Light-induced degradation in compensated n-type Czochralski silicon solar cells

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This study focuses on the evolution under illumination of the electrical performances of solar cells made with n-type boron–phosphorus compensated Czochralski silicon. First, we show via carrier lifetime measurements that this material is sensitive to light-induced degradation (LID) effects due to the formation of BO_{i2} complexes. Solar cells were then processed with this compensated material. The cells performances were found to be dependent on the position of the wafer along the ingot height.

This dependence is due to carrier lifetime variations along the ingot height and is not directly linked with the differences in concentration between boron and phosphorus. LID experiments were then performed on the same cells. Unlike what was suggested from previous studies, we highlighted a weak decrease of the cell performances under illumination, consistent with the electrical characterizations at the wafer level. These degradations have been quantified and linked with the chemical composition of the material.

1 Introduction The need of the photovoltaic (PV) industry in low cost Si leads to the use of solar-grade Si (SoG). This material often purified via the metallurgical route (SoG_M-Si) contains more impurities than electronic-grade Si (EG-Si). Moreover, this SoG_M-Si is often compensated: both B and P are present and the total dopant content is very high (around $10^{17}\,cm^{-3}$). The high B concentration ([B]) is partly responsible to the so called light-induced degradation (LID) effects on p-type SoG_M-Si [1]. LID is due to the presence under illumination of recombination-active complexes associating an interstitial O dimer (O_{i2}) [2, 3] and a B atom [substitutional (B_s) [3] or interstitial (B_i) [4]] reducing the carrier lifetime (τ). LID has been widely studied and most of published studies are based on p-Si [2, 5, 6]. Results based on compensated Czochralski (Cz) p-Si show that the concentration of BO_{i2} complexes is depend on the net doping, *i.e.* [B]–[P] rather than the total [B] [7]. This behaviour could be explained by an association of a B atom with a P atom, forming BP pairs [7, 8]. Thus, B–P compensated n-Si should not be affected by LID effects since all the B is compensated [9]. Even if some BO_{i2} are formed,

their recombination activity should be weaker in n-Si than in p-Si, due to the asymmetric electron and hole capture cross sections (σ) [10]. Thus the study of the behaviour under illumination of compensated n-Si solar cells is very important. Notice that n-Si possesses some other advantages compared to p-Si like a reduced sensitivity to several metallic impurities [11, 12] due to a smaller σ for holes than for electrons. Moreover, n-Si presents a low variation of τ with the injection level. These advantages explain the growing interest around n-type SoG_M-Si.

In this paper, we study the variation under illumination of the electrical properties of n-type B–P compensated solar cells. For this study, an ingot was grown from an intentionally compensated feedstock. First, we showed from τ measurements that contrary to previous assumptions, B–P compensated n-Si is sensitive to LID effects due to the formation of BO_{i2} complexes. Then, solar cells were processed from this ingot. Their performances were compared with those of standard solar cells. They were then placed under illumination, and we highlighted and quantified their sensitivity to the LID effects.

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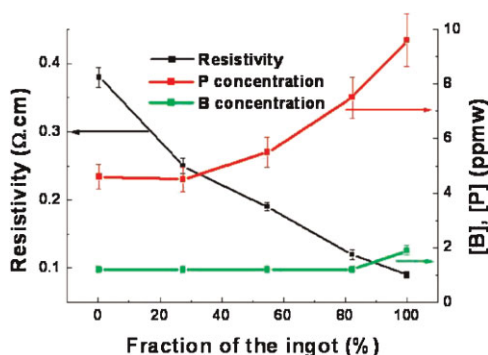
Figure 1 (online colour at: www.pss-a.com) Variation of the resistivity and the B, P concentrations along the ingot. 0% corresponds to the first crystallized part and 100% corresponds to the last crystallized part.

2 Experimental details

2.1 Description of the ingot For these experiments, we crystallized a single-crystalline Cz ingot from an EG-Si feedstock in which we deliberately added B and P. The grown ingot was only n-type. The ingot was sliced into 4 inch. wafers (500 μm thickness). The resistivity (ρ) (determined with the four point-probes measurement) and [B], [P] using glow discharge mass spectroscopy (GDMS), are given in Fig. 1. The ρ decreases steadily along the ingot height while [B] and [P] increase. This variation in [B] and [P] is due to segregation mechanisms during the ingot growth. The small variation in [B] is due to its high partition coefficient (k) equal to 0.8, whereas the strong variation of [P] is due to its lower k equal to 0.35.

