23.83% efficient mono-PERC incorporating advanced hydrogenation

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Abstract
LONGi Solar Energy Technology Co. Ltd. has achieved 23.83% for a commercial p-type Cz PERC cell. From a batch of over 40 000 cells, the average line efficiency achieved was 22.5%. R&D studies investigating hydrogenation and degradation show the importance of hydrogenation processes for efficiency improvements and controlling the hydrogen to prevent light-induced degradation. Such degradation is shown to appear very differently under different illumination and temperature conditions. This degradation impacts \(V_{OC}\), \(I_{SC}\), and especially fill factor. Current injection and thermal anneal can be used to recover the degradation, but the recovery may not be stable. Reducing the hydrogen content within the cell is shown to minimise degradation without sacrificing performance, provided that enough hydrogen is retained to passivate boron-oxygen defects.

1 | INTRODUCTION

The advanced hydrogenation technology developed at University of New South Wales (UNSW) Sydney is focused on controlling the hydrogen in silicon solar cells to enable enhanced bulk defect passivation and minimise light-induced degradation (LID). Typically studied on lab produced samples and cells, this work with LONGi Solar Energy Technology Co., Ltd. investigates the advanced hydrogenation technology on LONGi’s high efficiency p-type Cz commercial cells. LONGi focuses on the R&D, production and sales of monocrystalline silicon wafers, and cells and modules, and at present (Q1, 2019), has 5.5 GW cell and 6.5 GW module capacities.

LONGi has always attached great importance to R&D. The cost of R&D investment in the last 5 years has reached 2.38 billion Chinese RMB. The cell R&D department has always been committed to the research and development of high-efficiency monocrystalline solar cell technology. Among them, Cz PERC cells have repeatedly broken the world record; here, LONGi has achieved an efficiency of 23.83%. This cell performance is already almost equal to a 2017 forecasted industrial efficiency prediction of 24% and on the path towards commercial implementation of the 25% efficient PERL lab cell of 1999.

LONGi has a long-term partnership with the UNSW Sydney and has in-depth collaborative research on advanced hydrogen passivation technologies to improve the performance and long-term stability of silicon solar cells. In Cz silicon material, hydrogenation is very effective for passivating boron-oxygen(BO) defects that otherwise cause LID. The BO defect system can be understood using a three-state model of (1) defect precursors, that under light form (2) active BO defects, and can be passivated by hydrogen to form (3) passivated BO defects. More recently, there has been a phenomenon of a new LID caused by hydrogen, which is commonly referred to as light and elevated temperature-induced degradation (LeTID), but perhaps more...
appropriately referred to as hydrogen-induced degradation (HID).\textsuperscript{10} This type of LID, even identified in higher purity float-zone silicon wafers,\textsuperscript{11} displays more complex behaviours. In Vargas et al,\textsuperscript{12} it was shown that higher firing temperatures led to increased defect densities, while in Chan et al,\textsuperscript{13} it was shown that varied dark annealing before LID could affect the degradation and recovery rates. The late Professor S. R. Wenham from UNSW Sydney proposed a "bucket theory" of hydrogen,\textsuperscript{10} which can be represented by introducing an additional "reservoir" state of defect precursors to feed into a three-state model similar to the BO defect model.\textsuperscript{14} Therefore, in order to maintain the long-term stability of silicon solar cells, the control of the hydrogen within the cells becomes particularly critical.

This paper presents LONGi's recent commercial cell results, hydrogenation and LID investigations on LONGi cells (focused explicitly on LID caused by LeTID/HID defects), and field stability of modules.

## 2 | CELL FABRICATION

Cells were fabricated on 180-μm-thick p-type Cz wafers with an M2 (156.75 mm × 156.75 mm) size and resistivity of 0.5 to 3 Ω cm. Wafers were textured with ~2 μm pyramids. A diffusion was performed in a POCl\textsubscript{3} tube to form a 120 to 150 Ω□ emitter, and a selective emitter was subsequently formed using a 532-nm pulsed DR Laser tool to melt through and incorporate dopants from the phosphosilicate glass. After a subsequent acidic rear etch, the final wafer thicknesses were approximately 150 to 170 μm. A Meyer Burger MAiA PECVD reactor was used to deposit a dielectric stack on the rear, and a 70- to 85-nm hydrogenated silicon nitride (SiN\textsubscript{x}: H) on the front to act as an antireflection coating with refractive index (RI) 2.03 to 2.13 (measured at a wavelength of 633.2 nm), a surface passivation layer, and a hydrogen source. A 532-nm pulsed DR laser tool was used to create openings in the rear dielectric stack. The rear-side was screen-printed with aluminum, and the front fingers and five busbars were screen printed with silver aligned to the selective emitter using an applied materials camera. The cells were fired in a Despatch belt furnace, with peak temperature between 810 and 830 °C to form the front contacts and create local rear doping in the openings akin to what is found in the PERL cell.\textsuperscript{15} An advanced hydrogenation process was then carried out after firing using a laser hydrogenation system with a laser power of 3000 W, a temperature of 220 °C, and a 4-s process duration. The cell structure is shown in Figure 1. The degradation studies in this work are typically conducted at 75 °C using a hotplate placed under a source of illumination.

