

BORON-OXYGEN RELATED DEFECTS IN CZ-SILICON SOLAR CELLS DEGRADATION, REGENERATION AND BEYOND

Axel Herguth and Giso Hahn

University of Konstanz, Department of Physics, 78457 Konstanz, Germany

ABSTRACT: This contribution addresses the stability of Cz-Si solar cells subsequent to the so called Regeneration process which virtually eliminates the losses due to the well known boron-oxygen related defect. The stability of the regenerated state is vital for the industrial application of the Regeneration process. As recent experiments have shown, at least one sample was unstable after the completed Degradation-Regeneration cycle at elevated temperatures. However, this instability was not found for other samples investigated. Furthermore, different possible interpretations of this instability are discussed.

Keywords: Degradation, Czochralski, Stability

1 INTRODUCTION

A high lifetime of minority charge carriers or in other words a long diffusion length compared to the solar cell thickness is essential for high conversion efficiencies especially of comparably thick silicon solar cells.

Monocrystalline silicon materials like Floatzone or the more cost effective and hence more common Czochralski grown silicon (Cz-Si) can provide this property more easily than multicrystalline silicon due to the absence of grain boundaries and less defects and impurities. It is also well established that the maximal achievable conversion efficiency of silicon solar cells with a front side emitter rises with increasing doping concentration while on the other hand the lifetime decreases. As calculations have shown, an optimal result is expected for a specific resistivity of about $1 \Omega\text{cm}$ of the bulk material.

In reality, these expectations are not met for common oxygen-rich and (highly) boron-doped Cz-Si as the electrical parameters of solar cells show a temporal degradation in the form of an asymptotic saturating decay. These changes originate from a degradation of the bulk lifetime which results from a formation of recombination active complexes consisting of at least boron and oxygen [1,2]. Therefore this special type of degradation is referred to as 'boron-oxygen related degradation'. The boron and oxygen contents mainly determine a fundamental limit of the bulk lifetime after degradation [3]. Other components involved in the complex or at least indirectly contributing to the complex formation are currently discussed, e.g. carbon [4] or phosphor in compensated material [5].

Even though this special type of degradation was subject to many investigations since its first publication in 1973 [6] and many properties of complex formation and the complex itself were clarified in the past, data published in 2006 have proven a subsequent reaction following the degradation called 'Regeneration' [7,8]. Triggered or accompanied by the presence of (excess) minority charge carriers injected by light or forward voltages and supported by elevated temperatures, the bulk lifetime and in consequence the electrical parameters of the Cz-Si solar cell begin to recover in the course of time (see Fig. 1).

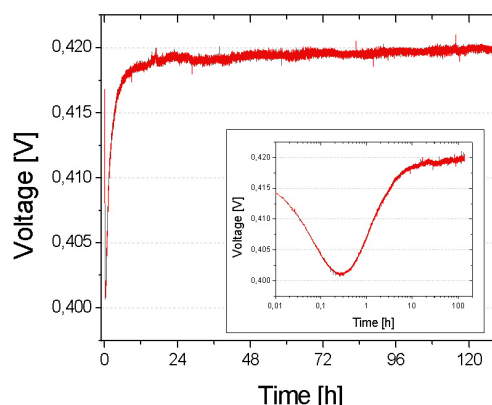


Figure 1: Linear and logarithmic representation (small) of V_{oc} during degradation and regeneration of a Cz-Si solar cell measured in-situ at around 120°C and 1 sun illumination.

2 EXPERIMENTAL

2.1 The reaction model

In general, the minority charge carrier lifetime is limited by the most active recombination channel which in this special case of degradation is correlated to the boron-oxygen complexes. A recovery of lifetime requires a partly (or complete) elimination of this channel until another channel becomes lifetime limiting. In other words, the recombination active boron-oxygen complexes have to become recombination inactive by a conversion into another state of the complex. Whether this new state provides only another configuration of the same components or a more complex interaction with other impurities could not be clarified so far.

Starting with dissolved components (state A), the formation of the recombination active complexes (state B) and a subsequent conversion into an inactive state C can be described by the reaction scheme shown in Fig. 2 (left part only).

The conversion of large numbers of complexes becomes macroscopically observable in the reaction paths implied by the arrows, each appearing under specific conditions (e.g. Degradation under illumination etc.). Even though the path of Redegradation (from

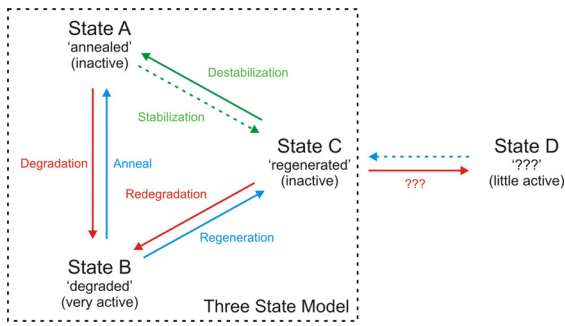


Figure 2: Three state model describing the boron-oxygen related degradation and regeneration [8] with extension of an additional fourth state.

state C back to state B) is shown in Fig. 2, its general existence could not be clarified so far. An inherent instability of the regenerated state towards the annealed state A could be proven at elevated temperatures exceeding 170°C in the dark for longer times [8] when Regeneration vanishes due to the missing injection of charge carriers. At temperatures below 170°C and carrier injection, this instability plays no role at all. In consequence, for temperatures below 170°C the regenerated state C should remain stable if the dynamic of the boron-oxygen complex is completely described by this three state model.

