

# Complete regeneration of BO-related defects in n-type upgraded metallurgical-grade Czochralski-grown silicon heterojunction solar cells

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Complete regeneration of boron-oxygen-related (BO) defects has been demonstrated on n-type upgraded metallurgical-grade (UMG) Czochralski-grown silicon heterojunction solar cells. Under accelerated regeneration conditions (93 suns, 220 °C),  $V_{OC}$  fully recovered in 30–100 s and remained stable during a subsequent stability test. Under milder regeneration conditions (3 suns, 180 °C), the kinetics were slowed down by more than an order of magnitude, but the recovery of  $V_{OC}$  was still complete and stable. The stabilized  $V_{OC}$  of the UMG cells is 709 mV–722 mV, similar to the electronic-grade control cells. We conclude that a significant amount of hydrogen, sourced from the a-Si:H films and possibly the hydrogen plasma treatment, has been introduced into the bulk during the solar cell fabrication processes or the regeneration step. This results in abundant hydrogen concentrations in the bulk of the cells for the purpose of regeneration of BO defects, whether the cell was pre-fired with silicon nitride films (600 °C for 5 s) or not. Published by AIP Publishing. <https://doi.org/10.1063/1.5042460>

The potential of low-cost n-type upgraded metallurgical-grade (UMG) Czochralski-grown (Cz) silicon materials for high-efficiency solar cells has been demonstrated recently, with efficiencies above 20% being reported.<sup>1–4</sup> A remaining disadvantage of this material, however, is the strong light-induced degradation caused by boron-oxygen-related (BO) defects, due to the simultaneous presence of boron and oxygen.<sup>5</sup> Recent results on p-type Cz silicon have demonstrated that BO defects can be eliminated completely by applying a regeneration process, which is the permanent deactivation of the defects happening under illumination at elevated temperatures, usually in the range of 100–300 °C.<sup>6–8</sup> However, the application of this process to compensated n-type silicon (n-Si) has shown more inconsistent results: Ref. 3 showed significantly incomplete regeneration in Passivated Emitter Rear Locally diffused (PERL) solar cells. Reference 9 proposed that the regeneration in n-Si is unstable at room temperature under illumination. Reference 10 achieved >90% completeness in samples with lighter net doping levels ( $\sim 10^{15} \text{ cm}^{-3}$ ); however, the completeness reduced to 51% and below in samples with net doping levels above  $10^{16} \text{ cm}^{-3}$ . Complete regeneration in such highly-doped n-type wafers was reported in Ref. 11, however, without any report on the long-term stability of the regenerated defects.

Hydrogenated amorphous silicon (a-Si:H) thin films are known to passivate crystalline silicon surfaces very well, leading to very high-efficiency silicon heterojunction (SHJ) solar cells,<sup>12–14</sup> with the current record efficiency being 26.6%.<sup>14</sup> The role of hydrogen in the regeneration of BO defects and how it interacts with the defect are debatable in the literature: hydrogen is found to be crucial for the

regeneration to occur in some studies,<sup>15–18</sup> while it is denied in other studies.<sup>19,20</sup> In spite of this, numerous studies have shown faster regeneration rates with a higher concentration of hydrogen ([H]) present.<sup>9,11,15–18,21</sup> Especially, in Ref. 21, the authors applied different firing parameters (peak temperature, peak temperature duration, and cooling rate) on  $\text{SiN}_x$ -passivated p-type wafers and investigated their effects on the regeneration kinetics. They were able to conclude that higher regeneration rates clearly correlated with higher [H] in the bulk introduced by the firing step. Thus, the hydrogen-rich a-Si:H films are also potentially beneficial for the regeneration of BO defects. In this work, we will test the regeneration of BO defects in n-type SHJ solar cells, by relying on hydrogen sourced from the a-Si:H films and possibly the hydrogen plasma treatment (which is further discussed in the following paragraph). We will also investigate the effect of a pre-firing step with silicon nitride films on the regeneration kinetics, which will indicate how the hydrogen concentration introduced by the firing step compares to that introduced by the a-Si:H films.

