Mitigating Light and Elevated Temperature Induced Degradation in Multicrystalline Silicon Wafers and PERC Solar Cells Using Phosphorus Diffusion Gettering

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Reducing light and elevated temperature induced degradation (LeTID) is important for the industrial success of PERC (passivated emitter and rear cell) solar cells fabricated on high-performance multicrystalline silicon (multi-Si) wafers. Although there has been a lot of progress in understanding the degradation kinetics, the defect(s) responsible for LeTID in multi-Si wafers at elevated temperatures (≈80 °C, 1 Sun) has yet to be identified. In this study, we look at the possibility of using phosphorus diffusion gettering (PDG) for reducing LeTID in multi-Si wafers and solar cells. By measuring light induced defect concentrations in multi-Si wafers before and after LeTID, we observe that PDG can substantially reduce the average defect concentration. Trace element analysis using inductively coupled plasma mass spectrometry reveals that multi-Si wafers from the edge of the ingot contain a high concentration of Cu, Ni and Ti in grains that degrade more than neighboring grains. To explore PDG for reducing LeTID in multi-Si PERC solar cells, we fabricate cells with two different emitter profiles. Etching back a heavily diffused emitter to obtain a high sheet resistance is observed to improve the LeTID performance of the solar cells, an effect that is very likely related to a reduced impurity concentration within the wafer.

1. Introduction

Multicrystalline silicon (multi-Si) grown by directional solidification continues to be the most commonly used substrate for industrially produced silicon solar cells.[1] Conventional solar cells were typically made with the aluminium back surface field (Al-BSF) structure.[2] In recent years, the promise of higher efficiency has driven the industry to adopt the PERC (passivated emitter and rear cell) architecture that was first demonstrated by Blakers et al. in 1989.[3] The localized rear contact in a PERC cell makes it operate at a higher injection level as compared to an Al-BSF cell under the same illumination condition,[3] but it suffers from higher degradation at elevated temperatures (≈75 °C). Since degradation depends primarily on the bulk minority carrier density, it has been referred to in the recent literature as light and elevated temperature induced degradation (LeTID) or carrier induced degradation (CID).[4,5]

Light induced degradation at room temperature in Czochralski (Cz) monocrystalline Si cells have been attributed to the boron-oxygen (B-O) and iron-boron (Fe_i-B) defects.[6] However, at an elevated temperature (≈75 °C) and 1 Sun intensity, Ramspeck et al. reported in 2012 a strong degradation of multi-Si PERC cells which could not be explained by the existing defect models.[4] This was the first report of this phenomenon, which received a lot of research interest in the coming years. LeTID was recently also reported for mono-Si PERC cells.[7] The significant degradation was a barrier for the success of multi-Si PERC cells. Kersten et al. reported a significant (10%) decrease in V_{oc} after 150 h of light exposure at an elevated temperature of 50–90 °C.[8] They also showed that the degradation is accelerated by higher temperatures, suggesting that the degradation rate could be injection level dependent. The extent of degradation was also found to vary with the wafer's ingot height, and can be as high as 14% for certain wafers.[9] Although the degradation has been reported to be a bulk phenomenon that depends on wafer characteristics,[8] some reports have distinguished between the bulk and surface components.[10] The process parameters during the surface passivation step can influence the degradation characteristics.[11] However, since the influence of the bulk is predominant,[12] in the present study the contribution of the surface passivation layer to the degradation process will not be investigated.

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Injection dependent lifetime spectroscopy (IDLS),[13] temperature and injection dependent lifetime spectroscopy (TIDLS)[5] and light beam induced current (LBIC)[14] measurements have been used to investigate the degradation mechanism in multi-Si. Nakayashiki et al. observed uniform degradation across the multi-Si wafers and suggested the possibility of Ti, W and Mo impurity atoms being involved in the defect complex.[13] Vargas et al. showed that the recombination parameters for the defect were like those for interstitial Ti and Mo.[5] Using solar cells fabricated from industrially produced multi-Si wafers, Luka et al. observed Cu precipitates in regions which experienced more degradation.[14] The search for the actual defect continues, and it is possible that a combination of defects may be involved.[6]