2.2 Stability or Instability?

In the past, the stability of the regenerated state was checked under carrier injection by illumination (shown in Fig. 2) as well as applied voltage both at room temperature (25°C). Also shown is the behaviour of the cell prior to the Regeneration step, demonstrating again the devastating impact of Degradation.

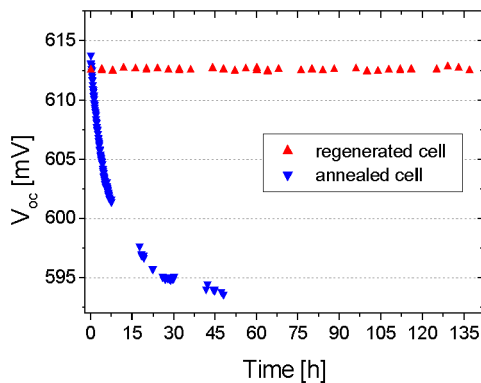


Figure 1: Temporal development of a solar cell before (blue) and after (red) the Regeneration process under illumination (top) and an applied voltage of 0.5 V (bottom) both monitored at room temperature.[8]

As can be seen from Fig. 3, after Regeneration the open circuit voltage V_{oc} remains stable at 25°C under both illumination and bias voltage in the dark for more than 100 hours.

The samples used in the following experiments were typical industrial crystalline Cz-Si solar cells, featuring a textured surface, phosphorous non-selective emitter, silicon nitride PECVD anti-reflexion coating and screen printed silver front and aluminium back contacts.

In further experiments the Degradation-Regeneration cycle was monitored in-situ using illumination to trigger the process at around 120°C. Fig. 1 shows an example where the voltage shows the typical dip due to Degradation and subsequent Regeneration. The voltage remains perfectly stable for a very long time showing actually a small increase as time goes by.

The experiment was repeated using another solar cell which was manufactured out of the same Cz-Si material but with a slightly different process. For the first few hours, the monitored voltage shown in Fig. 4 shows an analogue progression as the solar cell in Fig. 1, resulting in the expected stabilized plateau due to the completed regeneration.

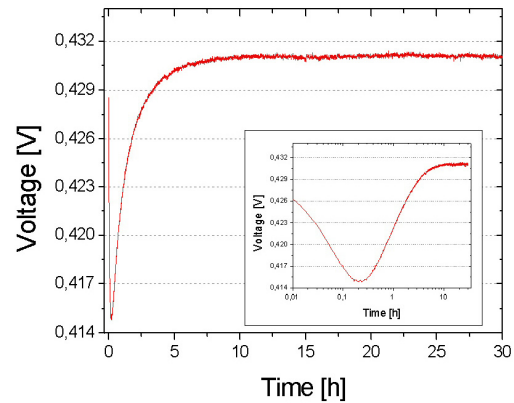


Figure 4: Linear and logarithmic representation (small) of V_{oc} of the first few hours of the degradation-regeneration cycle of a Cz-Si solar cell measured in-situ at around 120°C and 1 sun illumination.

Normally, the experiment is stopped at this point. In this case, the experiment was resumed resulting in the progression shown in Fig. 5.

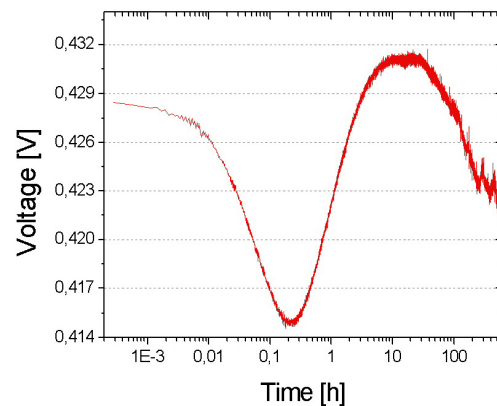


Figure 5: In-situ measurement of V_{oc} of a Cz-Si solar cell under illumination of 1 sun at 120°C. The long time measurement shows an instability of the voltage saturating for longer times resulting in a quasi-oscillating shape.

The voltage keeps dropping for a long time compared to typical Degradation and Regeneration times before the voltage stabilized around 7 mV lower than it was at the Regeneration plateau, but around 10 mV above the minimum due to Degradation. In logarithmic scaling the 'quasi-oscillating' behavior is exceptionally well observable featuring the dip due to Degradation, the

subsequent recovery due to Regeneration and the instability afterwards.

