

Research

SHORT COMMUNICATION

Investigations on the Long Time Behavior of the Metastable Boron–Oxygen Complex in Crystalline Silicon

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Boron and oxygen contamination in Czochralski-grown (Cz) silicon leads to a degradation of the minority charge carrier lifetime within short times due to the formation of recombination active complexes. The formation of these complexes is investigated for longer times showing a further development of the defect. This development called ‘regeneration’ is triggered by illumination or applied forward voltages and leads to a new state of the defect. This new state of the defect is proven to be less recombination active allowing higher stable minority carrier lifetimes and conversion efficiencies of solar cells. The influences of temperature and light intensity are discussed. Copyright © 2007 John Wiley & Sons, Ltd.

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INTRODUCTION

Lifetime degradation in standard Czochralski-grown (Cz) silicon due to the formation of boron–oxygen complexes with high recombination activity limits the efficiency potential of highly boron doped Cz silicon solar cells.^{1,2}

The minority charge carrier lifetime after complete degradation can be described by a fundamental limit mainly determined by the boron and oxygen concentration³ as well as marginally influenced by the carbon concentration.⁴ The formation of these complexes already takes place at room temperature and is driven by charge carriers injected by light or external voltages.^{5,6} The total number of complexes scales linearly with the boron concentration^{7–10} and a loss in

efficiency up to 2% absolute in highly boron doped ($N_D > 10^{16} \text{ cm}^{-3}$) oxygen rich material under the typical working conditions of solar cells may occur.

The total number of complexes scales about quadratically with the interstitial oxygen concentration^{9–11} suggesting a stoichiometric composition of one substitutional boron and two oxygen atoms. Optimized temperature ramps within the manufacturing process can limit the negative impact of defect formation but cannot avoid it completely.^{7,11,12}

The observable degradation consists of two parallel reactions,¹⁰ one known as the fast process which occurs in the first few minutes and the other as the slow asymptotic process. The two processes lead at first to two different states but for longer times a subsequent reaction seems to transform both into the final state of the slow asymptotic process and the fast process can be neglected.

The formation of the boron–oxygen complexes is a thermally activated reaction^{10,11,13} and hence higher

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temperatures increase the generation rate of the complexes. It is also observable that the recombination active complexes become instable at elevated temperatures around 140°C in an anneal step in the dark thus making these complexes metastable.^{10,11,14} This behavior of degradation and anneal can be roughly understood by a conversion of two possible states of the complex into each other as it is shown in the left part of Figure 1, neglecting the fast process as mentioned before. The annealed state A features only marginal recombination activity while the degraded state B is highly recombination active.

EXPERIMENTAL SETUP

For our experiments, $12.5 \times 12.5 \text{ cm}^2$ Cz silicon solar cells with a base boron doping around $0.5\text{--}1 \times 10^{16} \text{ cm}^{-3}$ were prepared using an industrial type solar cell process including NaOH saw damage etch, a 50 Ω/sq . phosphorus emitter from a POCl_3 diffusion, a $\text{SiN}_x\text{:H}$ antireflection coating by plasma enhanced chemical vapor deposition and a screen printed silver front and aluminum back contact. For reproducible starting conditions, all samples were annealed at 200°C in the dark for 30 min directly before starting the experiments to ensure that the boron–oxygen complexes are mainly present in the annealed state A.

PRINCIPLE RESULTS AND INTERPRETATION

In a first experiment, the sample was placed on a temperature controlled chuck and illuminated by a halogen lamp with an intensity leading to a current equivalent of one sun (1 kW/m^2 , AM 1.5). The temporal development of the electrical parameters is monitored by placing the sample at a different measurement setup and collecting dark $I(V)$ characteristics of the solar cell at 24°C independent from the temperature during illumination. These $I(V)$ characteristics were used to deduce the saturation current density J_{01} of the first diode using the two-diode model. The results of this experiment are shown in Figure 2.

