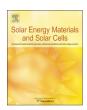
FISEVIER

Contents lists available at ScienceDirect

# Solar Energy Materials and Solar Cells

journal homepage: www.elsevier.com/locate/solmat



## In-situ characterization of electron-assisted regeneration of Cz-Si solar cells

L. Helmich<sup>a,\*</sup>, D.C. Walter<sup>a</sup>, D. Bredemeier<sup>a</sup>, R. Falster<sup>b</sup>, V.V. Voronkov<sup>b</sup>, J. Schmidt<sup>a,c</sup>



- <sup>a</sup> Institute for Solar Energy Research Hamelin (ISFH), Am Ohrberg 1, 31860 Emmerthal, Germany
- <sup>b</sup> SunEdison Semiconductor, Via Nazionale 59, 39012 Merano, Italy
- <sup>c</sup> Department of Solar Energy, Institute of Solid-State Physics, Leibniz Universität Hannover, Appelstraße 2, D-30167 Hanover, Germany

### ARTICLE INFO

Keywords: Solar cell LID Czochralski-grown silicon Boron-oxygen defect Regeneration

#### ABSTRACT

We examine the regeneration kinetics of passivated emitter and rear solar cells (PERCs) fabricated on boron-doped p-type Czochralski-grown silicon wafers in darkness by electron injection via application of a forward bias voltage at elevated temperature (140 °C) in order to discriminate between electronic and photonic effects. Based on these dark regeneration experiments, we address the existing inconsistency regarding the measured linear dependence of the regeneration rate constant on the excess carrier density. Using the method of dark regeneration by current injection into the solar cell, we are able to measure the total recombination current of the solar cell at the actual regeneration temperature under applied voltage, i.e., at the physically relevant regeneration conditions. The direct comparison of the regeneration rate constant as a function of electronically injected carrier concentration in the dark and the regeneration rate constant during illumination clearly shows that the regeneration is a purely electronically stimulated effect and that photons are not directly involved.

## 1. Introduction

The boron-oxygen (BO)-related defect center limits the efficiency of silicon solar cells fabricated on boron-doped Czochralski-grown silicon (Cz-Si) after light-induced degradation (LID). As previously shown, however, the BO defect can be permanently deactivated, i.e. the efficiency can be fully regenerated, if the solar cell is exposed to illumination or, alternatively, if electrons are injected by application of a forward bias voltage at elevated temperatures [1-4]. For the regeneration under illumination, a dependence of the regeneration rate constant  $R_{\rm de}$  on the average excess carrier density  $\Delta n_{\rm avg}$  in the bulk of the silicon base, determined from room-temperature measurements, has been reported by several research groups [5,6]. R<sub>de</sub> increases proportionally with the illumination intensity [5,6]. However, a proportional dependence of  $R_{de}$  on  $\Delta n$  seems to be inconsistent with the strictly mono-exponential decay of the effective defect concentration during the regeneration process, as  $\Delta n$  is expected to increase strongly during the process of regeneration, due to a loss of the BO recombination centers. One possible explanation would be that the lifetime is in fact constant at the increased temperature applied during regeneration [7], which would result in a constant  $\Delta n$  value at the regeneration temperature. In order to examine the regeneration at well-defined  $\Delta n$  and to isolate the impact of electron injection on the regeneration kinetics, we measure the current flow in-situ through PERC solar cells under

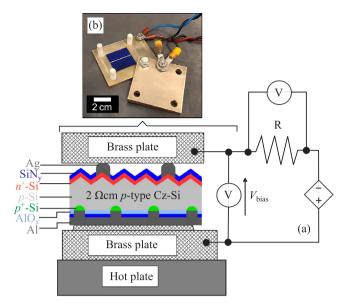
different constant forward bias voltages in the dark at elevated temperature.

