

## FURTHER INVESTIGATIONS ON THE AVOIDANCE OF BORON-OXYGEN RELATED DEGRADATION BY MEANS OF REGENERATION

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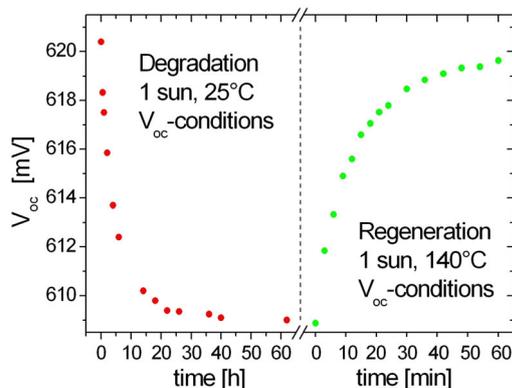
**ABSTRACT:** Boron and oxygen contamination in Czochralski (Cz) grown silicon leads in the short term to a degradation of the charge carrier lifetime due to the formation of recombination active complexes. For longer times these harmful complexes may be neutralized by a ‘regeneration’ called reaction. Supported by elevated temperatures, a conversion of the recombination active species into an inactive species is induced by the presence of charge carriers injected by light or bias voltages. In this contribution, the influence of light intensity and bias voltages is discussed.

**Keywords:** Czochralski, Degradation, Boron-oxygen complex

### 1 INTRODUCTION

A high lifetime of minority charge carriers is essential for high conversion efficiencies especially of thick crystalline silicon solar cells. Monocrystalline silicon materials like 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 in general. It is also well established that the maximal achievable conversion efficiency of silicon solar cells with an emitter on the front side rises with increasing doping concentration and as calculations have shown, an optimal result is expected for a specific resistivity of about 1 Ωcm 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 (see Figure 1, left) when excess charge carriers are injected by light or bias voltages. These changes originate from a degradation of the bulk lifetime which results from a formation of recombination active complexes consisting of boron and oxygen [1,2]. Therefore, this special type of degradation is called ‘boron-oxygen related degradation’. The level of boron and oxygen contamination mainly determines a fundamental limit of the bulk lifetime after degradation [3] with slight influence of the carbon content [4].



**Figure 1:** Open circuit voltage monitored during the degradation phase at 25°C (left) and the regeneration phase (right) at 140°C.

Even though this special type of degradation was subject to many investigations over the past 30 years and many properties of complex formation and the complex itself were clarified, data published only recently have proven a subsequent reaction following the degradation called ‘regeneration’ [5,6]. Triggered or accompanied by the presence of (excess) minority charge carriers injected by light or forward bias 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 Figure 1, right).

If the injection of charge carriers takes place at elevated temperatures, degradation and regeneration cannot be divided clearly like it is shown in Figure 1 (note: different temperatures for degradation and regeneration) and form a closed curve (see e.g. Figure 2). These curves show at first the negative impact of the degradation and afterwards the recovery by regeneration. Both reactions, degradation [7,8] as well as regeneration [6], have been shown to be thermally activated reactions, or in other words the conversion probability  $P_{conv}$  of one specimen of the complex towards the specimen formed during the degradation or regeneration respectively follows in both cases the Arrhenius equation in the form

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

Besides the mean thermal energy  $k_B T$  this equation includes a reaction specific activation energy  $E_a$  and a characteristic conversion rate  $v_{char}$ . The activation energies of both reactions have already been determined to  $E_a \sim 0.45$  eV for the degradation [6,7,8] and  $E_a \sim 0.61$  eV for the regeneration [6].

The number of converted complexes per time unit determines the time constant of the macroscopically observed reaction. Understanding the dynamics of conversion and hence what determines the rate of conversion is the key to clarify what is physically going on and how to manipulate the reaction.

The activation energy of the conversion is unchangeably given by nature and reflects microscopic processes like statistical diffusion of components hindered by specific energy barriers. In contrast, temperature and partly the characteristic conversion rate  $v_{char}$  are accessible for the experimenter.

Changing temperature has great influence due to the exponential function in Eqn. 1. But changing temperature may create other problems like implying thermal stress at the contacts or, when applied on the module level, seriously damage the common EVA (Ethyl-Vinyl-Acetat) lamination foil. So controlling the characteristic frequency might be the better approach to influence the reaction rate.

As the regeneration is triggered or at least accompanied by the presence of (excess) charge carriers, their quantitative influence is subject of the following investigations. It has to be distinguished between charge carrier injection by light or bias voltages.