Reduction of LID in solar cells fabricated from Cz-Si can be achieved through hydrogen passivation,[15] impurity gettering,[16] and/or dark annealing.[17,18] Multicrystalline silicon usually has a higher concentration of transition metal impurities, and limited success has been achieved in reducing the extent of degradation. Bredemeier et al. observed that annealing cells at a high temperature leads to regeneration.[18] Padmanabhan et al. reported that PERC cells fabricated with a heavily doped emitter that was then etched back to a higher sheet resistance show less degradation.[19] The beneficial role of phosphorus diffusion gettering (PDG) in reducing lifetime degradation in passivated high-performance multi-Si wafers was investigated by Zuschlag et al. in ref. [20]. The firing temperature seems to play an important role in activating the defect that causes LeTID in multi-Si. A defect model based on the dissolution of metal precipitates at a high firing temperature was proposed in ref. [18]. Wafers fired at a lower peak temperature and under a gradual temperature gradient experienced less LeTID.[13,21]

Although the PV industry has succeeded in reducing the degradation extent in multi-Si cells by optimizing the firing profile of the screen-print metallisation process,[13] there is an opportunity to improve the degradation performance by exploring the role of phosphorus diffusion gettering on PERC cells made from industrially produced high-performance multi-Si wafers. Also, there is a need to investigate the impurity distribution in multi-Si wafers and explore if there is a possible link between the impurity concentration in different regions and the extent of degradation. In this study, inductively coupled plasma mass spectrometry (ICP-MS) is used to determine impurity concentrations in multi-Si wafers before and after phosphorus diffusion gettering (PDG). In Section 2, the results of an experiment to confirm the successful reduction of light induced defects (excluding Fe_i concentration) after PDG are discussed. In Section 3, a method for improving the LeTID performance using the so-called SERIS etch[22] is discussed.

2. Experiment Details and Results

2.1. Measuring Light Induced Defect Concentration in Multi-Si Lifetime Samples

Boron-doped high-performance multi-Si wafers ($156 \times 156\,mm^2$, 170 µm, 1 Ω cm) were processed by removing the saw damage by a saw damage etch (SDE) in a KOH bath (78 °C), followed by RCA-1 and RCA-2 cleaning and a 1% hydrofluoric acid (HF) dip. Phosphorus diffusion was carried out with a Tempress Quantum HD $POCl_3$ tube diffusion furnace at 840 °C to arrive at a sheet resistance of $50\,\Omega\,square^{-1}$. After etching off the phosphosilicate glass (PSG) and the diffused layer, the samples were passivated by depositing a 5 nm AlO_x layer using a SoLayTec atomic layer deposition (ALD) system followed by annealing for 20 min in a Protherm furnace. Surface photovoltage (SPV) diffusion length measurements were used to map the interstitial iron (Fe_i) equivalent light induced defect concentration.[23] The process involves three diffusion length measurements: the first step is to deactivate the BO_i by annealing the sample in the dark at 200 °C for 3 min followed by the deactivation of the Fe_i at 85 °C for 5 min; the second measurement involves selective activation of the BO_i defects by light exposure at 120 °C (accelerated light induced degradation, ALID) for 10 min, followed by deactivation of the Fe_i at 85 °C for 5 min; the third step involves Fe_i activation by exposing the wafer to repeated flashes of light at room temperature.[23,24] This metric includes all defects that are activated during the degradation process. It does not isolate the nature of the defect that causes LeTID in multi-Si wafers, but its magnitude indicates the extent of defect generation in different regions of the wafer. To get a better perspective on how PDG affects the degradation process, SPV measurements were repeated after an extended degradation for 24 h in a light soaking chamber at elevated temperature (1 Sun, 75 °C). **Figure 1** shows that the light induced defect concentration measured for the control and gettered sample (sister samples from the same ingot) differ by 21% after ALID. This difference increases to 83% after extended LeTID at an elevated temperature (75 °C, 1 Sun, 24 h), which suggests that impurity gettering significantly improves the degradation performance of the wafer. The significantly high standard deviation is representative of the inhomogeneous degradation in multi-Si grains.[25]

