LETID- AND (EXTENDED) BO-RELATED DEGRADATION AND REGENERATION IN B- AND GA-DOPED MONOCRYSTALLINE SILICON DURING DARK AND ILLUMINATED ANNEALS

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ABSTRACT: We study the degradation effects of boron-oxygen related light-induced degradation (LID) and light- and elevated temperature-induced degradation (LeTID) on both B- and Ga-doped Cz-Si wafers from the same industrial producer. The wafers of the two doping types were subjected to the same sample processing and degradation conditions. The studied conditions include dark anneal (DA) at 175°C and illuminated anneals at 75°C and either 1 or 0.1 sun eq. illumination intensity, which allow a good direct comparison of the influence of the dopant elements on the degradation effects. We find an atypical injection dependence of LeTID in the Ga-doped samples compared to the "standard" behavior in B-doped silicon. The Ga-doped samples degrade strongly only when the carrier injection is low. Degradation of Ga-doped samples during DA is only observed on long timescales, resulting in an injection-dependent lifetime dissimilar to LeTID-degraded Ga-doped samples and B-doped samples after both DA and LeTID. The results indicate that the dopants have a strong influence on the degradation behavior.
Keywords: Crystalline silicon, Ga-doping, Degradation, LeTID, boron-oxygen defect

1 INTRODUCTION

It is believed that hydrogen and some other component are involved in Light- and elevated Temperature-Induced Degradation (LeTID), e.g. [1]. The differences between LeTID in Ga- and B-doped silicon samples reported for both multicrystalline [2] and monocrystalline [3] silicon can possibly help in understanding the detailed physical mechanisms behind LeTID. The published results show in particular a lower degradation extent and slower progression in Ga-doped materials indicating an interesting influence of the dopants. However, the comparison between the two differently doped materials in the mentioned studies is not unambiguous: influences of different crystalline structures (in the case of mc-Si [2]) or different pre-treatments (in the case of mono-Si [3]), which both can have a severe impact on the outcome, could not be entirely excluded. In addition, for the greater picture many more variations in sample processing and degradation conditions – most of which have already been performed on B-doped Si – have to be examined also in Ga-doped Si. This statement pertains particularly in light of the current shift of the industry's attention toward Ga-doped silicon materials (see e.g. ref. [4]).

Therefore, the present study aims to compare LeTID degradation and regeneration in B- and Ga-doped Czochralski-grown silicon (Cz-Si) by using monocrystalline wafers from the same industrial producer, ensuring the same crystalline structure. On both material types, the exact same processing and degradation sequences are applied. However, application of illumination for LeTID testing gives rise to several obstacles for the physical understanding of the occurring processes: (i) Different initial carrier lifetimes and their changes due to LeTID result in large variations of the excess carrier densities which strongly affects kinetics. (ii) The metastable BO-related defect in B-doped Cz-Si strongly affects carrier lifetimes and must be expected to react to LeTID testing.

To avoid these obstacles, a dark anneal at temperature around 170°C has been proposed to activate the LeTID defect without the need of illumination [5]. On the other hand, it was reported that significant lifetime instabilities are observed after subjecting B-doped Cz-Si modules to increased temperatures for an extended time, such as during Damp Heat testing [6]. Therefore, both dark and illuminated anneals at different light intensities are employed on all materials in order to be able to discriminate between the different, complex degradation phenomena.

2 EXPERIMENTAL

The Cz-Si wafers used for this experiment were sourced from one industrial producer and consisted of two boron-doped materials (1.6 and 1.4 Ωcm, $[O_i] = 8 \times 10^{17}$ and 5.5×10^{17} cm^{-3}, respectively) and one Ga-doped material (1.0 Ωcm, $[O_i] = 6.5\text{-}8 \times 10^{17}$ cm^{-3}).

After saw damage etch and wet chemical cleaning, the wafers underwent an oxidation step at 1050°C for 80 min followed by an oxide etch, a $POCl_3$ diffusion at 810°C (60 min., resulting in a sheet resistivity of ~100 Ω/sq) and subsequent etch back of the diffused region. Such treatments have been demonstrated to improve the material quality of monocrystalline silicon [7],[8]. Both wafer surfaces were passivated with a stack of 6 nm Al_2O_3 (Fast-ALD, Solaytec) and 150 nm SiN_x (PECVD MAiA, MeyerBurger). Finally, the wafers were fast-fired at a measured sample peak temperature of 800°C. The final thickness of the wafers was 145±4 µm.

