



7th International Conference on Silicon Photovoltaics, SiliconPV 2017

Temperature dependent degradation and regeneration of differently doped mc-Si materials

Jakob M. Fritz*, Annika Zuschlag, Daniel Skorka, Andreas Schmid, Giso Hahn

University of Konstanz, Departments of Physics, 78457 Konstanz, Germany

Abstract

Light and elevated temperature induced degradation is observed for multicrystalline Si PERC-type solar cells, strongly limiting solar cell parameters under operation conditions. In this contribution, we investigate the effect of temperature on the degradation and regeneration kinetics of lifetime samples with different p-doping. While there is no fundamental difference visible between B- and Ga-doped materials, Ga-doped samples generally had a lower starting lifetimes and showed a slower degradation process. Ungettered Ga-doped samples did not regenerate within the applied time frame. For higher treatment temperatures ($\geq 200^\circ\text{C}$) lifetimes after regeneration exceeded the initial values before degradation for both gettered materials. There are first indications that the degradation reaction is diffusion limited (following Arrhenius-like kinetics), while the observed regeneration kinetics might change for higher temperatures ($\geq 150^\circ\text{C}$).

© 2017 The Authors. Published by Elsevier Ltd.

Peer review by the scientific conference committee of SiliconPV 2017 under responsibility of PSE AG.

Keywords: multicrystalline Si; lifetime; degradation; regeneration; illumination; temperature; PERC

1. Introduction

Light and elevated temperature induced degradation (LeTID) affects the performance of multicrystalline (mc) silicon passivated emitter and rear cell (PERC) solar cells [1-3]. The underlying effect or mechanism of LeTID is still unknown. The effect can also be observed on lifetime samples as already shown (e.g., [3, 4]). The type of surface passivation [5], effective external gettering steps [6] as well as firing conditions [7, 8] strongly influence

* Corresponding author. Tel.: +49-7531-88-3728; fax: +49-7531-88-3895.
E-mail address: Jakob.Fritz@uni-konstanz.de

LeTID. Regeneration can be observed at longer timescales (after ~1,000 h) when treated at 75°C and 1 sun, a kind of standard conditions for LeTID experiments. It is known that the kinetics of the LeTID effect is influenced by illumination / carrier injection and temperature. Increasing the temperature accelerates the effect (e.g. [3]). Since the regeneration effect can be observed at 75°C only at longer timescales, an increase in speed by increasing the temperature would be interesting if the underlying effect is only accelerated but not altered otherwise.

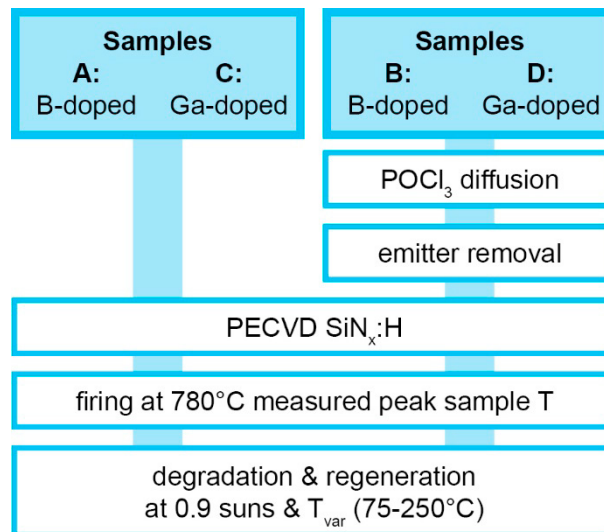
This contribution presents a study of effective minority charge carrier lifetimes τ_{eff} to identify the temperature dependency of LeTID that might lead to a better modelling of the effect. It shows that even on equally processed sister samples with comparable grain structure the regeneration behaviour seems to change for temperatures above 200°C.

2. Experiment

For the experiment 5x5 cm² adjacent mc-Si wafers in ingot height (sister samples) with either B-doping (~1 Ωcm) or Ga-doping were used. By using sister wafers, a comparable material quality as well as very similar grain and defect structure can be achieved. All samples were etched to remove saw damage. To compare samples with and without P-gettering step, half of the samples received a POCl₃ diffusion step (55 Ω/□) and the created emitter was removed again by etching. All samples got a PECVD (plasma-enhance chemical vapour deposition) silicon nitride layer as surface passivation and were fired at 780°C measured peak sample temperature. The applied process sequences are also shown in Fig. 1.

