Large-Area Boron-Doped 1.6 Ω·cm p-type Czochralski Silicon Heterojunction Solar Cells with a Stable Open-circuit Voltage of 736 mV and Efficiency of 22.0%

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Abstract

In this letter, we fabricate large-area defect-engineered p-type silicon heterojunction (SHJ) solar cells using standard 1.6 Ω·cm commercial-grade boron-doped Czochralski (Cz) silicon wafers. We demonstrate that despite achieving an open-circuit voltage of 735 mV with an efficiency of 21.6% for gettered samples, without appropriate treatment, the cells are heavily susceptible to boron-oxygen related light-induced degradation (LID), with the effective lifetime at maximum power point decreasing to 13 µs. This degradation results in a loss of efficiency of more than $3.1\%_{abs}$ ($14.3\%_{rel}$) after 48 hours of light soaking. However, the addition of an advanced hydrogenation post-cell fabrication process increases the efficiency by $0.2\%_{abs}$ to 21.8%, and dramatically reduces susceptibility of LID, decreasing the extent of degradation to $0.2\%_{abs}$ ($0.9\%_{rel}$). A peak stable independently measured efficiency of 22.0% with an open-circuit voltage (V_{OC}) of 736 mV is achieved with the addition of a dedicated high-temperature pre-fabrication hydrogenation. These results indicate that p-type Cz wafers can be used to fabricate stable, next-generation high-efficiency solar cells using SHJ or other passivated contact architectures requiring V_{OC}s well above 700 mV.

Silicon heterojunction (SHJ) solar cells are responsible for the world-record 1-sun silicon solar cell efficiency of 26.7% (with an open-circuit voltage (V_{OC}) of 738 mV).[1] From an industrial perspective, Hanergy has reported a daily average efficiency of 23.6% on a 120 MW pilot line and a record efficiency of 25.11% on a full-area R&D n-type SHJ solar cell (V_{OC} of 747 mV).[2] The remarkably high V_{OC} in SHJ solar cells are enabled by the excellent surface passivation provided by the hydrogenated amorphous silicon (a-Si:H) films. However, a-Si:H films impose a maximum temperature constraint of 200 °C during the fabrication process due to a potential loss of hydrogen at elevated temperatures that can deteriorate the surface passivation quality.[3] Thus, silicon wafers used for SHJ solar cells do not benefit from the gettering of metallic impurities and hydrogenation of bulk defects that are naturally incorporated in the fabrication sequence of aluminium back surface field (Al-BSF) and passivated emitter and rear cell (PERC) solar cells.[4][5] Therefore, high-quality n-type Czochralski (Cz) silicon with bulk lifetimes (τ_{bulk}) > 1 ms are required in the fabrication of SHJ solar cells.[6][7] Although there have been cost reductions on n-type Cz silicon over the last ten years, p-type Cz silicon is still 8% cheaper than n-type Cz (at a thickness of 180 µm).[7],[8] As a result, moving to cheaper wafer stocks such as p-type Cz silicon could reduce the cost of SHJ solar cells if the efficiency can be maintained.