## 3 | RESULTS AND DISCUSSION

### 3.1 | Production line performance data

This part reports results from the LONGi pilot line, including average efficiency, cell efficiency trends in mass production for 2018, and performance parameters of the PERC champion cell.

#### 3.1.1 | Line performance

The following results in Figure 2 show the average IV performance characteristics from a batch of 40 228 production cells. Figure 3 shows the pilot line cell average efficiency trends for 2018. The 244.43 cm\textsuperscript{2} cells were measured under standards test conditions at 25 °C, under 1000 W/m\textsuperscript{2} standard solar spectrum illumination by IEC 60904-3 using a golden cell calibrated by Fraunhofer ISE.

#### 3.1.2 | Champion cell

The following results in Figure 4 show the 23.83% efficient champion cell IV and PV characteristics, as measured under standards test conditions at 25 °C, under 1000 W/m\textsuperscript{2} standard solar spectrum illumination by IEC 60904-3, measured externally by the Wuxi National Quality Inspection Center. The cell area is 244.43 cm\textsuperscript{2}.

![Cell Structure Diagram](image-url)
3.2 | Hydrogenation

A laser hydrogenation process was applied to 10 finished cells from the production line, which have already undergone a more typical hydrogenation process in the belt furnace. The cells were heated to 250 to 300°C on a hotplate and illuminated with 3 to 5 kW of laser power for 1 to 8 s. The efficiencies before and after hydrogenation are shown in Figure 5, and the average performance parameters before and after hydrogenation are shown in Table 1.

From Figure 5, it can be seen that all cells improved a small but still significant amount (0.08% absolute) due to the added laser hydrogenation process. The efficiency spread also became tighter as some of the poorer performing cells were brought up by the process; however, the poorest performing outlier cell only gained an average improvement remaining an outlier. Table 1 shows that on average the open circuit voltage ($V_{OC}$), short circuit current ($I_{SC}$), fill factor (FF), and reverse saturation current of the ideal diode ($J_{01}$) all improved a small amount leading to an overall average efficiency improvement of 0.08% absolute despite a slight worsening of $J_{02}$. $R_s$ remained unchanged. Overall the seconds’ long laser hydrogenation process provides added benefit in the form of efficiency improvement and less deviation.

3.3 | LID with a varied hydrogen content

Three finished cells were prepared with varied hydrogen concentrations within the cells. The hydrogen concentration was manipulated through a change in the film composition and RI. Within a certain range of RI, an increasing RI would increase the amount of hydrogen in-diffusion into the silicon wafer during firing. The measured RIs for these films were 2.1, 2.2, and 2.3 for the low, medium, and high
hydrogen concentrations, respectively. To test the stability, the cells were heated to 75°C under one sun light-emitting diode (LED) illumination at open circuit (conditions typical for testing LeTID/HID\textsuperscript{16}) for 40 hours. Suns-V\textsubscript{OC} measurements were taken in situ at 75°C, and the V\textsubscript{OC} normalised to the starting V\textsubscript{OC} prior to degradation for the cells over the 40 hours of testing can be seen in Figure 6. The cell performance measured under STC conditions using a HALM IV tester at the start and after 40 hours of LID testing can be seen in Table 2.

It is clear from both Figure 6 and Table 2 that the higher the hydrogen content in the cells, the more severe the degradation. With low hydrogen content, minimal degradation is seen, which is in line with the expected behaviour of hydrogen-induced degradation (HID\textsuperscript{10} or LeTID\textsuperscript{8,16} under such testing conditions. This highlights the importance of controlling the hydrogen to prevent this form of LID occurring in the field, noting that even in the low H content cell, the overall performance of the cell is not harmed due to less hydrogen for passivation, with similar cell efficiencies, even slightly better in this case.

