

A NEW APPROACH TO PREVENT THE NEGATIVE IMPACT OF THE METASTABLE DEFECT IN BORON DOPED CZ SILICON SOLAR CELLS

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ABSTRACT

A new reaction model concerning the boron-oxygen related degradation is presented, introducing a third recombination inactive state, that stabilizes the electrical parameters of Cz-Si solar cells, and the transition to this new inactive state is proven by experimental data. Furthermore, the stability under solar cell working conditions and the formation kinetics of this additional state are discussed.

INTRODUCTION

Performance degradation in boron doped Czochralski (Cz) silicon solar cells caused by the formation of a boron-oxygen related defect has a big impact on photovoltaics, as it partly compensates the advantage of higher lifetimes achieved in not yet degraded Cz material compared to more cost effective multicrystalline material. The defect is activated under illumination or by applying a forward bias voltage in the dark. The degradation can be completely reversed at elevated temperatures and thus making the defect metastable.

Recent investigations [1] have proven the independent formation process of two different defects after a complete anneal, the first occurring within the first few minutes and the second forming in several hours. The fast process shows strong recombination activity and thus rules the degradation process in an early stage, but for longer times the defect complexes formed in the slower process give a limit for minority lifetime, even though their recombination activity is lower. These investigations [1] also showed, that both defects seem to have a similar composition probably consisting of one substitutional boron atom and two interstitial oxygen atoms or better an interstitial oxygen dimer, but that they exist in two different configurations causing different recombination activity. Furthermore, a thermal activated transition of the fast forming configuration to the slow one is assumed to occur with a low energy barrier of about 0.3 eV.

In the past, the formation as well as the annihilation kinetics of the slowly forming recombination centres were target of many investigations (e.g. [1,2]) revealing that both effects are likely to be thermally activated, i.e. that both processes meet the Arrhenius equation. The transition probability P_{trans} of the defect from an inactive state (annealed) to an active state (degraded) or vice versa is then given by a reaction specific characteristic trial frequency v_{char} weighted by the probability of having enough

mean thermal energy $k_B T$ compared to the activation energy E_a , given by the exponential Boltzmann factor.

$$P_{trans} = v_{char} \cdot \exp\left(-\frac{E_a}{k_B T}\right) \quad (1)$$

The activation energy deduced from this relation for the slowly forming degradation process is in the range of 0.4 – 0.5 eV [1,2] with a characteristic frequency strongly dependent on the underlying process, that is assumed to be recombination enhanced accounting for the activation by light and forward bias voltage.

The activation energy for the annihilation process is about 1.3 – 1.4 eV [1,3] in accordance with the elevated temperatures needed for annealing. The characteristic frequency of the annihilation process was determined to be about 10^{13} Hz, noticeably close to phononic frequencies, indicating that the defect complex is probably disrupted by lattice vibration.

CLASSICAL WAYS OF AVOIDANCE

For avoidance of boron-oxygen related degradation, the disadvantageous interaction of the critical components boron and oxygen has to be prevented. The common approaches for avoidance mainly aim at the reduction of critical complexes by lowering the boron and/or oxygen concentrations.

As it is easier to reduce boron concentration, nowadays Cz with bulk resistivities $>3 \Omega\text{cm}$ is frequently used in the PV industry, accepting a loss in the efficiency potential as the optimum resistivity would be around $1 \Omega\text{cm}$. More complicated is the reduction of oxygen in Cz silicon, as it originates from an inevitable quartz crucible melting during crystal pulling. Protective layers are under investigation but due to the high thermal load this approach was not capable of reducing the oxygen contamination significantly. A promising new approach using magnetic fields to confine the silicon melt without contact to a crucible has resulted in a sufficiently low oxygen contamination of the so called MCz silicon.

Although this problem mainly affects highly doped Cz material, standard mc-Si is not immune to degradation. In fact, the degradation influences the lifetime in a comparable way, but in general numerous other recombination active defects like grain boundaries limit lifetime.

Another possibility is the use of other p-type dopants like gallium or aluminium instead of boron. At a first glance, this rules out boron-oxygen complexes as a matter

of principle, but only if there is a low residual boron background requiring pure feedstock material. The same consideration holds for n-type silicon. But both alternatives implicate a problem with doping homogeneity, as their segregation coefficient is well below unity and thus a loss in efficiency potential for parts of the ingot is inevitable. In addition, the industrial production technology for n-type silicon is nowadays by far less common than for p-type material.

In summary, all alternatives implicate new and so far unsolved problems. In the following, a complete new approach for the solution of the well known problem of boron-oxygen related degradation is described.