Substantial progress on high-efficiency p-type silicon solar cells has recently been made, such as work by Haase *et al.* with an interdigitated back contact solar cell featuring tunnel oxide doped polycrystalline silicon contacts with efficiency of 26.1% (float-zone (FZ) silicon with resistivity of 100 $\Omega\cdot$cm and V_{OC} of 727 mV)[9] and by Descoeudres *et al.* on a SHJ structure with efficiencies of 23.8% (FZ silicon with V_{OC} of 723 mV) and 23.6% (Cz silicon with V_{OC} of 740 mV).[10] While the V_{OC} of the champion p-type Cz SHJ solar cell from Descoeudres *et al.* is comparable with the V_{OC} of the world-record n-type SHJ solar cell from Yoshikawa *et al.*, the FF of the p-type device is 4.1%$_{abs}$ lower. However, the average efficiency of larger batches of identically processed n-type and gettered p-type SHJ solar cells were at the same level,[10] suggesting that p-type SHJ solar cells may be able to achieve the same average efficiencies as n-type SHJ solar cells in production. It is important to note that with the addition of a dedicated gettering step to improve material quality, Descoeudres et al. observed an efficiency gain of ~ 0.2%$_{abs}$ in batches of p-type SHJ solar cells.[10] In previous studies, we have also demonstrated the role of gettering in increasing the lifetime of p-type Cz silicon,[5],[11],[12] which translated to a ~ 1%$_{abs}$ increase in the efficiency of SHJ solar cells. These results together indicate the need for gettering as a defect-engineering process to enhance the quality of p-type silicon wafers for SHJ solar cells applications. As such, all wafers used in this manuscript were gettered to improve material quality and remove metallic impurities such as iron. However, if the quality of commercial-grade p-type silicon wafers improves to a point where the concentration of impurities is negligible for the performance of the SHJ solar cells, a dedicated gettering step may not be necessary.

A key barrier for the mass production of p-type Cz SHJ solar cells is its susceptibility to boron-oxygen (BO) related light- or more specifically, carrier-induced degradation,[13] the key degradation mechanism investigated in this manuscript. This can reduce the efficiency by 0.7%$_{abs}$ in Al-BSF and 1.5%$_{abs}$ in PERC architectures.[14],[15] The efficiency reduction due to BO degradation in SHJ solar cells with V_{OC}S well above 700 mV is expected to be much larger. It is important to note that the use of gettering is not expected to significantly change the stability of the solar cells in this work related to BO related degradation.

However, BO light-induced degradation (BO-LID) can be treated with post-cell fabrication processes[16], and hence the cells made stable under typical working conditions. Substantial progress has been made recently in developing rapid solutions for BO-LID p-type Cz silicon PERC solar cells suitable for industry.[17] As such, significant reductions in LID from 5%$_{rel}$ to less than 0.5%$_{rel}$ have been demonstrated, resulting in stable efficiencies of > 21.5% in mass production.[18] Presumably, the LID in record 23.83% efficient p-type Cz silicon PERC cells with V_{OC}S of 687 mV[19] could be limited to < 2%$_{rel}$ degradation, with V_{OC}S of > 680 mV.

However, to date, little work has been done investigating LID in p-type SHJ solar cells.[20],[11] For example, LID testing was not performed for the record cells from Descoeudres *et al.* although it was noted such wafers are likely to suffer from bulk degradation due to light-induced effects,[10] albeit with presumably a reduced total defect concentration due to the high wafer resistivity (6 $\Omega\cdot$cm after gettering and the annihilation of thermal donors). In our recent work, we fabricated p-type SHJ solar cells that were susceptible to an efficiency degradation of 0.9%$_{abs}$ (4.7%$_{rel}$),[20] however, the degradation could be greatly reduced to 0.2%$_{abs}$ (1%$_{rel}$) using an advanced hydrogenation process. This processing yielded a stable V_{OC} > 700 mV on lab-scale SHJ solar cell fabricated with 1.6 $\Omega\cdot$cm p-type Cz silicon wafers. However, a significant gap in V_{OC} remained to achieve the values approaching 740 mV required for high-efficiency SHJ solar cells. In this letter, we combine gettering, hydrogenation and advanced hydrogenation processes with an industrial SHJ structure to demonstrate stable full-area p-type SHJ solar cells with voltages > 736 mV and an efficiency of 22%.