To investigate the impurity distribution in regions of the wafer that degrade to different extents, samples were extracted from the edge (region A in **Figure 2**(a)) and centre (region B in Figure 2(a)) of a wafer that came from the ingot edge. Edge

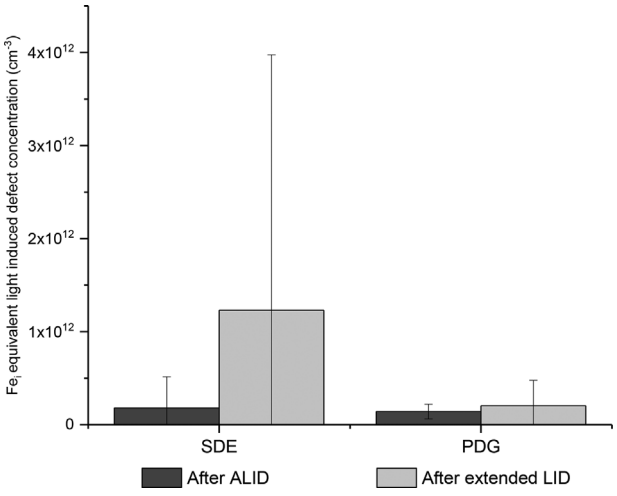

Figure 1. Fe_i equivalent light induced defect concentration (averaged over wafer area) before and after phosphorus gettering. The detection limit is $10^8\,cm^{-3}$ for Fe_i.

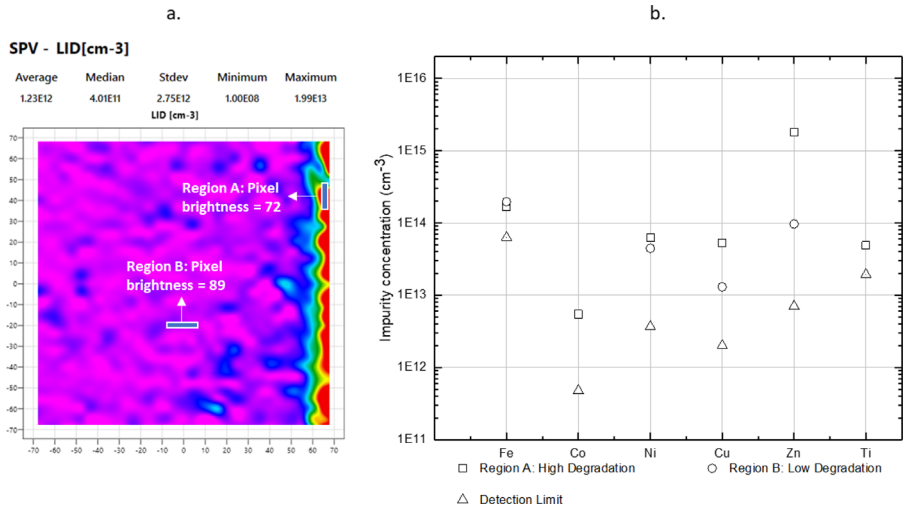

Figure 2. a) Light induced defect concentration map of a passivated lifetime sample from the edge of the ingot after 24 h degradation (at 75 °C, 1 Sun); (b) Trace element analysis for two regions of a high-performance multi-Si wafer from the edge of the ingot. The average concentration of light induced defects in region A is 60% higher than in region B.

wafers contain a higher concentration of impurities from the crucible. Light induced defects are more concentrated in region A, and this is reflected by the 24% lower pixel brightness compared to region B. The trace element analysis results in Figure 2(b) show that Ni, Cu, and Ti are some of the elements present at a higher concentration in region A. This does not prove that the difference in concentration causes the aggravation of degradation characteristics, although it shows that light induced defects are more concentrated in regions containing more of these transition metals.