Looking closer at the FF changes in Table 2 shows small changes in R\textsubscript{s} with hydrogen content; however, the more significant changes are seen in the lower H content samples. J\textsubscript{01} seemed to be slightly worsened by increasing H content and decreased slightly in the low-med H content cells and increased slightly with high H content. The most significant changes are seen again in J\textsubscript{02}, where the high H content layer causes J\textsubscript{02} to increase ~4.5x (342% increase) again, possibly indicating increased junction recombination.

### 3.4 | LID under varied temperature

Three finished cells were LID tested using different temperatures (65, 85, and 110°C) on a hotplate under one sun LED illumination at open circuit. Figure 7 shows the normalised V\textsubscript{OC} over the 5 hours of LID testing, measured in situ at elevated temperatures; Table 3 shows HALM measurements at room temperature (STC) at the beginning and after degradation.

Figure 7 shows that minimal degradation is seen at the lowest temperature (65°C) in 5 hours. At the higher temperatures, degradation is seen, with a much faster degradation and recovery occurring at the higher temperature. The performance data in Figure 2 show that the degradation after 5 hours at 85°C is very similar to the degradation seen after 1 hour at 110°C (roughly the minima for 110°C as shown in Figure 11 before recovery processes dominate). This shows that the worst case temporary performance loss for these cells is <1% relative in V\textsubscript{OC}, ~1% relative in J\textsubscript{sc}, and ~3% relative in FF, resulting in ~4.5 to 5% relative (1-1.05% absolute) efficiency loss, should the cells reach such elevated and sustained temperatures in the field.

| Hydrogen Content | Time | Efficiency, % | V\textsubscript{OC}, V | I\textsubscript{SC}, A | FF, % | R\textsubscript{s}, Ω | J\textsubscript{01}, fA/ cm\textsuperscript{2} | J\textsubscript{02}, nA/ cm\textsuperscript{2} | LID (\Delta η), % |
|------------------|------|---------------|-----------------|--------------|-------|-------------|-----------------|----------------|----------------|
| Low H content    | Start | 22.15         | 0.6835          | 9.845        | 80.44 | 0.00239     | 140             | 4.45           | -0.95          |
|                  | 40 hrs| 21.94         | 0.6829          | 9.821        | 79.92 | 0.00252     | 133             | 4.30           |                |
| Med H content    | Start | 21.96         | 0.6809          | 9.843        | 80.06 | 0.00244     | 150             | 3.20           | -1.96          |
|                  | 40 hrs| 21.53         | 0.6790          | 9.800        | 79.04 | 0.00257     | 147             | 8.50           |                |
| High H content   | Start | 22.02         | 0.6841          | 9.841        | 79.91 | 0.00255     | 131             | 3.73           | -4.59          |
|                  | 40 hrs| 21.01         | 0.6779          | 9.723        | 77.87 | 0.00257     | 139             | 16.5           |                |

Abbreviations: FF: fill factor; LID: light-induced degradation.
Three finished cells were LID tested using different LED illumination intensities (0.5, 1, and 1.6 suns) at 85°C on a hotplate at open circuit. The results are shown in Figure 8.

Figure 8A depicts the change in normalised $V_{OC}$ as a function of light soaking time for varying illumination intensities. Given that the voltage lowers at lower light intensities, the change in $V_{OC}$ in a quantifiable normalised defect density ($N_{VOC}$) using the equations described by Shen et al.\textsuperscript{17} is presented in Figure 8B. It is found that by using a lower light intensity, the magnitude of degradation increases, which is somewhat surprising for a “light-induced” degradation. One possibility to explain this effect is that there are competing degradation and recovery processes occurring simultaneously, of which the recovery process is accelerated much more by the light, resulting in lower perceived apparent degradation. This can be explained in relation to “buckets” or stores of hydrogen that cause the degradation patterns (as described in Ciesla et al.\textsuperscript{10}); the increased light does not accelerate release from non-recombination active buckets 1 and 2 significantly but could help to clear out the hydrogen in recombination active “bucket 3,” or perhaps enable freed hydrogen to disperse before even entering “bucket 3.”