A NEW APPROACH: THREE STATE MODEL

For the better understanding of the experimental results, the underlying new model is introduced first. The details about the regeneration process itself used later on can only be partly published here due to the patent pending situation.

Three state model

The formation and annihilation of the complexes responsible for degradation can be described as a chemical reaction of microscopic systems from a less recombination active state A to a strongly recombination active state B. The macroscopic system (solar cell) is thereby a composition of a multitude of microscopic defects in different states. Degradation as well as annealing is therefore a relaxation of a non-equilibrium state of the system. Since both ways of reaction are observed, the equilibrium is adjustable by external excitation and temperature as shown by Glunz et al. [2].

One way of limiting degradation is therefore to disturb this equilibrium by introducing a third state C, which is at least less recombination active as state B and stable regarding a reaction to state A and B under typical working conditions of the solar cell. A scheme of this hypothetical system is shown in Fig. 1.

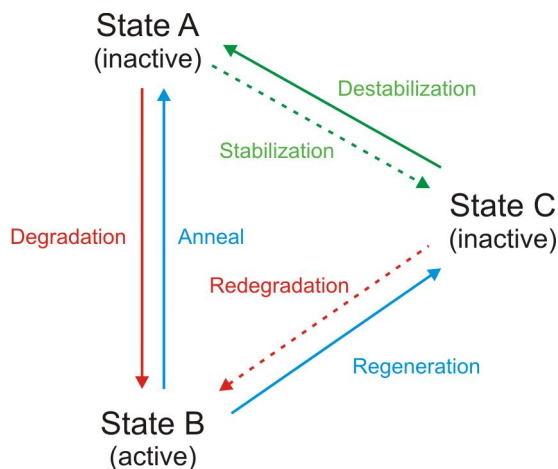


Fig. 1: Microscopic reaction scheme of the three state model. Recombination activity is marked in brackets. Dashed Lines were not observed so far.

The left part containing state A and B and the reactions of degradation and anneal represents a simple model for the degradation process neglecting the fast defect formation process mentioned in the introduction, because its defects probably transform in the cause of time to the defects of state B. State C is connected to this system by potential reactions described in Fig. 1.

Later on the existence of the 'Regeneration' as well as the 'Destabilization' reaction is verified, and their formation kinetics are discussed. The existence of the 'Redegradation' and 'Stabilization' channels is unknown up to now.

Sample preparation and experimental setup

For the following investigations, 12.5x12.5 cm² semi-square boron doped Cz silicon solar cells with resistivities of 1-3 Ωcm were fabricated using an industrial standard process consisting of alkaline saw damage etch and/or texture, POCl₃ diffused emitter with about 50 Ω/sq., PECVD SiN_x anti-reflection coating and a screen printed metallization.

For degradation of solar cells both, illumination under a halogen lamp at a current equivalent to AM 1.5 and forward bias voltage were used in combination with a temperature controlled environment. Annealing of solar cells (state B to A) was performed on a hot plate at a temperature of ~200 °C for 30 min in complete darkness.

Confirmation of boron-oxygen related degradation

To make sure that the samples suffer from the typical boron-oxygen related degradation as described in the introduction, some experiments were performed including time resolved recording of IV parameters. This allows the determination of decay constants from a single exponential fit, which are characteristic for this specific type of degradation. Combining these records at different temperatures results in the Arrhenius plot shown in Fig. 2, from which an activation energy of 0.44 ± 0.07 eV could be extracted.

Taking its error into account, this is in good agreement with values published from other groups [1,2] and it confirms that the samples behave according to the well known boron-oxygen related degradation.

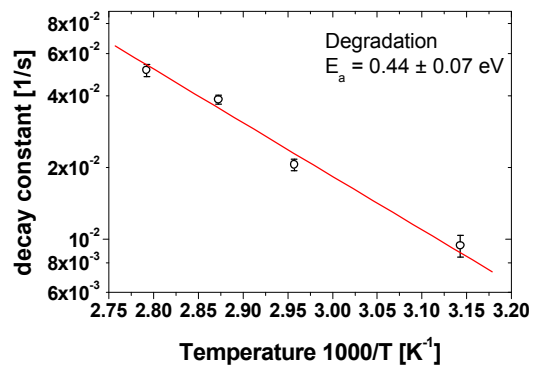


Fig. 2: Arrhenius plot deduced from V_{oc} degradation decay curves at different temperatures.

Time resolved regeneration process

As the regeneration reaction aims at the already existing active defects (state B), the sample was first degraded at 25°C under illumination until an asymptotic stable performance was reached, indicating the complete degradation (Fig. 3). Afterwards our new process was applied and interrupted multiple times for determination of IV parameters. This results in a time resolved record of the regeneration process within the cell shown in Fig. 3.