The UMG Cz ingot used in this work was supplied by Apollon Solar in the framework of the PHOTOSIL project.<sup>22</sup> The wafers were obtained from two positions in the ingot—middle and tail. The concentrations of boron and phosphorus ([B] and [P]) in the wafers were measured by secondary ion mass spectrometry (SIMS), as shown in Table I. The wafers were chemically etched and went through a Tabula Rasa step at 1000 °C for 0.5 h in oxygen to prevent the ring defects and then a phosphorus gettering process at 785 °C for 0.5 h to remove mobile impurities.<sup>23</sup> These pre-treatment steps have been shown to significantly improve the carrier lifetime to above 4 ms in this material.<sup>23</sup> After removing the diffused layers, Fourier transform infrared (FTIR) spectrophotometry measurements were conducted to determine the interstitial

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TABLE I. Materials, doping levels, and  $[O_i]$  of the wafers.

Wafers	[P] ( $\text{cm}^{-3}$ )	[B] ( $\text{cm}^{-3}$ )	Net doping $n_0$ ( $\text{cm}^{-3}$ )	$[O_i]$ ( $\text{cm}^{-3}$ )
UMG Cz middle	$1.2 \times 10^{16}$	$1.1 \times 10^{16}$	$1 \times 10^{15}$	$7-8 \times 10^{17}$
UMG Cz tail	$2.0 \times 10^{16}$	$1.3 \times 10^{16}$	$7 \times 10^{15}$	$6-7 \times 10^{17}$
EG Cz	$1.2 \times 10^{15}$	Negligible	$1.2 \times 10^{15}$	Not measured

oxygen concentrations, applying the same standard as reported in Ref. 23. The results are shown in Table I, with the ranges reflecting the non-uniformity of  $[O_i]$  on each wafer. Then, for half of the wafers from the middle and tail regions, a 80 nm thick plasma-enhanced chemical vapour deposited (PECVD) hydrogenated  $\text{SiN}_x$  film was deposited on both sides, in a Roth and Rau AK400 chamber. The sample temperature during the deposition was approximately 250 °C. A firing step at 600 °C for 5 s, with a 30 °C/s ramp up rate, and a 14 °C/s average cooling down rate, was then performed on the coated wafers, in a rapid thermal processor—these wafers are hereafter referred to as “pre-fired.” The processing parameters of the firing step were previously optimised for this  $\text{SiN}_x$  film, based on the hydrogenation effects of grain boundaries in multicrystalline wafers.<sup>24</sup> The pre-firing step did not significantly improve the lifetime of the wafers, mainly because the lifetime was not dominated by bulk recombination after the Tabula Rasa and phosphorus gettering steps.<sup>23</sup> The  $\text{SiN}_x$  films were then removed and SHJ solar cells were made on all of the wafers at Arizona State University. The a-Si:H thin films were deposited using an Applied Materials P-5000 multi-chamber PECVD tool, with a 30 s hydrogen plasma treatment after deposition of the intrinsic layers and prior to the deposition of the doped layers. The temperature for both the deposition and hydrogen plasma treatment was 250 °C. Reference 25 provides further details of the solar cell processes. Several SHJ solar cells with the same structure, but made from n-type electronic grade (EG) Cz materials, were also included in this study as control cells. The doping level of the EG Cz material was determined by four-point probe measurements (shown in Table I).