For the degradation and regeneration treatment, an illumination of 0.9 ± 0.1 suns at various temperatures between 75°C and 250°C was used to investigate temperature dependent kinetics of the degradation and regeneration behaviour.

The minority charge carrier lifetime measurements of the samples were performed repetitively using TR-PLI (time resolved photoluminescence imaging [9, 10]) at room temperature. This is a fast, spatially resolved and self-calibrated way to obtain lifetime measurements.



at different states during the degradation and regeneration at 200°C and 0.9 suns. Within the first minutes, τ_{eff} decreases significantly in all sample areas. After approximately 30 min τ_{eff} recovers due to regeneration.

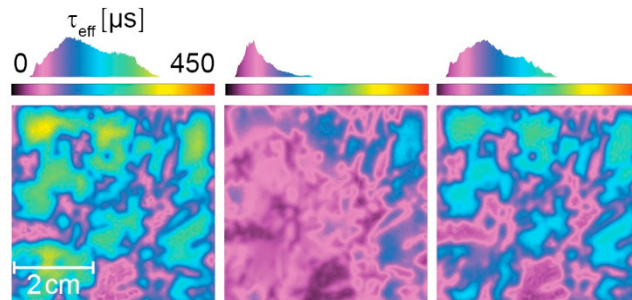


Fig. 2. Lifetime maps of a Ga-doped, P-gettered sample after different durations of treatment at 200°C and 0.9 suns. From left to right: initial measurement, after degradation ($t=5$ min) and during regeneration ($t=30$ min).

There are many different ways to visualize and interpret these lifetime measurements depending on the focus of what should be compared. Often average values are compared [3, 7], effective defect lifetime maps are obtained [11], or different regions of the same sample can be investigated [12, 13].

To study the influence of the applied temperature during degradation experiments, the average τ_{eff} values of several samples are compared in section 3.1. In section 3.2 a more detailed view on the degradation and regeneration behaviour is obtained by looking at different regions of the same sample using “rainbow” plots as introduced in [4]. A comparison with a model based on Arrhenius-like behaviour is shown in section 3.3.

3.1. Influence of degradation temperature and dopant

To focus on the influence of temperature and dopant on the degradation and regeneration behaviour, the harmonic average τ_{eff} of each lifetime map is calculated and plotted over time for differently treated samples. In this way, the development of different samples can be compared easily but the spatial information and the influence of different regions on the harmonic average is lost.

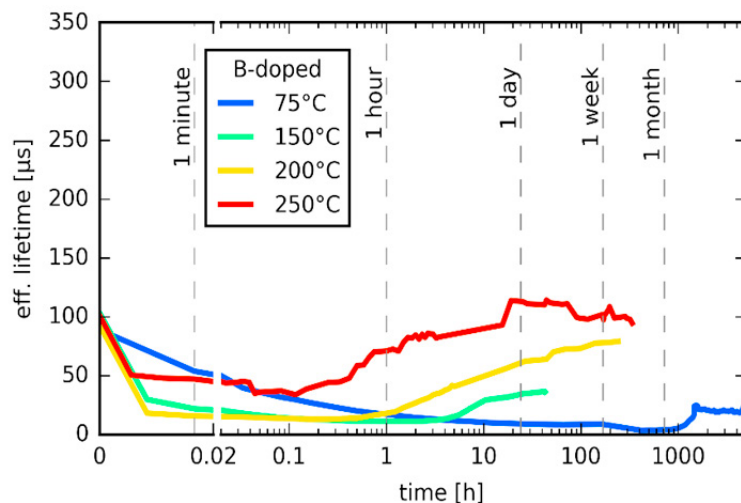


Fig. 3. Harmonic averages of B-doped, ungettered samples treated at different temperatures and 0.9 suns.

In Fig. 3 the harmonic average τ_{eff} values of the B-doped, ungettered samples A treated at different temperatures are shown. As in all upcoming graphs where development of τ_{eff} values over time is shown, the first part of the

graph is plotted on a linear scale to show the behaviour within the first minute. After that, the graph is plotted in logarithmic scale to show the τ_{eff} behaviour over long timescales (up to $\sim 4,000$ h).