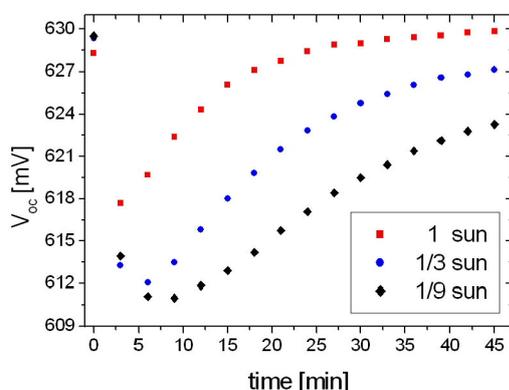
## 2. EXPERIMENTS

For the following investigations, solar cells were processed from standard 1.4  $\Omega\text{cm}$  boron doped Cz silicon material using an industrial standard process consisting of alkaline saw damage etch,  $\text{POCl}_3$  based emitter diffusion resulting in a sheet resistance of 50  $\Omega/\text{sq.}$ , PECVD  $\text{SiN}_x\text{:H}$  anti reflection coating and a screen printed metallization.

Before each experiment, the samples were tempered at 200°C in the dark to guarantee comparable starting conditions.

### 2.1 Influence of light intensity

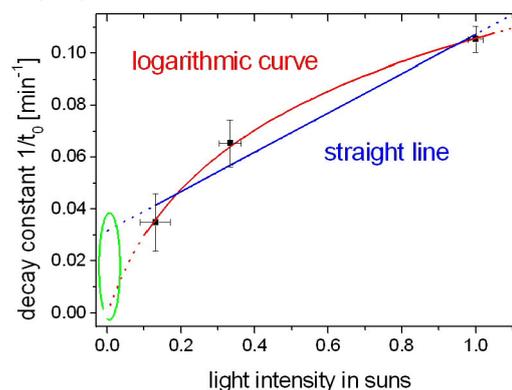
The samples were illuminated with a common halogen lamp which exhibits a broad band spectrum reaching at least from infrared to ultraviolet. The lamp's intensity of one sun was adjusted to the current equivalent of one sun of a calibrated solar cell. The intensity on the sample could be weakened by metal gratings placed above the sample. The shadowing was adjusted by different metal coverage in the range of 0% (no grating) up to 80%. The use of metal gratings avoids relative changes in the spectral composition of the halogen lamp's spectrum as no wavelength dependent absorption occurs. For temperature control, the samples were placed on a heated chuck under  $V_{oc}$ -conditions. The open circuit voltage  $V_{oc}$  of the solar cell was measured periodically at room temperature to monitor the progress of degradation and regeneration as shown in Figure 2 for three different intensities.



**Figure 2:** Open circuit voltage  $V_{oc}$  monitored during degradation and regeneration cycles induced by illumination at 140°C and different intensities. The data set for 1/9 sun was cut off at 45 min.

As can be seen from Figure 2, the degradation and regeneration cycle varies with intensity. The few data points describing the drop due to the degradation do not allow any further conclusions on the kinetics of degradation. In contrast, a significant change in the kinetics of the regeneration process is visible. The data for 1/3 and 1/9 suns in Figure 2 were cut off to emphasize the starting phase but each measurement series reached a final level of  $V_{oc}$  close to 630 mV.

To quantify the influence of light intensity, the increasing part of each data set presented in Figure 2 was fitted by a single exponential decay to determine a characteristic time constant  $t_0$ . Figure 3 shows a comparison of the inverse time constants at different light intensities.



**Figure 3:** Inverse time constants  $1/t_0$  of the regeneration part deduced from Figure 2 plotted versus light intensity. The drawn lines are only guides to the eye and represent two possible curve progressions in the investigated intensity range. Taking the error bars into account both extreme curve progressions could support the data. Note that for vanishing intensity (marked in green), the time constant of a straight line remains finite and results for higher intensities in a steadily decrease of the time constant.

The few data points and the error bars do not allow a reliable prediction on the exact correlation of light intensity and time constant. The drawn lines are therefore only two possible curves for further discussion. Two points should be denoted. First, the drawn curves fundamentally differ for vanishing intensities. A linear correlation (blue line) would suggest that regeneration may occur in the dark without any external influence. The existence of this 'dark regeneration' cannot be ruled out as a matter of principle due to the permanent presence of intrinsic charge carriers that could support complex conversion, but it should be taken into account that thermal statistics at a doping concentration of about  $10^{16} \text{cm}^{-3}$  allow only about  $10^4 \text{cm}^{-3}$  minority charge carriers in the bulk region. As it can be assumed from Shockley-Read-Hall recombination calculations, the boron-oxygen related complexes do exceed the minority carrier concentration by several orders of magnitude. Hence it is unlikely that these few minority charge carriers remarkably support the regeneration reaction even if a continuous supply by thermal excitation is given. Thus the inverse time constant should tend towards zero even if it remains finite. A logarithmic slope (red curve) would better support this argumentation.