Full size textured 156 mm $\times$ 156 mm p-type boron-doped commercial-grade Cz grown silicon wafers with a resistivity of 1.6 $\Omega\cdot$cm were etched in an alkaline solution to remove saw-damage, resulting in a wafer thickness of approximately 180 μm. This was followed by a cleaning

step using the Radio Corporation of America (RCA) processes 1 and 2. In RCA 1 the wafers were submerged in a mixture of ammonium hydroxide, hydrogen peroxide and deionised water (DIW) in a ratio of 1:1:5 for 6 minutes at 75 °C and then rinsed in (DIW) at room temperature. Directly after, in RCA 2, the wafers were submerged for 6 minutes in a solution of hydrochloric acid, hydrogen peroxide and DIW (1:1:6) heated to 75 °C. The wafers were then rinsed in DIW and dipped in a 2% HF solution at room temperature.

Wafers were then rinsed in DIW and spin-dried. Directly after, a phosphorus gettering process at a peak temperature of 840 °C for 45 minutes was performed in a quartz diffusion tube furnace with a phosphoryl chloride source to form n^+ emitters with a sheet resistance of 35 Ω/□ on both sides of the wafers. A 2% HF solution was used to remove the surface phosphosilicate glass layers. Approximately 2 μm of each side of the wafers, including the diffused layers, was removed by an alkaline texturing step. The wafers underwent an RCA cleaning step prior to the deposition of 75-nm-thick hydrogenated silicon nitride (SiN_x:H) films (refractive index of 2.08 at 633 nm) with a mixture of ammonia and silane (SiH_4) on both sides of the wafers.[21] The deposition was performed using a Meyer Burger MAiA remote plasma-enhanced chemical vapour deposition (PECVD) tool. During the process, the wafers were kept at a tempereature of 400 °C for approximately 5 minutes per side. This is the standard SiN_x:H layer used at UNSW on the front surface to fabricate PERC solar cells.

The wafers were split into two groups, the first group was pre-gettered only (G), wafers in the second group underwent both pre-gettering and a pre-hydrogenation step (G+H). Wafers in the G+H group were annealed at a peak-temperature of 740 ± 6 °C in an in-line fast-firing furnace at a belt speed of 4.5 m/min (pre-fabrication hydrogenation, H). The SiN_x:H films of all wafers from both groups were removed.

Front junction p-type SHJ solar cells were fabricated with the defect-engineered wafers in an industrial pilot line by Meyer Burger. A radio frequency PECVD tool was used to deposit an intrinsic hydrogenated amorphous silicon a-Si:H(i) layer with a mixture of hydrogen (H_2) and SiH_4 onto the front of the wafers. This was followed by the deposition of an n-type hydrogenated amorphous silicon a-Si:H(n) layer also on the front of the wafers, by adding a doping gas containing phosphorous to the mixture of H_2 and SiH_4. A a-Si:H(i) layer was similarly deposited on the rear of the wafers. Directly after, a p-type hydrogenated amorphous silicon a-Si:H(p) layer was also deposited on the rear of the wafers, by adding a doping gas containing boron the the mixture of H_2 and SiH_4. Direct current magnetron sputtering was then used to deposit indium tin oxide (ITO) layers in both sides of the wafers. Silver contacts were formed by screen printing, followed by low temperature curing. The cells were bifacial and busbarless with an area of 244.32 cm^2. It should be noted that the identical process was applied for these p-type Cz SHJ solar cells as the standard process used by Meyer Burger for their n-type Cz SHJ solar cells.

After cell fabrication, the G and G+H cells were separated into two groups, one group was the control while the cells from the other group were treated with a modified UNSW advanced hydrogenation process (AHP) to mitigate BO-LID.[11] During AHP, excess carriers are generated via illumination to manipulate the hydrogen already existing in the solar cell [22]. No additional hydrogen source is provided during this process. The AHP process was performed using an in-line pilot production tool. A continuous-wave laser with a wavelength of 980 nm was used to illuminate the whole solar cell area simultaneously with an illumination intensity equivalent to approximately 100 suns for a period of 10 seconds. During the process, solar cells were heated on a hot plate with a temperature of 250 °C. During AHP, the solar cell's temperature was monitored with an infrared thermometer, and a peak temperature of 295 °C was recorded at 10 s under illumination.