All wafers were measured by QSSPC with a WCT-120 Sinton Instruments Lifetime tester in fast flash mode directly after the firing step. Next, the wafers were degraded in ambient light for ~48 h in order to ensure that all boron-oxygen related defects had been formed and the impact of the metastable iron-acceptor pair dissociation was assessed by the proceeding suggested in ref. [9]. The Fe-content was found to be negligible for this experiment. After these initial tests, the wafers were cut into halves.

Several wafer halves of each material were then degraded in the dark (anneal, DA) at 175°C and their respective counterparts were degraded under illumination at 75°C with either 1 or 0.1 sun eq. halogen lamp illumination. In this way, LeTID can be observed and compared with and without carrier injection. Between the degradation steps, the wafers were repeatedly characterized by QSSPC and PLI measurements always in the same sequence. For the DA samples, care was taken to minimize exposure to light between the anneal and the first QSSPC measurement. This gave the carrier lifetime in the BO-annealed, but LeTID-degraded state. After that, injection-dependent PL imaging as well as harmonically modulated PL [10] ensued. Subsequently, the samples were BO-degraded and once again measured by QSSPC to characterize the BO- and LeTID-degraded state. Samples degraded under illumination could not be measured in the BO-annealed state because the necessary annealing steps at ~200°C are known to change the LeTID behavior entirely [11],[12]. Therefore, such wafers were measured only in the fully BO- and LeTID-degraded state.

3 RESULTS AND DISCUSSION

As can be seen in Figure 1, during DA the B-doped Cz-Si samples show an initial degradation and also regeneration as expected from literature, e.g. [5],[13]. The degradation starts after 1 h and is mostly completed after 10 h. After 20 h the lifetime curves split up: The LeTID-related defect begins to regenerate, whereas the lifetime in the BO-degraded state stays at the same level as during the fully degraded state of both defects (hence, it does not recover to its initial state prior to DA, indicated by the green bar in Figure 1). After approx. 100 h, the regeneration seems to reach an inflection point. Interestingly, during that time span the BO-related defect density appears to increase even further. We believe that these observations are related to the extended BO degradation, which was recently reported to have an impact during the damp heat testing of modules consisting of Cz-Si solar cells [6]. The lifetime regeneration in BO-annealed state continues afterwards to very high lifetimes. The surface-related recombination current J_{0s} (not shown here) [14] remains at a very low level during the entire DA. This indicates that surface degradation is not of relevance in our experiment in accordance with our previous stability tests of similar Al_2O_3/SiN_x stacks [15]. Please note that the BO-degraded state during the first few hours was not recorded due to experimental difficulties.

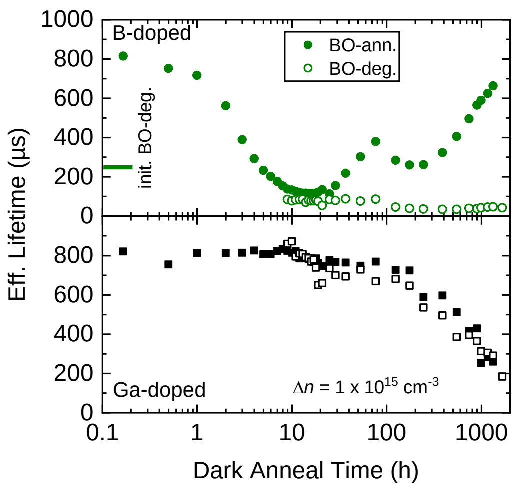

Figure 1: Effective carrier lifetime extracted at Δn = 10^{15} cm^{-3} during dark anneal at 175°C of B-doped (top graph) and Ga-doped (bottom graph) samples in the BO-annealed (closed symbols) and BO-degraded (open symbols) states.

The Ga-doped samples remain stable under dark annealing for a long time and begin to degrade after approx. 100 h, which was verified to be not related to an increase in J_{0s}. The set-in of the degradation coincides with the inflection point of LeTID-regeneration and further BO-degradation in the B-doped samples. It is still unclear whether this is a mere coincidence. However, it is to be noted that the DA excludes influences of excess carrier differences between Ga- and B-doped samples. Due to this and the fact that both Ga- and B-doped wafers underwent the same processes and have the same thicknesses, this observation happening on the same timescales may well be related to each other.