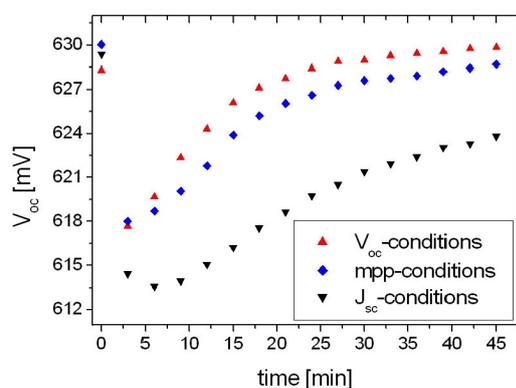
For higher intensities a contrary argumentation is possible. It is unlikely that an extremely high charge carrier concentration will lead to a steadily decreasing time constant (as indicated by the blue line). Instead, saturation is more likely to be reached as other components (needed for formation of the complex) than the charge carriers will become the limiting parameter for the reaction. However, in the range investigated in this contribution, an approximately linear behaviour just as well as a logarithmic-type behaviour could be assumed.

## 2.2 Influence of working conditions under illumination

Under illumination, the (excess) charge carrier density or the position of the quasi Fermi levels, respectively, may be influenced also by the working point of the solar cell, or in other words whether a voltage may build up across the cell and/or whether an external current may flow.

Three working conditions were chosen:  $V_{oc}$ -,  $I_{sc}$ - and mpp-conditions. For  $V_{oc}$  conditions, the front and rear contact remained isolated. For  $I_{sc}$ -conditions, the front and rear contact were directly connected. For mpp-conditions, a small resistor (with constant value) was interconnected between front and rear contact. This does not fix the working point of the solar cell exactly at maximum power output due to the changes in the electrical parameters of the cell in the course of degradation and regeneration, but it should provide an indication of the behaviour close to maximum power output. The samples were illuminated again by a halogen lamp at the current equivalent of one sun and placed on a temperature stabilized chuck at 140°C. Again the electrical parameters were periodically measured at room temperature. The collected data are shown in Figure 4.

The data from  $V_{oc}$  and  $I_{sc}$  differ significantly regarding the time constants of the recovery. Defining again a characteristic time constant  $t_0$  from a single exponential decay, regeneration under  $I_{sc}$ -conditions takes about 24 min compared to only 9.5 min for  $V_{oc}$ -conditions and thus about 2.5 times longer (see Table I). This behaviour could be roughly expected from the previous experiments as the injection level is lower in the case of  $I_{sc}$ -conditions. For mpp-conditions, an intermediate behaviour is observed resembling almost the  $V_{oc}$ -conditions. This can be understood as the charge carrier concentration in the bulk region is almost similar to the  $V_{oc}$ -conditions.



**Figure 4:** Open circuit voltage  $V_{oc}$  monitored during degradation and regeneration cycles under constant illumination of one sun at 140°C but varying working conditions of the solar cell.

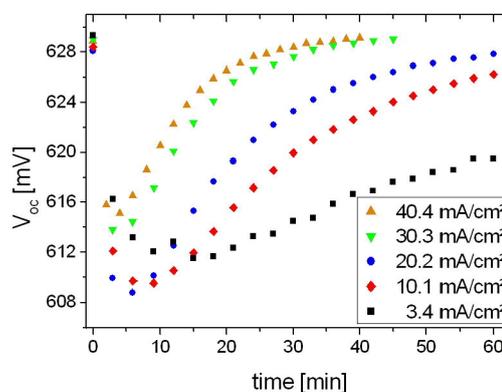
**Table I:** Comparison of the time constants  $t_0$  of regeneration under different working conditions

Condition	$V_{oc}$	mp	$I_{sc}$
Time constant [min]	9.49 ( $\pm 0.22$ )	9.53 ( $\pm 0.60$ )	23.81 ( $\pm 0.94$ )
Relative to $V_{oc}$ [%]	100 $\pm$ 2	100 $\pm$ 7	250 $\pm$ 5