Current-Voltage (J-V) measurements were performed at Meyer Burger using standard testing conditions. The stability under illumination was tested by in-situ monitoring on a SunsV_{OC} stage (Sinton Instruments). The V_{OC} was monitored during 48 hours light soaking (LS) under an illumination intensity of approximately 0.02 Wcm^{-2} from a white LED light source at room temperature. The minority carrier effective lifetime (τ_{eff}) of the finished SHJ solar cells was extracted from the Suns-V_{OC} measurements at an injection-level corresponding to the maximum

power point (MPP) and open-circuit (OC) conditions. The stable champion cells had their performance externally measured at Solar Energy Research Institute of Singapore (SERIS).

The J-V characteristics of the SHJ solar cells fabricated with the defect-engineered wafers are shown in Table 1. An average V_{OC} of 735 mV was achieved for the G group, corresponding to a τ_{eff} at open-circuit ($\tau_{eff,OC}$) of 520 µs and resulting in an average efficiency of 21.6%. After 48 hours LS a 3.1%$_{abs}$ (14.3%$_{rel}$) drop in the average efficiency was observed, resulting in an average efficiency of 18.5% for the G+LS group. One sample from the G group was selected for in-situ SunsV$_{OC}$ monitoring during LS (Figure 1(a)). The $\tau_{eff,OC}$ and $\tau_{eff,MP}$ as a function of light soaking time are shown in Figure 1(b). An astonishing V$_{OC}$ drop of 63 mV was measured after LS, resulting in a V$_{OC}$ of 658 mV (G+LS). This corresponded to a $\tau_{eff,OC}$ of 70 µs and a $\tau_{eff,MPP}$ of 13 µs for the G+LS group, highlighting the inherent susceptibility to LID for the wafers used to fabricate the SHJ solar cells in this work. Although the most significant reduction was observed in V$_{OC}$, FF and J$_{SC}$ also reduced with LS.

Table 1: J-V characteristics of the defect-engineered p-type SHJ solar cells before and after AHP and LS. Data for the stable champion cells, externally measured at SERIS, is also shown.

Process	Number of cells	J_{SC} [mA cm^{-2}]	V_{OC} [mV]	FF [%]	η [%]
G	7	39.7 ± 0	735.4 ± 0.9	73.8 ± 0.3	21.6 ± 0.1
G + LS	2	38.7 ± 0.1	658.1 ± 3.9	72.3 ± 0.5	18.5 ± 0
G + AHP	4	39.6 ± 0	736.7 ± 1.4	74.8 ± 0.8	21.8 ± 0.3
G + AHP + LS	2	39.6 ± 0.1	735.4 ± 0.1	74.1 ± 0.5	21.6 ± 0.2
G + H	8	39.6 ± 0.1	731.1 ± 1.4	73.1 ± 0.2	21.2 ± 0.1
G + H + LS	1	38.9	673.6	72.1	18.9
G + H + AHP	4	39.5 ± 0	733.3 ± 0.5	74.8 ± 0	21.7 ± 0
G + H + AHP + LS	2	39.5 ± 0	729.2 ± 1.2	73.8 ± 0.1	21.3 ± 0.1
Champion stable cells measured at SERIS					
G + AHP + LS	1	39.1	734.1	76.0	21.9
G + H + AHP + LS	1	39.1	736.2	76.3	22.0