In the first test, the following processing sequence was performed on four UMG cells (pre-fired and non-fired cells from both the middle and tail regions) and a control cell:

**Test 1:** 1-sun degradation  $\rightarrow$  93-sun, 220 °C regeneration  $\rightarrow$  1-sun stability test.

The 1-sun illumination intensity was provided by a halogen lamp and was measured by a reference cell. The temperature of the cells was 40–45 °C, as monitored by a thermocouple. The regeneration process was conducted at UNSW using a 938 nm laser, with 57 kW/m<sup>2</sup> illumination intensity.<sup>26</sup> The photon flux was equivalent to 93 suns, based on the reference spectrum ASTM G173.<sup>27</sup> The regeneration process was conducted on a hotplate and the sample temperature was controlled at 220 °C.<sup>26</sup> During the degradation and regeneration, the open-circuit voltage ( $V_{OC}$ ) of the cells at 25 °C was measured using a Sinton Instruments FCT-450 Light-IV tester or a Suns- $V_{OC}$  system (*ex situ*). The  $V_{OC}$  degradation of all four UMG cells approximately saturated in 5–6 days. Accordingly, we fixed the time length of the stability test (1 sun, 40–45 °C) as 6 days for the remainder of this study.

The results of Test 1 are summarized in Fig. 1. The almost constant  $V_{OC}$  measured on the control cell confirms that the a-Si:H films were stable through these treatments. In contrast, a 50 mV drop in  $V_{OC}$  during the degradation is observed on all four UMG cells, due to the activation of the BO defects. The  $V_{OC}$  completely recovered during the subsequent regeneration step and remained stable during the stability test, indicating that the BO defects that caused the  $V_{OC}$  drop have been completely regenerated. The recovery of  $V_{OC}$  is much more stable than that reported in Refs. 3 and 9: both studies were performed on compensated n-Si and reported significant re-degradation of lifetime or  $V_{OC}$  during the stability test after regeneration. It is difficult to calculate the exact degree of completeness of the regeneration to compare with those reported in Ref. 10, mainly due to the relatively large uncertainties associated with extracting the relative concentration of BO defects from the  $V_{OC}$  data.<sup>28</sup> This is because the injection levels at which the  $V_{OC}$  was measured varied significantly throughout the degradation-regeneration cycle, while the recombination lifetime of the BO defects in n-Si is still injection-dependent.<sup>29,30</sup> Another reason is that if the carrier recombination rate at BO defects is reduced, other forms of recombination like surface recombination and Auger recombination in the heavily doped layers start to dominate the  $V_{OC}$  to the level of the control cells.

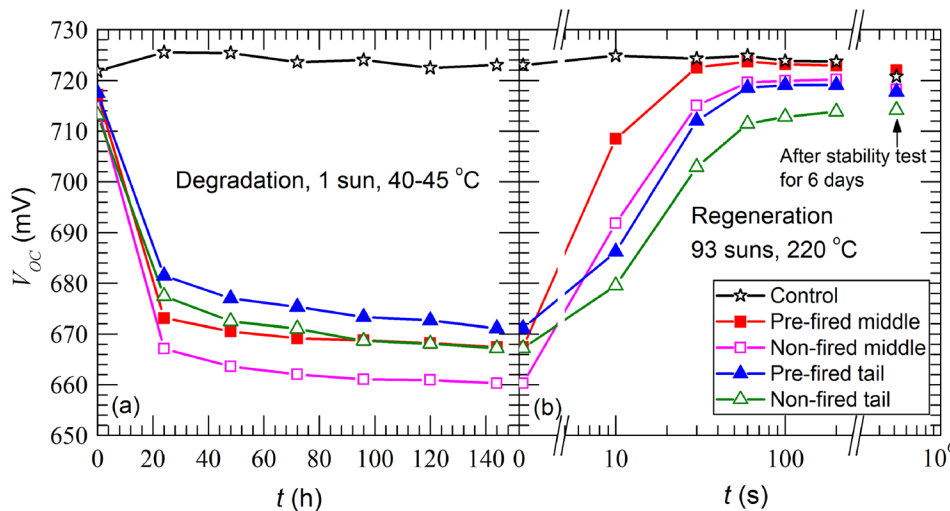


FIG. 1.  $V_{OC}$  as a function of time during (a) degradation, (b) regeneration, and after stability test (1 sun, 40–45 °C) for 6 days, measured on cells from Test 1.