However, when looking at the recovery portion also, it can be seen that all samples, irrespective of light intensity and magnitude of degradation, reach a minimum at around 10 hours and then reach a full recovery around 50 hours so that the rate of recovery is the highest under the lowest light intensity. Assuming that light does increase recovery rates, it, therefore, appears that the recovery is also dependent on defect concentration, so that the more hydrogen in bucket 3, the faster the rate of emptying/recovery (in agreement with Ciesla et al.\textsuperscript{10}).

### 3.6 | LID recovery

To reverse the effects of LID, either current or thermal treatments were applied to cells after 5 hours of LID testing at 75°C on a hotplate under one sun LED illumination at open circuit.

### Table 3 | Cell performance before and after LID testing at different temperatures

| Sample, °C | Measured | $V_{OC}$, V | $I_{SC}$, A | FF, % | Efficiency, % | LID Efficiency Change |
|------------|----------|-------------|-------------|-------|---------------|-----------------------|
| 65         | Before   | 0.6855      | 9.833       | 79.75 | 22.00         | −1.27%                |
|            | After 5 h| 0.6853      | 9.794       | 79.05 | 21.72         |                       |
| 85         | Before   | 0.6855      | 9.831       | 79.70 | 21.98         | −4.55%                |
|            | After 5 h| 0.6810      | 9.722       | 77.42 | 20.98         |                       |
| 110        | Before   | 0.6855      | 9.826       | 79.80 | 22.00         | −4.77%                |
|            | After (1 h)| 0.6808    | 9.723       | 77.31 | 20.95         |                       |
|            | After (5 h)| 0.6851    | 9.778       | 78.94 | 21.65         | −1.59%                |

Abbreviations: FF: fill factor; LID: light-induced degradation.
3.6.1 | Current

Current was applied to each of two degraded cells for 1 hour at room temperature. One cell received 2 A of reverse current (~21.2 V reverse biased), while the other received 10.3 A (slightly higher than $I_{SC}$) of forward current (~3.1 V forward biased). The results are shown in Figure 9 and Table 4.

Figure 9 and Table 4 show that applying a reverse current to a cell degraded under these LID conditions appears to have negligible benefit. The $V_{OC}$ got a bit worse, while the $I_{SC}$ improved slightly. The most significant change (in relative %) due to LID is FF and also only gains a little improvement, despite almost a full recovery in Rs. Overall, efficiency showed a small improvement.

On the other hand, the forward current resulted in the efficiency mostly recovering. The $V_{OC}$ ended up higher than it started before LID, perhaps indicating some improved H passivation, or there was already some preformed defect to be deactivated. The $I_{SC}$ regained half of what was lost due to LID, while the FF mostly improved, despite the Rs getting worse due to the current treatment.

Assuming the hydrogen causes the degradation, it seems that the forward bias helps to shift the hydrogen causing the bulk or junction recombination, but worsens Rs, perhaps moving the hydrogen to the contacts. At the metal-silicon interface, hydrogen can bind to and passivate the silver, thus reducing the conductivity of the contact.

### Table 4

| Bias  | Stage        | $V_{OC}$, V | $I_{SC}$, A | FF, % | Efficiency, % | $R_s$, Ω |
|-------|--------------|-------------|-------------|-------|---------------|-----------|
| Reverse | start       | 0.6808      | 9.797       | 80.08 | 21.86         | 0.00254   |
|        | 5-h LID     | 0.680       | 9.750       | 79.26 | 21.51         | 0.00259   |
|        | treated     | 0.6796      | 9.757       | 79.37 | 21.54         | 0.00255   |
| Forward | start       | 0.6856      | 9.841       | 80.23 | 22.16         | 0.00257   |
|        | 5-h LID     | 0.6846      | 9.877       | 79.56 | 21.82         | 0.00255   |
|        | treated     | 0.6869      | 9.813       | 80.06 | 22.09         | 0.00253   |

Abbreviations: FF: fill factor; LID: light-induced degradation.

While the reverse current does not manage to shift the recombination active hydrogen but does manage to improve the Rs, perhaps moving hydrogen away from the contact might be passivating, consistent with Fung et al. 14

3.6.2 | Thermal

Three samples after 5 hours of LID were each treated with 5 hours of thermal annealing at 110, 210, and 310 °C, respectively, in the dark. The results are shown in Figure 10 and Table 5.

