Acceleration and mitigation of carrier-induced degradation in p-type multi-crystalline silicon

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Recently, a new carrier-induced defect has been reported in multi-crystalline silicon (mc-Si), and has been shown to be particularly detrimental to the performance of passivated emitter and rear contact (PERC) cells. Under normal conditions, this defect can take years to fully form. This Letter reports on the accelerated formation and subsequent passivation of this carrier-induced defect through the use of high illumination intensity and elevated temperatures resulting in passivation within minutes. The process was tested on industrial mc-Si PERC solar cells, where degradation after a 100 hour stability test was suppressed to only 0.1% absolute compared to 2.1% for non-treated cells.

1 Introduction Multi-crystalline silicon (mc-Si) has been shown to degrade over long time scales when subjected to carrier injection with particularly severe losses demonstrated in passivated emitter and rear contact (PERC) cell structures [1–4]. The degradation has primarily been reported as being light-induced and has most commonly been observed under elevated temperature conditions leading it to be described as light and elevated temperature induced degradation (LeTID) [4]. However, the degradation rate has been shown to vary depending on whether the solar cell is operated under V_{oc} or I_{sc} mode [4], indicating that it can be more accurately described as carrier-induced degradation (CID). This CID effect is a significant problem for the photovoltaics (PV) industry as mc-Si based devices currently account for over 65% of the total market with PERC predicted to become the dominant device structure over the next 10 years [5, 6]. Full defect formation and passivation is possible under field conditions but can take more than 10 years [7]. Some groups have reported to have been successful in at least partially suppressing this degradation [4, 8, 9], predominantly due to changes in their solar cell processing, however their exact methods remain unpublished for commercial reasons.

There is currently no consensus in the literature about which particular defect or defects are responsible for this

observed degradation in mc-Si. Ramspeck et al. showed that defect formation occurs not only in B-doped mc-Si wafers, but also in Ga-doped mc-Si wafers and therefore could not be explained by the boron-oxygen (BO) defect [1], which is the well-known cause for carrier-induced degradation in B-doped Cz silicon [10]. In addition, Kersten et al. showed that the mc-Si degradation does not correlate with interstitial oxygen content [4]. The BO defect in Cz silicon also forms on a much shorter time scale than the defect in mc-Si under similar degradation conditions [11]. It has also been shown that this degradation in mc-Si is not due to boron-iron (FeB) pair dissociation [1]. Despite some suggestions that the defect has some dependence on the aluminium oxide (AlO_x) rear side passivation layer on mc-Si PERC cells [2], the effect has been shown to occur on both symmetrical mc-Si lifetime samples passivated either by AlO_x or silicon nitride (SiN) [4], and thus appears to be a bulk effect. It is quite possible that there are multiple defects responsible for the CID observed in mc-Si, and the extent to which this defect or defects are present are expected to differ along position in the ingot as well as between wafer manufacturers. This study shows that the formation of the defect can be accelerated through the use of carrier injection, in this case using high intensity light, and subsequently be permanently passivated. This accelerated

formation and passivation appears to be similar to that recently shown for the BO defect in Cz silicon [12] in the sense that the defect must be formed prior to passivation, and that increased illumination and elevated temperatures can be used to accelerate the degradation. However, in the case of mc-Si, the timescales are substantially increased.

2 Methods Symmetrical lifetime test structures were prepared using randomly selected commercially available 156 mm × 156 mm boron-doped (∼1.6 Ω cm) high performance (HP) mc-Si wafers from three commercial sources, these sources will be referred to as A, B and C for the remainder of this Letter. In addition, commercial grade 156 mm × 156 mm boron-doped (1.6 Ω cm) Czochralski (Cz) wafers were included in the experiment as a reference. The saw damage was removed from both surfaces of the mc-Si wafer from source A through acidic texturing, whilst for mc-Si wafers from source B and C an alkaline etch was used. It is not expected that the difference in wet chemical treatment will have a significant impact on the experiment, which is focussed on determining whether or not CID can be significantly accelerated rather than the determination of exact degradation rates. All wafers underwent an RCA clean and HF dip, followed by phosphorus diffusion in a POCl$_3$ tube furnace at 795 °C for 30 minutes with a drive-in step at 885 °C for 30 minutes to achieve an average emitter sheet resistance of 72 Ω/sq which has been shown to provide effective gettering [13, 14]. The phosphosilicate glass (PSG) was removed in dilute HF prior to the deposition of a hydrogen-rich silicon nitride (SiN$_x$:H) film onto both surfaces via plasma enhanced chemical vapour deposition (PECVD, Roth & Rau MAiA). The resulting films had a thickness of 75 nm and refractive index of 2.08 nm at 633 nm. Samples then underwent firing in an infra-red fast-firing furnace with a peak firing set-temperature of 700 °C. The wafers were then cut into 39 mm × 39 mm samples for ease of processing. Subsequently, lifetime samples were initially split into two groups:

– Standard degradation, light soak at 70 °C with a broadband halogen source (irradiance of 0.46 kW m^{-2}).