The τ of different wafers along the ingot height were measured by the quasi-steady-state-photoconductivity (QssPC) method (Table 1). This method requires the knowledge of the majority (μ_{maj}) and minority (μ_{min}) carrier mobilities. The effects of compensation on μ_{min} and μ_{maj} were – at least partially – taken into account using Arora's mobility model [13] based on the GDMS results for [B] and [P]. The τ mappings of the same wafers were done by using the micro-wave-phothoconductance-decay (μW-PCD) technique (Table 2), which was also used in order to study the LID effects. The low τ in the last part of the ingot can be

Table 1 Carrier lifetime measurements along the ingot by QssPC at 1 sun. The wafers at 83 and 99% of the ingot height were not measurable by the QssPC technique (because the detected photoconductivity signal being too low on these two wafers).

position in the ingot (%)	1	30	55	83	99
carrier lifetime (μs)	20	63	41	–	–

Table 2 Carrier lifetime measurements along the ingot by the μWPCD technique at moderately high injection level. The values presented here are the average of the wafers mappings.

position in the ingot (%)	1	30	55	83	99
carrier lifetime (μs)	23	46	44	21	12

explained by a strong [P] and a low compensation level (C_l), probably inducing a high Auger recombination rate. The low τ in the first part of the ingot could be explained by a higher density of crystallographic defects.

2.2 Solar cells fabrication and characterization 50×50 mm^2 solar cells were processed on wafers selected at seven different positions along the ingot height. The fabrication steps are chronologically: KOH texturing, front side BCl$_3$ diffusion, rear side POCl$_3$ diffusion, thermal SiO$_2$ growth, SiN deposition on both sides, screen-printing of contacts and firing. The fabricated cells were measured in terms of short circuit current (J_{sc}), open circuit voltage (V_{oc}), fill factor (FF) and energy conversion efficiency (η) by standard $I–V$ measurements (AM 1.5 at 25 °C).

Finally, LID experiments were carried out on the cells fabricated. For the LID experiments, the cells were placed under an illumination intensity of 2 suns (0.2 W/cm^2) at 50 °C for at least 60 h.

3 Results and discussion

3.1 Carrier lifetime variation under illumination: Highlighting of BO$_{i2}$ complexes in n-Si For this experiment, we used a wafer from the described ingot, located at 30% of its height. [B] and [P] were, respectively, equal to 1.6×10^{17} and 2.1×10^{17} cm^{-3} ($\rho = 0.25$ Ω cm). Two reference uncompensated Cz n-Si wafers were used for comparison, with [P] = 1.2×10^{15} and 2.0×10^{17} cm^{-3}. The effective τ (τ_{eff}) was measured under illumination by μWPCD. The illumination of the sample was locally done (degraded area $\approx 3 \times 3$ mm^2) by the laser pulses of the μW-PCD technique (intensity of 1650 W/cm^2).

The wafers used for this study were chemically polished and electrically passivated by a deposition on both sides of Si hydrogenated nitride (SiN:H) layers with a plasma-enhanced-chemical-deposition (PECVD) equipment. For this experiment, τ_{eff} under illumination was followed until complete degradation. Figure 2 shows the evolution of τ_{eff} under illumination for the compensated wafer and for the control samples. The compensated wafer is degraded while
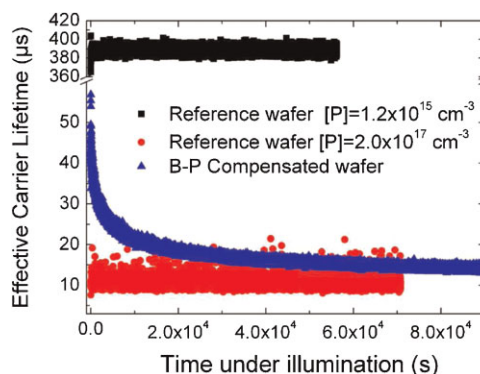
Figure 2 (online colour at: www.pss-a.com) Evolution of the carrier lifetime under illumination for the reference and the compensated wafers.