## 2. Experimental details

In this contribution, we examine passivated emitter and rear cells (PERCs) fabricated on 2.0-2.2 Ωcm boron-doped Cz-Si wafers using an industrial-type screen-printing process [8]. The interstitial oxygen concentration [Oi] is according to the wafer supplier in the range of  $(7-8) \times 10^{17}$  cm<sup>-3</sup>. The 156 × 156 mm<sup>2</sup> sized solar cells have an efficiency in the range of  $(20.52 \pm 0.22)\%$  before they were laser-cut into  $25 \times 25 \text{ mm}^2$  cells to increase the number of identical cells and to reduce the total current flow through the cell. First, we characterize all cells by measuring their *I-V* characteristics in the fully degraded and the dark-annealed states, respectively. The solar cells are degraded at room temperature using a halogen lamp with an illumination intensity of  $P_{ill}$ = 10 mW/cm<sup>2</sup> for 65 h (fully degraded state). Dark annealing is performed under ambient environment on a hot plate at 200 °C for 10 min (annealed state). The measured efficiencies in the fully degraded state are (19.06 – 19.35)%, whereas the efficiencies after dark annealing, which temporarily deactivates the BO defect, are in the range (19.43 – 19.85)%. Directly after dark annealing, we place the solar cell between two brass plates connected with Teflon screws, as shown in Fig. 1.

E-mail address: l.helmich@isfh.de (L. Helmich).

<sup>\*</sup> Corresponding author.



**Fig. 1.** (a) Schematic of our set-up for the in-situ regeneration experiments in darkness. (b) Photo of the clamped solar cell placed on the hot plate.

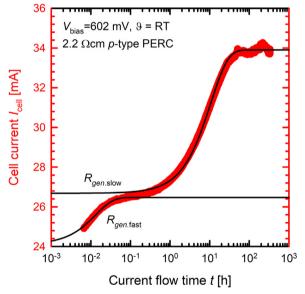
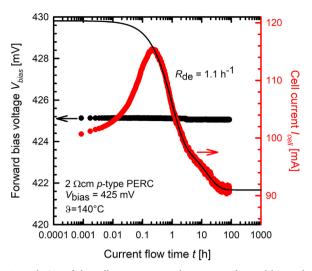
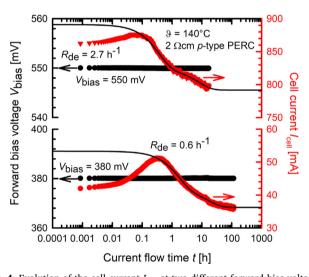


Fig. 2. The typical two-stage degradation, as known from the literature [9], can also be observed in the dark cell current, if a constant forward bias voltage  $(V_{\text{bias}} = 602 \,\text{mV})$  in this case) is applied to the cell at room temperature.

This sandwich-like structure is then put onto a conventional hot plate. After 30 mins, the thermal equilibrium is reached and a voltage is applied, which is kept constant during the entire experiment. The cell current  $I_{\rm cell}$  (red symbols in Fig. 2(b)), which is proportional to the overall recombination rate in the cell, is measured by a voltage-drop over a resistance, which is connected in series (see Fig. 1(a)). We choose the resistance (0.1  $\Omega$  or 1  $\Omega$ ) according to the examined current range. The initial state of the solar cells was after dark annealing and the temperature of the cell temperature on the hot plate was kept constant at 140 °C during regeneration. After complete regeneration, we characterize each solar cell again by illuminated  $\emph{I-V}$  measurements (25 °C, AM1.5 G spectrum, 1sun) using the LOANA solar cell characterization tool (pvtools, Hamelin, Germany).



**Fig. 3.** Evolution of the cell current  $I_{\rm cell}$  under constant forward bias voltage  $V_{\rm bias} = 425\,\mathrm{mV}$  at  $140\,^{\circ}\mathrm{C}$  in darkness. The solid black line shows a double-exponential decay function. The forward bias voltage  $V_{\rm bias}$  is constant during the entire regeneration experiment.