– Accelerated degradation, light soak at 140 °C with a 938 nm laser (irradiance of 44.8 kW m^{-2}).

The standard degradation process was performed on a hotplate under a halogen light source with the irradiance (0.46 kW m^{-2}) measured using a thermal power sensor (S305C, Thorlabs). The wafer temperature was measured using an IR thermometer and the hotplate set-temperature was adjusted to result in a sample temperature of 70 °C whilst illuminated. This temperature was chosen based on previously demonstrated results in the literature for field relevant conditions that are known to form the defect on an experimentally feasible timescale [1, 2, 4]. The accelerated degradation process was performed on a hotplate under laser illumination. A 938 nm fibre-coupled diode laser was used, operating in quasi-continuous wave mode (0.5 ms pulse length at a repetition frequency of 2 kHz). A beam shaper was used to illuminate the entire sample and the ir-

radiance (44.8 kW m^{-2}) was calculated from measurements obtained from a thermal power sensor (S305C, Thorlabs). The temperature of the wafers was monitored in situ using an infrared thermometer (PC301HT-0, Calex) and the hotplate was adjusted such that the wafer temperature was 140 °C under illumination. This temperature was chosen based on a coarse preliminary sweep of treatment conditions in which this setting showed clear degradation within a short timescale. In both arrangements, samples were removed from the hotplates at fixed intervals for measurements of the injection-level-dependent effective minority carrier lifetime (referred to as lifetime for the remainder of the Letter). In each case, samples were left in the dark at room temperature for at least two hours prior to measurement to minimise the potential effects of interstitial iron [15]. Lifetime measurements were performed using a commercial photoconductance lifetime tester (WCT-120, Sinton Instruments) [16]. The measured data was analysed using the generalised method [17] and corrected for Auger recombination [18]. To examine the trends due to processing, the effective lifetime was extracted at an excess minority carrier density (Δn) of 9.1 × 10^{14} cm^{-3} (corresponding to one tenth of the bulk doping density).

3 Results and discussion The relative change in lifetime under standard and accelerated degradation conditions for a representative sample from each of the mc-Si wafers along with a Cz reference sample is shown in Fig. 1.

In the case of the Cz sample under standard degradation conditions, the effective lifetime reached its lowest value after 16 hours, after which the lifetime began to recover as is typically seen for such samples and has been attributed to the formation and subsequent passivation of BO defects [11, 19]. For the accelerated case, the lowest effective lifetime of the Cz sample was measured after only one minute. However, the true minimum was likely to have occurred prior to the initial one-minute test interval. For each of the mc-Si samples, a slow-forming defect was clearly apparent under standard degradation conditions. For the samples from wafers B and C, most of the degradation occurred within the first 50 hours with little to no recovery shown even after 1000 hours. The sample from wafer A continued to degrade even after 1000 hours. In the accelerated case at 140 °C, most of the degradation occurred within one minute and was followed by a relatively gradual recovery. Within 120 minutes, samples from wafers B and C recovered to at least their original lifetime value, whilst the sample from wafer A recovered to 2.5% below its original value. The stability of the recovered lifetime characteristics was assessed by subsequent light soaking under the standard test conditions of 0.46 kW m^{-2} irradiance at 70 °C. After 100 hours of light soaking, all mc-Si samples showed further improvements in lifetime, indicating that defect passivation in these samples was still ongoing and was not halted or reversed at these conditions. It should be noted that using a high illumination intensity (28.7 kW m^{-2}) at 70 °C also showed a clear acceleration of defect forma-
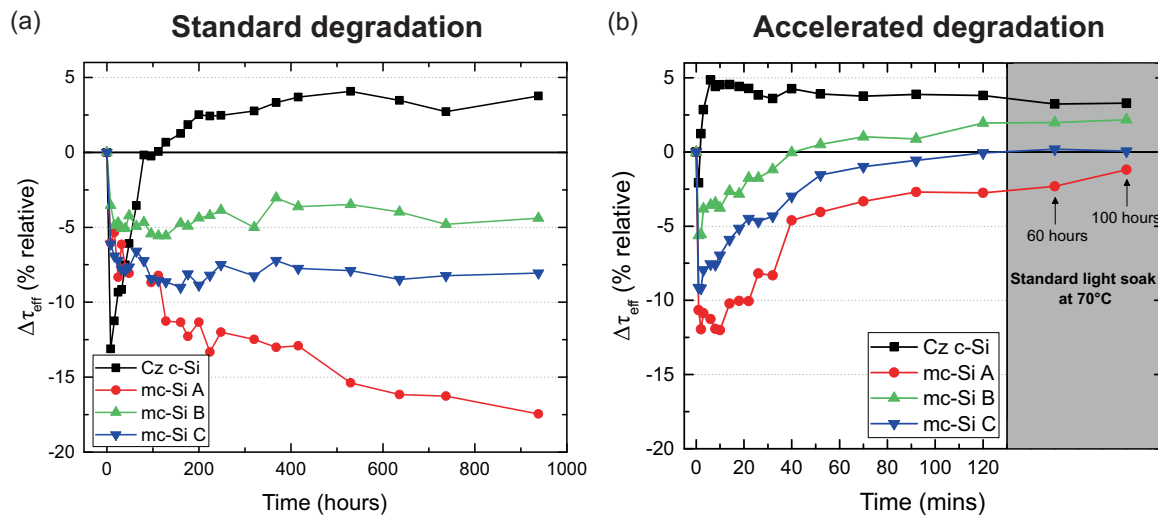
Figure 1 Relative change in effective lifetime for a Cz sample (black squares) and mc-Si samples from three sources for both (a) standard degradation conditions (0.46 kW m^{-2} at 70 °C), and (b) accelerated degradation conditions (44.8 kW m^{-2} at 140 °C).