Table 3 Solar cell results as a function of the ingot height and the compensation level (C_1). Each result is an average of three cells.

ingot height (%)	$C_1 = ([P] + [B])/([P]-[B])$	V_{oc} (mV)	J_{sc} (mA/cm^2)	FF (%)	η (%)
reference FZ n-Si cell		629	35.6	77.6	17.4
2	11.4	585	24.8	73.5	10.7
30	7.4	606	29.5	73.5	12.8
43	–	606	29.1	72.8	12.9
58	4.3	619	30.4	74.5	14.0
72	–	617	30.4	74.1	13.8
86	3.2	622	29.3	75.0	13.7
99	3.6	621	28.4	74.5	13.2

the uncompensated wafer is not affected by degradation under illumination. This result first means that the degradation observed on the compensated wafer is not due to any depassivation of the surfaces, because τ_{eff} of the control wafers remains stable. The second conclusion is that the cause of this degradation is related to the addition of B in the sample. The interstitial O (O_i) concentration ($[O_i]$) was determined by Fourier-transform infrared (FTIR) spectroscopy measurements and is equal to about 10^{18} cm^{-3}. This LID of the compensated sample suggests that the formation of BO_{i2} complexes is possible in n-Si. It should be noticed that this LID could not be attributable to FeB pairs because there is no recovery of τ in the dark. Moreover, the contribution of other metallic impurities (like Cu [14]) towards the observed LID is strongly unexpected since the studied ingot was grown from high purity EG feedstock, meaning that the concentrations in metallic species in the wafer being probably below 10^{11} cm^{-3}.

The BO_{i2} hypothesis in this material was verified by annihilating this defect in the dark [15] for temperatures ranging between 200 and 250 °C. The study of the annihilation kinetics led to an annihilation energy (E_{ann}) of 1.7 ± 0.2 eV. This result is in good agreement with literature data concerning this mechanism, 1.3 and 1.8 eV [3, 16, 17], for uncompensated p-Si.

This result confirms that BO_{i2} complexes exist in compensated n-Si. Previous studies on compensated p-Si evidenced that LID effects were reduced for a given $[B]$, when increasing the C_1. This behaviour has been linked with the possible existence of BP complexes. Our work, by showing that BO_{i2} is efficiently formed in compensated n-Si, appears as a contradiction with these previous studies, since in this Si, the pairing of B with P should leave no B available for BO_{i2} formation. Therefore, it suggests that BP complexes, if they do exist, are present in a minor amount. This supports the study conducted by Macdonald and Liu [18] based on measurements of the hole mobilities and the characteristic crossover point caused by interstitial iron in compensated Si, and the work of Lim et al. [19] on the deactivation of the BO centres. These results are consistent with the recent model described by Voronkov and Falster [4], in which only B_i is responsible for the LID effects. Thus, our contribution brings further evidence that BP pairs cannot be responsible for the reduced LID in compensated Si.

In the following part, we present the results of LID experiments at the cell level. This LID phenomenon should be less pronounced than for p-Si, because as already mentioned, the capture cross-section ratio k (σ_n/σ_p) of BO_{i2} being equal to 9.3 [10], these complexes are more virulent in terms of carrier recombination in p- than in n-Si.

3.2 Solar cells results The η varied from 10.7 to 14.0% (see Table 3). The same fabrication process on uncompensated FZ n-Si wafers ($\rho = 5\,\Omega$ cm) led to η of 17.4%. These differences in η are probably due to the high amount of dopant in our compensated Si.

The V_{oc} increases steadily along the ingot height. This is probably due to the increase in the equilibrium electron density (n_0), equal to $[B]-[P]$, along the ingot height:

$$V = \frac{k_B T}{q} \ln\left(\frac{\Delta p_{front} n_0}{n_i^2}\right), \tag{1}$$

$k_B T$ is the Boltzmann thermal energy, q the electron elementary charge, Δp_{front} the excess minority carrier concentration and n_i is the intrinsic carrier concentration.

