Bulk and surface instabilities in boron doped float-zone samples during light induced degradation treatments

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Abstract

Float-zone silicon is often used as a supposedly stable high lifetime reference material. Here it is shown, however, that boron doped float-zone samples that underwent a fast firing step may suffer from a severe degradation in bulk lifetime during illumination at elevated temperatures. Furthermore, it is observed that silicon nitride related passivation may be affected by a long-term decrease in chemical passivation quality. A time and injection resolved visualization is introduced to quickly distinguish between these degradation features. Both bulk lifetime and chemical passivation quality are shown to recover at the same treatment conditions after longer treatment times.

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1. Introduction

Many experiments investigating phenomena such as boron oxygen (BO) related degradation (e.g., [1-3]) in Czochralski (Cz) silicon or light induced degradation (LID) in multicrystalline (mc) silicon (e.g., [4-6]) require a separation of changes in bulk and surface passivation quality. Frequently, reference samples made out of float-zone (FZ) silicon are assumed to have high and stable bulk lifetimes \( \tau_p \) and are therefore used to check for changes in surface passivation quality. However, a number of possible defects is reported in the literature for FZ silicon. These

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include grown-in defects like vacancies, self-interstitials, dislocations, swirl defects and fast-cooling defects which can be influenced by the crystal growth process (e.g., [7-9]). Sample processing and especially high temperature steps may also result in formation or dissociation of defects, as observed in [10-13].

Recently, it has been shown that boron doped FZ material can be prone to severe degradation of $\tau_b$ during treatments at elevated temperature and illumination [14-16]. Additionally, it was found that SiN$_x$:H related surface passivation quality may degrade and recover under these treatment conditions as well [14]. To gain further insight, an injection dependent evaluation of measurement data is used in this study to distinguish between different degradation features.

2. Experimental

Samples were made out of either boron doped (1 $\Omega$cm) or phosphorous doped (2.5 $\Omega$cm) FZ silicon. All samples first received a cleaning step in a solution of H$_2$O$_2$ and H$_2$SO$_4$ at 80°C followed by a dip in HF (Piranha clean) in a cleanroom environment. Hydrogenated silicon nitride (SiN$_x$:H) layers were deposited on both sides using direct plasma enhanced chemical vapor deposition (PECVD) at a set temperature of 450°C. Finally, all samples received a fast firing step in a belt furnace at around 800°C (sample temperature) and were subsequently stored in darkness until degradation treatments started.

The samples were treated at an illumination intensity of around 1 sun equivalent intensity and at elevated temperatures up to 250°C on hotplates. In order to monitor the effective minority carrier lifetime $\tau_{\text{eff}}$ during such a treatment, samples were repeatedly taken from a hotplate and $\tau_{\text{eff}}$ was determined by a photo conductance decay (PCD) measurement at 30°C using a Sinton Instruments lifetime tester (WCT-120).

3. Results and discussion

3.1. Injection resolved visualization of LID at 80°C

First, a PCD measurement series of a boron doped FZ sample will be discussed. The sample was treated at a temperature of 80°C and 1 sun illumination intensity for an accumulated treatment time of several hundred hours. The measurement data shown in Fig. 1 are already corrected for Auger and radiative recombination according to the parameterization of Richter et al. [17] and therefore reflect only recombination at defect levels either in the bulk or at the surface. Fig. 1 (a) shows PCD measurement data at three different injection levels. As can be seen, the sample is far from stable during the treatment both at a time scale of minutes up to a time scale of weeks. Additionally, it can be seen that the shape of the curves differs significantly at different injection levels.

To fully visualize the measurement data over a wide range of injection levels, different colors are used in Fig. 1 (b). Already after a short treatment time (~1 h) a minimum $I$ in $\tau_{\text{eff}}$ is reached, especially at low injection levels (bluish colors). This is characteristic for a deep level defect that can be described by the Shockley-Read-Hall (SRH) mechanism featuring a low $\tau_b$ at low injection and a higher $\tau_b$ at high injection [18, 19]. Afterwards, a recovery can be seen leading to a local maximum II (~10 h) where the injection dependency gets inverted: reddish colors drop below bluish colors and the injection dependency resembles the one at the beginning of treatment. In the subsequent drop, high injection levels still show the lowest $\tau_{\text{eff}}$. This indicates a surface limitation of the sample: The commonly used description of surface recombination with the surface saturation current density $J_{\text{sat}}$ is known to result in higher recombination at higher injection [20].

The different injection behavior correlates very well with other measurements. Using a combination of corona charging series, capacitance voltage measurements and re-passivation of the surface, it was found out for identically processed samples that feature I is caused by a degradation of bulk lifetime $\tau_b$ [14]. This bulk degradation and the subsequent rise of $\tau_{\text{eff}}$ leading to feature II can be described with a 3-state defect model [15] including a regeneration reaction of the underlying bulk defect. Assuming a single deep defect level, the capture cross section ratio $\sigma_n/\sigma_p$ was determined to be $\sim$20, suggesting a positively charged defect [15].

