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Rapid passivation of carrier-induced defects in p-type multi-crystalline silicon

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ABSTRACT

A slow forming carrier-induced degradation effect has previously been reported for p-type multi-crystalline silicon (mc-Si) solar cells and has been observed to be most severe in passivated emitter and rear contact (PERC) designs. The as yet undetermined defect (or defects) responsible for this degradation is typically described as being light-induced. However, in this work we confirm that a directly equivalent degradation also occurs when subjecting a cell to current injection, thus the effect can therefore be more accurately described as being carrier-induced. The defect can take years to form under normal operating conditions, but acceleration of this formation and an apparent subsequent passivation through the use of high intensity illumination at elevated temperatures has recently been demonstrated. In this work we further investigate this approach, analyzing the effects of temperature and time on degradation, regeneration, and resulting stability, as well as the variations in treatment response for mc-Si materials from two different manufacturers. Susceptibility to carrier-induced degradation after 225 h of light soaking at 70 °C is shown to be reduced by 80% using a rapid, 10 s treatment with an illumination intensity of 44.8 kw/m^2 at 200 °C. Stability is shown to further improve by extending treatment time but is reduced with increasing treatment temperature.

1. Introduction

In recent years, there have been an increasing number of reports of a slow forming, light-induced degradation (LID) effect observed in multi-crystalline silicon (mc-Si) solar cells [1–4]. The effect has been shown to be most severe in passivated emitter and rear contact (PERC) cells [1,3] which are predicted to become the dominant device structure in industry within the next few years [5,6]. With mc-Si currently accounting for around 65% of the PV market [5], and the PERC structure rapidly increasing in popularity, the understanding and mitigation of this degradation effect is of critical importance.

The exact defect (or defects) responsible for this degradation has not yet been determined, but it has been shown that the degradation cannot be wholly attributed to the intensively studied B-O complex or Fe_i-B pair dissociation known to be the primary causes of LID in Czochralski (Cz) silicon solar cells [1]. Evidence of this has been presented through observed degradation in gallium-doped wafers [1] and through a lack of correlation with interstitial oxygen concentration [4]. Additionally, the degradation observed in mc-Si occurs on significantly longer timescales than those reported for B-O or Fe_i-B effects on Cz silicon, with mc-Si typically requiring hundreds of hours of light soaking for full defect formation, even when accelerated using elevated temperatures [4]. The defect responsible is likely produced from one or several of the various impurities typically present in mc-Si due to contamination in the material feedstock or the crucible walls/coating. Copper is one such impurity, which has recently been shown to lead to LID in both Cz and mc-Si materials, however, the timescales reported for Cu related LID appear to be too rapid to explain the degradation recently observed in mc-Si PERC cells [7,8]. Further investigation is therefore required in order to determine the root cause in this case.

The lengthy timescales required to observe the full extent of degradation in mc-Si have led to the necessity to increase defect formation rates in order to make experimental studies and rapid mitigation feasible. Hanwha Q-cells have therefore advocated an elevated temperature of 75 °C whilst light soaking to be used as standard and the terminology of 'light and elevated temperature induced degradation' (LeTID) to be used [4]. Whilst such terminology is useful for isolating this defect from others, such as the

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B-O complex, it has the potential to mislead as the degradation can occur at temperatures lower than the 75 °C recommended for studying LeTID and can be induced without light [1,4]. Furthermore, the formation rates of other defects, including the B-O complex can also be increased using elevated temperatures and illumination [9,10]. Throughout this work we have therefore used the broader terminology of carrier-induced degradation (CID), this is further discussed in Section 2.

In mc-Si solar cells, this CID manifests as a reduction in V_{oc}, I_{sc} and *fill factor* (*FF*) leading to diminished power output and efficiency, with absolute efficiency losses of up to 2.1% recently observed in mc-Si PERC cells [4,11]. Kersten et al. have reported that symmetrically passivated mc-Si wafers exhibited CID as a reduction in effective minority carrier lifetime with a strong injection level dependence. Furthermore, this degradation was observed to occur when passivating with either silicon nitride (SiN_x) or aluminium oxide (AlO_x) layers, indicating that the CID was primarily within the bulk [4]. However, studies on solar cell structures with differing sensitivity to bulk diffusion length have been shown to exhibit a similar extent of degradation, suggesting that bulk defects alone may not fully account for the degradation [3,12].