As can be seen in Fig. 3, all samples A degrade fast within the first minutes and regenerate at longer timescales depending on the used temperature (e.g., after $\sim 1,000$ h at 75°C). In general, it can be said that increasing temperature accelerates degradation and regeneration. The Ga-doped, ungettered samples C (not shown) are on a lower lifetime level compared to the B-doped samples and do not regenerate within the observed time (e.g., $\sim 4,000$ h at 75°C).

As expected, the B-doped, P-gettered samples (Fig. 4) show a significantly higher initial lifetime compared to the B-doped ungettered sister samples (Fig. 3). Apart from that, the degradation kinetics is similar and the lifetime minimum, respectively maximum degradation, is at a very similar lifetime level for the samples treated at 75°C and 150°C . As for the ungettered samples, the lifetime minimum gets less pronounced with increasing temperature. Due to the higher initial lifetimes, this behaviour can be seen more clearly in Fig. 4. The time where the onset of regeneration starts to be seen is nevertheless similar for the B-doped samples with and without P-gettering. For higher temperatures above 150°C , the lifetime exceeds the initial lifetime measured before degradation which could not clearly be detected for the ungettered samples.

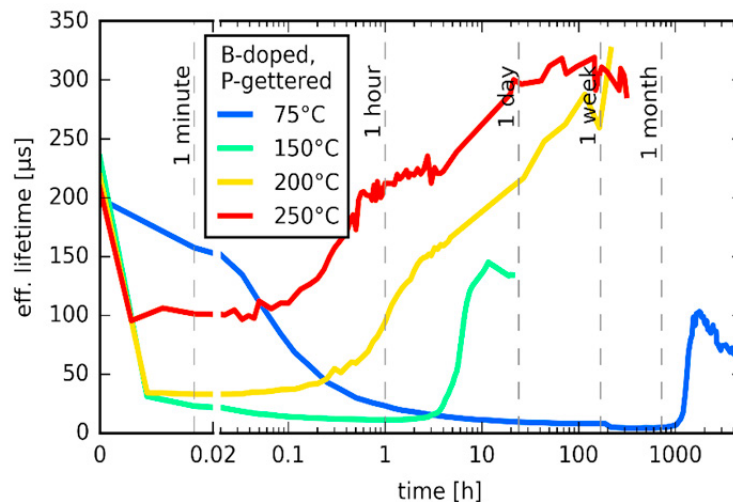


Fig. 4. Harmonic averages of B-doped, P-gettered samples treated at different temperatures and 0.9 suns.

Comparing the Ga-doped, P-gettered samples shown in Fig 5 with the B-doped, P-gettered samples shown in Fig. 4, the general trend for increasing temperatures is the same, as for both type of dopants the degradation speeds up and regeneration starts earlier for higher temperatures. Also for the P-gettered samples, the initial lifetime level for the Ga-doped samples is lower compared to the B-doped ones. The degradation of the Ga-doped, P-gettered samples is significantly slower than for the B-doped samples as can be seen most clearly at the sample treated at 75°C (blue lines in Fig. 4 and Fig. 5). The lifetime in the minima on the other hand is comparable for the two differently doped materials. Although the regeneration kinetics itself seems to be slower, the regeneration sets in after similar treatment times comparing the B- and Ga-doped P-gettered samples treated at the same temperature. As for the B-doped samples, the Ga-doped samples exceed the initial lifetime value if treated at high enough temperatures. However, this behaviour is less pronounced for the Ga-doped samples.

Taking a closer look at the Ga-doped, P-gettered sample treated at 200°C (yellow line in Fig. 5) it can be seen that the average lifetime increases towards 1 h and then decreases again to form a second minimum before it increases to a lifetime higher than the initial value on longer timescales. If the temperature is increased further, the first maximum and second minimum move towards each other and form a shoulder on the increase between the first minimum and the maximum on longer timescales. Looking at the B-doped samples in Fig. 4, a similar shoulder for

the sample treated at 250°C and also slightly for the sample treated at 200°C can be observed, although it is less pronounced.

The first lifetime minimum forms due to bulk effects [6] whereas further experiments (not shown) suggest the second minimum detectable at higher temperatures to be due to surface passivation. This investigation is still in progress, taking into account changes in surface passivation quality as described in [14, 15]. So the observed regeneration behaviour probably shows a combination of bulk and surface effects.

