

Light-Induced Degradation in compensated mc-Si *p*-type solar cells

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Abstract — Light-induced degradation (LID) due to boron-oxygen complex formation seriously diminishes the efficiency of *p*-type solar cells. The influence of dopants concentration, net doping and oxygen on the degradation process is investigated using a large variety of B and P compensated mc-Si ingots. Our experiments indicate that the trend of LID depends on the amounts of interstitial oxygen [O_i] and total boron [B]. No clear dependence was found on net doping.

Index Terms — boron, degradation, doping, oxygen, photovoltaic cells, silicon.

I. INTRODUCTION

A strong need for low-cost technologies for the production of silicon for Photovoltaic (PV) applications has emerged during the last decade.

When compared to the traditional Siemens process, new purification processes are less effective on dopants like boron and phosphorous due to their high segregation coefficients. For this reason a thorough knowledge of the effects related to dopants is of great importance for the PV industry.

Several studies were performed in order to understand how the presence of dopants complicates the light induced degradation (LID) that is commonly observed in B doped Cz-Si [1]-[2]. It is also well known that degradation is a result of the B-O complex formation which acts as a recombination centre reducing the minority carrier lifetime and therefore the solar cell performance [1]. Some recent works based on the performance degradation of solar cell have suggested that the formation of B-O defects in compensated solar-grade silicon is not increased compared to non-compensated material of similar properties [3]-[4]. It was suggested by Krühler *et al.* [5] that this could be due to the formation of B-P pairs which leads to the dependence of the dominant recombination process on the net doping $p_0 = N_A - N_D$ rather than the total boron concentration. These findings are further supported by the result of Macdonald *et al.* [6]. However, in the last few years, several aspects of the degradation process have been brought into question including the formation of B-P pairs [7], the parameters on which the defect concentration rely on [8] and the charge-state-driven mechanism of the oxygen dimer on which the accepted degradation mechanism was based [9]. An alternative model has been recently proposed by Voronkov and Falster [10] which is able to overtake some of the raised issues. However, those reports imply that a full understanding

of the degradation process in compensated material has not yet been achieved and more studies are required.

The intention of this work is to investigate the degradation process in several mc-Si *p*-type ingots with different intentional doping levels; each ingot was analysed along the whole height since the different segregation coefficients of the dopants and the varying oxygen concentration influence the electrical parameters and the response to the illumination.

II. EXPERIMENTAL SET UP

The cells degradation was evaluated through open circuit voltage (V_{OC}) measurements and its behaviour when light soaking was applied on the sample.

In this work a WACOM sun simulator was used for the IV measurements: this facility is a continuous light simulator with a 5kW Xe lamp. A light beam of 1000W/cm² (1sun) intensity with AM1.5 spectrum (class A) was used. The lamp illuminated a vacuum chuck on which the sample was positioned and held at a standard temperature of 25°C.

The degradation of the samples was carried out using an array composed of three 50W halogen lamps positioned above a second vacuum chuck at a distance of about 30 cm, which resulted in a light exposure with a light intensity of about 1sun. During this process the temperature of the chuck was held constant at 25°C using a water cooling system.

A box oven was used to carry out the thermal process required to split the B-O complexes. The solar cells were annealed at temperatures maintained in the range of 200-215°C for 20 minutes. During this procedure the sample was positioned between two metal plates in the oven in order to minimize the temperature variations that could occur because of the handling operations. To guarantee a good accuracy the temperature was measured with a thermocouple positioned between the metal plates.

The annealing was followed by a relatively fast cooling to the room temperature before each V_{OC} measurement was taken.

Before every degradation cycle the samples were annealed in order to re-set any partial degradation and then measured with the sun simulator. Once the degradation was completed and recorded, the samples were subjected to a second annealing in order to re-establish the initial condition and to finalize the annealing-degradation cycle.