2.2. Step Toward Mitigating LeTID in Multi-Si PERC Cells

There has been considerable interest in developing processes for reducing LeTID in multi-Si PERC cells. To explore the application of phosphorus gettering to a production ready solar cell manufacturing process, multi-Si PERC cells were fabricated with two emitter types on high-performance multi-Si wafers ($156 \times 156\,mm^2$, 170 µm, 1 Ω cm). The first cell type (A) had an emitter diffused to 90 Ω square^{-1}. The second cell type (B) was fabricated from a wafer diffused to 50 Ω square^{-1} and then etched back to 90 Ω square^{-1} using the SERIS etch.[22] This process partially removes impurities gettered in the diffused layer of the wafer. After metallization, the cells were fired at 740 °C in a belt furnace. Except the emitter fabrication, all other processing steps for cells A and B were identical. The V_{oc}, I_{sc} and efficiency of cells A and B are 630 mV, 37.03 mA cm^{-2}, 18.36% and 630 mV, 37.03 mA cm^{-2}, 18.13%, respectively. The performance parameters are quite similar for both cells.

After fabrication, the cells were degraded for 152 h at 1 Sun intensity and 80 °C in a light soaking chamber. **Figure 3** depicts the photoluminescence (PL) image (model R2 from BTI) taken from the central regions of cells A and B at different stages of the degradation process. While there is a 34% decrease in the average number of PL counts (limited to the central part of the PL image) for cell B, counts from cell A decrease by 43% during the same period. PL counts are representative of the electronic quality of the solar cell, and the higher degradation for cell A suggests that it experiences more LeTID than cell B. The inhomogeneity of PL counts in the samples after degradation has been reported earlier.[25]

Since the hypothesis for this difference in degradation rates is related to impurity gettering during the etch-back process, trace element analysis was performed by selecting a 1-cm^2 region from the base wafers of the two cells. **Figure 4** shows that the base wafer for cell B has a lower concentration of Ti, Cr, Mn, Fe, Cu, and Mo. Ni is slightly higher in the wafer for cell B, while the Cr concentration is almost the same. In the literature, Ti and Cu have been associated with the degradation process,[13,14] and our experiment confirms that a difference in concentration exists in wafers that degrade to different extents. The wafers used for cells A and B were from the centre of the ingot, while the samples used in Section 2 were from the ingot edge. Since impurity concentrations depend on the position of the ingot from which the wafer was cut, the concentrations presented in Figure 4 are slightly dissimilar to the samples discussed in Section 2.1.

The cell performances under 1-Sun illumination were measured using a LED-based *I–V* tester (Wavelabs, model Sinus-220) under standard test conditions (STC; 25 °C cell temperature, 1000 W m^{-2}, AM1.5 global). **Figure 5** summarizes the performance characteristics due to degradation at 1 Sun and 80 °C in a light soaking chamber. After 152 h of LeTID, the decrease in V_{oc} is about 1% for cell A and 0.5% for cell B. This is a significant improvement for cell B, especially since there is only one additional process step when compared to the conventional process of cell manufacturing.

3. Discussion

LeTID in multi-Si wafers needs to be understood and addressed to improve the economic viability of the multi-Si PERC cell. Unlike Cz-Si, the degradation phenomenon cannot be explained by either

