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## Effects of germanium doping on the boron-oxygen complex formation in silicon solar cells

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The light-induced degradation (LID) due to the boron-oxygen (B–O) complexes is particularly harmful for solar cells made from the boron-doped *p*-type Czochralski silicon (Cz-Si). Many studies focused on this phenomenon and some processes have been proposed to reduce it. Recently, Cz-Si voluntarily doped with germanium (Ge) was used to inhibit the effect of the B–O complexes activation. We studied here both conventional Cz-Si (CZ) and Ge-doped Cz-Si (GCZ), and compared their sensitivity to the LID. The first result was that solar cells produced with GCZ had the same performances than solar cells made with CZ despite the impurities like iron unintentionally introduced in GCZ by the Ge powder. Then, we found that the degradation under illumination of the

efficiency was lower in GCZ only for the solar cells produced from the last solidified part of the ingot (where the Ge content is the highest). These differences were correlated with the amount of interstitial oxygen (O<sub>i</sub>) which was found to be lower for the GCZ wafer, possibly due to the formation of Ge–O<sub>i</sub> related defects and/or to Geenhanced oxygen precipitation effects. At the cell level, we also compared the kinetics of the LID in both materials and confirmed that the degradation was slower in GCZ. Finally, we showed that the mechanism of light-induced regeneration (LIR) also occurs in GCZ solar cells, with similar kinetics with respect to conventional Cz-Si cells.

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**1 Introduction** The light-induced degradation (LID) due to the boron–oxygen complexes (B–O) is an important drawback for solar cells containing boron (B) and interstitial oxygen (O<sub>i</sub>) [1]. The Czochralski-grown silicon (Cz-Si), which represents a large part of the materials used to produce solar cells, is thus particularly sensitive to the LID. Indeed, Cz-Si contains a large quantity of O<sub>i</sub> because of the reaction between the quartz crucible (SiO<sub>2</sub>) and the silicon (Si) melt during the crystallisation of the ingot.

The LID of Cz-Si solar cells was reported for the first time in 1973 by Fischer and Pschunder [2]. Since then, this phenomenon has been intensively studied. It has been shown that the LID is due to the activation of B-O complexes under photogeneration of charge carriers, which degrade the carrier lifetime and consequently the efficiency

( $\eta$ ) of solar cells. A B atom and an oxygen dimer ( $O_{2i}$ ) are involved in this complex. However, the state of the B atom (substitutional or interstitial [3] point defect) and the formation mode of the complex (diffusion under illumination of the  $O_{2i}$  species and association with the B atoms, or reconfiguration of an electrically inactive  $BO_{2i}$  complex initially formed during the ingot growth or the solar cell fabrication) are controversial. Previous experimental studies showed that the density of activated B–O has approximately a linear dependence on the net doping density in p-type Si ( $p_0$ ) [4] and a quadratic dependence on the  $O_i$  concentration ( $O_i$ ) [1].

In order to reduce the LID by influencing the properties of oxygen (O) atoms, Yu *et al.* introduced germanium (Ge) into the Si melt [5]. Indeed, it has been shown that Ge

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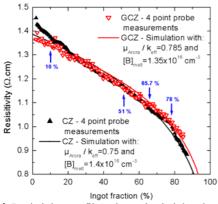
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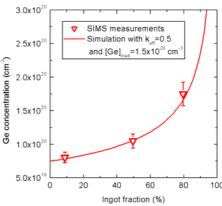
doping reduced the LID because of steric effects (Ge atoms are larger than Si atoms) and led to interaction between Ge and O<sub>i</sub>. Two combined explanations can be proposed [5, 6]. First, Ge atoms would increase the energy barrier of O<sub>i</sub> diffusion in the Si crystal. As a consequence, the amount of O<sub>2i</sub> would be lower, as finally the B–O concentration. Secondly, [O<sub>i</sub>] would decrease as a result of the formation of complexes involving Ge, Oi atoms and sometimes vacancies (V). Indeed, they could directly reduce [O<sub>i</sub>] when they are formed, and they also could be nucleation sites for the O precipitation. Finally, Ge doping reduces the kinetics of the LID. The energy barrier for O2i diffusion would be increased by the presence of Ge [7]. Solar cells were produced with Ge-doped Cz-Si and their performances were similar to those processed with conventional Cz-Si [5, 8]. In parallel, the addition of Ge developed other positive effects. For instance, Ge-doped Si is interesting for processing thin wafers because its mechanical strength is higher than that of conventional Cz-Si [9].