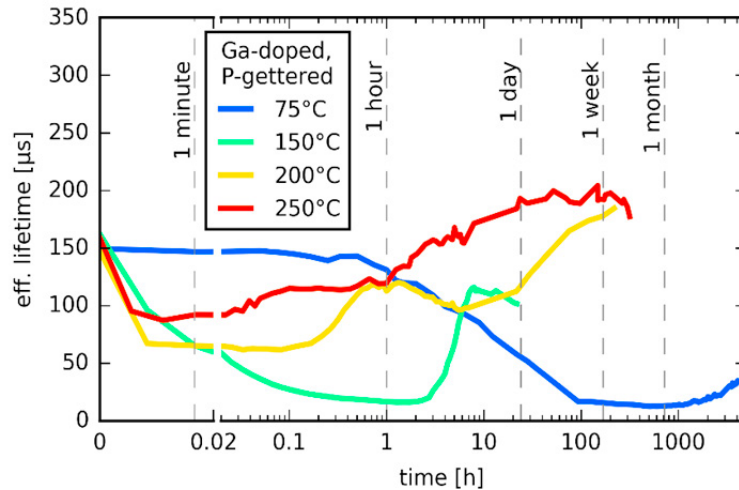


Fig. 5. Harmonic averages of Ga-doped, P-gettered samples treated at different temperatures and 0.9 suns.

3.2. Rainbow plots

Especially for mc-Si material with differing material quality due to local differences in defect structures and defect densities, the series of spatially resolved TR-PLI lifetime maps over degradation time provide additional information on the degradation and regeneration behaviour of sample areas of different lifetime. Plotting each of these different areas of the same sample as one line into the same plot helps to get an insight on how areas of different lifetimes evolve over time. To make the lines more distinct, the individual lines are colour-coded according to the lifetime in this area at the initial measurement. This leads to the so-called “rainbow plots” (introduced in [4]). These plots bear the advantage of being able to distinguish the different areas and see how initially good or initially bad areas develop during degradation and regeneration. The drawback of this kind of visualization is that only one sample can be shown per graph which makes direct comparison of multiple samples difficult. Such a plot is shown in Fig. 6 representing the different small areas of a Ga-doped, P-gettered sample treated at 200°C. This sample is chosen to trace back the observed regeneration behaviour and the second lifetime minimum regarding the harmonic average lifetimes as described above in section 3.1.

One thing that can clearly be seen is that the relative lifetime distribution within the sample stays the same during the whole treatment (e.g., red coloured lines are always above green or blue coloured ones). The second lifetime minimum is observed for all sample areas, independent of the initial lifetime. Therefore, the underlying effect affects the whole sample and cannot be attributed to certain defect structures in certain sample areas. Lifetime studies on similarly treated FZ wafers hint to changes in surface passivation quality [14, 15]. Assuming changes in surface passivation quality, the observed lifetime behaviour might be an overlay of an increasing bulk quality and a temporarily decreasing surface passivation quality. Further experiments will focus on the influence of bulk and surface regarding the second lifetime minimum.

Another point is that the regeneration to the first maximum sets in earlier for areas with higher initial τ_{eff} (as already observed in [6]). This may be a hint that regeneration kinetics might depend on Δn . The second decrease and increase on the other hand seem to set in at similar times for all areas regardless of initial lifetime. Most of the areas

fully recover and many even exceed the initially measured τ_{eff} . This is especially true for areas with high initial lifetime (e.g., red and yellow lines).

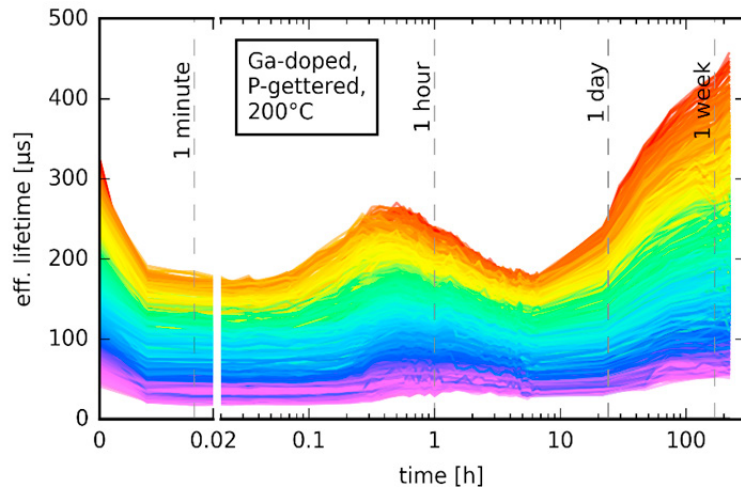


Fig. 6. Rainbow plot of a Ga-doped, P-gettered sample treated at 200°C where the development of individual areas of the sample is shown.