In terms of the kinetics, the regeneration was completed in approximately 30–100 s in all four UMG cells, in very similar timescales. It is likely that a significant amount of hydrogen (comparable or even more than that introduced during the pre-firing) has been introduced into the bulk of the cells, during the solar cell fabrication processes, the degradation step and/or the regeneration process, resulting in comparable [H] in both the non-fired and pre-fired cells. We identify the following 3 possible hypotheses to explain our results:

**Hypothesis A:** A significant amount of hydrogen sourced from the a-Si:H films is introduced into the bulk during the degradation step.

**Hypothesis B:** The regeneration in Test 1 is too fast to reveal the effect of the firing step.

**Hypothesis C:** A significant amount of hydrogen, sourced from the a-Si:H films and possibly the hydrogen plasma treatment,<sup>31</sup> has been introduced into the bulk during the solar cell fabrication processes or the regeneration step.

To test Hypothesis A, we conducted a second test, where another 4 UMG cells (pre-fired and non-fired cells from both the middle and tail) and another control cell were subjected to the same regeneration conditions, but without degradation.

**Test 2:** 93-sun, 220 °C regeneration → 1-sun stability test.

The results of Test 2 are shown in Fig. 2. A larger  $V_{OC}$  variation is observed on the control cell than before. However, the changes in  $V_{OC}$  of the 4 UMG cells are much larger and are therefore attributed to the activation and regeneration of the BO defect. Again, the  $V_{OC}$  of the UMG cells completely recovered within 30 to 100 s and remained stable during the subsequent stability test. The time scales of the recovery of  $V_{OC}$  are still comparable for all four cells in Test 2 and are also comparable to Test 1. This indicates that without the degradation step, [H] in the pre-fired cells and the non-fired cells is still comparable. This contradicts Hypothesis A.

To test Hypothesis B, we conducted a third set of experiments, where we significantly slowed down the regeneration rate:

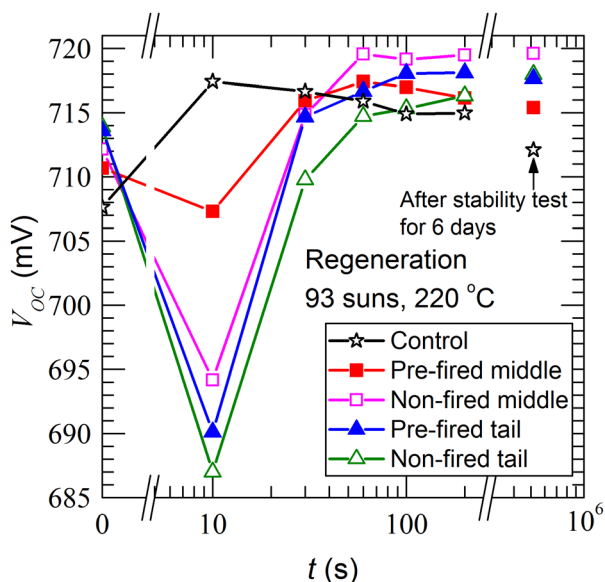


FIG. 2.  $V_{OC}$  as a function of time during regeneration and after stability test (1 sun, 40–45 °C) for 6 days, measured on cells from Test 2 without degradation.

**Test 3:** 1-sun degradation or no degradation → 3-sun, 180 °C regeneration → 1-sun stability test.

The 3-sun illumination intensity was provided by a halogen lamp and measured by a reference cell. Four middle UMG cells and a control cell were included: we degraded one pre-fired and one non-fired UMG cell and the control cell before regeneration (for 6 days), while subjected another pre-fired and one non-fired UMG cell directly to the regeneration step without degradation.

The results of Test 3—shown in Fig. 3—indicate that the regeneration was slowed down by more than an order of magnitude. The recovered  $V_{OC}$  was still approximately stable during the stability test, as shown in Fig. 3(b). After 100 s, the kinetics of the degraded cells and the non-degraded cells are very similar, again invalidating Hypothesis A.