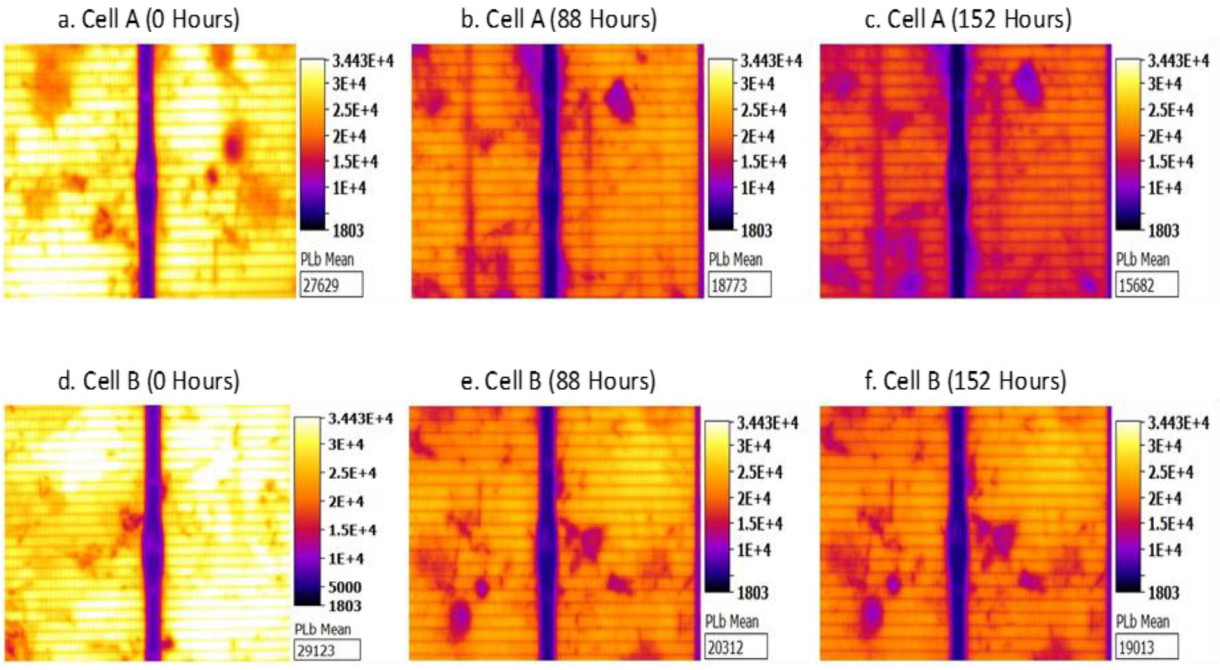

Figure 3. Central section of the PL map captured in the quasi-steady-state mode (large-area illumination, 2 Suns, 0.05 s pulse time) for cell A (a–c) and cell B (d–f) during the degradation process.

the Fe_i-B or the B-O defect kinetics. Recent studies have suggested the possibility of transition metal defect complexes being involved, based on experiments involving lifetime spectroscopy[13] and intentional contamination with a metal impurity.[14] The observation of denuded zones during spatial analysis of defect kinetics in samples fired at different temperatures also suggest the involvement of metallic precipitates.[26] While these methods can be insightful, there was a need to investigate the effects of metallic impurities present in industrially manufactured multi-Si wafers on the degradation characteristics. The experiments in the present work aim to further the understanding of LeTID defect characteristics in multi-Si. The first experiment involved isolating the effect of Fe_i-B pairs using SPV. Measuring a significantly lower light induced defect concentration after PDG showed that there is a possibility that the defect(s) responsible for LeTID at elevated temperature (≈80 °C) can be gettered effectively. It may be conjectured that the thermal processing steps that the wafer undergoes during PDG are responsible for the better degradation performance, rather than the gettering process itself. However, this possibility was addressed by measuring the reduction in transition metal impurities after gettering, thereby suggesting that there could be a correlation between the impurity concentration

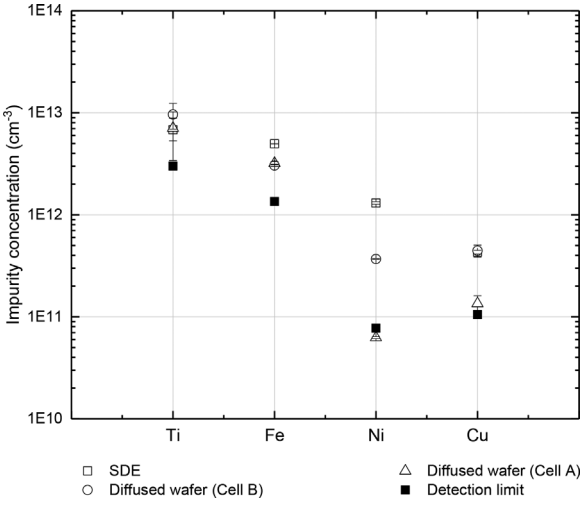

Figure 4. Trace element analysis for impurity measurements in the base wafers (after diffusion) used for fabricating cells A and B.