III. MATERIAL USED

The material for the analysed solar cells (125x125 mm²) originated from several lab scale (12 kg) mc-Si ingots. For each of the ingots prime quality polysilicon feedstock was intentionally doped with B and P (see Table I). The ingots have been produced within the CrystalClear integrated project at Sintef in Norway. They show a varied degree of compensation grade $R_c = (N_A + N_D) / (N_A - N_D)$ and are divided into two groups with different value of net doping $p_0 = (N_A - N_D)$ and therefore resistivity. We will refer to the materials from the 1st group as Standard because of their resistivity values included in the range of 0.6-1.0 Ω·cm which is very close to resistivity commonly used for mc-Si material; the 2nd group materials have a characteristic low resistivity in the range of 0.15-0.30 Ω·cm and will be marked as Low. The table below reports some ingots characteristic where B and P refer to the dopants amount introduced to the virgin poly-silicon before growing the ingots. The resultant degree of compensation and the measured net doping, both varying along the ingots, refer to the 70% of the ingot height. The measured data come from quasi state steady photoconductivity (QSSPC) measurements.

Label	B [ppma]	P [ppma]	(N _A -N _D) measured [cm ⁻³]	R _c
<u>Std-ref</u>	0.33	-	1.60x10 ¹⁶	1
<u>Std-1</u>	0.50	0.24	1.63x10 ¹⁶	2
<u>Std-2</u>	0.85	0.76	2.13x10 ¹⁶	4
<u>Std-3</u>	1.50	1.72	1.51x10 ¹⁶	8
<u>Low-ref</u>	1.60	-	6.97x10 ¹⁶	1
<u>Low-1</u>	2.40	1.17	6.97x10 ¹⁶	2
<u>Low-2 (+Fe)</u>	2.40	1.17	6.97x10 ¹⁶	2

Table 1. Ingots parameters. B and P refer to the dopants amount introduced to the poly-silicon before growing the ingots. The degree of compensation and the measured net doping (N_A-N_D) refer to the 70% of the ingot height.

The last ingot (*Low-2*) in Table I contains the same amount of dopants as the ingot *Low-1*, but some Fe was also added to the material.

In all the ingots the interstitial oxygen was measured with Fourier transform infrared spectroscopy (FTIR) at different ingot heights. The oxygen trend over the ingots does not show always the typical reduction towards the top (i.e. ingots *S-ref* and *S-3*).

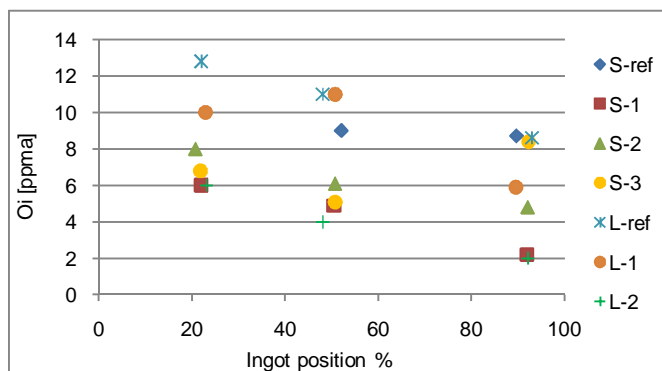


Fig. 1. O_i concentration through all the ingots. The *S-ref* data contains only two points since the value at 20% of the height is not available.

The solar cell process used was a *p*-type state-of-the-art industrial process including P-diffusion, Al-Back Surface Field (Al-BSF) and SiN_x:H firing through.

IV. RESULTS AND DISCUSSION

For each ingot at least three solar cells, each from a different position, were analysed in order to gather data along the whole ingot height. This was required since both the oxygen and dopants concentrations change along the height of the ingots, the latter according to the Scheil equation:

$$C_x = kC_0(1 - x)^{k-1} \quad (1)$$

where C_0 is the initial concentration of added dopant, k is the segregation coefficient and C_x is the concentration at height x .