For the two degraded cells in Test 3, we extracted the relative defect concentration  $N_t^*$  of the BO defects despite the aforementioned uncertainties, by first calculating  $\Delta n(t)$  from  $V_{OC} = (kT/q) \ln(np/n_i^2)$ .<sup>32</sup> We then calculated  $N_t^*(t) = C_I(1/\Delta n(t) - 1/\Delta n_{max})$ , where  $C_I$  is a constant and  $\Delta n_{max}$  is the maximum injection level (calculated from  $V_{OC}$ ) during the regeneration. This equation is valid under the assumption that the recombination lifetime of the BO defect is largely injection-independent. Then, we fitted  $N_t^*$  with the exponential relation  $N_t^*(t) = C_2 \exp(-t/\tau_{regen}) + C_3$ ,<sup>6</sup> to extract the regeneration time constant.  $C_2$  and  $C_3$  are constants. The fits are shown in Fig. 3. The regeneration time constants for the pre-fired cell and the non-fired cell are 360 s and 510 s, respectively, yielding a ratio of 1.4 for the regeneration rates. Applying the same method for calculating the regeneration rate to the four cells in Test 1, the ratios of the regeneration rates in the pre-fired/non-fired cells are 1.6 and 1.2 for the middle and tail cells, respectively. These values suggest that a significant amount of hydrogen is introduced during the solar cell processes and the regeneration, which counts against Hypotheses A and B, but supports Hypothesis C. The higher rates in the pre-fired cells also indicate that the firing of the SiN<sub>x</sub> films injects additional hydrogen into the devices.

In addition, in Ref. 3, a UMG PERL cell with a similar substrate material went through the same regeneration step and the stability test as the cells in Test 3. The PERL cell was not fired, but had a SiN<sub>x</sub> film present, and was degraded under 1-sun illumination before regeneration.<sup>3</sup> Unlike in the SHJ cells, significant incompleteness was observed on the PERL cell, which may be attributed to the lower injection level or [H] in it, based on the theoretical model discussed in Refs. 11, 26, 33, and 34.

In conclusion, we have demonstrated the application of the BO defect curing process in n-type UMG Cz SHJ solar cells. Under 93 suns at 220 °C, the  $V_{OC}$  fully recovered in 30–100 s, and remained stable during a subsequent stability test, in both pre-fired and non-fired, middle and tail cells, whether degraded or not. This indicates a fast and complete regeneration of BO defects in compensated n-Si SHJ cells. Combined with the experiments conducted under 3 suns at 180 °C, we have concluded that a significant amount of hydrogen, sourced from the a-Si:H films and possibly the hydrogen plasma treatment, has been introduced into the bulk during the solar cell fabrication processes or the



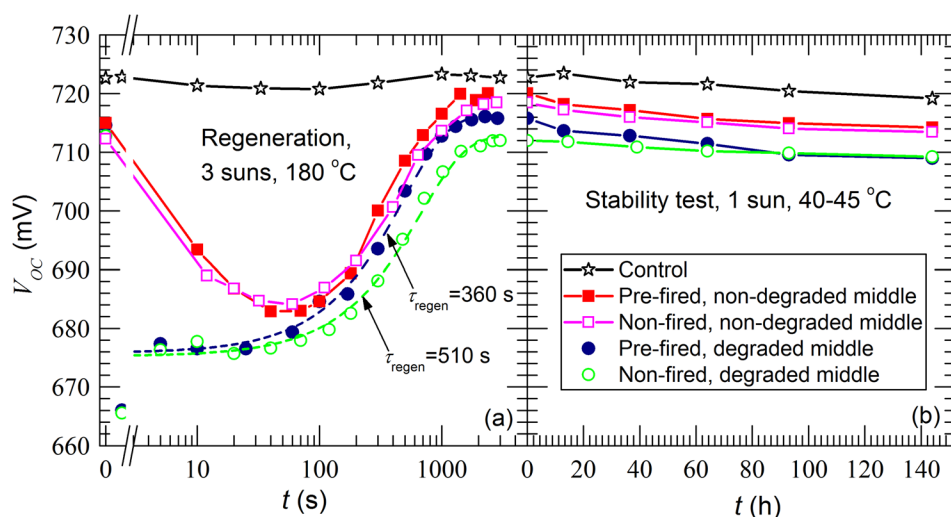


FIG. 3.  $V_{OC}$  as a function of time during (a) regeneration and (b) stability test, measured on cells from Test 3. In (a), the data points to the left of the axis break were measured after degradation on the degraded cells.