A surprising result is obtained by degradation under illumination at 75°C, as can be seen in Figure 2: Whereas B-doped Cz-Si behaves as expected – i.e. the degradation being faster at higher illumination intensity – the opposite seems to be true for the Ga-doped samples: upon illumination with 1 sun eq., only a small dip in the carrier lifetime – if any at all – can be seen. By contrast, low intensity illumination equivalent to 0.1 sun provokes a distinct and strong degradation effect. This result has been verified on several samples.

In order to clarify whether the higher intensity illumination resulted in a very fast or very slight LeTID degradation - regeneration cycle in the Ga-doped sample, it was subjected afterwards to degradation at 0.1 sun eq. (open blue rectangles in Figure 2). As can be seen, it degrades strongly and approximately follows the same extent and kinetics as the fresh sample which was degraded at 0.1 sun eq. directly after firing (open triangles). Further work is required to determine whether a similar strong degradation at low injection conditions is also observed after the application of a rapid stabilization step which makes use of extremely high carrier injection by means of laser illumination [11].

Previously, a four-state model has been proposed to describe the transition from the precursory state A into the degraded state B with the LeTID defect being active, which then continues to the permanently regenerated state C (to account for influences of DAs, an additional reservoir state has been suggested) [16]. In the

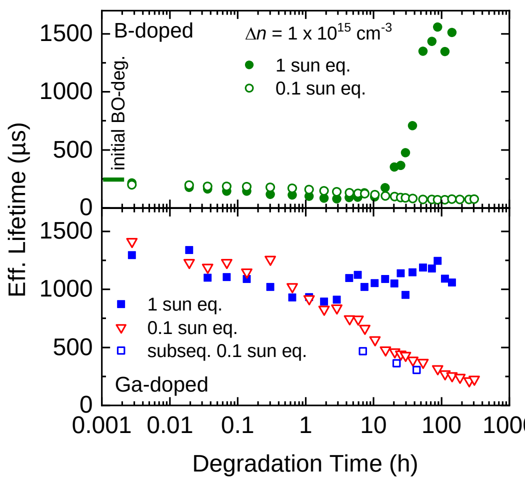

Figure 2: Effective carrier lifetime extracted at Δn = 10^{15} cm^{-3} during illuminated anneals at 75°C of B-doped (top graph) and Ga-doped (bottom graph) samples illuminated with 1 sun eq. (closed symbols) and 0.1 sun eq. (open symbols), respectively.

framework of this model, our interpretation of these observations is that the excess carrier concentration has a significant influence on the equilibrium LeTID defect concentration: At higher injection, in Ga-doped samples the precursory state A is preferred; only at lower injection, the equilibrium shifts toward the state B enabling significant carrier lifetime degradation.

As PL images of B-doped samples in Figure 3 reveal, there is a fundamental difference between the regeneration in the dark and under illumination: During LeTID, the regeneration begins first at locations of highest lifetimes (in our case at the upper wafer edge) and spreads from there, which is in line with previous studies [17],[18]. Please note that interestingly in this Cz-Si case, this lateral regeneration effect seems to also include the BO-related defect. With regard to the LeTID defect, it was hypothesized previously that the regeneration is due to the diffusion (in or out) of a component leading to the regeneration [19]. If the regeneration during DA follows the same mechanism, we would expect to see a very similar distribution in both wafer halves. However, our results indicate that the dependence of regeneration on injection is very strong and might have influenced the thickness-dependent analysis in ref. [19]. An obvious future task is therefore to investigate the LeTID-related regeneration in material of varying thickness during dark anneals.