Continued exposure to conditions that induce degradation has been shown to lead to an eventual recovery of minority carrier lifetime, often termed 'regeneration' [4,13]. Under typical field conditions for a solar cell this could take several years. However, we have recently demonstrated that significant acceleration of the defect formation and subsequent recovery rate can be achieved with the use of elevated temperatures (140–320 °C) and very high irradiance illumination (44.2 kW/m^2) [11]. Similar approaches have previously been proven to be effective for accelerating reaction rates of other defects, such as the B-O complex [10,14]. The state of the system after this degradation/recovery process is significantly more stable than the initial state, strongly indicating that the process has led to passivation of the defect, with the resulting material being less susceptible to CID. In this work, we further investigate the effects of this passivation technique by firstly examining the variability of results across mc-Si material from different manufacturers and ingot positions. In addition, the effect of treatment time on mc-Si PERC cells is investigated in order to gauge the minimum time required for effective stabilisation.

2. Methods for inducing degradation

The gradual degradation of mc-Si based solar cells has typically been reported in the literature as being light-induced or, more recently, as light and elevated temperature induced. However, whilst incident photons are obviously present under typical operating conditions, it is in fact the *excess carriers* generated by the photons that induce the degradation effect. The distinction between light-induced and carrier-induced is important as the commonly used terminology of LID neglects that current can also be used to study these effects. Evidence that the degradation in mc-Si PERC cells is carrier-induced has previously been presented by Kersten et al. who show similar degradation for modules exposed to light or current injection [4]. The carrier-induced nature of the degradation is further supported by the differing rates of degradation that have been observed for cells under identical illumination conditions but operating in either V_{oc} or I_{sc} mode, with those operated at V_{oc} showing a significantly faster decline [4]. In this section we aim to verify these results at the cell level using mc-Si PERC solar cells from neighboring ingot positions in order to confirm that degradation induced by either current or light is directly equivalent.

2.1. Experimental methods

For this experiment, mc-Si PERC solar cells known to exhibit CID effects were sourced from an industrial manufacturer (*Manufacturer A*). Two cells from neighboring ingot positions (sister cells) were subjected to approximately equivalent degradation conditions using illumination or current injection. In both cases the cell was placed on a hotplate with the cell temperature maintained at 70 °C as confirmed by an IR thermometer. For the light soaking case, the cell was illuminated with 0.46 kW/m^2 of broadband light from a halogen source. For the current injection case, the cell was kept in the dark and connected in forward bias to a source measure unit (SMU) power supply operating in current control mode. In order to achieve similar carrier injection levels between the two experiments, the V_{oc} was measured in the illuminated case and the current of the SMU was adjusted to provide a matching voltage drop in the dark case. In both arrangements the cells were removed at regular intervals for Suns-V_{oc} (Sinton Instruments) measurements in order to track the degradation.

2.2. Results and discussion

The resulting change in V_{oc} for each cell with time is shown in Fig. 1. The two degradation curves show excellent agreement, verifying that the degradation effect is in fact carrier-induced and can be equally triggered by current or light.

Whilst light is logically the primary concern for solar cells, fundamentally it is the carriers generated by the incident photons that induce the degradation effect. Alternative methods for carrier injection are therefore applicable and should not be neglected as they may lead to new methods to study or alleviate the problem, as demonstrated by Hyundai's recent use of current injection to avoid destabilisation of the passivated B-O complex in Cz silicon solar cells during the lamination process [15].

3. Rapid passivation, variability and stability

Accelerated passivation of carrier-induced defects in *p*-type mc-Si has recently been demonstrated through the use of high intensity illumination and elevated temperatures [11]. It was shown that identically diffused and SiN_x passivated mc-Si wafers, sourced from three different manufacturers, exhibited significant variance in CID susceptibility when light-soaked for several hundred hours. However, in all cases, substantial passivation was achieved within 120 min at 140 °C, with the results showing

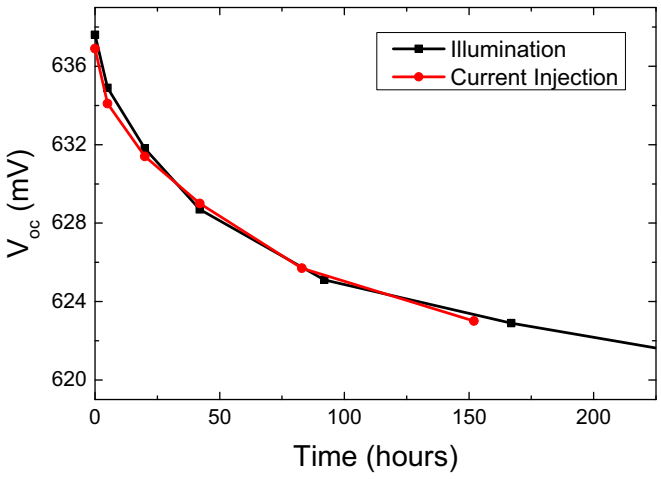

Fig. 1. Change in V_{oc} with time for sister mc-Si PERC cells subjected to equivalent carrier injection using light and current.