regeneration step. To further confirm the conclusions, techniques to directly measure the hydrogen concentration in the bulk are under development. In addition, the ability of this a-Si:H film (possibly in combination with the hydrogen plasma treatment) to inject abundant hydrogen throughout the silicon bulk at below 250 °C is potentially very meaningful for bulk hydrogenation in defect-rich silicon materials. How hydrogen interacts with BO defects cannot be answered by the results of this study. Further studies are required to shed more light upon this question.

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<sup>1</sup>R. Einhaus, J. Kraiem, J. Degoulange, O. Nichiporuk, M. Forster, P. Papet, Y. Andrault, D. Grosset-Bourbange, and F. Cocco, "19% efficiency heterojunction solar cells on Cz wafers from non-blended upgraded metallurgical silicon," in *Proceeding of the 38th IEEE Photovoltaic Specialists Conference (PVSC)* (2012), pp. 003234–003237.

<sup>2</sup>Y. Schiele, S. Wilking, F. Book, T. Wiedenmann, and G. Hahn, *Energy Procedia* **38**, 459 (2013).

<sup>3</sup>P. Zheng, F. Rougieux, C. Samundsett, X. Yang, Y. Wan, J. Degoulange, R. Einhaus, P. Rivat, and D. Macdonald, *Appl. Phys. Lett.* **108**, 122103 (2016).

<sup>4</sup>P. Zheng, F. E. Rougieux, X. Zhang, J. Degoulange, R. Einhaus, P. Rivat, and D. H. Macdonald, *IEEE J. Photovoltaics* **7**, 58 (2017).

<sup>5</sup>T. Schutz-Kuchly, J. Veirman, S. Dubois, and D. Heslinga, *Appl. Phys. Lett.* **96**, 093505 (2010).

<sup>6</sup>A. Herguth, G. Schubert, M. Käs, and G. Hahn, *Prog. Photovoltaics: Res. Appl.* **16**, 135 (2008).

<sup>7</sup>G. Hahn, S. Wilking, and A. Herguth, "BO-related defects: Overcoming bulk lifetime degradation in crystalline Si by regeneration," *Solid State Phenom.* **242**, 80–89 (2015).

<sup>8</sup>B. Hallam, A. Herguth, P. Hamer, N. Nampalli, S. Wilking, M. Abbott, S. Wenham, and G. Hahn, *Appl. Sci.* **8**, 10 (2017).

<sup>9</sup>B. Lim, "Boron-oxygen-related recombination centers in crystalline silicon and the effects of dopant-compensation," Ph.D. thesis, University of Hannover, 2012.

<sup>10</sup>T. Niewelt, J. Broisch, J. Schön, J. Haunschild, S. Rein, W. Warta, and M. C. Schubert, *Energy Procedia* **77**, 626 (2015).

<sup>11</sup>S. Wilking, M. Forster, A. Herguth, and G. Hahn, *Sol. Energy Mater. Sol. Cells* **142**, 87 (2015).

<sup>12</sup>M. Taguchi, A. Yano, S. Tohoda, K. Matsuyama, Y. Nakamura, T. Nishiwaki, K. Fujita, and E. Maruyama, *IEEE J. Photovoltaics* **4**, 96 (2014).

<sup>13</sup>K. Masuko, M. Shigematsu, T. Hashiguchi, D. Fujishima, M. Kai, N. Yoshimura, T. Yamaguchi, Y. Ichihashi, T. Mishima, and N. Matsubara, *IEEE J. Photovoltaics* **4**, 1433 (2014).