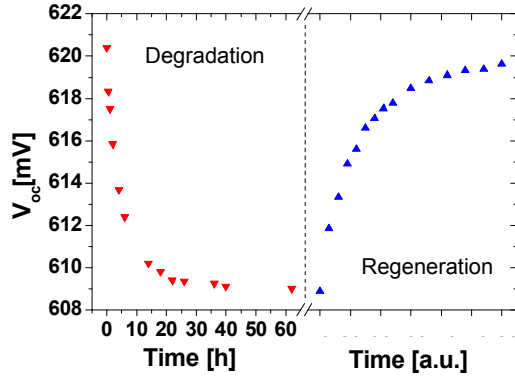


Fig. 3: Degradation and subsequent Regeneration cycle. The long time limit of regeneration probably equals the annealed state at the beginning of degradation.

Similar to the degradation process, the temporal development is described by a saturating exponential decay (for the trap density), and as the harmful defects are neutralized, the electrical parameters begin to regenerate. QSSPC measurements on equivalent samples also showed this effect.

Stability of the regenerated state

To confirm that the regeneration process leads to a third state C differing from the also inactive annealed state A, a subsequent monitored degradation is carried out. The results of this process, carried out under both illumination and applied forward voltage, are shown in Fig. 4 with V_{oc} representative for electrical parameters. For a direct comparison, the degradation of the same cell was recorded before the regeneration process also shown in Fig. 4. It is obvious, that the solar cell after this new process step is not only far more stable than without it but that the stable performance level is significantly higher than for the degraded cell. The difference in V_{oc} compared to the first measurements of the annealed cell originates from an incomplete regeneration cycle due to the saturation character of the process.

This property of the regenerated state provides the possibility to distinguish between the so far electrically not distinguishable annealed and regenerated state. As a result, the fundamental lifetime limit published by Bothe et al. [4] is not valid for regenerated samples, showing effective lifetimes up to 140 μ s on 1.4 Ω cm material with SiN_x surface passivation. The effectiveness of the regeneration is proven for materials with resistivities of 1.4 – 14 Ω cm received from at least three suppliers.

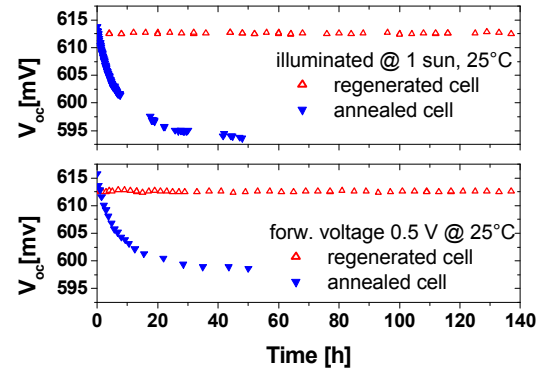


Fig. 4: Stability test of a regenerated cell compared to a completely annealed cell. Degradation was induced by illumination (top) and applied forward voltage (bottom).

Formation kinetics of regeneration

To determine the formation kinetics of regeneration, time resolved IV data was recorded at different temperatures. As expected for chemical reactions, a strong temperature dependence is observed as shown in Fig. 5.

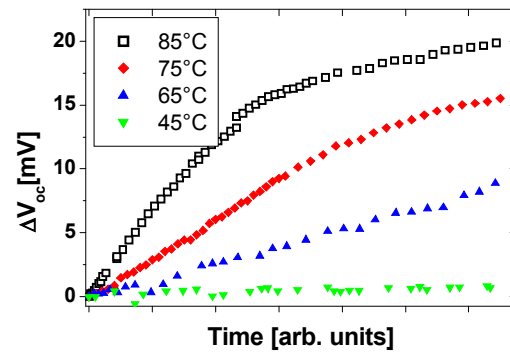


Fig. 5: Gain in V_{oc} within the regeneration process for different temperatures and constant other parameters. At low temperatures (down triangles), the regeneration hardly appears, higher temperatures accelerate the process significantly.

For low temperatures, the time needed for regeneration is far longer than investigated here, indicating that the reaction is constricted by an energy barrier.

The gain in V_{oc} for higher temperatures reveals that regeneration can be approximated by an (inverse) exponential decay and thus the extraction of a decay constant $1/t_0$ with t_0 being the time necessary for an amplitude drop to $1/e$ is feasible. Using these decay constants extracted at even higher temperatures (not shown) in combination with the Arrhenius equation (Eq. 1), the activation energy can be determined to be 0.62 ± 0.02 eV as shown in Fig. 6. Other measurements provide with higher uncertainties values up to 0.92 eV and thus the correct value remains ambiguous. The characteristic frequency of the regeneration process can be adjusted in several orders of magnitude by the applied parameters in the regeneration process step.