AHP improved the efficiency of G samples by 0.2%$_{abs}$ to 21.8%, which is related to an increase in both FF and V$_{OC}$. The increase in V$_{OC}$ is expected to be caused by both improved surface passivation[23] and bulk lifetime,[12] which may also increase the τ_{eff} at maximum power point ($\tau_{eff,MPP}$), which increased from 70 µs (G) to 140 µs (G+AHP). The increased $\tau_{eff,MPP}$ translated to an enhancement in pseudo fill factor (pFF) from 73.9% (G) to 75.2% (G+AHP). The $\tau_{eff,OC}$ was significantly higher, increasing from 520 µs (G) to 710 µs (G+AHP). This result is in agreement with the literature, confirming that while the key-feature of SHJ solar cells of enabling high V$_{OC}$ is preserved on p-type silicon, the low τ_{eff} at low injection ($\tau_{eff,low}$) results in reduced FF.[24] Although the use of AHP on the finished p-type SHJ solar cells enhanced the FF, the average FF of 74.8% (G+AHP) is still a limiting factor, approximately 6%$_{abs}$ lower than the recent p-type Cz SHJ solar cell results from Descoeudres et al.[10] It is expected that this is due to a surface-related effect rather than a bulk effect, reducing the lifetime at low injection.[24] Olibet et al. suggested that the lower $\tau_{eff,low}$ on p-type than on n-type are due to the discrepancy between the capture cross-section for electrons and holes at the a-Si:H/c-Si interface.[25],[11] N-type SHJ solar cells can also be susceptible to this injection level dependency of $\tau_{eff,low}$, the problem can be solved by improving the passivation quality of the a-Si layer.[26] Thus, the optimization of the a-Si passivation layers could reduce the injection level dependency of $\tau_{eff,low}$ on p-type SHJ solar cells.

The stability of the G + AHP samples was also investigated using in-situ SunsV$_{OC}$ monitoring (Figure 1). Remarkably, after 48 hours of LS, almost no change in V$_{OC}$ was observed with AHP. The application of AHP on the finished solar cells of the G group resulted in an average stable efficiency of 21.6% (G+AHP+LS), which matches the average efficiency of the G group before LS. The efficiency loss of 0.2%$_{abs}$ (0.9%$_{rel}$) is less than that required by manufacturers (typically 1-2%$_{rel}$). The 3.1%$_{abs}$ boost on the stable efficiency of the solar cells from 18.5% to

21.6% with AHP demonstrates the necessity of incorporating an AHP to enhancing the efficiency of p-type Cz SHJ solar cells and ensure that the cells do not suffer from BO related LID.
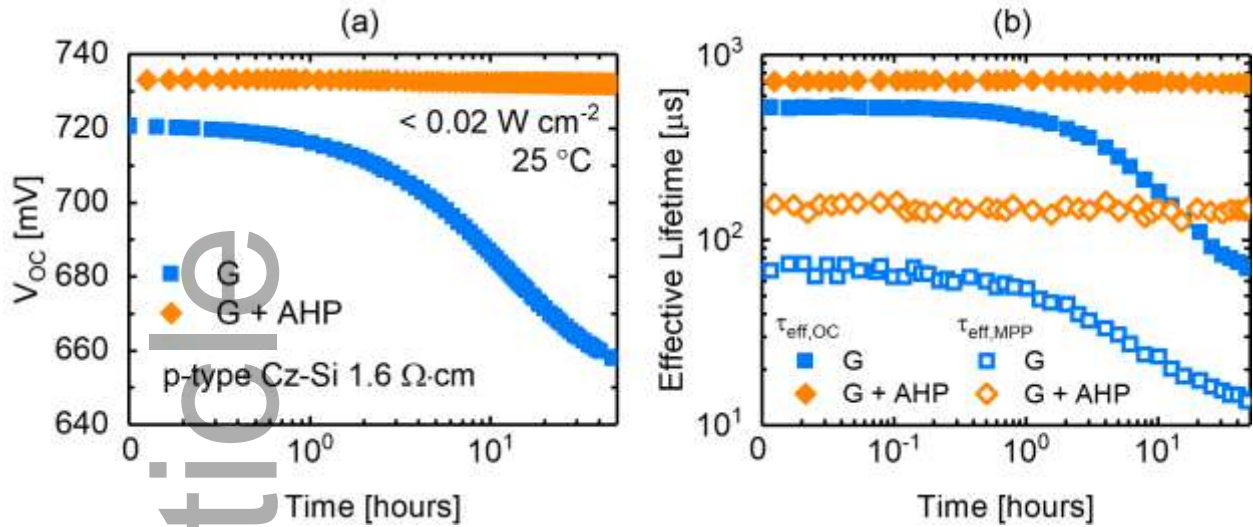