## 2 Experimental details

**2.1 Crystallisation of the ingots** In order to study the LID due to the B-O in Ge-doped Si, we crystallised two similar ingots. The first one, named CZ, was used as reference and was made from an ultra pure Si feedstock. The second one, named GCZ, was made from the same feedstock, which was intentionally doped with Ge. Both ingots were obtained by using exactly identical growth conditions, in the same furnace. The same amount of B was added in the crucible for both ingots (the B concentration ([B]) was equal to  $1.9 \times 10^{16}$  cm<sup>-3</sup> in the melt at the beginning of the ingot growth). Figure 1 shows that the resistivity profiles (4-point probe measurements) of both ingots are superimposed. As a consequence, supposing that Ge does not influence the majority-carrier mobility, this confirms that [B] was identical in both ingots. This is crucial to compare the LID effects since their amplitudes depend on p<sub>0</sub>, which is equal to [B] in non-compensated B-doped Si (for such [B], the incomplete ionization of the B atoms



**Figure 1** Resistivity profiles along the height obtained by 4-point probe measurements on wafers. The solid lines are obtained by simulating the resistivity with the Arora's model (majority-carrier mobility [10]) and the Scheil's law ([B]). The blue arrows indicate the position of the cells used to study the LID.



**Figure 2** SIMS measurements of the [Ge] in GCZ. The solid line represents [Ge] along the ingot by using the Scheil's law. The fit parameters are [Ge] in the melt ([Ge]<sub>melt</sub>= $1.5 \times 10^{20}$  cm<sup>-3</sup>) and the effective segregation coefficient ( $k_{eff}$ =0.5).

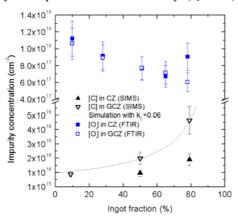
can be neglected). Consequently in this study, the effects of Ge on the LID can be rigorously evaluated by using wafers or cells from the same location in both ingots. Ge was introduced in the Si feedstock from a Ge powder at a concentration of  $1.5 \times 10^{20}$  cm<sup>-3</sup> (5N purity). According to [5], the Ge concentration ([Ge]) expected within the growth wafers should be sufficiently high to obtain reduced LID effects.

Figure 2 shows the secondary ion mass spectrometry (SIMS) measurements of [Ge] in GCZ for three positions in the ingot. The red solid line corresponds to the [Ge] profile computed by the Scheil's law. The fitting parameters are the [Ge] added in the melt ([Ge]<sub>melt</sub>) and the Ge effective segregation coefficient (keff). In order to fit the experimental [Ge], we used a k<sub>eff</sub> value equal to 0.5. This value is a little higher than the equilibrium coefficient  $(k_0=0.33)$ , that is why we also compared it with the value of keff computed by using the Burton-Prim-Slichter (BPS) theory [11]. For a pulling rate of 60 mm/h, a crystal rotation rate of 13 rpm, a kinematic viscosity of the melt of 3.5×10<sup>-7</sup> m<sup>2</sup>.s<sup>-1</sup>, and a liquid-phase solute diffusion coefficient of about 10<sup>-8</sup> m<sup>2</sup>.s<sup>-1</sup>, we obtained a k<sub>eff</sub> equal to 0.43. Even if we do not find exactly the same value than our experimental  $k_{eff}$ , the computed  $k_{eff}$  is also higher than  $k_0$ , which is mainly due to the high pulling rate used in our growth process (about 60 mm/h) [12]. The SIMS analyses show that no Ge powder was lost during the crystallisation. Moreover, a wafer coming from the seed end of CZ was analysed but [Ge] was lower than the detection limit of the SIMS technique (<1×10<sup>15</sup> cm<sup>-3</sup>), as expected.

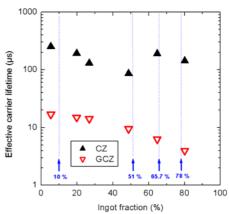
**2.2 Characterisation of the materials** Various physical, chemical and electrical characterisations were carried out on both ingots. Figure 3 shows along the ingot height the concentrations of carbon ([C]) measured by SIMS and  $[O_i]$  determined by Fourier transformed infrared spectroscopy (FTIR) at room temperature. The [C] measured here are standard for Cz-Si. We correctly fitted these concentrations by the Scheil's law with a segregation coefficient close to the value reported in [13] ( $k_C$ =0.07±0.01).