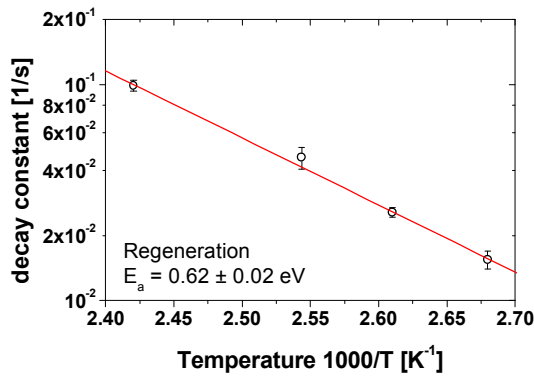


Fig. 6: Arrhenius plot of the regeneration process.

Kinetics of the destabilization

At elevated temperatures, a transition from state C to state A can be assumed. Due to the electrical indistinguishability, the effect cannot be directly investigated. Therefore, a subsequent degradation can be applied, converting all defects in state A to B. This does not influence stable defects in state C, thus reducing the problem to the well known distinction between state B and C.

For the determination of a decay constant of this process, multiple very similar samples are treated in the dark at the same temperature for different durations and are afterwards degraded under illumination until no more change in IV parameters could be detected. The resulting decay curves of destabilization are shown in Fig. 7.

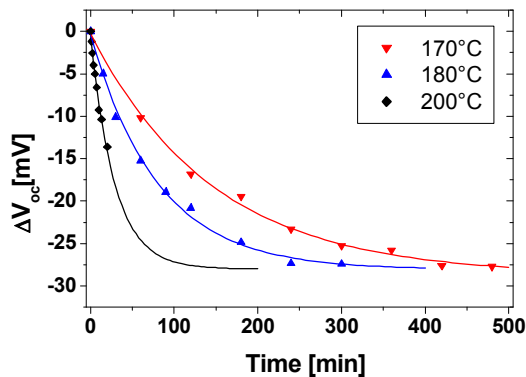


Fig. 7: Decay curves of the destabilization recorded after subsequent degradation. The lines are exponential decay fits for determination of the decay constants.

The data at 200 °C show the main problem of this method. The number of samples was limited to eight and thus only eight different times could be investigated. Measured points in the strongly decaying phase support a good fit in this region but do not allow a determination of the long time limit. Thus the limiting value has to be given manually according to the other decay curves.

The extracted decay constants give rise to another Arrhenius plot with an extracted activation energy in the range of 0.96 – 1.02 eV, as shown in Fig. 8.

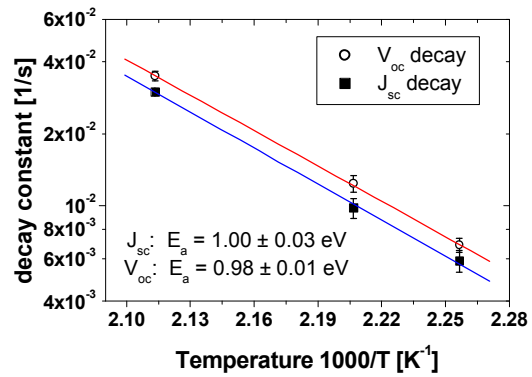


Fig. 8: Arrhenius plot of the destabilization. The data points were extracted from J_{sc} and V_{oc} decay curves.

The characteristic frequency resulting as a byproduct of the Arrhenius plot is approximately in the order of 10^9 Hz. This is about 3-4 orders of magnitude lower than phononic frequencies, being expected for simple complex dissociation by lattice vibrations. Thus it could be an indication for a more complex dissociation reaction, during which one or more intermediate stages are traversed in analogy to the two stepped annealing reaction of the fast forming defects as mentioned in the introduction.

CONCLUSIONS

In this contribution the impact of boron-oxygen related defects and its formation kinetics in Cz silicon were investigated. Converting most of the boron-oxygen related defects to the newly introduced third state C results in a reliable stabilization of the electrical parameters of highly boron doped Cz silicon solar cells at a level comparable to the annealed state. For temperatures according to the working conditions of encapsulated solar cells the regenerated state is proven to be stable for at least 192 hours. Thus boron-oxygen related degradation is not the limiting factor for the cell performance anymore, allowing the use of more cost-efficient highly boron doped material, which may tap the full efficiency potential and may reduce W_p costs. In addition to standard front contact cell concepts, also advanced cell concepts like back contact cells may benefit from higher stable minority carrier lifetimes.

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