Figure 1: (a) Open-circuit voltage and (b) $\tau_{eff,MPP}$ and $\tau_{eff,OC}$ as a function of time under illumination (0.02 W cm^{-2} intensity, 25 °C) for the AHP treated (orange diamonds) and non-treated (blue squares) defect-engineered p-type Cz SHJ solar cells.

The addition of a dedicated high-temperature H process resulted in a slightly reduced V_{OC} when comparing G (735.4 mV) and G+H (731.1 mV) samples before LS. The cause is still under investigation. With the addition of H, the extent of degradation in efficiency due to BO-LID also reduced from 3.1%$_{abs}$ (14.3%$_{rel}$) to 2.3% $_{abs}$ (10.8%$_{rel}$), with a reduced V_{OC} loss of ~20 mV. It is known that fast-firing can reduce the equilibrium concentration of BO defects.[27],[28] However, this level of degradation is unacceptable for manufacturers. Therefore, AHP was still required to sufficiently eliminate LID, to achieve a stable efficiency of 21.3% after a 0.4%$_{abs}$ efficiency loss (1.8%$_{rel}$). The slightly larger degradation on the G+H+AHP group compared to the G+AHP group is currently under investigation.

It is important to note that the mitigation of BO related degradation on the G group was also achieved without the application of the high-temperature H step, which is known to introduce hydrogen from the SiN$_x$:H films into the silicon bulk.[29] Recently, Sun *et al*. reported the complete regeneration of BO defects in compensated n-type UMG Cz SHJ solar cells without any high-temperature H process.[30] For hydrogen incorporation under 250 °C , the a-Si(i)/a-Si(p) stack deposition was found to naturally enable bulk hydrogenation.[31] Considering the extrapolation of Van Wieringen and Warmoltz diffusivity data as an upper limit for hydrogen diffusion in silicon,[32] a diffusion length of 23 μm is estimated for hydrogen with the AHP process used in this work. Hydrogen diffusion from the wafer's surface to the bulk, which would require a diffusion length of at least 90 μm, doesn't take place during AHP alone. This suggests that a significantly amount of hydrogen was introduced in the wafer's bulk prior the AHP process, which could occur during PECVD processes or the drying and curing of the screen-printed contacts (typically performed around ~200 °C).[3] Still, the addition of AHP to the standard SHJ fabrication processes was vital to mitigate BO defects in both G and G+H group wafers. This suggests that, although the addition of the H step resulted in an efficiency increase of ~ 0.1%$_{abs}$, it may not be required to ensure stability of the finished SHJ solar cells. However, further work is required to determine whether the pre-fabrication SiN$_x$:H PECVD process in this work provided bulk hydrogen for the G group samples, or if hydrogen from the a-Si:H films in the industrial PECVD tools and rapid pumping/thermal cycles was sufficient to passivate BO defects in p-type Cz silicon SHJ solar cells. The understanding of the hydrogenation mechanism in SHJ solar cells would also benefit from the investigation of the role of other processes, such as the

H$_2$ dilution in SiH$_4$ during the a-Si:H films deposition, in providing hydrogen for bulk defect passivation.

A notably high stable efficiency of 22.0% (V$_{OC}$ of 736.2 mV) was achieved for the champion solar cell (Figure 2) from G+H group (and an efficiency of 21.9% (V$_{OC}$ of 734.1 mV) on the champion cell from the G group) as independently measured by SERIS. We note that there is a discrepancy in the IV parameters of the champion SHJ solar cells, particularly for the G+H+AHP+LS sample, measured at Meyer Burger and the external measurements performed at SERIS. At this stage, the reason for the discrepancies is not understood. However, differences may arise from contacting schemes and chuck reflectivities.

