Techniques for mitigating light-induced degradation (LID) in commercial silicon solar cells

Brett Hallam[1], **Catherine Chan**[1], **David Payne**[1], **Dominik Lausch**[2], **Marcus Gläser**[2], **Malcolm Abbott**[1] & **Stuart Wenham**[1]

[1]University of New South Wales (UNSW), Sydney, Australia; [2]Fraunhofer Center for Silicon Photovoltaics (CSP), Halle (Saale), Germany

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ABSTRACT

Light-induced degradation (LID) in both Czochralski (Cz) and multicrystalline p-type silicon is one of the biggest challenges currently faced by the PV industry. Over the next few years it will be necessary to develop cost-effective solutions and integrate them into manufacturing lines. This is particularly important for the successful adoption of the passivated emitter rear cell (PERC), since this cell architecture has been shown to be highly susceptible to degradation. Given this motivation, the PV research community has been hard at work studying and developing methods to solve this problem. This paper presents a summary of this work, specifically the application to commercial solar cells. For Cz silicon it is demonstrated that numerous solutions exist, including rapid processes with operation times of the order of seconds and which result in completely stable PERC efficiencies. Solutions are also emerging for the more difficult multicrystalline silicon substrates, although hitherto these techniques have tended to be slower and less effective.

LID in silicon solar cells

Solar cell manufacturers strive to improve cell efficiencies and to produce modules with stable performance during operation in the field. However, almost all modules are subject to degradation mechanisms that can significantly affect their long-term energy yield; these mechanisms have implications for the warranties that manufacturers offer, typically of the order of 25 years. One degradation mechanism in silicon solar cells of particular importance is caused by light, or, more specifically, by the charge carriers generated by illumination. Light-induced degradation (LID) can severely impact the performance of solar cells. An example degradation curve of a p-type Cz solar cell is shown in Fig. 1, highlighting a reduction in efficiency of more than $0.6\%_{abs}$ within 50 minutes of light soaking at 100°C.

LID is caused by a variety of impurities, and can reduce cell performance by more than 10% [1]. One source of LID is the metallic impurities, such as copper and iron, which can be incorporated into the silicon during crystal growth. However, because of the high diffusivity of such impurities, the associated degradation can be treated relatively easily through gettering processes [2,3].

A much more significant source of LID in the PV industry occurs predominately in p-type Czochralski (Cz) grown silicon [4]. In this material,

LID is dominated by a defect that is mostly thought to be a boron–oxygen (B–O) complex [5]. This has been the most prominent LID mechanism in solar cells, and is generally what is meant when the term 'LID' is used. However, despite more than a decade of study, there is still no consensus on the actual defect composition.

In the case of multicrystalline silicon (mc-Si), another significant LID mechanism was recently identified [1,6] that can be even more severe than B–O-related degradation in p-type Cz solar cells. While it has been confirmed that the defect is not related to the B–O complex or to iron–boron pair dissociation, the true source is still unknown.

The extent of degradation can depend on the solar cell structure. For example, the LID in p-type Cz aluminium back-surface field (BSF) solar cells may be $3–4\%_{rel}$ [7],
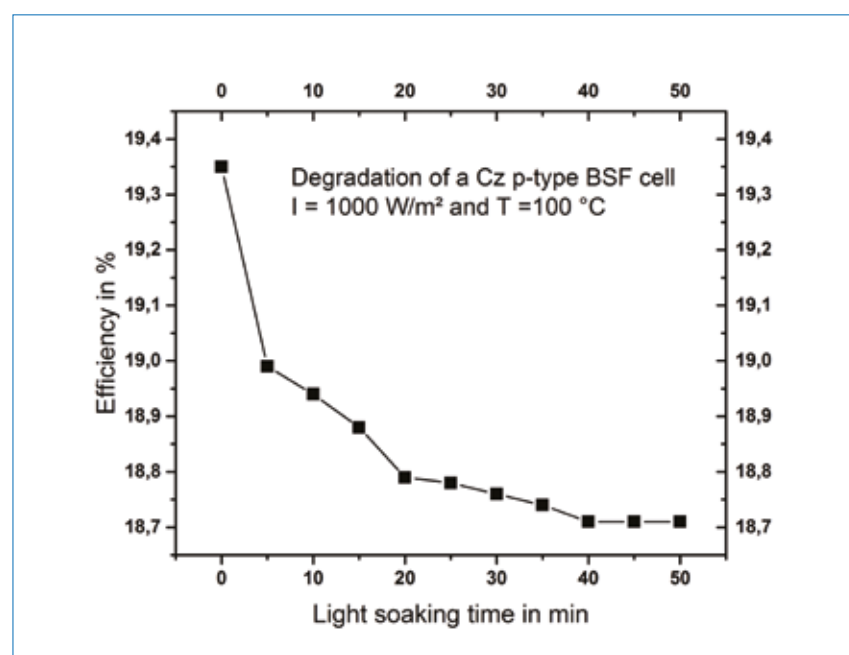