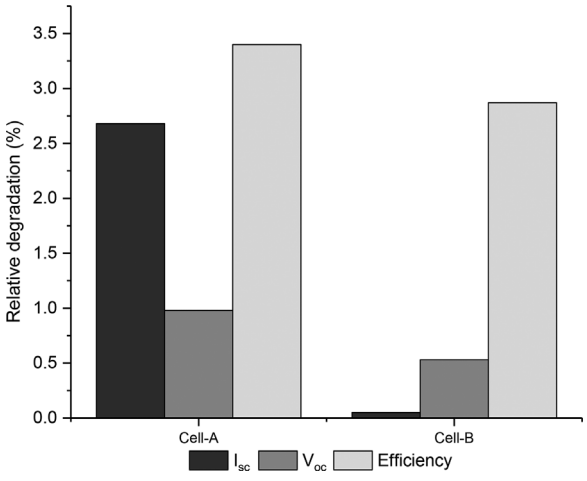

Figure 5. Relative degradation of the 1-Sun electrical parameters of cells A and B due to LID (80 °C, 1 Sun) after 152 h.

and degradation performance. Our next attempt was to identify the difference in the nature and concentration of impurities present in different parts of an edge wafer. The results showed that light induced defects are more concentrated in regions containing a higher concentration of transition metal impurities. In the last experiment, we introduced a method to improve the LeTID performance (at 80 °C, 1 Sun) using an etch-back step during the emitter fabrication process. Trace element analysis performed on two samples with different degradation characteristics further support our hypothesis. Since none of the wafers was intentionally contaminated, and all processes were like those in a standard PV cell production line, these experiments could be an important step towards developing an industrially relevant LeTID mitigation process (at 80 °C, 1 Sun) for multi-Si solar cells.

4. Conclusion

Transition metal impurities affect the carrier lifetime and aggravate the light induced degradation performance of multi-Si wafers and solar cells. By measuring impurity concentrations in two regions of the same multi-Si wafer, we observed that the region with larger LeTID has a higher concentration of Cu, Ni, and Ti. To demonstrate the possibility of reducing the extent of degradation using phosphorus diffusion gettering (PDG), light induced defect concentrations were measured before and after extended degradation. For a particular sample, it was found that wafers subjected to PDG have 83% lower concentration of light induced defects when compared to samples that did not undergo phosphorus diffusion. To use PDG for improving multi-Si PERC cell degradation performance, we fabricated two cells that underwent different diffusion steps. While characterizing the cell performance using PL imaging and *I*–*V* tests, we noted that using an etch-back step on a heavily diffused emitter to achieve a high sheet resistance removes certain transition metal impurities, which could be the reason for the better cell performance after LeTID conducted over 152 h.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords

emitter etch-back, light-induced degradation, multicrystalline silicon, phosphorus diffusion gettering