improved stability with a greatly reduced extent of degradation after a subsequent 100-h light soak. Increased temperatures were also shown to have the potential to speed up the required treatment time, however, higher temperatures were found to be less effective at mitigating the extent of subsequent degradation, and hence led to reduced stability. In the current work, these initial findings are expanded upon through investigation of industrial mc-Si PERC cells from two different manufacturers. Standard degradation tests were used to gauge the level of variability that can be expected across samples from different suppliers, as well as from wafers sourced from different ingot heights. A variety of rapid passivation treatments were tested on sister cells in order to examine the effects of treatment time and temperature on resulting stability.

3.1. Experimental methods

Industrially fabricated mc-Si 156 mm × 156 mm PERC solar cells were sourced from two different manufacturers, referred to here as *Manufacturer A* and *Manufacturer B*. In each case the as-received cells were laser cleaved into several 30 mm × 30 mm samples for ease of subsequent processing. Samples were then split into several groups in order to investigate material variability, rapid passivation and stability. Throughout the various sample treatments, Suns-V_{oc} (Sinton Instruments) measurements were carried out between crucial processing steps and at regular intervals throughout the degradation/passivation process in order to track the effects of CID. The individual groups are described below:

Group 1: Four samples from each manufacturer were selected to investigate variations in CID severity between suppliers. These sample sets were subjected to light soaking at 70 °C under halogen lamps with an incident irradiance of 0.46 kW/m^2. For cells from *Manufacturer A*, information on the wafer's position within the mc-Si ingot was not provided and samples were therefore selected at random. For cells from *Manufacturer B*, cells were available from both the top and bottom of the ingot and two cells from each position were therefore selected. Light soaking was carried out for a minimum of 225 h.

Group 2: To investigate the effect of a wafer's ingot position on CID severity, sister cells from *Manufacturer B* were selected to undergo laser treatment using a 938 nm diode laser with an incident irradiance of 44.8 kW/m^2 at a sample temperature of 140 °C. This process has previously been shown to accelerate defect formation and passivation to a timescale of minutes [11]. Processing was carried out for a cumulative duration of 120 min, the laser treated cells were then subjected to light soaking under the same conditions as Group 1 and compared to a group of sister cells light soaked with no prior treatment.

Group 3: In order to investigate the effects of treatment time and temperature on resulting stability, two sets of five sister cells were selected from *Manufacturer A*. One cell in each set was kept as a non-treated control sample, and the four other samples were subjected to a laser treatment with an irradiance of 44.8 kW/m^2 for different durations of 10 s, 30 s, 2 min and 8 min. Set 1 was processed at 200 °C whilst Set 2 was processed at 250 °C. All samples were then subjected to the light-soaking stability test as detailed for Group 1.

3.2. Results and discussion

3.2.1. Variability

Results from the Group 1 samples, exposed to elevated temperature light soaking with no prior treatment, showed significant reductions in V_{oc} due to CID. The range in overall extent of degradation for samples from each supplier is summarised in Table 1.

In this case a substantial difference in the overall degree of degradation was observed, with samples from *Manufacturer A* typically showing more than double the reduction in V_{oc} in comparison to samples from *Manufacturer B*. Whilst the two suppliers investigated here by no means provide the quantity of results required to statistically estimate the variance in CID across mc-Si PERC cells, the dramatic variation in CID susceptibility between these two test cases does highlight the considerable extent to which a combination of different source material and different cell processing can affect the severity of degradation in cell performance.

Fig. 2 shows the rapid defect formation and passivation of the laser treated Group 2 samples from *Manufacturer B* followed by a stability test carried out on the treated samples as well as untreated sister samples for controls.

The results of Fig. 2(a) shows a trend of increased degradation extent for cells produced with wafers from the bottom of the mc-Si ingot, with bottom cells degrading almost twice as much as cells from the top of the cast ingot. Interestingly, the bottom cells also appear to exhibit a faster and more complete recovery. For all treated samples the cells returned to within at least 0.5% of their initial V_{oc} values at completion of the 120-min process. Subsequent stability testing shown in Fig. 2(b) reveals that the treated cells were substantially more stable than the untreated controls with 225 h of light soaking resulting in an average V_{oc} reduction of 0.2% for the treated cells and 1.9% for the controls.