Figure 1. Example efficiency degradation of a p-type Cz aluminium back-surface field solar cell.

compared with the higher values often reported for passivated emitter rear cells (PERCs) of up to 4–6%$_{rel}$ [8], and may approach 10%$_{rel}$ [9]. This is primarily due to a stronger dependence of efficiency on bulk lifetime in high-efficiency solar cell structures, although this may not be the only cause of the higher sensitivity in PERC cells. Similarly, stronger degradation has been observed in mc-Si PERC cells than in mc-Si BSF cells [10]. At UNSW, LID effects in industrial PERC cells from various manufacturers have been studied. The worst impact observed was 1.8%$_{abs}$ for Cz and 2.1%$_{abs}$ for mc-Si. With the current adoption of PERC technology by the industry, a trend that is predicted to continue well into the future [11], LID will have an increasingly significant impact on the PV industry.

International experts have predicted a \$3.7 trillion investment in PV by 2040 [12]. Assuming that 50% of PV devices are fabricated on wafers subject to a 10%$_{rel}$ LID performance loss, this could equate to a \$185 billion loss for the industry. The loss in efficiency also has a significant impact on greenhouse gas emissions. By 2025, predictions indicate a global PV installed capacity of 1TW, and 1,500TWh of PV-based electricity generation [13]. The reduced yield due to LID could equate to an additional 75GWh of electricity being required from other electricity sources. If such electricity is generated using fossil fuels, this could correspond to the generation of greenhouse gas emissions of approximately 66M tonnes CO_2 equivalent (CO_{2-e}) (based on an average of 888 tonnes CO_{2-e}/GWh of electricity production from coal [14]), which would be mitigated if LID were eliminated.

Various techniques have demonstrated the ability to reduce the extent of LID in silicon solar cells. This article reviews different approaches for reducing LID, both on the incoming material level and during cell and module production. It demonstrates that the mitigation of LID in Cz and mc-Si is not only technically feasible but can also be achieved in various ways, and that further work is required to explore which solution (or combination of solutions) is best suited to the manufacturing environment.

Selecting source material to avoid LID

Fundamentally, LID in both mono and mc-Si wafers occurs because of sub-optimal bulk properties; one option to avoid LID is therefore to modify the source material used to make the solar cells. Decreasing the boron and/or interstitial oxygen concentrations can reduce the extent of LID associated with B–O defects.

Reducing interstitial oxygen

In monocrystalline silicon material, interstitial oxygen concentrations may be reduced in Cz silicon by using crucibles with coatings such as silicon nitride [15], or by applying magnetic fields during crystal growth [16]. Float-zone (FZ) silicon may also be used, with interstitial oxygen concentrations typically two orders of magnitude lower than those in Cz material [17]; however, this is significantly more expensive than Cz silicon, and hence not favoured by silicon solar cell manufacturers. FZ silicon can also be subject to various other defects, such as nitrogen-related defects, which can have significant detrimental effects on bulk lifetime [18].

Casting affords another opportunity to reduce oxygen content in the silicon. Again, the crucible walls are typically coated in silicon nitride to reduce oxygen incorporation. The casting method, however, can introduce other contaminants and structural defects into the silicon that typically reduce material quality. The development of cast-mono silicon by BP Solar [19] offered a promising approach for producing essentially full monocrystalline silicon wafers with the low oxygen content of cast silicon, and therefore reduced LID. However, cast-mono silicon can suffer from significant variations in material quality throughout the ingot due to the generation of high dislocation densities [20]; as a result, the industry has moved away from this material [11]. The more recent development of 'high-performance multi' [21] has similarly used seeded casting methods, but has deliberately reduced the grain size and dislocation densities in the crystallized material.

Modifications to wafer doping

As an alternative approach, wafers with a higher bulk resistivity, and hence lower boron doping concentration, can be used; this also has the benefit of reducing the sensitivity to Shockley-Read-Hall (SRH) recombination for certain defects. This is not ideal in a PERC solar cell structure, however, as majority carriers (holes) are required to flow laterally through the bulk to the p-type contacts. Hence, increasing the resistivity will increase the series resistance and lower the fill factor of the device.

Boron can also be replaced by other dopants: if retaining a p-type substrate, typically gallium dopants are used. However, gallium has a significantly lower segregation coefficient than that of boron; this can introduce large variations in the resistivity of wafers throughout a Cz ingot, which reduces the usable portion of the ingot.