The degradation of our samples occurring during the exposition to the light soaking showed two different stages in accordance with the model presented by K. Bothe and J. Schmidt [1] with the degradation curves composed of a fast initial decay preceding a slower asymptotic trend (see Fig. 2). Nonetheless, it's been recently reported by T.U. Nærland *et al.* [11] that the fast initial degradation can totally be attributed to the heating of the cell occurring during the illumination of the sample and that only the slower decay is related to the photo-induced cell degradation. In order to separate the effect of the temperature from the effect of the degradation mechanism due to BO complex formation, we used a FZ-Si solar cell in which oxygen content was negligible. The result was that just a small decrease in V_{OC} was recorded for the FZ sample which is negligible in comparison to the total amount of the initial V_{OC} decay occurring in the mc-Si material (see Fig. 2). This contribution was easily eliminated by cooling down the cells before the measurements took place.

It's well known that a heating treatment with T~200°C carried on for about 15 minutes in the dark is able to split the B-O centres and recover the solar cell from LID effects. Each

sample was subjected to this treatment both before and after every degradation process in order to re-establish the initial conditions. In Fig. 2 this effect is shown for a mc-Si cell. After the first degradation process the sample was subjected to the heating treatment and the initial V_{OC} value was fully re-established. The degradation occurring on a FZ-Si cell is also shown in order to compare the effects related to the temperature with those due to B-O complexes formation.

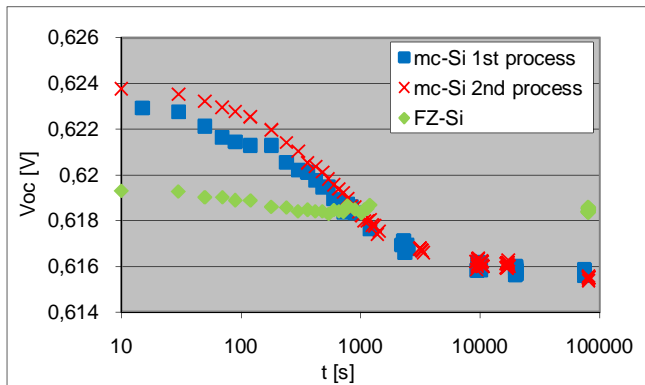


Fig. 2. Two subsequent degradation processes on a mc-Si cell and a process on a FZ-Si cell are shown. Annealing has been carried out at the beginning and at the end of each degradation cycle.

The V_{OC} of the solar cells varies along the height of the ingots since it is a function of the amount of dopants, impurities and defects present at different heights of the ingots (see Fig. 3).

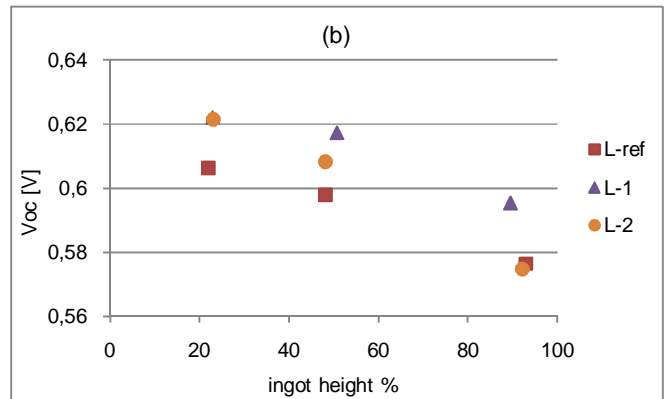
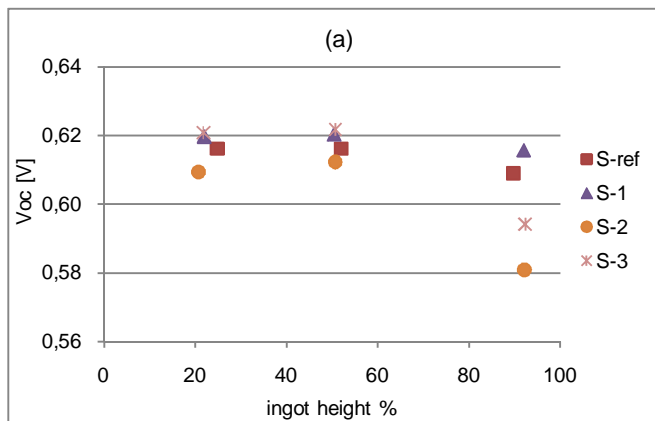
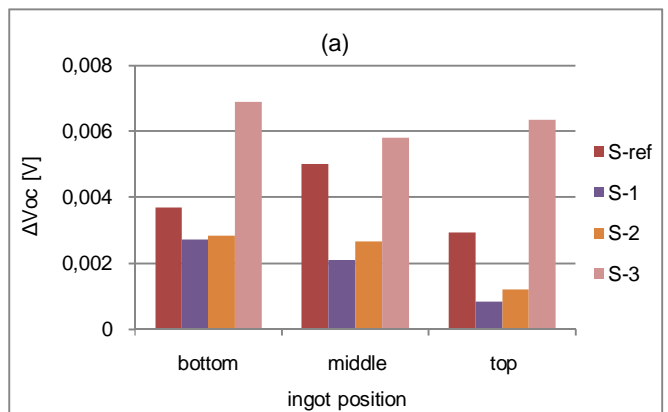