3.3. Temperature dependent kinetics

For further discussion of the effect, single features of the data sets are used. Here we use the time at which the observed minimum or maximum (respectively shoulder) in τ_{eff} is reached (harmonic average values). These features can be compared better with existing models than the whole series of lifetime maps. In the previous graphs only four temperatures were shown to make the plots not too packed. Here all investigated temperatures between 75°C and 250°C are displayed leading to a more significant conclusion. The drawback of this visualization is that the rest of the data remains unused and because of this, other parts of the data that might lead to another quantitative result that cannot be seen by this approach. In addition, the observed minima and maxima are strictly speaking not the correct pieces of information for a quantitative evaluation of the degradation and regeneration process. The minima are forming because of the onset of regeneration, and not because degradation has come to its completion. Similarly, the maxima (or shoulders) are formed because of an onset of decrease in surface passivation. Therefore, care has to be taken in interpreting the following results quantitatively. But nevertheless, the results can give some hints about the underlying processes or reactions.

The specific question to be examined here is if the times, at which the first minimum and the maximum (or shoulder for higher temperatures) is reached, follow the law of Arrhenius. For higher temperatures, the shoulder is used because the maximum exceeding initial lifetime values afterwards is probably due to additional effects. The times after which the minima (and maxima) are reached are plotted versus temperature in Fig. 7. With a logarithmic x-axis showing time and a linear temperature y-axis a straight line forms.

Such a straight line would also be predicted for diffusion limited processes by the Arrhenius law. So it is quite probable that the effect leading to the minimum (degradation) is diffusion limited. The Ga-doped samples (not shown) show a very similar behaviour.

Doing the same for the time at which the maxima (or shoulders) are reached, a different behaviour can be observed. Up to roughly 150°C the maxima show an Arrhenius-like behaviour but deviate for higher temperatures. The minima (or shoulders) are reached later than expected for a simple Arrhenius-like behaviour. This suggests that for these higher temperatures the underlying effect is not purely driven by first order diffusion kinetics. Further experiments show that the second minima might be due to a decrease in surface passivation quality but also the effect kinetics in the bulk may change additionally. The Ga-doped samples D (not shown) show a less pronounced deviation from the Arrhenius-like behaviour for the maxima (or shoulders).

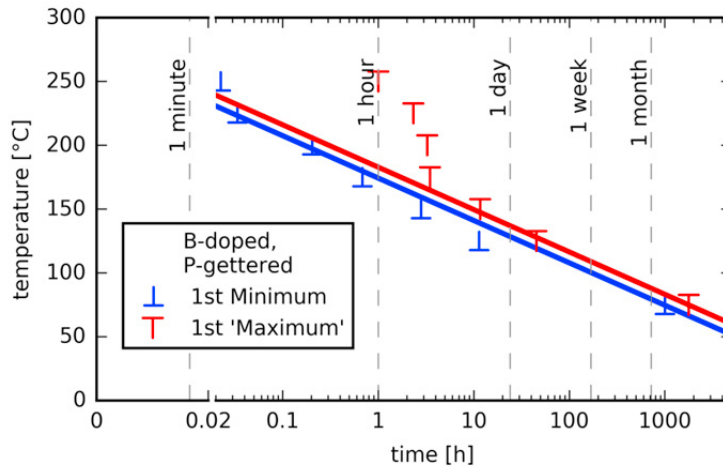


Fig. 7. Extraction of the positions of minima and maxima (respectively shoulders) for the different degradation treatments. Solid lines are guides to the eye to indicate an Arrhenius-like diffusion driven behaviour.

4. Conclusion & outlook

This paper showed that an increase in temperature accelerates the degradation and also the regeneration reaction (if regeneration is observed). Ga-doped, ungettered samples did not regenerate within the observed time ($\sim 4,000$ h at 75°C) regardless of the used temperature.