Phosphorus-doped n-type wafers can also be used to completely eliminate boron–oxygen defects, provided that the material is not compensated. The highest-efficiency industrial solar cells are fabricated on n-type substrates [22]; however, the use of n-type wafers generally results in the requirement for significant processing and equipment changes in the production line. The processing sequence can also be thermally and energy intensive, and is more complicated than that required for p-type substrates. Furthermore, the high thermal budget can induce a significant degradation of the material lifetime through the formation of other oxygen-related defects, such as oxygen precipitates [23]. These defects can be just as detrimental as the B–O defects, and can reduce performance by more than 10% [24]. Generally, the use of n-type material is confined to monocrystalline substrates, because of the inability of the mc-Si to achieve the high lifetimes required in n-type structures, as well as its inability to tolerate the high thermal budget required. Similarly to gallium, phosphorus has a smaller segregation coefficient than boron, leading to larger variations in the bulk doping throughout the ingot.

> **"**The susceptibility of PERC cells to the hotly debated light-induced degradation (LID) is closely related to the casting or pulling process of the ingot from which the wafers are cut. (T. Hengst – Meyer Burger [25])**"**

Modifications to multicrystalline silicon material

In looking for ways to avoid LID in mc-Si PERC solar cells, a dependence of the degradation on the incoming wafers has been reported [1,10,25], which suggests that crystallization and/or impurity concentrations influence degradation. Manufacturers producing mc-Si PERC

Manufacturer	Stable efficiency enhancement with hydrogenation [%$_{abs}$]
A	0.8
B	1.0
C	0.7
D	0.9
E	1.5
F	0.8
G	1.8
Average	1.1

Table 1. Efficiency enhancements from an 8s advanced hydrogenation process for the treatment of B–O defects in industrial p-type monocrystalline PERC solar cells.

solar cells therefore carefully choose the wafers to be compatible with their specific solar cell processes in order to reduce the extent of degradation. The factors that influence the degradation and the changes to crystallization and/or wafering required, however, have not been publicly disclosed.

Manufacturers producing PERC cells may also avoid the use of mc-Si substrates. In this case, p-type Cz silicon wafers are used, as the LID associated with the B–O defect is often smaller than that associated with mc-Si PERC solar cells.

Mitigating B–O-related LID during cell/module fabrication

In instances where B–O-related LID cannot be completely eliminated by carefully selecting the incoming material, the extent of LID can be reduced or eliminated at various stages of cell/module fabrication.

Illuminated annealing

While illumination can cause a degradation of solar cell performance through the generation of defects, the same conditions that induce the degradation can also result in a permanent recovery of performance. Illuminated annealing at elevated temperatures to stabilize the bulk lifetime of boron-doped Cz wafers was first demonstrated at the University of Konstanz by Herguth et al. in 2006 [26]. At the time, however, the mechanisms were not understood; furthermore, the recovery time was of the order of hours, and not suitable for mass production.

Since then, several key advances in the understanding of the mechanisms have been presented, and have helped in reducing the time required to mitigate B–O-related LID. First, the importance of hydrogen was noted in 2009 by Centrotherm: solar cells fabricated with hydrogenated silicon nitride layers using plasma-enhanced chemical vapour deposition (PECVD) saw a degradation and subsequent recovery of the lifetime during illuminated annealing, whereas solar cells fabricated using hydrogen-free silicon nitride layers did not show a

recovery [27]. This indicated a possible hydrogen-passivation-based mechanism for the permanent recovery. More recently, several studies have backed up these early findings and ruled out the potential impact of other factors in those initial experiments [28–31].

> "The detrimental LID effect of p-type solar cells was abolished by the application of a hydrogenated silicon nitride layer and a supplementary treatment with illumination and temperature. (K. Münzer – Centrotherm [27])"

The next breakthrough came from UNSW with the application of hydrogen charge state theory [32] to explain the role of the illumination in defect passivation [33–35]. The charge state of hydrogen can affect both the mobility [36] and the reactivity [37] of hydrogen in the silicon. In p-type silicon, nature drives hydrogen into a non-optimal charge state. It is only through the addition of extra carriers to provide charge state manipulation that it can take a form which is able to react with the B–O defect [33]. This understanding was subsequently adopted and expanded upon by several research groups [30,38,39]. It is worth noting that the control of hydrogen charge states has implications for the passivation of all defects in crystalline silicon, including the mysterious mc-Si defect discussed in the next section.

The final breakthrough of key importance to high-throughput manufacturing was the identification by UNSW of the role of defect formation [40–42] (which is often the rate-limiting step in the complete defect passivation process), and importantly of how it can be greatly accelerated [43]. To achieve short mitigation times with greater effectiveness, it is necessary to accelerate this formation rate [41,42]. This is particularly the case if higher temperatures are used to accelerate the overall reaction rates. When solar cells are produced on Cz wafers using screen printing, at the end of the line the bulk of the cells are relatively free of B–O defects (the defects have not yet formed). Thus, in a commercial cell it is necessary to first form the defects quickly so that they can be subsequently permanently passivated. Initial studies identified a saturation of the defect formation rate [44], which imposed a theoretical limit on the temperatures and times to achieve stabilized silicon. However, subsequent work has demonstrated that, through the use of extremely high-intensity light, it was possible to break through these limits and achieve a greatly accelerated defect formation rate [43], because of the dependence on the total hole concentration [45,46].