J_{sc} seems to be the limiting factor on η because the trends of J_{sc} and η are the same along the ingot. J_{sc} are lower where the initial τ are the poorest, i.e. the top and the bottom of the ingot. FF are relatively low ($\approx$74%) due to a high series resistance. This problem is mainly due to our cell process.

3.3 LID experiments Figure 3 presents the V_{oc}, J_{sc} and η losses after illumination. The parts of the ingot where
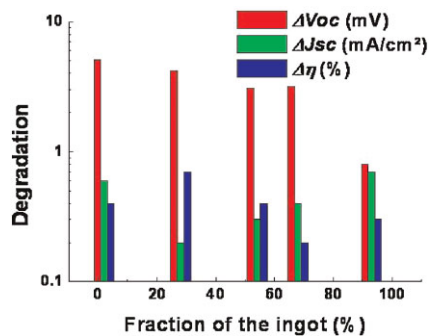
Figure 3 (online colour at: www.pss-a.com) V_{oc}, J_{sc} and η losses as a function of the position in the ingot.

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the decrease in η is the most important is due to a different FF (up to 3%) between each measurement (probably due to a weak oxidation of the metallic electrodes). For the cell at 72% of the ingot height, the FF measured before and after degradation was the same (75%), meaning that only the drops in V_{oc} and J_{sc} are responsible for the drop in η (0.2%), and meaning in this case that only BO_{i2} are suspected for the LID effect observed at the cell scale. Whatever the amplitude of the degradation, $\Delta\eta$ never exceeds 0.7%, whereas the drop of η in B-doped Cz-Si can reach 2% absolute. J_{sc} seems to be more affected at positions where the initial τ are the weakest, *i.e.* on the first and on the last part of the ingot. ΔV_{oc} also shows a dependence with the position along the ingot, *i.e.* the most compensated part of the ingot is associated to the greatest drop in V_{oc}.

An important point that should be stressed concerns the illumination time: is the time that we have used sufficient for a complete formation of the BO_{i2} complexes? In order to answer this question, we tried to estimate the time constant associated with the LID kinetics in our material. This can be done by adapting Palmer's model (which describes the LID kinetics in p-Si) to n-Si, and using the τ measurements presented earlier (Fig. 2). By using Palmer's model (in which we entered the hole concentration estimated from PC1D simulations and our measured [B] value), it is possible to estimate the generation rate (R_{gen}) of the complex for a cell taken at 30% of the ingot height. The numerical application gives R_{gen} (50 °C) $\sim 10^{-5}\,s^{-1}$. The time constant τ_{gen} (50 °C) is then $1/R_{gen}$ (50 °C) $\sim$26 h. Consequently the degradation can be considered complete after $3 \times \tau_{gen}$: about 80 h.

It is also possible to estimate τ_{gen} by using the τ measurements presented in Fig. 2. Indeed, by fitting the experimental data with an exponential function, a time constant of about 17 000 s is found. However, through this experiment the illumination was not constant. The μW-PCD uses a laser pulse with a duration of $200 \times 10^{-9}\,s$. The time between each laser pulse is fixed to $400 \times 10^{-6}\,s$. Thus the 'real' time constant is about 8.5 s. The power of each laser pulse being approximately 16 500 suns, this time constant corresponds to a hole concentration in the bulk of the cell of about $3 \times 10^{17}\,cm^{-3}$ (estimated from PC1D simulations). Under 1 sun illumination, in the cell, the hole concentration is estimated to be $3.4 \times 10^{13}\,cm^{-3}$. It is then possible to estimate the time constant under 1 sun at 25 °C which was found to be about 23 h. Both estimated time constants (determined, respectively, at 50 and 25 °C) are in good agreement, and show that our experimental conditions (60 h under 2 suns at 50 °C) were sufficient for a quasi-complete degradation of the cells.

4 Conclusions From the crystallization of an intentionally B–P compensated Cz ingot, it was shown that unlike what expected from the literature, B–P compensated n-Si is

sensitive to LID involving BO_{i2} complexes. In the second part of the study, we measured the amplitude of the LID on cells fabricated at different positions of the ingot. These degradations have a dependence on the position along the ingot height. These degradations in terms of η are weaker than in B-doped Cz-Si underlying the potential of n-type compensated solar Si for the PV industry.

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