passivation of acceptors can be used to determine the amount of fired-in hydrogen [20], [21]. Hydrogen complexes in silicon can also be studied through their localized vibration modes (LVM) using infrared (IR) absorption spectroscopy [41], [42].

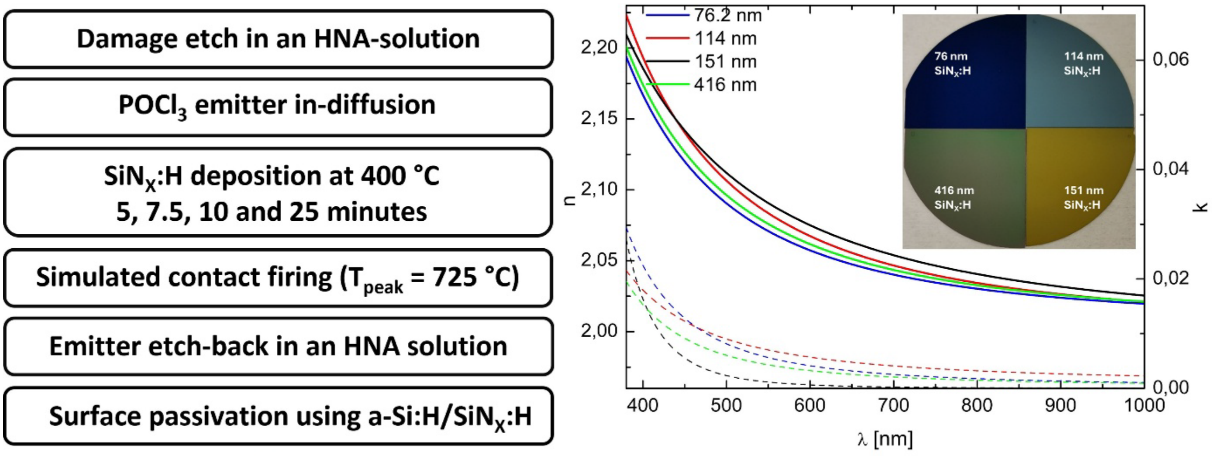
In this work we investigate the effect of carrier injection on light induced degradation in boron doped wafers with different hydrogen concentrations through illumination at room temperature (RT).

2. Experimental details

Cz wafers doped with boron with a resistivity of about 1 Ω-cm have been processed according to the process flow presented in Figure 1a). An initial saw damage etch in an HNA solution (hydrofluoric, nitric, and acetic acids) was followed by a two-sided emitter-in-diffusion in a $POCl_3$ tube furnace (ca. 70 Ω/sq.). Hydrogen was introduced by plasma enhanced chemical vapor deposition (PECVD) of a $SiN_X{:}H$ layer on both sides, followed by a simulated contact firing step in a belt furnace. A peak temperature of 725°C was measured. The $SiN_X{:}H$ layers and the emitters were then removed in a new HNA etch. An $a\text{-}Si{:}H/SiN_X$ stack (approximately 40 nm $a\text{-}Si{:}H$ and 60 nm SiN_X) deposited on both sides at a temperature of 230°C was then used for surface passivation of the wafers intended for minority carrier lifetime studies [43]. Furthermore, one as-fired and one surface passivated wafer have been measured for each $SiN_X{:}H$ thickness. In addition, a non-fired reference wafer without intentionally introduced hydrogen was measured, i.e. a wafer subjected only to the first and the last step in Figure 1a).

For characterization by ellipsometry $SiN_X{:}H$ films, with 5, 7.5, 10, and 25 minutes of deposition, were grown on 4-inch double-side-polished (DSP) Cz-wafers. We assume a representative deposition rate on the DSP wafers for isotropically etched semi-square Cz-wafers despite the different surface morphologies.