This progress has enabled complete stabilization from B–O-related LID in industrial solar cells to be achieved within 8s [40]. A demonstration of UNSW's advanced hydrogenation process for the rapid treatment of B–O-related LID, when applied to industrial p-type monocrystalline silicon PERC cells straight off the production line from various cell manufacturers, is shown in Table 1. The process forms and passivates the defects using high-intensity laser illumination (>100 suns, 938nm wavelength, quasi-continuous wave mode). An average efficiency enhancement of $1.1\%_{abs}$ was achieved for the cells from the seven manufacturers, with enhancements of up to $1.8\%_{abs}$ observed (manufacturer G). An example efficiency distribution with and without the 8s advanced hydrogenation treatment for manufacturer B is presented in Fig. 2: the image shows a $1\%_{abs}$ efficiency enhancement due to the passivation of B–O defects.
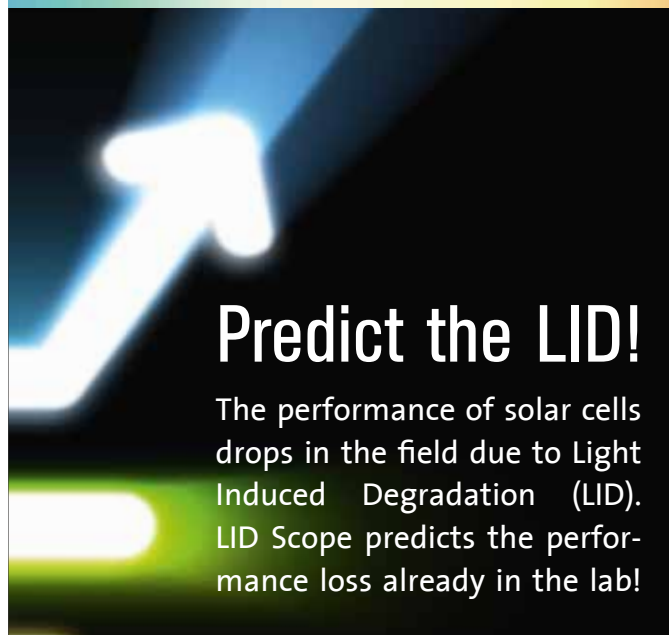
Integration of B–O LID mitigation processes into solar cell/module fabrication

It is possible to carry out LID mitigation in the field: operating conditions in the field provide the temperature and illumination required to drive the passivation reactions [8]. However, the timescales are too slow for this to be considered a viable option for modules, since hundreds of hours at elevated temperatures would be required, which could be equivalent to several years of operation in the field. Because of the strong temperature dependence of the reactions, the time required is also heavily dependent on the location of the installation and mounting type [47].

Performing LID mitigation during the actual solar cell and/or module fabrication therefore appears to be the most feasible option. Nonetheless, there some limitations on integrating the LID mitigation process into the fabrication sequence for solar cells/modules. Because of a potential destabilization of the B–O defect passivation at high temperatures [26], the advanced hydrogen passivation processes must be performed after the last high-temperature step; for screen-printed solar cells, this is the metal-contact firing step.