## 2.3. Influence of forward bias voltages

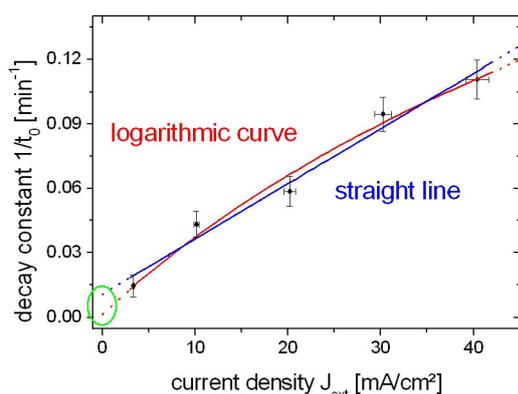
In addition to illumination, excess carriers can be injected by forward bias voltages. As the electrical parameters vary in the course of the degradation/regeneration cycle, two basically different ways of injection are possible. At the one hand, the (external) current can be kept constant and thus the voltage drop across the cell varies. On the other hand, the voltage drop can be kept constant and thus the (external) current varies. In the following experiments, a constant (external) current was chosen.

The sample was placed again on a temperature controlled chuck at 140°C and was connected to a power supply with current stabilization. The experiments took place in the dark to avoid any influence of light-induced regeneration. The samples were periodically measured at room temperature to monitor the progress of regeneration. It should be noted that the short circuit current density  $J_{sc}$  of the samples was about 32 mA/cm<sup>2</sup> at one sun. The results for five different (external) current densities are shown in Figure 5.



**Figure 5:** Open circuit voltage  $V_{oc}$  monitored during degradation and regeneration cycles induced by different bias voltages (constant external current densities) at 140°C in the dark. The data for 3.4 mA/cm<sup>2</sup> are systematically shifted relative to the other data and cut off at 60 min. Lower current densities lead to elongated time constants  $t_0$ .

As expected, the duration of regeneration increases with lower (external) current densities. The data from the 3.4 mA/cm<sup>2</sup> experiment were cut off for a better presentation of the other data but do increase further up to a level close to 630 mV. Again the data for each current density were fitted by a single exponential decay to determine a characteristic time constant  $t_0$ . These time constants are presented in Figure 6.



**Figure 6:** Inverse time constants  $1/t_0$  deduced from Figure 5. The drawn curves are only guides to the eye and represent two extreme cases of curve progression supported by the data (including error bars) in the investigated range of current density. In analogy to the illuminated case shown in Figure 3, vanishing current densities (marked in green) lead to a finite time constant and higher current densities result in a steadily decreasing time constant for the straight line (blue).

In contrast to Figure 3, which shows the correlation of the time constant with light intensity, only a slight slope is visible. The statistical spread points can support a linear dependence as well as a non-linear, possibly logarithmic dependence. However, it should be denoted that the linear dependence of the decay constant  $1/t_0$  leads to a non-vanishing value at 0 mA/cm<sup>2</sup>. This would mean again that the regeneration should occur in the dark without any external influence.

For (external) current densities beyond 40.4 mA/cm<sup>2</sup> the time constants  $t_0$  seem to drop further. Taking into account a  $J_{sc}$  of around 32 mA/cm<sup>2</sup>, the presented data in Figure 5 cover a current equivalent up to 1.25 suns but due to the lower slope a possible saturation is likely to be reached at higher current densities compared to Figure 2. However, it should be kept in mind that the excess charge carrier concentration of both cases cannot be directly compared.

### 3. DISCUSSION

$V_{oc}$ -based measurements of industrial-type solar cells can provide neither precise information about the injection level deep within the bulk region nor about the exact development of the bulk lifetime due to their complex I(V) behaviour (non-ideal two diode model). However, the use of these solar cells in the above experiments shows that the results are relevant for industrial-type solar cells.

As the experiments above have shown, the time constant of regeneration can be significantly influenced by the excess charge carrier concentration in the range of about 1/10 to 1 sun in the illuminated case as well as correspondingly in the case of forward bias voltages. As can be concluded from Figure 2 and Figure 5 a saturation of the time constant may be assumed and would be expected to be reached at considerably higher charge carrier concentrations than one sun, indicating that the charge carriers are of extreme importance for the regeneration reaction.

Comparable investigations for the dependence of the degradation kinetics on carrier concentrations have shown that saturation is already reached at light intensities of around 1/100 sun and thus charge carriers have minor importance in the range of one sun [9].

A considerable gradient of the time constant regarding light intensity or current density suggests that the regeneration reaction can be accelerated further by this parameter independent of the temperature. Hence an improvement may be possible compared to the recently published data [5,6].

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