LARGE AREA SOLAR CELLS MADE FROM DEGRADATION-FREE, LOW RESISTIVITY GALLIUM DOPED CZ WAFERS

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ABSTRACT: Boron doped Czochralski-wafers for industrial solar cells are negatively impacted by the fact that boron forms recombination active defects with oxygen under illumination, lowering the minority carrier lifetime of the bulk. This effect is known as light-induced degradation (LID) [1,2] and causes a voltage and current drop of the solar cells. It may be circumvented by using high-resistivity material to minimize the boron content of the wafer, but this leads to other negative effects.
A different approach is the replacement of boron by gallium as dopant. In this work, low-resistivity gallium doped HiCz™ wafers produced by Confluence Solar's proprietary process were processed into solar cells together with HiCz™ boron doped wafers. The 125x125 mm² cells were manufactured similarly to mass production conditions, employing screen printing and co-firing as the metallization technique.
The solar cell results showed that both the boron and gallium doped cells produced initial efficiencies of around 18%. Various degradation experiments were conducted, showing LID on boron doped samples. This degradation saturated after 48 hours with a 6 mV decrease in V_{OC} and an efficiency decrease of 0.3% absolute. On gallium doped samples however, no LID could be observed on a comparable timescale, the cells retained their initial efficiencies.

Keywords: Czochralski, Doping, Degradation

1 INTRODUCTION

Usually, boron concentrations in boron-doped monocrystalline Czochralski-wafers for industrial solar cell production are below those concentrations that would optimize efficiency leading to resistivities in the range between 3 and 6 Ωcm. This is done to address the widely known fact that boron forms defects with oxygen under illumination that lower the minority carrier lifetime of the bulk. This effect is known as light-induced degradation (LID) [1] and causes a significant open circuit voltage (V_{OC}) and short circuit current (J_{SC}) drop of the solar cells when in operation [2]. The first paper on the degrading effect induced by light on boron-doped wafers was published in 1973 [3] and since then it was subject in numerous experiments.

In the industry, this problem is circumvented by using high-resistivity substrates to minimize the boron content. However, laboratory cells on low-oxygen float-zone wafers yield better results when choosing lower resistivities around 0.5 Ωcm and below. It would therefore be desirable for solar cell manufacturers to use wafers that have a low resistivity and still do not show light-induced degradation. Also, advanced cell concepts with local contacts require a good lateral conductivity, therefore low resistivities are preferred.

Such properties can be achieved by replacing the p-type dopant boron by the equally trivalent element gallium. Gallium shows similar electronic behavior in the silicon band structure, but does not form recombination-active defects under illumination. The production of gallium doped Cz silicon is more complicated than producing boron doped Cz because of the very low segregation coefficient for gallium in silicon. Traditional batch Cz processes produce gallium ingots with a large axial resistivity variation. This can increase costs due to the limited acceptability of the material or the need to develop cell manufacturing processes that can accommodate the wide resistivity range. For this reason, gallium doped wafers have not been widely adopted in an industrial setting, though the advantages of gallium doped monocrystalline silicon wafers in terms of LID reduction have been known for some time.

Confluence Solar's proprietary HiCz™ silicon ingots with nearly uniform axial resistivity allow cell manufacturers to produce cells at comparable costs to traditional boron doped substrates without the effects of LID and enable high efficiency cell designs. In this study, HiCz™ Ga doped substrates were produced along with HiCz™ B doped substrates which both have a uniform axial resistivity.

2 SOLAR CELL FABRICATION

For this experiment, 40 solar cells were made from 125x125 mm² semisquare wafers. Next to a control group of 10 wafers for the optimization, 15 cells were made of B doped substrates and 15 cells were made of Ga doped substrates. The resistivities of the wafers are given in Tab. I. Note that Group 2 has approximately twice number of dopant atoms compared to Group 1.

Table I: Resistivities of the used substrates.

	Base doping	Resistivity
Group 1	p-type, Boron	2.1 Ωcm
Group 2	p-type, Gallium	1.0 Ωcm

The solar cell process used in this experiment (see Fig. 1) was a selective emitter approach oriented closely to standards used in the industry [4]: The cells underwent an alkaline texturing before $POCl_3$ emitter diffusion to about 30 Ω/sq and plasma edge isolation. Subsequently, an etch resist grid was applied by inkjet printing [5], followed by selective emitter formation via acidic etch-back to around 70 Ω/sq as described in [4]. Afterwards, a SiN_x anti-reflection coating was deposited by plasma-enhanced chemical vapor deposition (PECVD) and the cells were metalized by screen printing Ag-paste on the front and Al-paste on the rear side before being cofired in a belt furnace.
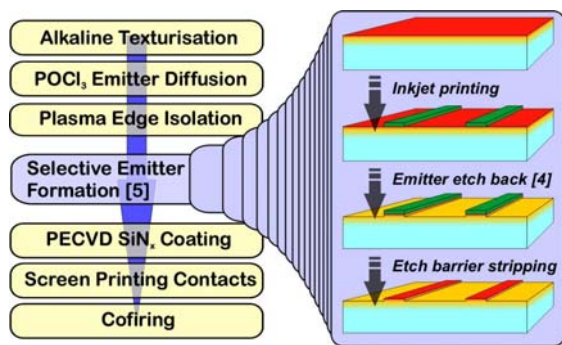
Figure 1: Illustration of the solar cell process.