**Fig. 4.** Evolution of the cell current  $I_{\rm cell}$  at two different forward bias voltages  $V_{\rm bias}$  at 140 °C in darkness. The solid black lines show fits of double-exponential decay curves. The forward bias voltage  $V_{\rm bias}$  is constant during each regeneration experiment.

## 3. Results and discussion

## 3.1. In-situ measured degradation and regeneration kinetics

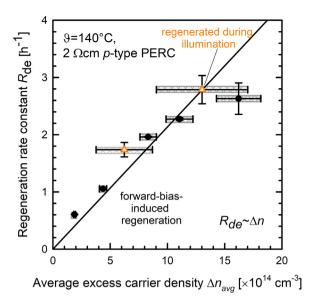
Figs. 2–4 show the time evolution of the dark-injected cell current  $I_{\rm cell}$ , which is directly proportional to the total recombination rate versus the logarithmically plotted time at the applied voltages  $V_{\rm bias}$ .

In Fig. 2 the typical degradation behavior at room temperature known from the BO defect activation under illumination is observed. For the fast initial increase of the cell current, we determine a rate constant of  $R_{\rm gen,fast}=2.1\times10^{-2}~{\rm s}^{-1}$  and for the second, slower rate constant we determine  $R_{\rm gen,slow}=2.6\times10^{-5}~{\rm s}^{-1}$ . These rate constants,  $R_{\rm gen,fast}$  and  $R_{\rm gen,slow}$ , are in excellent agreement with the fast and slow generation rate constants of the light-induced BO defect

activation  $R_{\text{gen,fast}} = 3 \times 10^{-2} \text{ s}^{-1}$  and  $R_{\text{gen,slow}} = 3 \times 10^{-5} \text{ s}^{-1}$  as published in the literature [9], which is an indication of the proper functioning of our measurement setup. Interestingly, also the regeneration, as shown in Figs. 3 and 4 at 140 °C, proceeds with a doubleexponential process with a fast and a slow component, corresponding to a decreasing cell current. This double-exponential behavior is not observed if the regeneration is performed in the traditional way, i.e. if the I-V measurements are performed after cooling down to room temperature [10]. Only the fast component is increasing with increasing  $V_{\rm bias}$  at the chosen regeneration temperature. The slow component shows no dependence on the forward bias voltage and seems to be a kind of measurement artefact not related to bulk recombination. Hence, we relate only the fast component to the regeneration kinetics of the boron-oxygen defect. However, the efficiency of the solar cells is the same in the dark-annealed state and after complete dark regeneration through current feed (see Fig. 5). Hence, we identify the fast component of the regeneration rate with the regeneration rate constant  $R_{de}$  of the BO-related regeneration.

## 3.2. Stability after electronically stimulated regeneration

Fig. 5 shows exemplarily the evolution of the efficiency  $\eta$  and the open-circuit voltage  $V_{\rm oc}$  of one solar cell after electronically stimulated regeneration in the dark during illumination with an intensity of  $P_{\rm ill}=10\,{\rm mW/cm^2}$  (0.1 suns) at room temperature. Also shown are the fully degraded and the dark-annealed states. The direct comparison reveals that the efficiency as well as the open-circuit voltage after electronic regeneration and the values after dark-annealing are practically the same. These results clearly prove that the solar cells have in fact been permanently regenerated by means of electron injection via current feeding in darkness and that photons are not a necessary prerequisite in the regeneration process, if electrons are generated alternatively.



**Fig. 6.** The in-situ-measured regeneration rate constants  $R_{\rm de}$  versus the average excess carrier density  $\Delta n_{\rm avg}$  (filled circles) shows a proportional dependence. PC1D simulations were used to extract  $\Delta n_{\rm avg}$  in the base of the PERC solar cells at a fixed forward bias voltage in darkness. The grey bars show the range of  $\Delta n_{\rm avg}$  during regeneration. In comparison, regeneration rate constants of solar cells regenerated during illumination are shown (open triangles). The straight black line is a proportional fit to the measurement data of the forward-bias-induced regeneration rate constant  $R_{\rm de}$  (circles), taking the range of  $\Delta n_{\rm avg}$ -values (grey bars) into account.