The high V$_{OC}$s demonstrated here are comparable to the V$_{OC}$ of the 26.7% record solar cell from Yoshikawa et al. fabricated with n-type Cz silicon (738 mV).[33] This indicates the capability of p-type silicon to achieve high stable efficiencies using an SHJ solar cell architecture. Furthermore, it is worth noting that the 23.6% p-type Cz silicon SHJ solar cell from Descoeudres et al. did not benefit from any dedicated hydrogenation process.[10] AHP could potentially increase the efficiency and mitigate BO related LID in their p-type Cz SHJ solar cells.
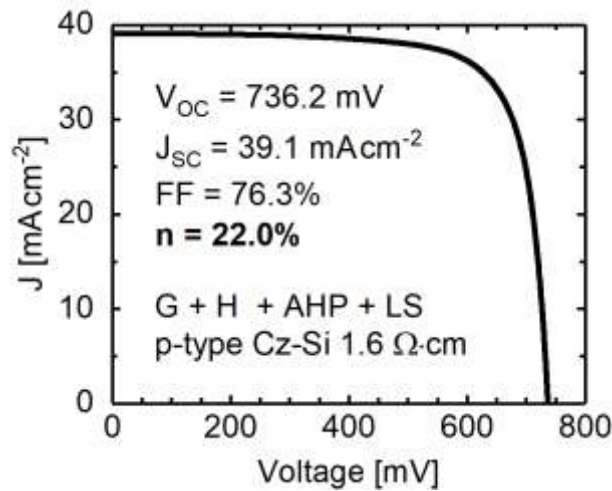

Figure 2: J-V characteristics of the champion stable p-type Cz SHJ solar cell measured at SERIS. The champion stable SHJ solar cell underwent pre-fabrication gettering and hydrogenation (G+H), post-fabrication advanced hydrogenation processing (AHP) and light-soaking (LS) prior to the IV measurement.

In this work, we fabricated large-area SHJ solar cells with pre-gettered p-type Cz silicon wafers. These cells were susceptible to significant BO related degradation, with a 3.1%$_{abs}$ loss in efficiency after 48 hours LS. A post-fabrication AHP process was used to mitigate BO related degradation, which not only increased the average efficiency by 0.2%$_{abs}$ but also reduced the extent of degradation to only 0.2%$_{abs}$. As such, the AHP was shown to be vital for p-type SHJ solar cells. A stable V$_{OC}$ > 736 mV was presented for the G+H group cells after AHP, with a corresponding efficiency of 22.0% (independently measured). On the other hand, a stable V$_{OC}$ > 734 mV was achieved without the need for a high-temperature H step (21.9% efficiency), suggesting that the H process may not be required to ensure stability. However, further work is required to ensure that this was not inadvertently due to the deposition of PECVD SiN$_x$:H on samples prior to SHJ solar cell fabrication. Although gettering is not expected to significantly change the stability of the SHJ solar cells, the AHP+LS process sequence should be tested in SHJ solar cells fabricated with non-gettered p-type Cz wafers to confirm this assumption. Future work is also required to increase the $\tau_{eff,low}$ in order to enhance the FF of the p-type SHJ solar cells. Importantly, this work demonstrates

the possibility of fabricating stable high-voltage SHJ and passivated contact solar cells using commercial low-cost p-type Cz wafers.

Acknowledgements

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Herein, we demonstrate large area silicon heterojunction solar cells with efficiency of 22.0% using commercial grade p-type Czochralski silicon wafers. An advanced hydrogenation process was developed to overcome the impact of boron-oxygen light induced degradation in these p-type cells, resulting in stable V_{OC} of 736 mV. This could be a potential pathway to lower-cost high-efficiency solar cells.