Usually, the emitter is a major contributor to overall recombination due to its heavily doped "dead layer". Application of a selective emitter helped to make the solar cells more sensitive to slight changes in the bulk lifetime since the recombination in the emitter region is suppressed.

3 SOLAR CELL RESULTS

Immediately after firing, the solar cells were IV measured to determine their undegraded initial state. The results are displayed in Tab. II

Table II: Solar Cell Results

	FF	J_{SC} [mA/cm²]	V_{OC} [mV]	Efficiency
B, avg.	78.7%	35.9	633	17.9%
B, best	79.0%	36.1	634	18.1%
Ga, avg.	79.2%	35.7	634	17.9%
Ga, best	79.6%	35.9	637	18.2%

Both groups are nearly identical in terms of efficiency. The gallium doped group shows a slight advantage in fill factor and V_{OC} while the boron doped cells have a higher J_{SC}. This could be an effect of the different resistivity (see Tab. I).

4 DEGRADATION EXPERIMENTS

4.1 Continuous irradiation

After the initial IV measurements, the cells were subjected to continuous irradiation under 1 sun at 25°C while their V_{OC} was recorded along with cell temperature and illumination intensity for normalization purposes. Graphs of these measurements are shown in Fig. 2 for the boron doped cells and in Fig. 3 for the gallium doped cells.
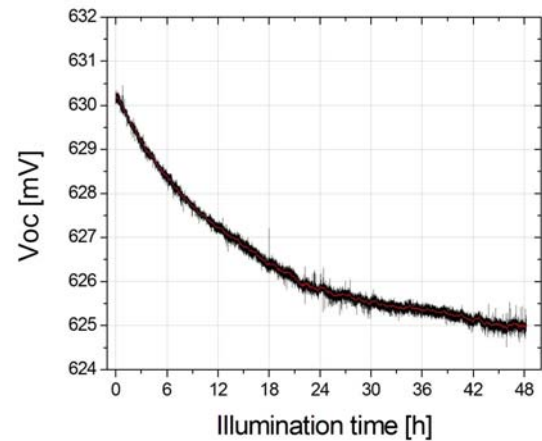
Figure 2: Normalized open circuit voltage of one boron doped solar cell over a 48 hour irradiation period.
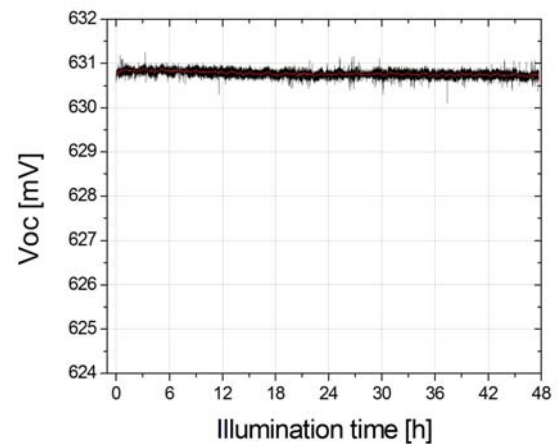
Figure 3: Normalized open circuit voltage of one gallium doped solar cell over a 48 hour irradiation period.

In Fig. 2 the well-known phenomenon of light-induced degradation can be observed: The cells lose around 5-6 mV due to the formation of recombination-active boron-oxygen complexes in an exponential decay over about 48 hours to a new plateau level. Observed time constants are in accordance to those published for the boron-oxygen complex [6] for which saturation at the new V_{OC} level is generally reached between 48 and 72 hours.

Quite a different picture can be seen with the gallium doped cells. Their V_{OC} development under illumination is displayed in Fig. 3 in which no degradation within reasonable measurement errors can be detected. It is noteworthy that no gallium doped cell showed more than 0.5 mV V_{OC} difference after 72 hours of continuous illumination.

4.2 Post-degradation measurements

After this procedure, the degraded cells were IV measured once again. A comparison of the cell parameter developments is given in Tab. III and IV for the aforementioned exemplary solar cells.

Table III: Boron cell before and after 48 hours of continuous irradiation at 25°C:

	Before	Diff.	After
FF	77.9%	-0.8	77.1%
J_{SC} [mA/cm²]	36.1	-0.1	36.0
V_{OC} [mV]	637	-6	631
Efficiency	17.9%	-0.3	17.6%

Table IV: Gallium cell before and after 48 hours of continuous irradiation at 25°C:

	Before	Diff.	After
FF	79.6%	0.0	79.6%
J_{SC} [mA/cm²]	35.9	0.0	35.9
V_{OC} [mV]	637	0	637
Efficiency	18.2%	0.0	18.2%

Here, the boron doped cells show a deterioration in all solar cell parameters, leading to a decrease of 0.3% absolute efficiency while the gallium doped cells' parameters remain largely unchanged within measurement error by the procedure.