We can notice that [C] is slightly higher in GCZ than in CZ probably because of the contamination by the Ge powder which was surely not as pure as expected. Concerning [O<sub>i</sub>], the true values may slightly differ from the measured ones because the samples used for the FTIR analyses were only chemically polished, and not optically polished. The polishing was performed CH<sub>3</sub>COOH/HNO<sub>3</sub>/HF solution and the thickness of the wafers was about 440 µm. Moreover, we did not take into account the possible effects of multiple internal reflections. However the comparison between each measurement remains highly relevant because the same procedure to extract the height of the peak at 1107 cm<sup>-1</sup> was used for each sample. Furthermore the data were confirmed by two other measurements on neighbouring wafers in each case. Then, [O<sub>i</sub>] was calculated with a calibration factor equal to  $3.14 \times 10^{17}$  cm<sup>-2</sup> [14]. In Fig. 3, we can see that  $[O_i]$  are almost the same along the ingots, except for both samples coming from the top parts (last solidified fraction), where [Ge] was the highest in GCZ. For the top part of the ingot, [O<sub>i</sub>] increases in the CZ wafer. This is often observed in conventional Cz-Si ingot, as reported in [15]. Indeed, at the end of the crystallisation, the contribution of the crucible's bottom to O<sub>i</sub> contamination of the melt is more important, and a higher content of O<sub>i</sub> is therefore incorporated into the ingot. However, we can see here that [O<sub>i</sub>] is still decreasing in the GCZ ingot despite the same growth process. This effect could be due to a Ge-enhanced O precipitation as reported in [16] and/or to a formation of Ge-O<sub>i</sub> related complexes which would consume O<sub>i</sub> atoms [5]. Nevertheless, this possible result should be strengthened by other studies.

Then we measured the effective carrier lifetime ( $\tau_{eff}$ ) for samples coming from both CZ and GCZ ingots. The wafers were first chemically etched. The surfaces were then electrically passivated on both sides by a standard plasma-enhanced chemical vapour deposited (PECVD) silicon nitride film. Finally, we measured  $\tau_{eff}$  by the quasisteady-state photoconductance decay (QSSPC) technique



**Figure 3** C (SIMS) and  $O_i$  (FTIR) concentration profiles in both CZ and GCZ ingots. The detection limit of the SIMS technique is  $5 \times 10^{15}$  cm<sup>-3</sup>. The dotted black line corresponds to the simulation of [C] by using the Scheil's law with a segregation coefficient close to the value from literature ( $k_C$ =0.07±0.01).



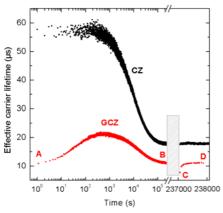
**Figure 4** Values of  $\tau_{eff}$  of CZ and GCZ samples. The excess carrier density was  $3\times10^{15}$  cm<sup>-3</sup>. The blue arrows indicate the location in the ingots of the wafers used to study the LID.

[17]. The results are presented in Fig. 4 (the uncertainties are about 10%). We notice that the  $\tau_{eff}$  values are much lower in GCZ samples than in CZ samples, which is not expected. Indeed, higher  $\tau_{eff}$  values should be obtained for GCZ wafers as a result of a decrease of void defects [6].

In order to understand the unexpected low  $\tau_{eff}$  values in the GCZ wafers, the dissolved iron (Fe) content was evaluated by applying the method described in [18] to two samples (CZ and GCZ) coming from the same ingot fraction (~ 50%). The procedure is based on repeated  $\tau_{eff}$  measurements by the microwave - detected photoconductance decay (µW-PCD) technique. The experimental data are presented in Fig. 5. With both carrier lifetimes before and after iron-boron (Fe-B) pair dissociation and by using the Shockley-Read-Hall statistics, we can calculate the concentration of dissolved Fe [19]. We found values of  $4.5\times10^{10}$  cm<sup>-3</sup> for the CZ sample and  $1.8\times10^{12}$  cm<sup>-3</sup> for the GCZ sample. As we can see, the GCZ ingot was unintentionally strongly contaminated by Fe, which explains why  $\tau_{\rm eff}$  was lower in GCZ than in CZ. The origin of this contamination is not completely proven but is probably due to the Ge powder. From the  $\tau_{eff}$  measurements the carrier lifetime limited by the B–O ( $\tau_{BO}$ ) was estimated to be 25.3  $\mu s$ for the CZ sample and 28.4  $\mu s$  for the GCZ sample.  $\tau_{BO}$  is here slightly higher in GCZ. However, the effects of Ge on the LID, if they do really exist, are very weak and have to be confirmed by complementary measurements.