Several options exist, however, for the treatment after metallization. First, the advanced hydrogen passivation process can be integrated into the cooling section of the fast-firing belt furnace for metallization; this has the benefit of not requiring an additional heating step, although the process duration is restricted by the firing of the metal contacts. Second, the process can be implemented in a stand-alone tool after metallization, which has the benefit of decoupling the metallization process from the LID mitigation treatment. Third, the
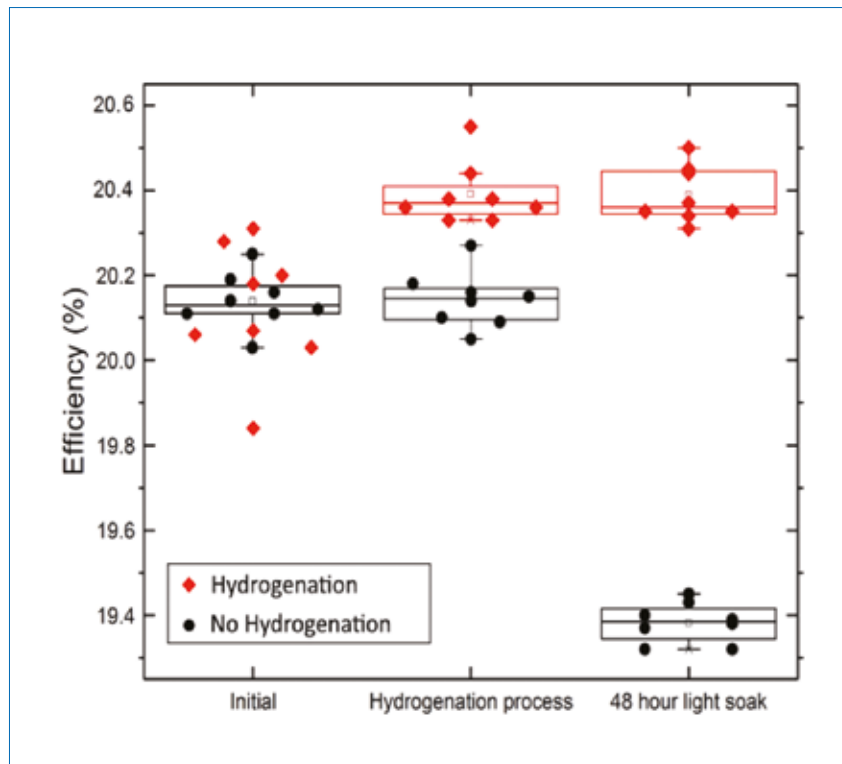

Figure 2. Efficiency enhancements for manufacturer B resulting from the addition of an 8s UNSW advanced hydrogenation process for the treatment of B–O defects.
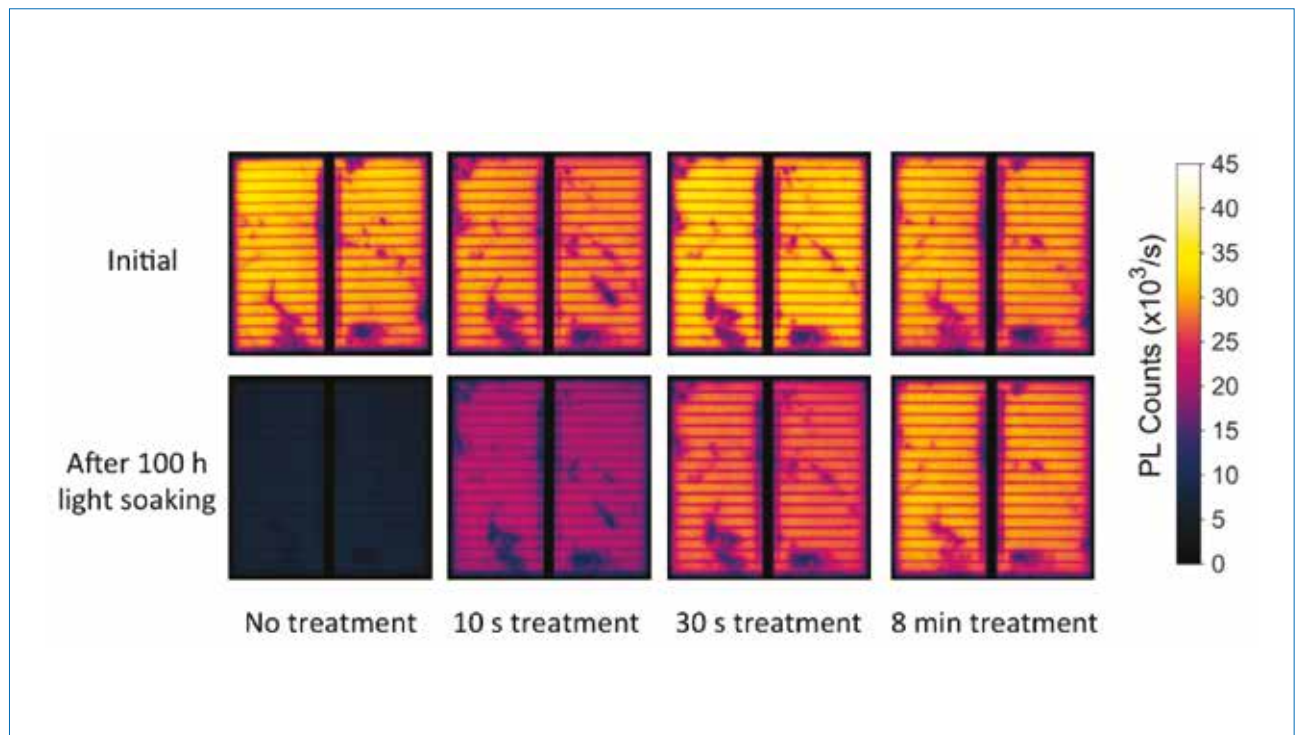

Figure 3. PL images (with point spread function deconvolution [53]) of industrial mc-Si PERC solar cells: initial images after cell fabrication, and additional images after a treatment at 250°C under 44.8kW/m^2 laser illumination for various durations and subsequent 100h of light soaking at 70°C (0.46kW/m^2).

process can be carried out during encapsulation [8]. One advantage of performing the hydrogenation during lamination is that a partial destabilization of the defect passivation during soldering and encapsulation (if the process was performed earlier) is avoided. A further advantage is that the relatively long processing time for encapsulation can allow a relaxation of the illumination intensity required for LID mitigation. However, it is unclear whether the integration of LID mitigation into the lamination could affect the encapsulant properties.