Fig. 3. V_{OC} behaviour along the ingots from the S Group (a) and the L Group (b). Measured are taken after annealing (not-degraded status).

The general trend observed was a large decrease in V_{OC} towards the top of the ingots: this result is mainly a consequence of the dopant concentrations. The presence of P having a smaller segregation coefficient than B yields an increased compensation in the ingot top, reducing the net doping and therefore reducing the V_{OC} . The V_{OC} is also lowered by the presence of defects and impurities which increases towards the ingot top as well. However, this is a second order effect in comparison to the effect of the doping. In fact the level of V_{OC} decrease is stronger for the ingots with higher compensation level while the amount of impurities and defects should be similar since all the ingots were crystallised in similar conditions.

In Fig. 4 the V_{OC} degradation after an illumination of about 23 hours is shown for all samples and reported as function of the ingot height for the two groups.



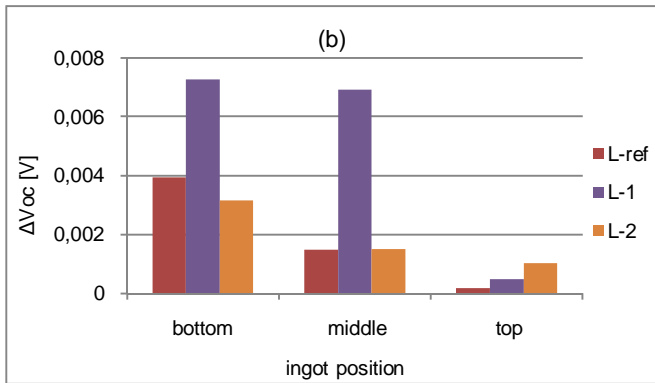


Fig. 4. Degradation along the ingots of the *S* Group (a) and the *L* Group (b). *S* stands for Standard and *L* for Low resistivity respectively. *Ref* indicates the reference uncompensated materials.

The LID (i.e. the drop of V_{OC}) along the height of each ingot showed a clear dependence with the amount of interstitial oxygen. In Fig. 5 this trend is reported.

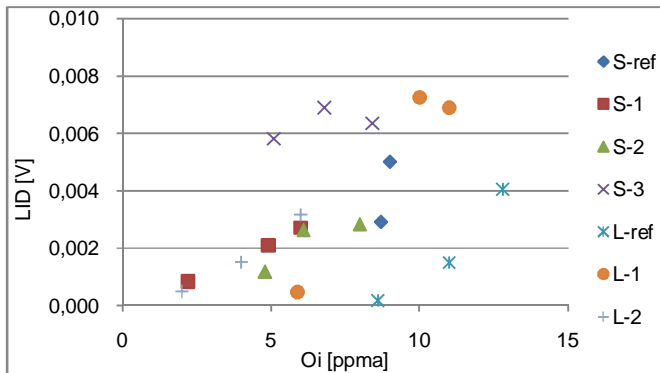


Fig. 5. LID as function of [Oi] in all the samples.