tion due to the increased light intensity in comparison to the standard degradation conditions, with further acceleration achieved by subsequently increasing the temperature. This highlights that both the illumination intensity and temperature should be increased to accelerate defect formation. It appears that the acceleration of the defect formation is pivotal in enabling rapid passivation of the defect. Results for higher temperatures and illumination have been focused on here in order to observe passivation within a practical timescale.

Two additional temperature conditions, 250 °C and 320 °C, were tested on samples from all three wafer sources in order to investigate the potential for further increasing reaction rates. At 250 °C the three mc-Si samples showed an average increase in lifetime of 8.5% after eight minutes of illumination at 44.8 kW m^{-2}. At the 320 °C test condition a similar average increase of 8.4% was observed after just one minute which increased slightly to 9.0% after a further three minutes of illumination. These samples were then subjected to a 100 hour stability test under the standard illumination conditions (0.46 kW m^{-2}, 70 °C). The resulting relative changes in effective lifetime for each of the tested conditions are shown in Table 1.

Table 1 Average relative change in effective lifetime after passivation and 100-hour post-passivation stability test for various processing temperatures. In each case an irradiance of 44.8 kW m^{-2} was used.

treatment conditions		average change in effective lifetime (%$_{rel}$)	
temperature (°C)	time (min)	after passivation	after stability test
not treated	N/A	N/A	−7.5
140	120	−0.3	0.3
250	8	8.5	10.2
320	4	9.0	5.6

Stability tests for the 140 °C and 250 °C treated samples both showed that the lifetime continued to increase under standard conditions with samples treated at 250 °C showing a remarkable 10.2% average increase after laser treatment and light soaking. However, in Fig. 1 it is apparent that the samples treated at 140 °C were still increasing in lifetime and are likely to further improve under additional light soaking. In contrast, for the samples treated at 320 °C the improvement in effective lifetime was shown to be less stable and the lifetime was significantly reduced under stability testing. One possible reason for the higher temperature being less effective could be the reduced availability of the defects for passivation. The formation and subsequent passivation of a defect typically competes against reverse reactions (defect dissociation and destabilization of the passivated defect) and this effect is exacerbated as those detrimental reaction rates increase at higher temperatures [20]. Another potential cause for the 320 °C process not being as effective could be the increased time in which the sample remained at a high temperature whilst not illuminated. Due to the interlock on the laser enclosure, the sample remained at process temperature for the few seconds it took to open the enclosure door and remove the sample, possibly resulting in partial destabilization of passivation achieved during illumination. Similar effects have been observed with passivated BO defects in Cz wafers when not kept illuminated during cooling from higher temperature as they effectively go through a "dark anneal" [19].