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[1] Fraunhofer Institute, *Photovoltaics Report* (**2017**).
[2] J. Mandelkorn, J. H. Lamneck, *J. Appl. Phys.* **1973**, *44*, 4785.
[3] A. W. Blakers, A. Wang, A. M. Milne, J. Zhao, M. A. Green, *Appl. Phys. Lett.* **1989**, *55*, 1363.
[4] A.S. K. Ramspeck, S. Zimmermann, H. Nagel, A. Metz, Y. Gassenbauer, B. Birkmann, in *Proc. 27th European Photovolt. Sol. Energy Conf.* (**2012**) pp. 861–865.
[5] C. Vargas, Y. Zhu, G. Coletti, C. Chan, D. Payne, M. Jensen, Z. Hameiri, *Appl. Phys. Lett.* **2017**, *110*, 92106.
[6] J. Lindroos, H. Savin, *Sol. Energy Mater. Sol. Cells* **2016**, *147*, 115.
[7] F. Fertig, R. Lantzsch, A. Mohr, M. Schaper, M. Bartzsch, D. Wissen, F. Kersten, A. Mette, S. Peters, A. Eidner, J. Cieslak, K. Duncker, M. Junghänel, E. Jarzembowski, M. Kauert, B. Faulwetter-Quandt, D. Meißner, B. Reiche, S. Geißler, S. Hörnlein, C. Klenke, L. Niebergall, A. Schönmann, A. Weihrauch, F. Stenzel, A. Hofmann, T. Rudolph, A. Schwabedissen, M. Gundermann, M. Fischer, J. W. Müller, D. J. W. Jeong, *Energy Procedia* **2017**, *124*, 338.
[8] F. Kersten, P. Engelhart, H.-C. Ploigt, A. Stekolnikov, T. Lindner, F. Stenzel, M. Bartzsch, A. Szpeth, K. Petter, J. Heitmann, J. W. Müller, *Sol. Energy Mater. Sol. Cells* **2015**, *142*, 83.
[9] K. Petter, K. Hubener, F. Kersten, M. Bartzsch, F. Fertig, B. Kloter, J. Muller, in *9th Int. Work. Cryst. Silicon Sol. Cells* (**2016**) pp. 1–17.
[10] K. Krauss, F. Fertig, D. Menzel, S. Rein, *Energy Procedia* **2015**, *77*, 599.
[11] Z. R. Chowdhury, N. P. Kherani, *Appl. Phys. Lett.* **2015**, *107*.
[12] B. Sopori, P. Basnyat, S. Devayajanam, S. Shet, V. Mehta, J. Binns, J. Appel, *Conf. Rec. IEEE Photovolt. Spec. Conf.* **2012**, pp. 1115–1120.
[13] K. Nakayashiki, J. Hofstetter, A. E. Morishige, T. T. A. Li, D. B. Needleman, M. A. Jensen, T. Buonassisi, *IEEE J. Photovoltaics* **2016**, *6*, 860.
[14] T. Luka, M. Turek, S. Großer, C. Hagendorf, *Phys. Status Solidi – Rapid Res. Lett.* **2017**, *11*, 1.
[15] L. Song, A. Wenham, S. Wang, P. Hamer, M. S. Ahmmed, B. Hallam, L. Mai, M. Abbott, E. R. Hawkes, C. Chong, S. Wenham, *Int. J. Photoenergy* **2015**, *2015*, 193892.
[16] L. J. Caballero, C. Del Cañizo, P. Sánchez-Friera, A. Luque, *Sol. Energy Mater. Sol. Cells* **2005**, *88*, 247.
[17] C. Chan, T. H. Fung, M. Abbott, D. Payne, A. Wenham, B. Hallam, R. Chen, S. Wenham, *Sol. RRL* **2017**, *1*, 1600028.
[18] D. Bredemeier, D. Walter, S. Herlufsen, J. Schmidt, *AIP Adv.* **2016**, *6*, 035119.
[19] M. Padmanabhan, K. Jhaveri, R. Sharma, P. K. Basu, S. Raj, J. Wong, J. Li, *Phys. Status Solidi – Rapid Res. Lett.* **2016**, *10*, 874.
[20] A. Zuschlag, D. Skorka, G. Hahn, *Prog. Photovoltaics Res. Appl.* **2017**, *25*, 545.
[21] R. Eberle, W. Kwapil, F. Schindler, M. C. Schubert, S. W. Glunz, **2016**, *865*, 861.
[22] P. K. Basu, J. Li, V. Shanmugam, A. Khanna, *RSC Adv.* **2016**, *6*, 35928.
[23] M. Wilson, P. Edelman, A. Savtchouk, J. D'Amico, A. Findlay, J. Lagowski, *J. Electron. Mater.* **2010**, *39*, 642.
[24] M. Tayyib, J. Theobald, K. Peter, J. O. Odden, T. O. Sætre, *Energy Procedia* **2012**, *27*, 21.
[25] T. Luka, S. Großer, C. Hagendorf, K. Ramspeck, M. Turek, *Sol. Energy Mater. Sol. Cells* **2016**, *158*, 43.
[26] R. Eberle, W. Kwapil, F. Schindler, S. W. Glunz, M. C. Schubert, *Energy Procedia* **2017**, *124*, 712.