Mitigating mc-Si PERC LID during cell/ module fabrication

Processes at the cell/module level can also greatly reduce the extent of degradation in mc-Si PERC cells. Hanwha Q CELLS has reported that their Q.ANTUM modules suffer less than 1%$_{rel}$ degradation after 1000h of light soaking at 75°C, compared with more than 10%$_{rel}$ for LID-sensitive modules [1]. However, the details of such processes have not been disclosed.

The mc-Si degradation and reports by Q CELLS have sparked significant interest within the PV industry. In the last two years, several approaches for LID mitigation have been presented.

Illuminated annealing

Illuminated annealing can be used to reduce LID in mc-Si PERC cells as well [48,49]; however, to date, the timescales for both the degradation and recovery are substantially longer than those for B–O-related LID. This generally results in the mitigation process requiring much longer exposures to illumination, such as a 30-minute treatment to reduce LID to 2%$_{rel}$ [48]. Reports have highlighted the influences of temperature, illumination intensity and process duration on the extent of LID mitigation [48–50]. For example, increasing the illumination intensity has been shown to reduce LID [48,49]; recent work using high-intensity illumination has demonstrated significant LID reductions (of up to 60%) for a processing time of 30s [51,52].

Fig. 3 shows an example of the influence of high-intensity illuminated annealing processes on mc-Si PERC LID. PL images of industrial mc-Si PERC cells are shown at the end of fabrication, and after a treatment with a high-intensity laser for various durations at 250°C (44.8kW/m^2, 938nm wavelength, quasi-continuous wave mode) and subsequent light soaking. As demonstrated in the figure, LID was substantially modified by the laser process.

Firing at a reduced temperature

The defect in mc-Si PERC cells is primarily activated by high-temperature firing, which is used to form the metal contacts. The extent of degradation can be regulated by varying the firing conditions [10,48,52,54]; in particular, firing at reduced temperatures can suppress the subsequent degradation. While the optimal firing may differ for each solar cell manufacturer, recently reported data by Chan et al. [52] demonstrated that reducing the firing temperature by 100–150°C was sufficient to eliminate most of the subsequent degradation in minority-carrier lifetime, while still allowing effective hydrogen passivation.

Fig. 4 shows an example of the impact of firing at various temperatures on the extent of degradation in lifetime after illumination, as well as the minimum value of lifetime throughout degradation for each firing temperature. The yellow region indicates the range of temperatures at which the highest absolute lifetimes can be obtained at maximum degradation. In the case of the samples and processing used here for screen-printed solar cells at UNSW, this occurred
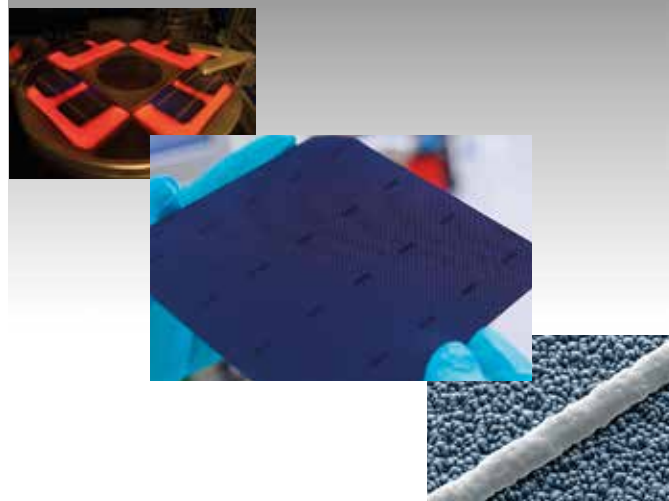
at firing temperatures approximately 100°C below the standard firing temperature.

Reducing the firing temperature, however, will potentially require a modification of the screen-printing pastes in order to ensure that appropriate contact resistances and adhesion can be achieved. For PERC solar cells, the aluminium pastes are also required to form localized BSF regions, the formation of which is heavily temperature dependent.

A second firing process
In the instance where a reduced firing temperature is not an option, a second firing process may be used to greatly reduce the extent of degradation. The second firing process can be implemented over the same timescale as the typical firing process, and can therefore be integrated into an in-line tool with multiple zones for the modified thermal profile. The second firing process to reduce LID is performed at a reduced temperature [52]. Using this approach, a reduction in degradation from 12.7%$_{rel}$ to 4.3%$_{rel}$ has been demonstrated [52].