At first J_{01} increases indicating a drop of the bulk lifetime in the solar cell due to the formation of the recombination active complexes (degradation). For longer times, a contrary trend sets in and J_{01} decreases which can be explained by a gain in bulk lifetime (regeneration). Further experiments on lifetime samples have given proof that this effect is indeed clearly associated with a recovery of the bulk lifetime.¹⁵ This can only be explained by a neutralization of the recombination active complexes. State A of the complex is not stable under illumination for the temperatures investigated (100–160°C), as can be concluded from the degradation within the first few

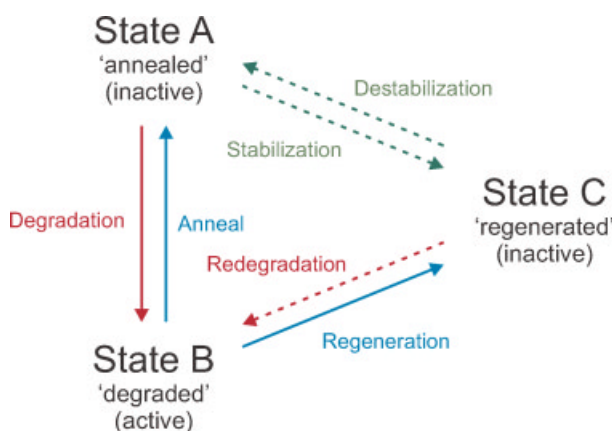


Figure 1. New proposed three state reaction scheme of degradation (left part only) and regeneration. Both degradation and regeneration are triggered by (excess) carrier injection. Degradation occurs already at room temperature while regeneration requires elevated temperatures around 140°C. The anneal as reversal reaction to the degradation principally takes place at elevated temperatures around 140°C but can be only observed if degradation and regeneration are suppressed. The observed conversion from state C to state A might be realized by a direct conversion (destabilization) or a two step reaction using state B as intermediate stage (redegradation and subsequent anneal). The direct conversion from state A to state C (stabilization) has not been observed so far

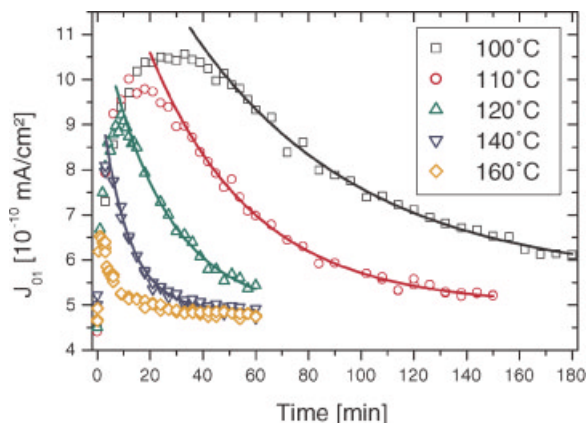


Figure 2. Temporal development of the saturation current density J_{01} during degradation (increase) and subsequent regeneration (decrease) both induced by constant illumination of 1 sun (current equivalent) at different temperatures. The base resistivity of the Cz Si solar cell was 1.4 Ω cm. The change in the amplitude results from the changing ratio between the time constants of degradation and regeneration

minutes. Thus the later increase in lifetime cannot be explained by a simple anneal reaction leading back from the degraded state B to the annealed state A. It rather necessitates an additional state C of the complex, which is recombination inactive and also stable towards a back reaction to the degraded state B for the temperatures investigated. The long time limit of the data shown in Figure 2 seems to resemble the starting values, when the sample is mainly in the annealed state A. Therefore, we suggest that this state C is characterized by a low recombination activity so

that other recombination channels apart from the one related to the boron–oxygen complex become lifetime limiting. The macroscopically observed recovery correlated to a conversion of large numbers of complexes from the degraded state B to this new ‘regenerated’ state C is called regeneration.

In consequence, the two state reaction scheme used for the degradation has to be extended by an additional state C with a recombination activity comparable to state A. The complete reaction scheme is shown in Figure 1, introducing the reaction path of regeneration leading from state B to this new state C.