# 4. Extraction of regeneration rate constant as a function of electron concentration

In order to calculate the excess carrier density in the cell base as a function of applied forward bias voltage, we perform device simulations using PC1D [11]. The used input parameters had been determined in a

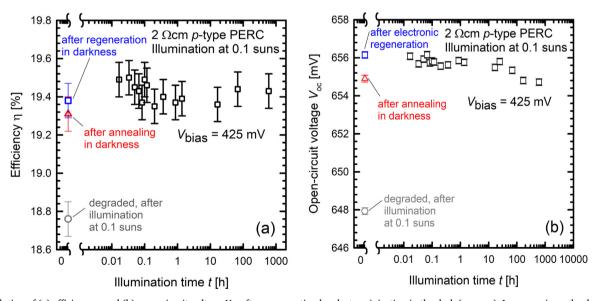


Fig. 5. Evolution of (a) efficiency  $\eta$  and (b) open-circuit voltage  $V_{oc}$  after regeneration by electron injection in the dark (squares). In comparison, the degraded state (circle) and the dark-annealed state (triangle) are shown. The scatter of measurement data refer to the reproducibility by the contacting of the solar cell.

previous study [12] and the series resistance has been determined using I-V measurements. In addition, we examine a lifetime sample of the same bulk Cz-Si material used in the cells. The lifetime measurements (not shown here) were performed using the photoconductance decay (PCD) method on a WCT-120TS Sinton lifetime tester at the regeneration temperature of 140 °C and an illumination intensity of P<sub>ill</sub> =  $100 \,\mathrm{mW}\,\mathrm{cm}^{-2}$ . In the fully degraded state, a lifetime of  $100 \,\mathrm{\mu s}$  was measured at an injection density  $\Delta n$  of  $1 \times 10^{15}$  cm<sup>-3</sup> and in the fully regenerated state the lifetime was 2000 µs at  $\Delta n = 1 \times 10^{15}$  cm<sup>-3</sup>. The PC1D simulations are always performed for the minimum bulk lifetime of 100 µs as well as for the maximum bulk lifetime of 2000 µs, defining the range of the average excess carrier density  $\Delta n_{\rm avg}$  in the solar cell base (shown as grey bars in Fig. 6) at a fixed applied voltage  $V_{\text{bias}}$ . Note, however, that in our in-situ regeneration approach, the electron concentration  $\Delta n$  during regeneration is almost constant, as can be seen by the very narrow grey error bars in Fig. 6, which is a major difference to previous regeneration experiments using illumination. Fig. 6 shows the regeneration rate constant  $R_{de}$  obtained from the fits to the in-situmeasured regeneration curves as a function of the average excess carrier concentration  $\Delta n_{\rm avg}$ . A proportional increase of  $R_{\rm de}$  with the voltage-induced  $\Delta n_{\rm avg}$  is observed. The in-situ measured  $R_{\rm de}$  values measured in darkness (filled circles) show a clear proportionality with  $\Delta n$ and the illumination-induced regeneration data points (open triangle) fit well to the dark-regenerated data set, suggesting that photons play in fact no role in the regeneration process and the regeneration is purely electronically stimulated.

## 5. Conclusions

In this contribution, we have investigated the regeneration process in boron-doped p-type Czochralski-grown silicon (Cz-Si) by current injection into solar cells in darkness at elevated temperature. Typical industrial PERC solar cells were examined in darkness at different forward bias voltages ( $V_{\rm bias}$ ), which define the electron concentration injected into the solar cell base via the pn-junction. The in-situ measurements of the total recombination current of the cells combined with the illuminated I-V characteristics showed a successful permanent regeneration. We extracted the regeneration rate constants  $R_{\rm de}$  at the different  $V_{\rm bias}$  values by fitting the time evolution of the measured injected dark current. The average excess carrier density  $\Delta n_{\rm avg}$  in the cell's base was determined using PC1D simulations. The measured data agree well with a proportional increase of  $R_{\rm de}$  as a function of  $\Delta n_{\rm avg}$ . The illumination-induced regeneration data fits in the dependence of the insitu measured  $R_{\rm de}$  values obtained in darkness by electron injection via

the *pn*-junction, suggesting that the regeneration process is a purely electronically stimulated process and photons play no role, thereby confirming previous defect models [13].