<sup>14</sup>K. Yoshikawa, W. Yoshida, T. Irie, H. Kawasaki, K. Konishi, H. Ishibashi, T. Asatani, D. Adachi, M. Kanematsu, and H. Uzu, *Sol. Energy Mater. Sol. Cells* **173**, 37 (2017).

<sup>15</sup>K. Münzer, "Hydrogenated silicon nitride for regeneration of light induced degradation," in *Proceedings of the 24th European Photovoltaic Solar Energy Conference* (2009), pp. 1558–1561.

<sup>16</sup>G. Krugel, W. Wolke, J. Geilker, S. Rein, and R. Preu, *Energy Procedia* **8**, 47 (2011).

<sup>17</sup>S. Wilking, A. Herguth, and G. Hahn, *J. Appl. Phys.* **113**, 194503 (2013).

<sup>18</sup>N. Nampalli, B. Hallam, C. Chan, M. Abbott, and S. Wenham, *Appl. Phys. Lett.* **106**, 173501 (2015).

<sup>19</sup>D. Walter, B. Lim, K. Bothe, V. Voronkov, R. Falster, and J. Schmidt, *Appl. Phys. Lett.* **104**, 042111 (2014).

<sup>20</sup>D. C. Walter and J. Schmidt, *Sol. Energy Mater. Sol. Cells* **158**, 91 (2016).

<sup>21</sup>S. Wilking, S. Ebert, A. Herguth, and G. Hahn, *J. Appl. Phys.* **114**, 194512 (2013).

<sup>22</sup>J. Kraiem, B. Drevet, F. Cocco, N. Enjalbert, S. Dubois, D. Camel, D. Grosset-Bourbange, D. Pelletier, T. Margaria, and R. Einhaus, in *High Performance Solar Cells Made from 100% UMG Silicon Obtained via the PHOTOSIL Process* (2010, IEEE), p. 001427.

<sup>23</sup>R. Basnet, F. E. Rougieux, C. Sun, S. P. Phang, C. Samundsett, R. Einhaus, J. Degoulange, and D. Macdonald, *IEEE J. Photovoltaics* **1**, 990 (2018).

<sup>24</sup>H. C. Sio, "Hydrogenation of high performance multicrystalline silicon," (to be published).

<sup>25</sup>B. Hallam, D. Chen, J. Shi, R. Einhaus, Z. C. Holman, and S. Wenham, *Sol. RRL* **2**, 1700221 (2018).

<sup>26</sup>B. J. Hallam, M. D. Abbott, N. Nampalli, P. G. Hamer, and S. R. Wenham, *IEEE J. Photovoltaics* **6**, 92 (2016).

<sup>27</sup>A. Herguth, *Energy Procedia* **124**, 53 (2017).

<sup>28</sup>K. Bothe and J. Schmidt, *J. Appl. Phys.* **99**, 013701 (2006).

<sup>29</sup>F. Rougieux, M. Forster, D. Macdonald, A. Cuevas, B. Lim, and J. Schmidt, *IEEE J. Photovoltaics* **1**, 54 (2011).

<sup>30</sup>T. Niewelt, J. Schön, J. Broisch, S. Mägdefessel, W. Warta, and M. C. Schubert, *Energy Procedia* **92**, 170 (2016).

<sup>31</sup>A. Descouedres, L. Barraud, S. De Wolf, B. Strahm, D. Lachenal, C. Guérin, Z. Holman, F. Zicarelli, B. Demareux, and J. Seif, *Appl. Phys. Lett.* **99**, 123506 (2011).

<sup>32</sup>R. A. Sinton, A. Cuevas, and M. Stuckings, in *Conference Record of the Twenty Fifth IEEE Photovoltaic Specialists Conference* (IEEE, 1996), p. 457.

<sup>33</sup>A. Herguth and G. Hahn, *J. Appl. Phys.* **108**, 114509 (2010).

<sup>34</sup>B. Hallam, M. Abbott, J. Bilbao, P. Hamer, N. Gorman, M. Kim, D. Chen, K. Hammerton, D. Payne, and C. Chan, *Energy Procedia* **92**, 42 (2016).