We can also notice that ingots with comparable amount of oxygen were subjected to a different grade of degradation (i.e. *S-2* with *S-3* or *L-ref* with *L-1*).

A further analysis was conducted in order to understand this finding. We selected cells taken at 20, 50 and 90% of the ingots height to allow a better comparison among samples with similar defects and impurities concentration and then we plotted LID as a function of different cell parameters (i.e. [B], [P], p_0 , R_c , Resistivity). All these parameter were calculated along the ingot height from the equation (1). The result showed that LID increases with increasing amount of boron. This trend is reported in Fig. 6 for samples taken at 20, 50 and 90% of the ingots height.

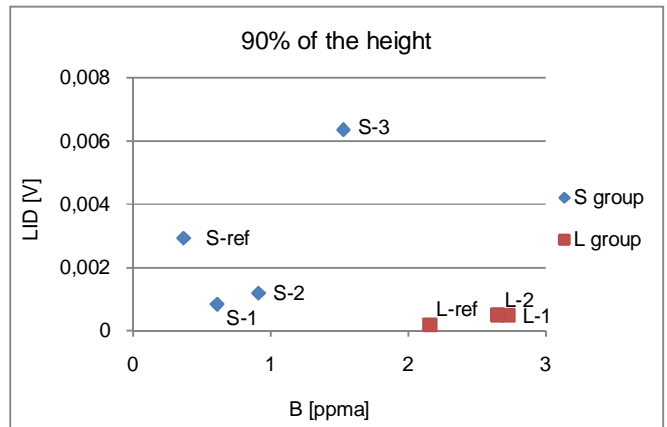
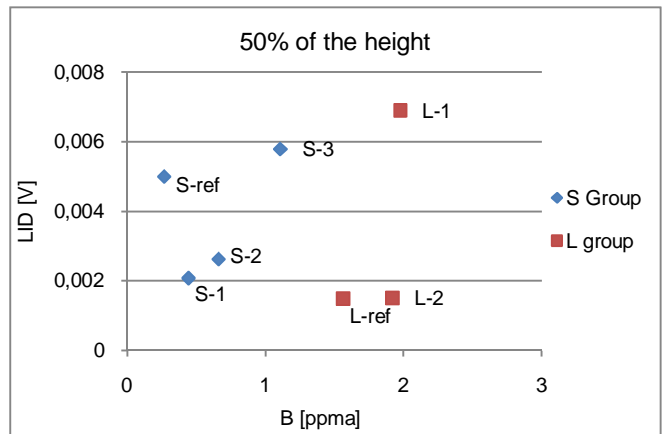
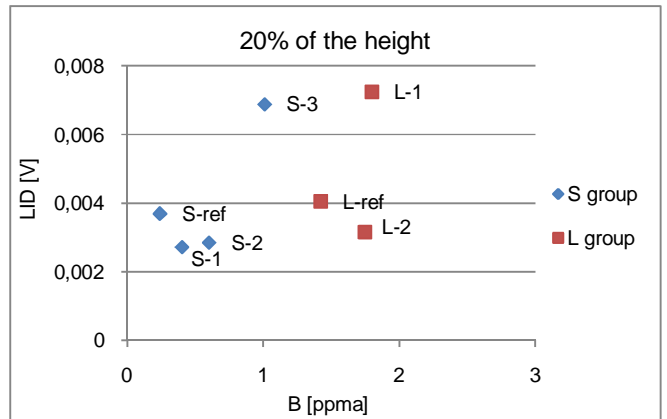


Fig. 6. LID as function of boron concentration in all the ingots at 20, 50 and 90% of the height.