There are several potential sources for this observed correlation between CID susceptibility and ingot position. Metal impurities, which are typically present in the feedstock used for material growth, are known to concentrate towards the top of the ingot due to their low segregation coefficient. Conversely, oxygen is primarily sourced from the quartz crucible, leading to higher concentrations towards the bottom of the ingot. Whilst previous work has shown no strong correlation between oxygen concentration and the extent of CID, results published by Ramspeck et al. do indicate that there may be a link between oxygen concentration and the rate of degradation [1]. The results of Fig. 2(a) appear to support this and indicate that not only does the degradation, or defect formation rate increase with oxygen concentration, but so too does the regeneration, or defect passivation rate. However, further work is required to confirm this as other factors such as typical grain and dislocation cluster size also vary with ingot height and are likely to have an effect on results. Changes in grain characteristics could also be the cause for the reduced severity of degradation in top ingot wafers which typically consist of larger grains and subsequently a lower grain boundary density. Wafers from the top of the ingot are also known to have a higher doping concentration which has been shown to correlate with a reduced rate of degradation in the case of Cu contamination [7]. However, this could be caused by a reduced minority carrier lifetime that is typically associated with higher doping and a similar trend could therefore be expected for other carrier-induced defect sources.

3.2.2. Rapid passivation and stability

Stability test results for laser treated Group 3 sample sets 1 and 2, treated at temperatures of 200 °C and 250 °C, are shown in Figs. 3(a) and (b) respectively. At these temperatures, the increased reaction rates mean that separate degradation and regeneration

Table 1.
Typical degradation characteristics for mc-Si PERC cells from two different manufacturers.

Manufacturer	Reduction in V_{oc} (mV)	Reduction in V_{oc} ($\%_{Rel}$)
A	38–43	5.9–6.7
B	10–19	1.6–3.0

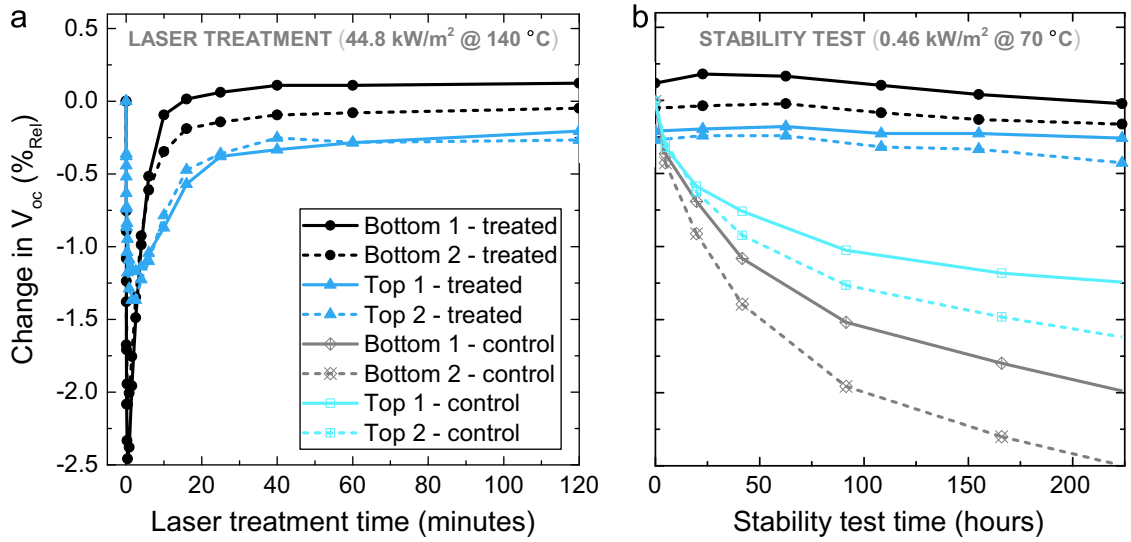

Fig. 2. Change in V_{oc} for mc-Si PERC cells from *Manufacturer B* sourced from top (blue) and bottom (black/grey) ingot positions undergoing accelerated defect formation and passivation (a) followed by stability testing for treated samples along with untreated controls (b). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article).