While this process is quite effective and rapid in reducing the extent of degradation, the process can introduce series-resistance problems associated with the contact resistance at the silver/silicon interface [52]; hence, the process window to avoid LID appears to be quite narrow. In addition, this process does not allow effective passivation of B–O defects.

A combined approach: firing and illumination
A combined approach may also be used, consisting of a second firing process and a subsequent illuminated anneal. This approach has benefits arising from the rapid nature of the firing process, as well as from the ability to passivate the remaining defects, including B–O defects. Furthermore, the combined approach can also be implemented within the tools for metal-contact firing by adding additional process zones. The combined approach has been shown to reduce degradation in open-circuit voltage from 5.6%$_{rel}$ to 0.1%$_{rel}$ after 500h of light soaking [52]; however, it can also lead to fill factor issues, presumably due to the second firing process, and requires further investigation.

The choice of current injection and illumination for LID mitigation

Although efforts for LID mitigation requiring carrier injection have typically focused on illumination, current injection can be used as an alternative method to provide the carrier injection. Both approaches may have strengths and weaknesses in their suitability for different applications.

In the case of approaches requiring short processing times, achievable through the acceleration of defect formation, illumination would appear the preferred one. While current injection can be used to provide carrier injection equivalent to low illumination intensities, series resistance effects limit the ability to achieve sufficient carrier concentrations throughout the device using high currents. Illumination allows operation in open-circuit conditions without series resistance effects, and can therefore facilitate accelerated defect formation. However, the necessary illumination intensities (typically > 20 suns) may be challenging to achieve in an industrial environment, and require high-powered LED or laser systems. Furthermore, the integration of such high-intensity illumination into industrial tools may face further challenges, such as safety concerns and energy requirements.

In certain instances, the application of current injection for LID mitigation may have advantages over illuminated approaches. One advantage of using current injection is the ability to process a large number of cells simultaneously, such as by stacking cells and applying current through the devices, without requiring a large processing area. Doing so can provide the high throughputs for the time required when using low current densities (below 2 suns equivalent), but this process requires contacting the solar cells and involves extra wafer handling. Furthermore, current injection is an efficient way to inject carriers and open up the opportunity for a flexible and accurate control of the injection conditions independently of the optical and electrical properties. Another advantage for tool/process integration is that current injection could be implemented during lamination without significant modifications in tool design to incorporate illumination.

Tools for mitigating LID

Industrial tools are now available for various implementations of the processes described above. One approach that appears popular is illuminated annealing. For example, Centrotherm, Despatch and Schmid are offering tools integrated with fast-firing and LID mitigation zones. The solutions appear popular, with companies such as Despatch claiming that several top-tier manufacturers in China and Taiwan have already ordered systems.
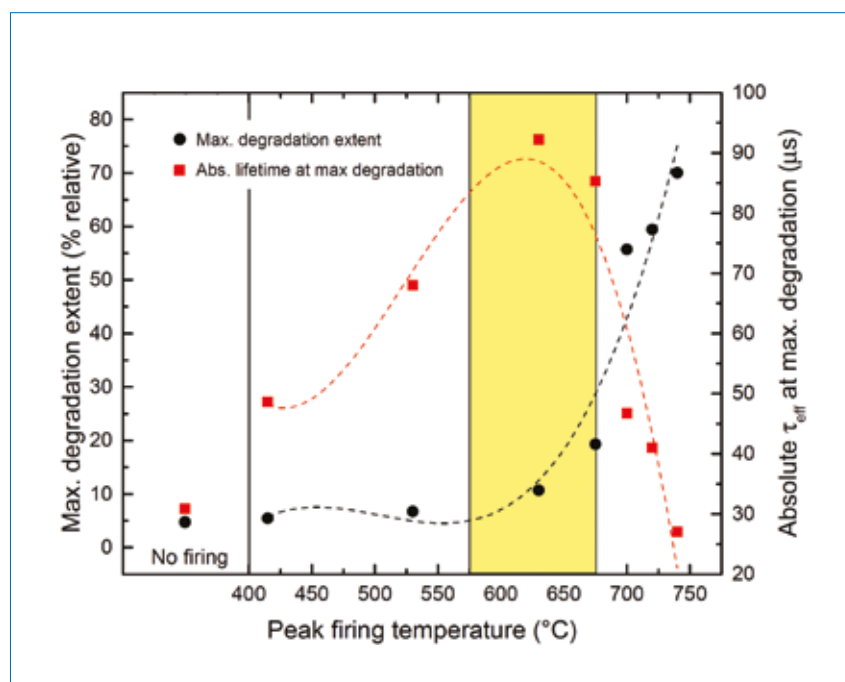

Figure 4. Maximum relative degradation of minority-carrier lifetime after firing at different temperatures and subsequent light soaking. Absolute values of minority-carrier lifetime at maximum degradation are also shown. The yellow region indicates the optimal firing temperature for the lifetime samples/processing used. (Data taken from Chan et al. [52].)