**2.3 Solar cells fabrication** Some wafers were also transformed into  $50 \times 50 \text{ mm}^2$  solar cells by using an industrial standard process. Both surfaces were texturized by the anisotropic chemical attack developed by the KOH solution. The n+ emitter was formed by phosphorus diffusion. Then a SiN-H layer used as antireflection coating was deposited on the front surface by PECVD. The silver front and aluminum rear electrodes were deposited by screen printing before rapid annealing. Junction opening was performed by laser cutting. We must notice that the process was not optimized for the geometry of solar cells studied here (small area and large thickness).

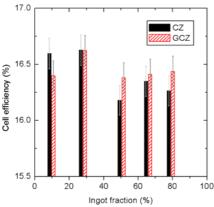




**Figure 5**  $\tau_{\rm eff}$  plotted versus time. Both samples come from the same ingot fraction (~50%). When the background is hatched, the sample is in the dark, otherwise the sample is illuminated. The points A, B, C and D correspond to different states of the B–O complexes and the Fe–B pairs (see Ref. [18] for more details).

## 3 Results and discussion

3.1 Performances of the solar cells The fabricated solar cells were characterized by current-voltage (I-V) measurements under standard illumination (AM1.5G: 0.1 W.cm<sup>-2</sup>; 25 °C). From these I-V measurements, the short-circuit current density (J<sub>SC</sub>), the open-circuit voltage (V<sub>OC</sub>), the fill factor (FF) and η were extracted. Figure 6 shows  $\eta$  for CZ and GCZ cells at several positions on the ingots. The values which are presented correspond only to the  $\eta$  of a cell at one position for a given material. As a consequence, we exclude the influence of manufacturing processes on the characteristics of the cells. Despite this assumption, we can see that the performances of the GCZ cells are almost as high as those of the CZ cells for each ingot fraction, which is consistent with literature [5, 8]. It is also worth noticing that the  $\eta$  of the GCZ cells are rather high compared to the low  $\tau_{eff}$  values previously measured (cf. Fig. 4). This result confirms that the GCZ ingot was contaminated by fast diffusing metal impurities, mainly Fe, which were extracted by the external gettering effect developed by the phosphorus diffusion [20]. Table 1 presents the averages of the cell parameters. They are almost identi-



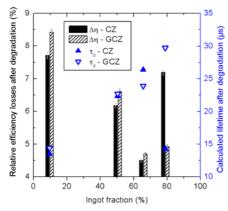
**Figure 6** Initial cell efficiency  $(\eta)$  plotted versus ingot fraction. The values correspond to one cell per position and material.

**Table 1** Averages of the electrical cell characteristics.

Cell parameters	CZ	GCZ
J <sub>SC</sub> (mA/cm <sup>2</sup> )	$34.0 \pm 0.1$	$34.0 \pm 0.1$
$V_{OC}(mV)$	$621 \pm 2$	$620 \pm 2$
FF (%)	$77.7 \pm 0.5$	$78.0 \pm 0.5$
η (%)	$16.4 \pm 0.1$	$16.4 \pm 0.1$

cal for both types of cells, CZ and GCZ. We can conclude that Ge doping is not harmful for the performances of solar cells. In particular, it seems that Ge-doped Si is poorly sensitive to the large presence of metal impurities even if this result should be confirmed with various Si qualities. It is consistent with the fact that Ge doping improves the electrical characteristics of a multicrystalline Si ingot formed from a medium-grade feedstock [21].