PROPERTIES OF THE REGENERATION REACTION

The significant decrease in the duration of the regeneration process with rising temperature as shown in Figure 2 indicates a strong temperature dependence and hence an Arrhenius plot based on Equation (1) for the conversion rate ν

$$\nu = \nu_{\text{ch}} \exp\left(-\frac{E_a}{k_B T}\right) \quad (1)$$

can be derived from the data in Figure 2. As the time constants for the regeneration at different temperatures support the Arrhenius equation as shown in Figure 3, the regeneration is likely to be a thermally activated reaction and an activation energy E_a of 0.61 ± 0.01 eV can be determined. This value differs strongly from the activation energies for the degradation with about

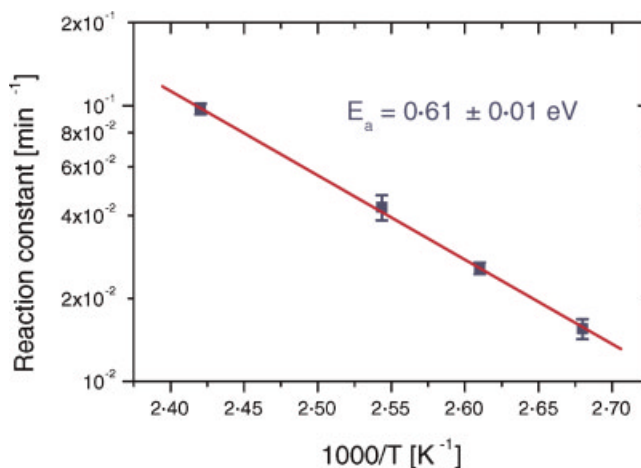


Figure 3. Arrhenius plot derived from the J_{01} measurements in Figure 2. The solid line is a linear fit according to Equation (1) allowing the extraction of the activation energy E_a of the regeneration

0.45 eV^{13,16,17} and for the anneal reaction with about 1.32 eV.¹⁴ Despite the activation energies the characteristic rates of the reactions play a key role for the observed time constants.

The pre-exponential characteristic rate ν_{ch} of the regeneration reaction depends on various factors such as the illumination intensity. The regeneration cycle for three different intensities ranging from 1 sun down to 1/9 sun is shown in Figure 4. We monitored the variation of the solar cell parameters by interrupting the regeneration process multiple times to measure illuminated $I(V)$ characteristics under standard reporting conditions (AM 1.5, 1 kW/m², 25°C). In contrast to the J_{01} data shown in Figure 2 these data do not require any further evaluation (like the two-diode model). The effect of regeneration shows up clearly in the short circuit current as well as the open circuit voltage and thus also the conversion efficiency. The fill factor remains mainly unaffected.

As shown in Figure 4 a variation of the illumination results in a significant change of the time constant of regeneration and hence the light intensity seems to be a limiting factor for the regeneration process. Referring to Figure 4 the reaction rate seems to depend approximately linearly on the light intensity in the range of one sun. In contrast to the regeneration process the degradation rate shows no significant dependence on light intensity in the range of one sun¹¹ suggesting that the (excess) carrier concentration is not a limiting factor for the degradation reaction.

Further experiments have proven that the regeneration process appears not only under illumination

but also under applied forward voltages. Both methods have in common that excess carriers are injected into the sample and thus we conclude that (excess) carriers are responsible for or at least accompany the conversion of complexes from the degraded state B to the regenerated state C. Therefore, we assume that ν_{ch} depends crucially on the (excess) carrier density, with higher densities accelerating the process.

As it is shown in Figure 2, the duration of the regeneration process is in the range of minutes to hours at elevated temperatures and varies strongly with temperature. Similar investigations at lower temperatures down to room temperature (25°C) suggest significantly longer durations and hence the regeneration becomes negligible on the timescale of degradation, which takes place in few hours at room temperature.

This allows proving the existence of the new regenerated state C which differs clearly from the annealed state A regarding typical degrading conditions like illumination or applied forward voltages at room temperature (25°C). Therefore, the temporal development of one solar cell was monitored under both conditions before and after the regeneration took place. The data resulting from this experiment are shown in Figure 5 (top) for the illumination with 1 sun at 25°C and Figure 5 (bottom) for an applied forward voltage of 0.5 V at 25°C.