LED illumination with light intensities of approximately 12, 48 and 89 mW/cm^2 at RT was used to degrade minority carrier lifetimes of the wafers. An automated setup for turning the LED lamps off for lifetime measurements was used [1], [11], [44], [45]. Quasi-steady state photoconductance (QssPC) measurements were performed at room temperature using a Sinton WCT-120TS unit. Carrier lifetimes have been extracted at an injection level of $0.1 \times p_0$, where p_0 is the equilibrium hole concentration. Injection dependent lifetime curves from QssPC measurements have been fitted to Shockley-Read-Hall (SRH) theory to extract the capture cross-section ratios for the dominant recombination mechanism [46].



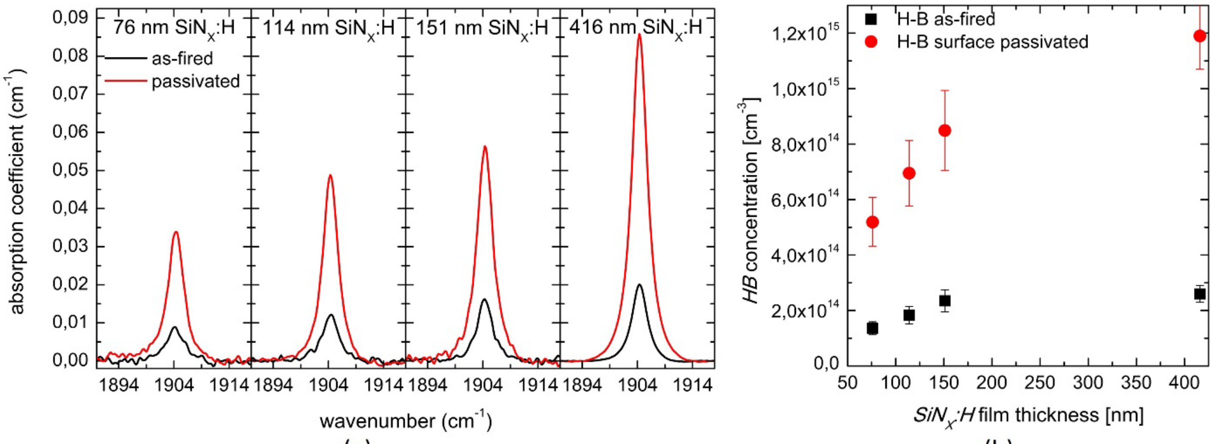
(a) (b)

Figure 1. *The process flow of the wafer processing (a). The thickness of the* $\boldsymbol{SiN_X:H}$ *layer is varied by changing the deposition time. Sectors of 4" DSP wafer with different* $\boldsymbol{SiN_X:H}$ *thicknesses and corresponding refractive indices determined using ellipsometry (b).*

Similarly processed wafers were cleaved into 1×1 cm^2 pieces for Fourier Transform (FT) IR spectroscopy measurements [11], [38], [39], [47]. Stacks of the pieces were cooled to 5 K in a cryogenic FT-IR spectrometer and measured by directing the light beam longitudinally through the stack. The resulting transmittance spectra of the LVMs were utilized to determine the concentration of the hydrogen boron (HB) complex by analyzing the peak areas in the absorption coefficient spectra [48].

3. Results and discussion

Figure 1b) shows refractive indices of 2.03-2.04 at a wavelength of 800 nm, and thicknesses of 76, 114, 151, and 416 nm that were found for deposition times of 5, 7.5, 10 and 25 minutes, respectively.