3.2 Amplitude of the LID Some cells were first annealed at 200°C in the dark during 40 min to deactivate all B-O. Then, they were placed under illumination to evaluate the amplitude of the LID effects on  $\eta$ . We studied here only the cells at 10%, 51%, 65.7% and 78% of the ingot fraction. They were placed on a T-controlled hotplate at either 42 °C or 50 °C under an illumination (halogen lamp) of about 0.5 Sun. We monitored the degradation by measuring the V<sub>OC</sub> of the cells and removed them only when this parameter was completely stable. Thus, we were able to ensure that the degradation was completely finished. Then, the solar cells were characterized again by I-V measurements under illumination and we compared η before and after the prolonged illumination. Figure 7 shows the relative efficiency losses after degradation ( $\Delta \eta$ ) for CZ and GCZ cells. In blue are plotted the expected carrier lifetime after degradation  $(\tau_d)$  determined with the formula proposed by Bothe et al. in [22] from our own [B] and [O<sub>i</sub>]. A strong correlation should exist between  $\Delta \eta$  and  $\tau_d$  because these both parameters are sensitive to the LID: the much lower  $\tau_d$  is, the much higher  $\Delta \eta$  should be. We observed that  $\Delta\eta$  was not very different between the CZ and GCZ cells, except for both solar cells taken from the highest part of the ingot. Indeed,  $\Delta\eta$  was here equal to 7.2 % for the CZ cell and to 4.9 % for the associated GCZ cell. This significant difference is well correlated with that of  $[O_i]$  which is reflected in  $\tau_d$  (identical [B] here). The [Ge]was higher in this cell ( $\sim 1.8 \times 10^{20}$  cm<sup>-3</sup>) than in the other studied GCZ cells  $(7.9 \times 10^{19} \text{ cm}^{-3} < [\text{Ge}] < 1.3 \times 10^{20} \text{ cm}^{-3})$ . As a consequence, we can suppose that for this Ge quantity, the O spatial distribution is influenced and [O<sub>i</sub>] is reduced, limiting the LID. The difference in B-O densities in CZ and GCZ cells seems to be related in our study only to the difference of [O<sub>i</sub>]. Although it has been shown that O<sub>i</sub> diffusion decreases with Ge doping [5, 23], the involvement of this phenomenon in the mechanism of the LID is controversial [3]. Thus we can suppose that the B–O density is reduced in GCZ mainly as a result of the formation of complexes involving Ge and Oi atoms and sometimes V [5]. Indeed, they firstly directly consume O<sub>i</sub> by their forma-



**Figure 7** Relative efficiency losses after degradation ( $\Delta \eta$ ) plotted versus ingot fraction (black columns and y-axis on the left). The blue triangles refer to the y-axis on the right and represent the calculated carrier lifetime after degradation ( $\tau_d$ ) [22].

tion. And secondly they are nucleation centres for the O precipitation, which leads to a decrease of [O<sub>i</sub>]. Finally, according to [5], we should observe a reduction of the LID in our GCZ cells even for those which are coming from the lowest part of the ingot. Contrary to what was published on the subject up to now, the effects of Ge atoms on the activated B–O density are not obvious. These results could be confirmed with samples with higher Ge content.

**3.3 The kinetics of the LID** From the previous  $V_{OC}$  measurements under illumination, we can calculate the normalized defect concentration  $(N^*_{Voc})$  which is proportional to the activated B–O concentration [1]:

$$N^{*}_{Voc}(t) = \frac{1}{\exp\left[qV_{OC}(t)/k_{B}T\right]} - \frac{1}{\exp\left[qV_{OC}(t=0)/k_{B}T\right]}$$
(1)

where q is the elementary charge,  $k_B$  the Boltzmann constant ( $k_B$ =1.38×10<sup>-23</sup> J.K<sup>-1</sup>) and T the temperature.  $V_{OC}(t=0)$  is the initial open-circuit voltage.

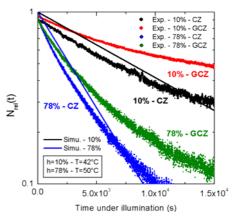
Then, we can transform these data in order to obtain the normalized concentration of non activated defects, noted  $N_{rel}(t)$  [24]:

$$N_{rel}(t) = \frac{N^*_{Voc}(\infty) - N^*_{Voc}(t)}{N^*_{Voc}(\infty)} = \exp[-R_{gen} \times t]$$
 (2)

 $R_{gen}$  is the generation rate of the B–O which is proportional to  $p_0^2$  in conventional Cz-Si, for a given temperature [1]. t is the time under illumination. Figure 8 shows the evolution under illumination of  $N_{rel}$  for CZ and GCZ cells corresponding to two positions along the height of both ingots. We compared the experimental data with the calculated  $N_{rel}$  based on empiric expressions from the literature obtained with conventional Cz-Si cells [1, 24, 25]. Our  $p_0$  values were set as input parameters in the latter expression. Despite the different [C] in both materials which could slightly influence the kinetics of the LID [26], we can notice that the degradation is significantly slower in GCZ