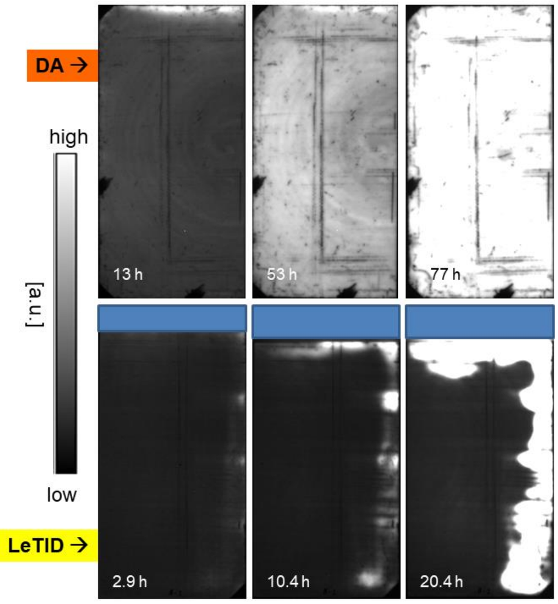

Figure 3: Progress of regeneration during dark anneal (upper row, BO-annealed state) compared to LeTID at 1 sun eq. (lower row) of two halves of the same B-doped wafer. All PL images were taken at a generation equivalent to 0.1 sun and scaled the same. During the measurements of the LeTID samples, the upper edge was masked in order to minimize the overflow of the camera detector (blue rectangles).

The characteristic injection-dependence in the charge carrier lifetime with a carrier cross section ratio *k* of ~20-30 (assuming a defect level at midgap) typical for the LeTID-related defect was observed for the B-doped samples for both DA and LeTID (not shown). Figure 4 depicts the injection-dependent effective lifetime measured on Ga-doped samples before degradation and in the most degraded states. Unlike the B-doped samples, the injection-dependent lifetimes of the Ga-doped wafers after the two different degradation treatments with and without illumination differ significantly: after DA, the lifetime curve is very flat, whereas significant injection dependence is obvious after degradation at 0.1 sun eq. illumination (independent of previous degradation at 1 sun eq.). Comparing the curves with the theoretical injection-dependent lifetime assuming only one midgap defect with a capture cross section ratio *k*=25 (black line), it seems clear that *k*~20-30 does not apply at least for the DA-degraded sample. Considering the negligible influence of the surface as mentioned above, this could indicate that the defect formed in Ga-doped Si during DA degradation is different to that in B-doped Si. However, for a more decisive statement, more investigations are necessary.

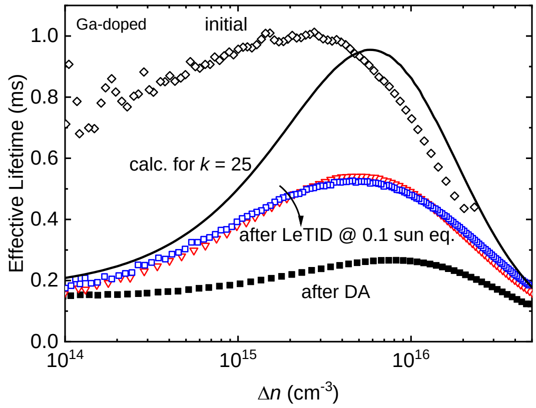

Figure 4: Injection-dependent carrier lifetime of Ga-doped samples before degradation (open diamond symbols), after DA (closed black rectangles), after only LeTID at 0.1 sun eq. (red open triangles), and after first degrading at 1 sun eq. and subsequently at 0.1 sun eq. (open blue rectangles) in the most degraded states. The colors correspond to the color coding in Figure 1 and Figure 2. In addition, the theoretical lifetime curve with a midgap level defect with *k* ~ 25 is displayed (black line).

4 CONCLUSION

In our study, industrial Ga-doped Cz-Si wafers are found to provide higher carrier lifetime and better lateral homogeneity than their B-doped counterparts. Also Ga-doped wafers are more stable under usual degradation conditions – namely BO-degradation and LeTID condition at 75°C and 1 sun eq, confirming earlier reports. However, it seems one must be careful with the conclusion that Ga-doped Cz-Si is less susceptible to LeTID. We observe pronounced degradation at lower illumination intensities. For this low intensity degradation to occur, it seems to be irrelevant whether the wafers had previously been subjected to LeTID degradation - regeneration treatment at high injection. This result is very important for the use of Ga-doped Cz-Si PERC solar cells in standard solar modules: Our results indicate that under usual operation conditions in hot climates, the relatively low carrier injection at MPP could favor significant LeTID degradation in Ga-doped Cz-Si.

With injection-dependent carrier lifetimes after degradation of Ga-doped samples being relatively flat compared to their degraded B-doped counterparts, we have first indications that the SRH defect parameters of the LeTID-defect in Ga-doped Si may differ from the ones in B-doped material.

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