## Acknowledgements

The authors would like to thank Ingo Ahrens and Sascha Wolter (ISFH) for their support concerning the experimental set-up, Helge Hannebauer (ISFH) for providing PERC solar cells and the State of Lower Saxony as well as the German Federal Ministry of Economics and Energy (BMWi) for funding within the research project "Upgrade Si-PV" under contract No. 0325877B. The content is the responsibility of the authors.

## References

- A. Herguth, G. Schubert, M. Kaes, G. Hahn, A new approach to prevent the negative impact of the metastable defect in boron doped Cz silicon solar cells, in: Proc. 32nd IEEE PVSC (4th WCPEC), Waikoloa, USA, 2006, pp. 940–943.
- [2] A. Herguth, G. Schubert, M. Kaes, G. Hahn, Avoiding boron-oxygen related degradation in highly doped Cz silicon, in: Proc. 21st EUPVSEC, Dresden, Germany, 2006, pp. 530–537.
- [3] B. Lim, S. Hermann, K. Bothe, J. Schmidt, R. Brendel, Permanent deactivation of the boron-oxygen recombination center in silicon solar cells, in: Proc. 23rd EUPVSEC, Valencia, Spain, 2008, pp. 1018–1022.
- [4] A. Herguth, G. Schubert, M. Kaes, G. Hahn, Investigations on the long time behavior of the metastable boron-oxygen complex in crystalline silicon, Prog. Photovolt.: Res. Appl. 16 (2008) 135–140.
- [5] A. Herguth, G. Hahn, Kinetics of the boron-oxygen related defect in theory and experiment, J. Appl. Phys. 108 (2010) 114509.
- [6] V. Steckenreiter, D.C. Walter, J. Schmidt, Kinetics of the permanent deactivation of the boron-oxygen complex in crystalline silicon as a function of illumination intensity, AIP Adv. 7 (2017) 035305.
- [7] V. Voronkov, R. Falster, Light-induced boron-oxygen recombination centres in silicon: Understanding their formation and elimination, Solid State Phenom. 205–206 (2013) 3–14.
- [8] T. Dullweber, J. Schmidt, Industrial silicon solar cells applying the passivated emitter and rear cell (PERC) concept – a review, IEEE J. Photovolt. 6 (2016) 1366–1381.
- [9] K. Bothe, J. Schmidt, Electronically activated boron-oxygen-related recombination centers in crystalline silicon, J. Appl. Phys. 99 (2006) 013701.
- [10] A. Herguth, G. Schubert, M. Kaes, G. Hahn, Further investigations on the avoidance of boron-oxygen related degradation by means of regeneration, in: Proc. 22nd EUPVSEC, Milan, Italy, 2007, pp. 893–896.
- [11] D.A. Clugston, P.A. Basore, PC1D version 5: 32-Bit solar cell modeling on personal computers, in: Proc. 26th IEEE PVSEC, Anaheim, CA, USA, 1997, pp. 207–210.
- [12] H. Hannebauer, T. Dullweber, U. Baumann, T. Falcon, R. Brendel, 21.2%-efficient fine-line-printed PERC solar cell with 5 busbar front grid, Phys. Stat. Sol. RRL 8 (2014) 675–679.
- [13] V. Voronkov, R. Falster, Permanent deactivation of boron-oxygen recombination centres in silicon, Phys. Status Solidi B 253 (2016) 1721–1728.