Analogous to the Degradation, the second drop in voltage is caused by a reduction of the minority charge carrier lifetime due to an increased recombination. As the saturation level differs significantly, four possible explanations come into question.

2.3 Interpretation

A first interpretation of Fig. 5 could be that the Regeneration reaction is limited while the Degradation continues to go on but is only intermittently superimposed by the Regeneration until this reaction ceases. As the time constant of the decay after the regeneration differs a lot from the time constant of the Degradation before Regeneration took place, this case is highly improbable but changing concentrations of the involved components may fundamentally alter the reaction kinetics.

A second argumentation could be that the recombination inactive state C becomes unstable towards a back-reaction to the degraded state B. In this case, the complex itself would feature the same recombination rate. The different level of the voltage shown in Fig. 5 then would imply that the concentration of the active defects is lower than directly after the Degradation. The maximum due to Regeneration process is a temporally decaying overshoot of the reaction equilibrium between the degraded and the regenerated state of the complex. This argumentation would contradict a kinetic theory in which the reaction rate features a linear proportionality towards the defect concentration as it does not support such an oscillating progression.

A third interpretation of Fig. 5 could be that the complex changes its composition and/or configuration once more from the regenerated state C to an unknown state D, as it is depicted in Fig. 2 extending the three state model by an additional state. The drop requires that this state D is more recombination active than state C. As the total recombination rate is ruled by both recombination strength of a single defect and its concentration, it is ambiguous whether there exists a large number of weakly active recombination centres or a small number of very active recombination centres. Therefore, it is unclear if the reaction equilibrium prefers state C or state D at the applied experimental conditions.

A last interpretation is that the observed drop of the voltage is caused by another effect than the boron-oxygen related Degradation/Regeneration. In this case the boron-oxygen complex is still recombination inactive but a completely different recombination channel becomes lifetime limiting. As the saturation value of the voltage lies above the degraded value, this effect could have been hidden by the boron-oxygen related Degradation in the past. Assuming that boron is not important for this alternative effect, a similar effect could then be observable in lowly doped solar cells.

3 CONCLUSIONS

The stability of the electrical parameters of the cells embedded in a module is of vital interest. Solar cells might change in generated current and the shape of their IV curve which might result in a mismatch of the cells in a module.

As module manufacturers in general guarantee for several years for the proper function of their modules, any process applied to solar cells or modules has to be qualified not to cause any problem within years. The Regeneration process has been proven to result in stabilized electrical parameters under normal testing conditions (1 sun, 25°C). The experiments in this contribution targeted on conditions far more extreme. As it was shown, at least one sample has shown an instability under these conditions.

The observed instability subsequent to the Degradation-Regeneration cycle saturated at a level higher than the low level of Degradation and therefore even if the regenerated state is not completely stable, a certain gain due to Regeneration would remain.

An interesting point, however, is that the instability was not observed on all samples or at least not with same time constant. Therefore, it is possible that the instability can be switched off or at least slowed down so much that a regenerated cell under outdoor conditions would never suffer from this instability. Anyway, the temperatures applied in the described experiments exceed the typical module temperatures observed under outdoor conditions by far and since the influence of the temperature is not clear so far, this has to be investigated more closely.

4 REFERENCES

- [1] J. Schmidt, A.G. Aberle and R. Hezel
Investigation of Carrier Lifetime Instabilities in Cz-grown Silicon
Proc. 26th IEEE PVSC, Anaheim 1997, 13
- [2] S. Rein, S. Diez, R. Falster and S.W. Glunz
Quantitative Correlation of the Metastable Defect in Cz-Silicon with Different Impurities
Proc. 3rd WCPEC, Osaka 2003, 1048
- [3] K. Bothe, R. Sinton and J. Schmidt
Fundamental Boron-Oxygen related Carrier Lifetime Limit in Mono- and Multicrystalline Silicon
Prog. Photovolt.: Res. Appl. 13, 287-296, 2005
- [4] G. Coletti, C.L. Mulder, G. Galbiati, L.J. Geerligs
Reduced Effect of B-O Degradation on Multicrystalline Silicon Wafers
Proc. 21st EU PVSEC, Dresden 2006, 1515
- [5] S. Dubois, N. Enjalbert, J.P. Garandet, R. Monna and J. Kraiem
Light-induced Degradation and Regeneration in Compensated Upgraded Metallurgical Silicon
Proc. 23rd EU PVSEC, Valencia, 2008
- [6] H. Fischer and W. Pschunder
Investigations on Photon and Thermal induced Changes in Silicon Solar Cells
Proc. 10th IEEE PVSC, Palo Alto 1973, 404
- [7] A. Herguth, G. Schubert, M. Kaes and G. Hahn
A new Approach to Prevent the Negative Impact of the Metastable Defect in Boron Doped Cz Silicon Solar Cells
Proc. 4th WCPEC, Waikoloa 2006, 940
- [8] A. Herguth, G. Schubert, M. Kaes and G. Hahn
Avoiding Boron-Oxygen related Degradation in Highly Boron Doped Cz Silicon
Proc. 21st EU PVSEC, Dresden 2006, 530