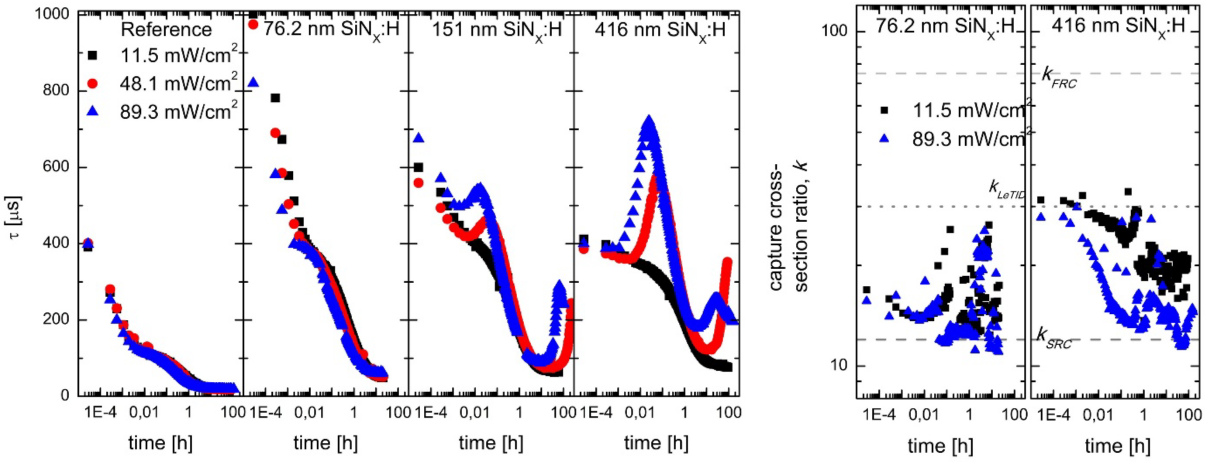


(a) (b)

Figure 2. *IR absorption coefficient spectra for the 1904 cm^{-1}* HB *related LVM (a) and corresponding* HB *pair concentrations (b) in as-fired (black) and passivated (red) wafers.*

IR absorption coefficient spectra of the LVM attributed to HB pairs are shown in Figure 2a), while Figure 2b) shows the corresponding HB concentrations calculated from the area of the absorption peaks in Figure 2a). A close to linear increase is observed in the hydrogen concentrations for 76, 114 and 151 nm $SiN_X{:}H$ film thickness. This confirms previous reports of increased amount of introduced hydrogen by increasing the thickness of the hydrogen source on the wafer [39]. For abundantly thick layers, i.e. 416 nm, the hydrogen-increase tapers off. HB concentrations between 1.4×10^{14} and 2.6×10^{14} cm^{-3} were measured in the as-fired wafers, while the passivated wafers show approximately four times higher concentrations. As the passivation process entails an additional process step of 20 minutes at 230°C, these increased concentrations are in accordance with the formation of HB pairs expected during dark annealing [35], [40]. Formation of HB pairs within minutes of dark annealing at temperatures exceeding 180°C has previously been demonstrated [36].

Figure 3a) shows the degradation of lifetime upon illumination at RT in both hydrogenated wafers as well as reference wafers. The reference wafers show quite comparable degradation curves for the different light intensities; similar initial lifetimes (τ_0) as well as comparable fast and slow decay curves. A 76 nm thick $SiN_X{:}H$ layer, close to the normal thickness for an anti-reflection coating, also produces similar degradation curves among the different illuminations. For increased light intensities minor increases in the degradation rates can be seen, best visible in the fast decay. This could, however, also be explained by a temperature increase of a few degrees for each increment in the light intensity. For thicker $SiN_X{:}H$ films and, thus, higher hydrogen concentrations, the results start to deviate from our current understanding of the BO-LID mechanism. Increasing the thickness results in a decreased τ_0, and at 416 nm it even diminishes to the plateau value which distinguishes the fast decay from the slow decay. As the lifetime is reduced approximately to the FRC/SRC plateau value it is tempting to postulate a pre-activation of the FRC defect centers. The FRC/SRC ratio in boron doped wafers can also be modulated using various dark annealing processes [49], however, this modulation did not reduce the initial lifetime. Alternatively, this lifetime decrease can be explained by a considerable LeTID defect density that may have been introduced by the passivation process at 230°C, as experienced by Vargas et al. under similar conditions [28]. For low intensity illumination the lifetime evolutions follow the expected slow decay curve for both the 151 nm and 416 nm thick films. For light intensities around 48 mW/cm^2 lifetime increase can be observed after a few seconds, followed by a decay that sets in after a few minutes of continued illumination. Increased illumination intensity triggers an earlier onset of this lifetime increase. The timeline for this lifetime increase fits well with the temporary recovery in boron doped float-zone wafers performed at 0.5 Suns illumination and 36°C [32]. Approaching 100 hours of illumination at RT a secondary lifetime increase is observed in the hydrogen rich wafers (416 nm). An increased BO-regeneration rate under illuminated annealing has been demonstrated for hydrogenated wafers [11]. The elevated hydrogen content may trigger a BO-regeneration at RT for our wafers. This secondary lifetime increase is followed by a new decay for the highest illumination.