To demonstrate the effect of this rapid defect formation and passivation on finished mc-Si solar cells, an industrially fabricated multi-crystalline 6-inch PERC cell was used. The cell was passivated on the rear surface by an industry standard layer of AlO$_x$ capped with SiN. The cell was cut into six 3 cm × 3 cm solar cells. Three of these cells underwent laser treatment using a 938 nm laser with an irradiance of 44.8 kW m^{-2} at a cell temperature of 250 °C (as measured during illumination) for eight minutes,

thus matching the conditions shown to give the best stabilised result in Table 1 for the mc-Si lifetime samples. The other three cells were used as controls and did not undergo laser treatment. All six cells were subjected to 100 hours of light soaking using the standard degradation process at 70 °C and 0.46 kW m^{-2}. Illuminated I–V measurements at standard test conditions were taken at each stage: (i) initial, (ii) after laser treatment (control samples were also re-measured at this point) and (iii) after light soaking. The measured open-circuit voltage (V_{oc}) results are presented in Fig. 2.

Initially, the V_{oc} of all six cells ranged from 628 mV to 638 mV. The varying performance of the cells was mostly due to the spatial variation across the mc-Si solar wafer, with some cells containing more dislocation clusters and grain boundaries than others. After laser treatment, the average V_{oc} of the treated cells increased slightly by approximately 2.8 mV. After 100 hours of light soaking at 70 °C and 0.46 kW m^{-2}, the average V_{oc} of the treated samples reduced by 2.3 mV, indicating a small amount of instability associated with the passivation. However, compared to the initial value, the average V_{oc} reduced by less than 0.5 mV, resulting in less than 0.1% absolute loss in efficiency. This is in stark contrast to the control samples, for which the V_{oc} decreased by 33.5 mV, corresponding to an absolute efficiency loss of 2.1% for these cells. The much larger degradation observed on these cells compared to the lifetime samples above could be due to a range of factors. First and foremost, the bulk material was different and thus the presence of the defect could have been more prominent in the cells. In addition, the AlO$_x$ passivation on the rear side must be considered, as this was not present on the lifetime samples used in this study. Whilst the lifetime samples showed degradation which indicated this defect is not related to AlO$_x$ passivation, it cannot be ruled out that AlO$_x$ passivation had some effect on the degradation observed in the cells. However, in both instances, the defect formation and subsequent passivation process was shown to be accelerated. It is possible that the slight instability observed on the treated cells was due to a non-optimum
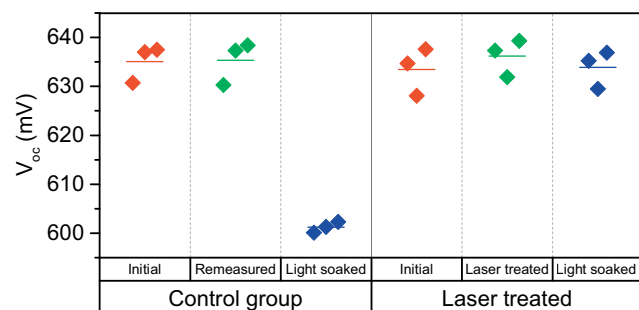
processing time and temperature for these particular samples, and further optimization may be required. As solar cells are fundamentally different from lifetime samples (due to factors such as the shading by the front metal fingers and rear local back surface fields), it is expected that for a given illumination intensity, the excess carrier density generated in the bulk will be lower for a solar cell than for a lifetime test structure. A longer treatment time or higher temperatures and/or irradiance may therefore be required for the complete passivation of the defect to occur.

4 Conclusion This work has demonstrated that the rate of the typically slow-forming defect recently observed in mc-Si can be significantly accelerated under high-intensity illumination and that passivation of the defect or defects responsible can be subsequently achieved in a matter of minutes during the same process. Furthermore, it has been shown that this process can be beneficially applied to finished solar cell devices. The quality and defect concentrations of mc-Si wafers from different sources and different ingot positions can vary significantly and the results in this paper are specific to those wafers studied and cannot necessarily be extended to all mc-Si wafers. However, in this work accelerated degradation and passivation was observed on all three different sources of material as well as cells fabricated on mc-Si from a separate source. An acceleration of defect formation appears to be vital in enabling a rapid passivation of the defects, and the high intensity light used may also accelerate the passivation rate. The nature and kinetics of the defect that is responsible for the process is not confirmed but the ability demonstrated here to greatly accelerate defect formation and passivation should help to enable practical and efficient further work in this area.

Figure 2 Open-circuit voltages of the control cells, and laser treated cells at three stages: 1. initial (red), 2. after rapid degradation and passivation using laser illumination (green), and 3. after 100 hours of light soaking at 70 °C and 0.46 kW m^{-2} to test stability (blue).

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