"Several furnace manufacturers have introduced solutions to the problem. (E. Anderson – Despatch Industries [55])"

Several tool manufacturers also offer stand-alone versions for LID mitigation, including Asia Neo Tech Industrial, Folungwin and DR Laser. Many other equipment manufacturers are probably working on developing tools for the market, and similarly for solar cell manufacturers because of the relative technical simplicity of applying heat and light to solar cells to facilitate the advanced hydrogenation processes. While earlier generations of the tools use relatively low illumination intensities (<10 suns), the newer generations are shifting towards higher illumination intensities (>20 suns) to allow the acceleration of defect formation that can drive rapid LID mitigation.

The significant efficiency enhancements that result from the application of LID mitigation processes mean that short payback times are possible. For example, efficiency enhancements of $1.1\%_{abs}$ (as shown in Table 1), obtained using a US$300,000 tool with a throughput of 3,600 wafers per hour, could have a payback time of the order of just one month.

Conclusions

LID can significantly affect the performance of p-type silicon solar cells, but there are many ways of managing and/or eliminating the degradation. Wafers may be carefully selected with reduced boron and/or oxygen concentrations in order to avoid B–O-related degradation.

In the case of multicrystalline silicon, there are reports that the degradation can be reduced by paying close attention to the crystallization process, but the details have not been disclosed. During cell/module fabrication, illuminated annealing may be used to treat B–O defects. Sub-10s processes have now demonstrated the complete mitigation of B–O-related LID on finished industrial solar cells. Current injection can also be used for LID mitigation; however, the timescales for such processes are probably longer because of the inability to build up carrier concentrations to the required levels for accelerating defect formation throughout the device.

For mc-Si PERC cells, changes to the firing conditions can reduce the extent of degradation. Subsequent treatments can also be carried out, such as illuminated annealing or a second firing step. With illuminated annealing processes, however, the timescales are typically longer than those for the treatment of B–O defects. Industrial tools for LID mitigation are now widely available, potentially with very short payback times. These new capabilities are giving strength to p-type silicon solar cell technologies.

Acknowledgements

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About the Authors

Brett Hallam is the co-director of core research for ARENA crystalline-silicon-based PV projects at UNSW. He received his Ph.D. from UNSW in the field of laser doping and hydrogen passivation for silicon solar cells. His current research activities focus on the development of advanced hydrogen passivation processes.

Catherine Chan completed her Ph.D. in photovoltaic engineering in 2014 at UNSW, where she is currently working as a postdoctoral research fellow in the areas of silicon solar cell degradation and advanced hydrogen passivation processes for silicon solar cells.

David Payne studied electronic engineering at the University of Southampton, where he went on to receive his Ph.D. in 2014 in the field of light trapping for photovoltaics devices. Since then he has been working as a research fellow at UNSW, primarily focusing on carrier-induced degradation in multicrystalline silicon.

Dominik Lausch obtained his Diploma degree (A) in physics from the University of Leipzig, Germany, in 2009. In 2012 he received his Ph.D. in natural science from the University of Halle, Germany, in cooperation with Fraunhofer CSP and Q-Cells SE. He is currently a postdoctoral researcher at Fraunhofer CSP, heading a team that is investigating plasma texturing and hydrogen passivation.

Marcus Gläser received a Bachelor's in solar technology (photovoltaics) from Anhalt University of Applied Sciences in 2011. After receiving his master's in 2014 in sustainable energy systems from Otto-von-Guericke University in Magdeburg, he began working on his Ph.D. with Fraunhofer CSP Halle, where he is investigating carrier-induced hydrogen passivation of bulk defects in crystalline silicon solar cells.

Malcolm Abbott received his Ph.D. in photovoltaic engineering in 2006 from UNSW, where he is currently the CTO of PV Lighthouse and a research director. His current research interests broadly span the crystalline silicon field and include developing new cell processes, advanced characterization techniques, mitigation of LID in wafers, and modelling of photovoltaic devices.

Stuart Wenham is director of the Photovoltaics Centre of Excellence at UNSW. His involvement in photovoltaics spans more than 30 years, and he has been honoured with numerous leading international awards. Along with his team he has achieved many cell and module performance world records and the successful large-scale commercialization of several technologies.

Enquiries

Brett Hallam
School of Photovoltaic and Renewable Energy Engineering
University of New South Wales
Sydney NSW 2052
Australia

Tel.: +61 415 415 156
Email: brett.hallam@unsw.edu.au

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