(a)

(b)

Figure 3. *QssPC-lifetimes for boron doped Cz-wafers with different hydrogen content during illumination at RT are shown in (a). A selection of capture cross-section ratios as well as literature values for* k_{FRC} *[18],* k_{SRC} *[21], and* k_{LeTID} *[50], [51], [52] (dashed lines) are shown in b).*

Figure 3b) shows a selection of k-values fitted from SRH models. For the thinnest $SiN_X:H$ layer, the k-values are in the 10-30 region for all light intensities, slightly above the range attributed to the k_{SRC} [21]. For the thickest $SiN_X:H$ layer the k-values start out higher and converge towards the expected SRC-values within minutes under high illumination. For low illumination intensity this reduction in the k-value is slower. The k-values are obtained assuming one dominant recombination mechanism. Thus, a gradual change in the k-value indicates a shift in the recombination mechanism that is limiting the carrier lifetimes. One can speculate, the increased k-value in the beginning of each degradation curve indicates that the FRC is not negligible due to its pre-activation and that both the FRC and the SRC contribute to the recombination at early stages of the illumination. On the other hand, the k-value for the light and elevated temperature induced degradation (LeTID) is in the 26-36 region [50], [51], [52]. Thus, an emerging contribution from LeTID defects formed during the additional processing steps, i.e. a dark annealing process, may also explain this early shift in the k-values. Thus, both a temporary recovery of the LeTID or a reversal of the proposed pre-activation of FRCs may explain the increase in the lifetime observed for elevated hydrogen concentrations and high illumination.

4. Summary

Silicon wafers with different hydrogen concentrations were produced through variation of the $SiN_X:H$ layer thickness during firing. An increased HB concentration is obtained by increasing the thickness of this layer. This increase is intensified by a subsequent surface passivation at 230°C.This is attributed to dissociation of H_2 and formation of HB pairs during this step.

Surface passivated wafers with different hydrogen concentrations were illuminated at RT and the lifetime degradation was monitored for three different light intensities. The initial lifetime prior to illumination decreases with increasing hydrogen content, reducing the fast decay part of the degradation curve. The characteristic lifetime plateau indicating the transition from the fast to the slow decay mechanism in wafers suffering from BO-LID is unaffected. With low intensity illumination, only the slow decay can be seen for the highest hydrogen concentration. However, higher light intensities trigger a temporary lifetime increase before the degradation once again sets in. Wafers with less hydrogen present exhibit similar degradation kinetics for all light intensities. This shows that a charge injection dependent effect has been introduced with an elevated hydrogen content. The reduced initial lifetime and the temporary increase may be explained by increased LeTID with elevated hydrogen content activated by the subsequent surface passivation, or by a proposed involvement of hydrogen in the fast recombination mechanism in BO-related LID.

Data availability statement

The data that support the finding of this study are available from the corresponding author upon reasonable request.

Author contributions

R. Søndenå: conceptualization; data curation; formal analysis; investigation; project administration; visualization; writing – original draft; writing – review and editing. **N. Aßmann:** data curation; formal analysis; investigation; writing – review and editing. **F. Mosel:** resources; writing – review and editing. **P-A. Hansen:** formal analysis; writing – review and editing.

Competing interests

The authors declare that they have no competing interests.

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