In both experiments, V_{oc} shows the well known instability before the regeneration process reducing the efficiency from 16.4% down to 15.2%. After degradation, the solar cell was treated at elevated

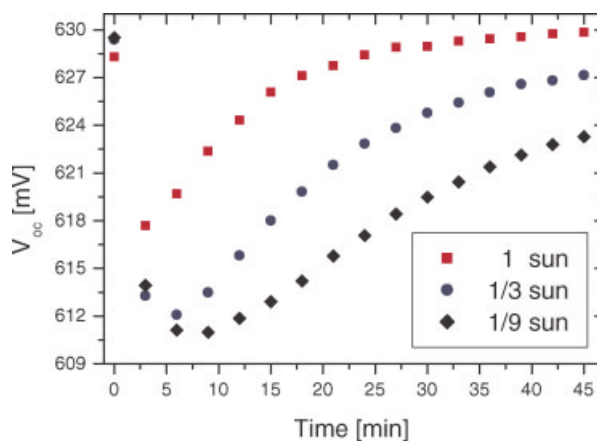


Figure 4. Temporal development of V_{oc} of a 1.4 Ω cm Cz Si solar cell during the regeneration at 140°C under different illumination intensities (in suns). Higher intensities accelerate the process. The change in the amplitude results from the changing ratio between the time constants of degradation and regeneration

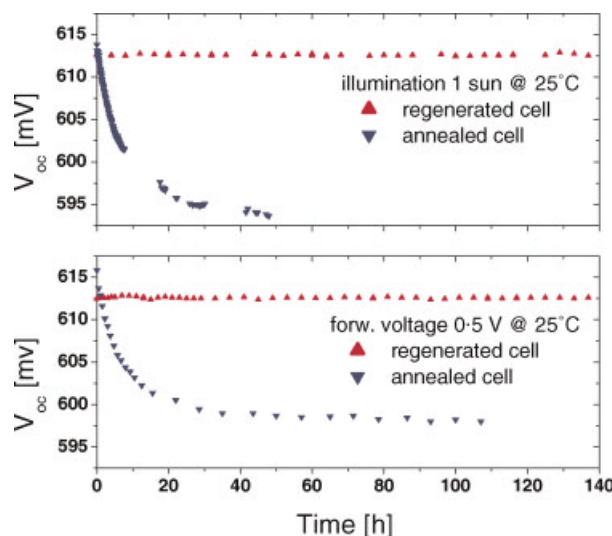


Figure 5. Temporal development of the open circuit voltage V_{oc} of a $2.8 \Omega \text{ cm}$ Cz Si solar cell under illumination of 1 sun (top) as well as under an applied forward voltage of 0.5 V (bottom). Both illumination and applied voltage cause a severe degradation of the annealed cell before the regeneration treatment, afterwards V_{oc} shows no instability

temperatures under illumination. As the regeneration shows an asymptotic behavior, the process was terminated as V_{oc} recovered about 80% of the loss due to the initial degradation. As both graphs show, V_{oc} remains totally stable after the regeneration process. The efficiency of the solar cell recovered to 16.2% but as the regeneration was terminated ahead of time it is expected that further improvement is possible.

This completely different behavior of the solar cell parameters (V_{oc} shown here) before and after the regeneration process proves that the new regenerated state exists.

Our investigations revealed that the regenerated state C becomes instable itself at elevated temperatures and is converted back into the annealed state A. This reaction also seems to be thermally activated and an activation energy of about 1.0 eV was determined.¹⁵ Whether this conversion follows the direct channel of destabilization as shown in Figure 1 or a two step reaction with state B as an intermediate stage, could not be clarified yet. In the experiments in the temperature range of 100–160°C presented here, this instability is covered by the parallel reaction cycle of degradation followed by regeneration and as the degradation–regeneration cycle dominates all other reactions, the equilibrium state of the system favors complexes in the regenerated state C.

CONCLUSIONS

The introduction of the regenerated state C with negligible recombination activity eliminates losses in the bulk lifetime due to the boron–oxygen related degradation and therefore leads to higher stable conversion efficiencies in highly boron doped Cz silicon solar cells.

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