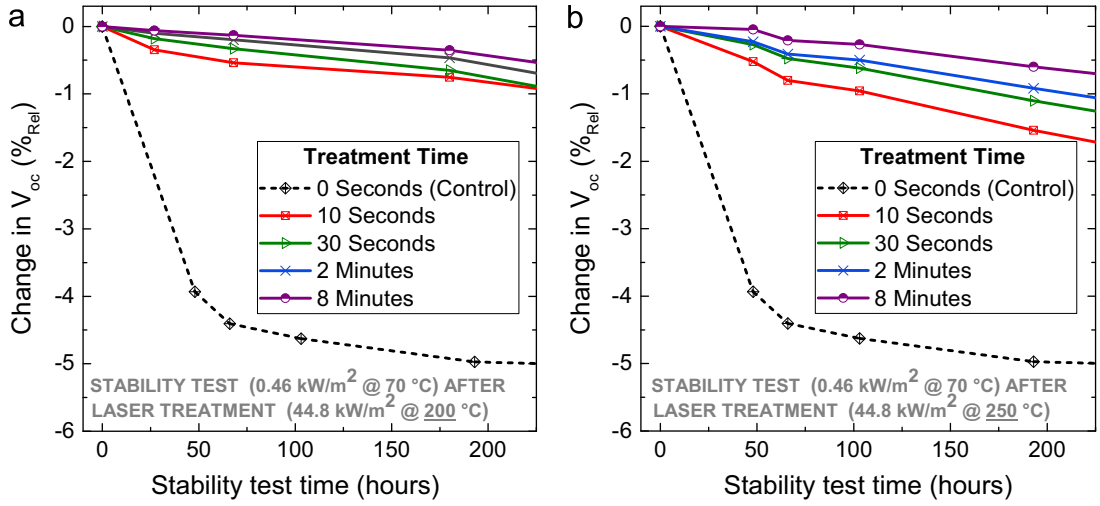

Fig. 3. Change in V_{oc} for mc-Si PERC cells sourced from *Manufacturer A* subjected to light soaking stability testing at 0.46 kW/m^2 and 70 °C for untreated samples (black dashed line) and samples treated for various durations with a treatment irradiance of 44.8 kW/m^2 at 200 °C (a) and 250 °C (b).

mechanisms cannot be clearly observed throughout treatment when using 10 s measurement intervals. The effectiveness of treatment can therefore not be determined by comparing initial and post-treatment V_{oc} values, which only show small variations of the order of single millivolts. Treatment efficacy must therefore be gauged by determining the resulting CID susceptibility, in this case presented as a change in V_{oc} relative to the post-treatment value plotted against time under illumination.

For all treatment conditions a dramatic increase in stability was observed in comparison to the untreated control sample with total CID effects after 225 h of light soaking reduced from 5% relative to less than 1% for samples treated at 200 °C (Fig. 3(a)) and less than 2% for those treated at 250 °C (Fig. 3(b)). A clear trend between increased treatment time and increased stability was also apparent with the largest differences shown in the 250 °C case. It could be expected that for equivalent treatment times, the 250 °C case would provide the best passivation treatment due to increased reaction rates at higher temperature. However, the stability results clearly show that this is not the case, indicating that under these conditions a partial destabilisation of the passivation and/or dissociation of defects may be occurring simultaneously. This could potentially be alleviated by increasing the rate of defect formation and subsequent passivation by using higher intensity illumination. With the current irradiance level of 44.8 kW/m^2, the 200 °C treatment has proven to be the most promising and showed a relatively low sensitivity to treatment time, with only a small change in stability between the 10 s and 8 min treatments. However, in all cases treated samples still showed a gradual decline due to CID suggesting that further treatment optimisation is likely required in order to achieve complete stability. It is also possible that several different defects are responsible for the overall degradation, with the current rapid passivation treatment only mitigating the most severe, faster forming defect.

4. Conclusions

The slow forming light-induced degradation effect increasingly reported for mc-Si solar cells has been confirmed to be equivalently activated by current injection and therefore can be more

accurately described as *carrier-induced degradation*. This effect was found in mc-Si PERC cells sourced from two different manufacturers with the extent of degradation in V_{oc} shown to vary dramatically between suppliers and across wafer ingot position. For samples where the ingot position was known, a stronger degradation and faster regeneration was determined for wafers from the bottom of the ingot, suggesting a dependence on non-uniformly distributed impurities, or potentially on grain boundary density.

Investigations into the accelerated mitigation of the CID effect through the use of elevated temperatures and high irradiance illumination revealed that substantial stabilisation can be achieved within an industrially relevant treatment time of just 10 s. At a treatment temperature of 200 °C the rapid, 10 s treatment was shown to reduce CID after 225 h of elevated light soaking by up to 80%, relative to an untreated control. Increasing treatment temperature from 200 °C to 250 °C resulted in a reduction in stability, whereas increasing treatment time led to a stability improvement. However, large increases in treatment duration were shown to result in a relatively small stability enhancement. Treated samples showed a significant reduction in CID susceptibility but in all cases, a gradual, ongoing degradation was still apparent. This suggests that further optimisation is required in order to achieve full passivation and complete, long-term resistance to CID.

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