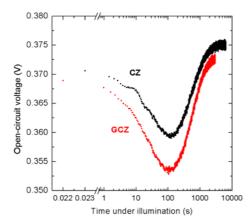
cells. This result is consistent with previous observations about the LID kinetics in Ge-doped Si wafers [7]. The proposed explanation is related to the reduction of O<sub>2i</sub> diffusion by Ge doping, which could be due to two reasons. First, it could be explained by the local increase of the energy of crystal field due to the larger size of Ge atoms than that of Si atoms. Secondly, the O2i diffusion could also be reduced by the association of O2i with Ge atoms. However, this assumption to explain the lower kinetics of the LID on GCZ cells is based on the hypothesis of a B-O complex formation by the diffusion under illumination of O2i dimers toward a substitutional B atom, which is a controversial model [3]. From a more practical point of view, we would like to emphasize that for Ge-doped Si solar cells, the amplitude of the LID has to be evaluated by placing the cells for longer durations under illumination. Otherwise the comparison between CZ and GCZ could be distorted.

3.4 The light-induced regeneration (LIR) Finally, we tried to apply the light-induced regeneration (LIR) [27] to a GCZ cell. This was performed by simultaneously illuminating (for generating charge carriers) and heating the cell to permanently deactivate the B-O. The initial performances of the cell can be recovered, and they are then stable under standard working conditions. Figure 9 presents the variation of V<sub>OC</sub> versus time under illumination of a CZ cell and a GCZ cell. They both come from the same ingot fraction ( $\sim 35.5\%$ ) and have the same  $[O_i]$  and [B]. Additionally, they were cut into samples of the same size (7×7 mm<sup>2</sup>). They were first annealed at 200 °C in the dark to deactivate all B-O before the experiment and were then placed on a hotplate at 150°C and under 5 Suns. From Fig. 2, we deduced that in the GCZ cell [Ge] $\sim 9.3 \times 10^{19}$ cm<sup>-3</sup>. Figure 9 shows that GCZ cells can be successfully regenerated by illuminating and heating them. Furthermore the presence of Ge into the crystal does not affect the LIR kinetics (for the studied [Ge]).



**Figure 8**  $N_{rel}$  plotted versus time under illumination for CZ and GCZ cells coming from two positions. The points correspond to the experimental data and the solid lines represent the calculated values of  $N_{rel}(t)$  for conventional Cz-Si. For cells located at 10% of the ingot's height, the measurements are obtained at 42°C, and at 50°C for cells located at 78%.





**Figure 9**  $V_{OC}$  plotted versus time under illumination. The cells were placed under 5 Suns on a hotplate. T was fixed at 150°C. Both cells come from the same ingot fraction (~35.5%) and have a size of  $7 \times 7$  mm<sup>2</sup>. [Ge]~ $9.3 \times 10^{19}$  cm<sup>-3</sup> in the GCZ cell.

**4 Conclusion** In this study we report on the effect of Ge doping on the initial and degraded (under illumination) performances of Si solar cells. No influence of Ge was observed on the initial cell performances, despite the high contamination of GCZ by impurities (other than Ge, mainly Fe) probably coming from the Ge powder. We also compared the degradation of  $\eta$  under illumination for CZ and GCZ cells. The  $\Delta \eta$  were not significantly different, except for the cells coming from the highest part of the ingots. This is in contradiction with other studies in which lower Ge doping were enough to reduce the LID. In our study, the GCZ cell coming from the highest part of the ingot was significantly less degraded than the associated reference CZ cell. This result was correlated with the lower [O<sub>i</sub>] value which could be due to the formation of Orelated complexes and/or to Ge-enhanced O precipitation effects. On the contrary, it is probably not related to the reduction of Oi diffusion in Ge rich Si. We pointed out that these conclusions need further confirmation. We also compared the kinetics of the B-O related complexes activation in both CZ and GCZ cells. The degradation was significantly slower in GCZ cells than in CZ cells. This could be due to the decrease of O<sub>2i</sub> diffusion in GCZ. Finally, we showed that the mechanism of LIR can be successfully transposed to GCZ, with similar kinetics.

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