The increasing temperatures clearly show an increased ability to recover degradation. After the 110 °C anneal, the efficiency dropped slightly more. The $V_{OC}$ got slightly worse, while the $I_{SC}$ showed negligible improvement. The most significant change was a continued reduction in FF despite the improvement in $R_s$. The sample annealed at 210 °C started at a slightly higher efficiency but showed similar trends due to LID testing. After the anneal, the $V_{OC}$ improved but not completely, similarly for $I_{SC}$, and the FF roughly half improved despite $R_s$ getting worse. Overall the efficiency improved but less than half of the performance that was lost due to the degradation. The sample that was annealed at 310 °C recovered the most, almost returning to its starting efficiency. Degradation trends were similar to the other
cells; however, after 310°C, almost all parameters that suffered from LID were almost entirely recovered.

### 3.7 LID treatment stability and implications discussion

Cells that were recovered from LID losses using thermal or current/bias treatments were tested for subsequent stability and unfortunately showed further LID. It seems that the current injection and thermal treatments are able to shift the hydrogen from problematic regions or forms (recombination active bucket 310), but only temporarily so that continued LID testing conditions allow the hydrogen to revert to problematic regions or forms (ie, shifted the hydrogen back to nonrecombination active bucket 1 or 2, where it can again move into bucket 3). For example, if the hydrogen is causing problems by building up at the surface, potentially interfering with surface passivation (via counter doping or interfering with the field passivation from charged dielectric layers), then the application of a forward bias can help shift H⁺ from the p-type surfaces, and H⁻ from the n-type surfaces (the dominant charge states for the respective polarities21), but this hydrogen can return to the surfaces under continued LID testing. Alternatively, it is possible that the treatment has not been able to solve hydrogen-related defects that have not yet formed so new defects form with continued LID testing.

Based on the above data, the most effective method is to reduce the hydrogen concentration in SiNx films as much as possible to reduce the corresponding degradation as in Section 3.3, while still ensuring that enough hydrogen is available to passivate any BO defects. Adjusting the firing recipe and hydrogen treatments using light and heat can also help control the hydrogen and reduce HID, which is a common treatment scheme in the PV industry.
3.8 Cell and module-related LeTID data

Based on the above, and understanding the involvement of hydrogen in causing LID, cell processes were continually further optimised. The hydrogen concentration in the SiNx layer was reduced as much as possible without affecting the cell efficiency or ability to passivate BO defects. Cell stability performance was monitored for cells produced during 2018 by measuring cell performance after 5 hours at 75°C, under one sun illumination as depicted in Figure 11. It can be seen that efficiency loss due to LID averaged less than 1% absolute and was very rarely above 1.5%. Towards the end of 2018, with continued improvements, LID stability was further improved, achieving significantly less than 1% LID loss on all cells in November 2018.

Outdoor testing of modules made from cells produced early in 2018 shows the actual stability in the field. Figure 12 shows the outdoor module performance data for eight modules as they were exposed to 580 kWh of illumination. The LID losses are comparable to that of the cells tested early in 2018 in Figure 11. The losses were rarely measured above 1.5% absolute. The majority of the degradation appeared within the first 40 kWh of outdoor exposure and reached a maximum average degradation of 1.32% absolute after 128 kWh of exposure. Modules fabricated using cells made post-October of 2018 (not shown) were also tested outdoor with degradation levels of 0.37% absolute (November 2018) and 0.45% absolute (December 2018) after approximately 61 kWh of exposure and at an ambient temperature of 25.4°C.

4 CONCLUSIONS AND FUTURE WORK

LONGi Solar Technology Co. Ltd. has fabricated commercial p-type PERC cells with an average $V_{OC}$ of 687.9 mV, $I_{SC}$ of 10.22 A, FF of 82.83%, and overall efficiency of 22.50%. A champion commercial cell of 23.83% efficiency was measured. This is already almost equal to 2017 industrial efficiency prediction of 24% and on the path towards commercial implementation of the 25% efficient PERL lab cell of 1999. Laser hydrogenation after a more typical firing hydrogenation process is shown to add a further 0.08% absolute efficiency improvement. LID testing at elevated temperatures is shown to be highly illumination and temperature dependent. The FF, in particular, $J_0$, seems to be most significantly impacted by LID potentially indicating increased junction recombination. Current injection and thermal anneals are able to recover LID losses but do not appear to be stable. Controlling the hydrogen content to low levels within the cell is seen to minimise degradation without sacrificing performance and results in cells and modules with around or less than 1% absolute LID performance losses. It is also important to study the hydrogen distribution within the silicon material in order to further understand the behaviour and impact of hydrogen, which will be included in future work.

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