The decline for long treatment times, on the other hand, was found to reflect a degradation of chemical passivation quality [14], in good agreement with the injection dependent analysis discussed before. A significant
recovery in passivation quality is caused by an increase of chemical passivation quality [14].

These attributions are verified and it is found that the observed degradation features at higher temperatures. According to Fig. 2, increasing the treatment temperature of a boron doped FZ sample leads to a significant acceleration of the observed behavior. Both degradation and recovery of $\tau_p$ happen in a couple of minutes at 150°C (blue dip) and are not visible at 250°C (maybe due to a lack of temporal resolution). With increasing temperature, also a minimum III and subsequent recovery of passivation quality can be observed. Again, using a combination of corona charging series, capacitance voltage measurements and re-passivation of the surface in identically processed samples, these attributions are verified and it is found that the recovery in passivation quality is caused by an increase of chemical passivation quality [14].

3.2. LID treatment at higher temperatures

The different injection behavior discussed in Fig. 1 can now be used as a characteristic “fingerprint” to identify degradation features at higher temperatures. According to Fig. 2, increasing the treatment temperature of a boron doped FZ sample leads to a significant acceleration of the observed behavior. Both degradation and recovery of $\tau_p$ happen in a couple of minutes at 150°C (blue dip) and are not visible at 250°C (maybe due to a lack of temporal resolution). With increasing temperature, also a minimum III and subsequent recovery of passivation quality can be observed. Again, using a combination of corona charging series, capacitance voltage measurements and re-passivation of the surface in identically processed samples, these attributions are verified and it is found that the recovery in passivation quality is caused by an increase of chemical passivation quality [14].
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Fig. 1. (a) Temporal evolution of 

Fig. 2. (a) Injection evolution of a boron doped FZ sample treated at 150°C and ~1 sun illumination intensity in the course of time. The data are already corrected for Auger and radiative recombination. Colors indicate the injection level. Data points are connected with lines to allow for easier readability. (b) The same representation for a boron doped FZ sample treated at 250°C and ~1 sun illumination intensity.

3.3. LID treatment of P-doped samples

Due to the significant changes in bulk and passivation quality in boron doped FZ samples, the question naturally arises whether there are similar degradation phenomena at play in phosphorous doped FZ samples. Fig. 3 shows injection resolved data of samples treated at 80°C and 250°C. In contrast to the B-doped samples, no degradation can be observed during the first hours of treatment at 80°C (no dip in blue). Instead, $\tau_{\text{eff}}$ increases during the first hours of treatment. After ~30 h of treatment, however, $\tau_{\text{eff}}$ starts to degrade and after ~1000 h of treatment, saturation sets in at significantly lower values. Due to $\tau_{\text{eff}}$ being most limited at high injection levels, the sample appears to be surface limited during the whole treatment. The similar injection dependency and time scale of degradation compared to B-doped samples lead to the assumption that this degradation is caused at the surface of the sample. This is backed up by $j_{\text{os}}$ values that decrease during the initial rise of $\tau_{\text{eff}}$ and increase significantly during degradation (data not shown).

A P-doped sample treated at 250°C shows a very similar evolution compared to B-doped samples: After degradation, surface passivation quality recovers, in this case to very high lifetime values. A similar behavior has been seen in B-doped 2 Ωcm samples, where $\tau_{\text{eff}}$ also recovered to much higher values compared to the initial level [14]. It is noteworthy that at 250°C treatment temperature the surface degradation does not lead to $\tau_{\text{eff}}$ values as low as at lower treatment temperatures. This is true for both B-doped and P-doped samples and is probably caused by a faster onset of the recovery reaction which is possibly obscuring the full potential of degradation at such high treatment temperatures.

4. Conclusions

It has been shown that a time and injection resolved visualization of $\tau_{\text{eff}}$ during illumination at different treatment temperatures is a useful tool for recognizing characteristic degradation features. Using this method and complementary measurement methods, first a degradation and recovery of bulk lifetime has been identified in boron doped FZ samples that underwent a fast firing step in a belt furnace. The injection dependency in the degraded state indicates a deep level defect.

Additionally, a subsequent degradation and recovery of chemical passivation quality has been observed and appears to be characteristic for SiNx:H related passivation that underwent a fast firing step. An inversion of the injection dependency allows to distinguish between bulk and surface degradation phenomena in the investigated samples. A similar degradation of surface passivation quality also occurs in boron doped FZ samples passivated with SiOx/SiNx:H or AlOx/SiNx:H [21, 22], also when using different PECVD tools. Additionally, it was shown that phosphorous doped samples show a similar degradation and recovery. It can therefore be supposed that the observed
changes in surface passivation quality are characteristic for a SiN\textsubscript{x}:H related passivation that underwent a fast firing step. All these findings should be taken into account when performing degradation experiments aiming at changes in the silicon bulk.

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