If the temperature is increased above roughly 150°C , a second τ_{eff} minimum and maximum can be observed (sometimes only as a shoulder). After this the second maximum (or maximum after the shoulder) reaches higher τ_{eff} than at the initial lifetime measurement in the corresponding areas. This is especially observed for areas with high initial τ_{eff} .

The times at which the minima are reached for different temperatures show Arrhenius-like kinetics. For the times at which the maxima (or shoulders) are reached, this is only true up to $\sim 150^\circ\text{C}$.

Further experiments should bring a differentiation between surface- and bulk-effects. Additionally the stability of the lifetimes exceeding initial values during regeneration is unclear.

Acknowledgements

The authors would like to thank Lisa Mahlstaedt, Johannes Fichtner, Noemi Mundhaas, Susanne Koch, and Clemens Winter for their assistance during sample processing and characterization. Part of this work was financially supported by the German Federal Ministry for Economic Affairs and Energy (FKZ 0325763B and 0324001). The content is the responsibility of the authors.

References

- [1] Ramspeck K, Zimmermann S, Nagel H, Metz A, Gassenbauer Y, Birkmann B, Seidl A. Light induced degradation of rear passivated mc-Si solar cells. Proc. 27th EU PVSEC; 2012. p. 861-5.
- [2] Fertig F, Krauss K, Rein S. Light-induced degradation of PECVD aluminium oxide passivated silicon solar cells. Phys Status Solidi RRL 2014;9(1):41-6.
- [3] Kersten F, Engelhart P, Ploigt H-C, Stekolnikov A, Lindner T, Stenzel F, Bartzsch M, Szpeth A, Petter K, Heitmann J, Müller J. Degradation of multicrystalline silicon solar cells and modules after illumination at elevated temperature. Sol En Mat & Sol Cells 2015;142:83-6.
- [4] Zuschlag A, Skorka D, Hahn G. Degradation and regeneration analysis in mc-Si. Proc. 43rd IEEE PVSC; 2016. p. 1051-4.
- [5] Kersten F, Heitmann J, Müller JW. Influence of Al_2O_3 and SiN_x passivation layers on LeTID. En Procedia 2016;92:828-32.
- [6] Zuschlag A, Skorka D, Hahn G. Degradation and regeneration in mc-Si after different gettering steps. Prog Photovolt 2016; DOI: 10.1002/ppp.2832

- [7] Bredemeier D, Walter D, Herlufsen S, Schmidt J. Lifetime degradation and regeneration in multicrystalline silicon under illumination at elevated temperature. *AIP Advances* 2016;6:035119.
- [8] Chan CE, Payne DNR, Hallam BJ, Abbott MD, Fung TH, Wenham AM, Wenham SR. Rapid stabilization of high-performance multicrystalline p-type silicon PERC cells. *Proc. 43rd IEEE PVSC*; 2016.
- [9] Kiliiani D, Micard G, Steuer B, Raabe B, Herguth A, Hahn G. Minority charge carrier lifetime mapping of crystalline silicon wafers by time-resolved photoluminescence imaging. *J Appl Phys* 2011;110:054508.
- [10] Kiliiani D, Herguth a, Micard G, Ebser J, Hahn G. Time-resolved photoluminescence imaging with electronic shuttering using an image intensifier unit. *Sol En Mat & Sol Cells* 2012;106:55-9.
- [11] Krauss K, Fertig F, Menzel D, Rein S. Light-induced degradation of silicon solar cells with aluminium oxide passivated rear side. *En Procedia* 2015;77:599-606.
- [12] Selinger M, Kwapil W, Schindler F, Krauss K, Fertig F, Michl B, Warta W, Schubert MC. Spatially resolved analysis of light induced degradation of multicrystalline PERC solar cells. *En Procedia* 2016;92:867-72.
- [13] Skorka D, Zuschlag A, Hahn G. Spatially resolved degradation and regeneration kinetics in mc-Si. *Proc. 32nd EU PVSEC*; 2016. p. 643-6.
- [14] Sperber D, Heilemann A, Herguth A, Hahn G. Temperature and light-induced changes in bulk and passivation quality of boron-doped float-zone silicon coated with SiN_x:H. *IEEE J Photovolt* 2017;7(2):463-70.
- [15] Sperber D, Graf A, Skorka D, Herguth A, Hahn G. Degradation of surface passivation and its impact on light induced degradation experiments. *Proc 44th IEEE PVSC*; 2017 accepted.