4.3 Long-term sunlight exposure

Some of the cells were exposed to daylight under open circuit conditions for 4 weeks. While the laboratory degradation experiments involving days of constant 1 sun illumination do not resemble realistic operation conditions, they match the voltage drop results found in these practical tests. They can be seen in Fig. 4.
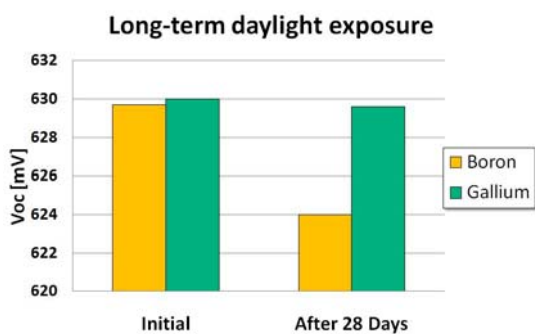

Figure 4: Average V_{OC} of the cells before and after 4 weeks of exposure to daylight.

Here, the boron doped cells show the same drop in V_{OC} as seen in the continuous irradiation experiment after the saturation time, around 6 mV. The gallium doped samples' performance loss was on average 0.4 mV, which lies in the range of the voltage measurements' reproducibility.

5 LOW-RESISTIVITY WAFERS IN ADVANCED CELL CONCEPTS

Certain advanced cell concepts favor a low-resistivity base material. This is the case for dielectrically passivated cells with local rear contacts or for interdigitated back contact cells. In these cases, the current is not only flowing perpendicular through the cell but has also a lateral component to the respective base contacts. This additional current path can be up to more than 500 μm depending on the cell concept, a rather significant distance compared to the 200 μm wafer width.

The series resistances of standard solar cells made from 1 Ωcm and 3 Ωcm material was measured. Usually, the series resistance of a standard industrial solar cell is dominated by the emitter and the front electrode. The influence of the base resistivity on the overall series resistance can be estimated to be about 60 mΩcm² on 3 Ωcm material or 20 mΩcm² on 1 Ωcm material. It therefore plays a minor role in the overall series resistances measured on complete solar cells, which lie in the range of 500 mΩcm²
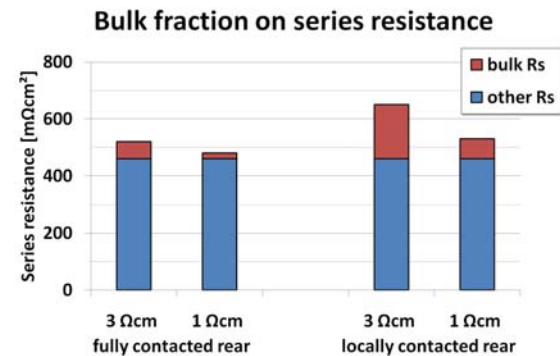

Figure 5: Series resistance R_S of standard and locally contacted cells with the fraction of the bulk highlighted in red.

The situation is somewhat different when lateral current transport in the base is necessary. In an additional cell manufacturing run using local contacts on the back (not further shown in this paper), wafers of the aforementioned two resistivities were included. The solar cell process used for their production is described in reference [7]. For a point-contacted rear side with a contact pitch of around 1 mm the overall series resistance rises up to 650 mΩcm² on 3 Ωcm material while this rise is much less pronounced on 1 Ωcm material, where 530 mΩcm² was measured. The fraction of bulk series resistance to overall series resistance is displayed in Fig. 5, for various cell structures and resistivities. It can be seen that the series resistance of the locally contacted cells was reduced by 20% by changing to a low-resistivity substrate, which in turn increased the fill factor by roughly 0.6% absolute.

6 SUMMARY

Large-area gallium doped Cz wafers were processed into solar cells in this work and compared to cells made of boron doped wafers. Both groups of cells showed equal efficiencies directly after firing. The gallium doped

cells showed virtually no degradation under illumination in the short and in the long term, while the boron-doped cells lost about 6 mV and had an efficiency drop of up to 0.3% absolute which could be attributed to boron-oxygen complex formation under illumination.

Continuous irradiation experiments showed that this LID effect on boron doped samples saturates after roughly 48 hours at 25°C, while the gallium doped samples retained the same V_{OC} level through even longer periods. These observations match those made with long-term tests on the cells which were closer to the operating conditions under daylight.

Since no degradation occurs, gallium-doped wafers can be recommended to cell manufacturers seeking to increase their long-term module efficiency just by exchanging their wafer supply. They also allow additional gains by moving towards lower base resistivities, an advantage exploited in high-efficiency cell processing.

The novel feature of Confluence Solar's proprietary process for producing HiCz™ Ga-doped wafers is in the high axial resistivity uniformity of the as-grown silicon ingot. This allows the selection of a narrow resistivity range that can be optimized to produce the most efficient cells without the need to bias the resistivity toward high values to avoid light induced degradation. This could be an enabling factor for the breakthrough of rear-passivated cells in industrial production, since low-resistivity gallium-doped wafers are degradation-free substrates that can be made to have low enough conductivity for reasonable back-contacting schemes.

7   ACKNOWLEDGEMENTS

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