The ingot *S-ref* shows a higher amount of degradation than the one occurring in the ingots *S-1* and *S-2* despite containing a lower amount of total boron. This is due to the substantially enhanced interstitial oxygen concentration in this material, much higher than in the other two mentioned ingots, which leads to the inversion of the general trend.

One can note that LID is lower than expected for the cells from the ingots of the 2nd group, especially at the top of the ingots. The exception is represented by the wafers from the ingot *L-1* at 20 and 50% of the height. These findings cannot be explained considering only the difference of interstitial oxygen amount among the samples. Our hypothesis is that the low LID observed for the 2nd group materials is related to the low absolute V_{OC} values obtained in these solar cells (especially towards the ingots top, see Fig. 3). In these samples the B-O complexes are a second order limiting factor to the solar cell performances; first one being the lifetime reduction due to impurities (in this way the high level of oxygen for *L-Ref* in the top is an indication of some issue during the crystallisation), which at high doping level dominates, and Auger recombination. The low V_{OC} values are the evidence that not-light-sensitive recombination mechanisms are dominant in these samples masking the effect of LID. The comparison of LID between the two groups (*L* and *S*) is not straightforward in absolute terms since the net doping and the J_{SC} of the cells are also different and therefore affect differently the V_{OC} . In order to make an absolute comparison among the two groups the real number of defect generated needs to be taken into account but for the same reason this cannot be done via the V_{OC} measurements. Additional characterisation on lifetime level is needed to discriminate the effects.

Previous models [6] suggested the dependency of the boron-oxygen defect density on the net doping concentration ($p_0 = N_A - N_D$) in compensated *p*-type samples. These models implied that the additional compensated boron exists in a form that is not able to bond with the oxygen dimers, thus prohibiting the formation of the BO defects. However, our results show that strong differences are found among ingots from the same group (i.e. same p_0). In order to avoid the effect of different amount of interstitial oxygen we focus on samples containing similar O_i concentration: *S-1* and *S-3* at 50%, *S-2* and *S-3* at 20%, *S-ref* and *S-3* at 90%, *L-ref* and *L-1* at 20 and 50%. In all these cases despite the same net doping a different amount of LID is found and, in agreement with our previous results, a higher degradation occurs in samples with higher amount of total. LID as function of net doping is shown in Fig. 7.

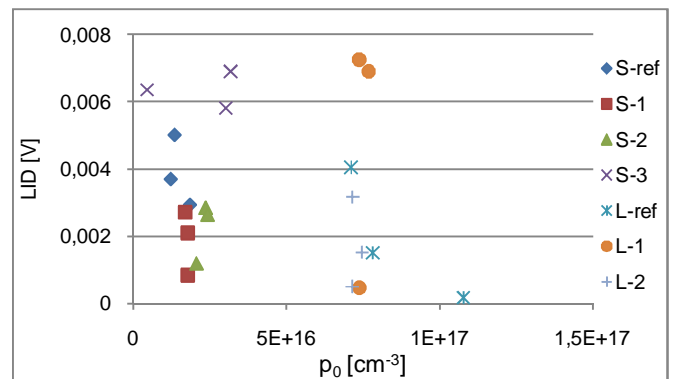


Fig. 7. Light-induced defects concentration versus net doping amount.

These findings support the dependence of LID process on [B]. At the same time not clear influence of the net doping has been found.

V. CONCLUSION

In this work we focused on the light-induced degradation (LID) of mc-Si *p*-type solar cells. We analysed several ingots divided into two groups with different net doping (p_0) values, each group containing ingots with different degree of compensation (R_c).

The general trend of LID depends on the amount of interstitial oxygen [O_i] as the degradation mechanism is based on the formation of recombination active B-O complexes.

More cell parameters were taken into account in order to explain the difference among various ingots: we found that LID increases with increasing amount of total boron. Few cases showing opposite trend are due to a considerable higher amount of interstitial oxygen.

Our results show no clear correlation to p_0 , which excludes the hypothesis of boron existing in a form not able to form complexes with oxygen and thus preventing the formation of B-O complexes.

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