

## ELECTRICAL AND THERMAL PROPERTIES OF THE METASTABLE DEFECT IN BORON-DOPED CZOCHRALSKI SILICON (CZ-SI)

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**ABSTRACT:** Lifetime degradation observed in boron-doped Czochralski silicon (Cz-Si) has its origin in a metastable defect that is activated under illumination or forward bias and deactivated under an anneal at around 200°C. To give insight into the physical mechanism underlying this defect transformation, the first part of this study is focused on the kinetics of defect formation and annihilation. For the process of defect formation, the quantitative analysis of this work clearly shows that it *cannot* be directly described by the mechanism of recombination-enhanced defect reaction (REDR) as it has been proposed in recent studies. While REDR predicts for the defect generation rate  $U_{gen}$  a linear dependence on the doping concentration  $N_A$  and the injection level  $\Delta n$ , a quadratic doping and a vanishing injection dependence is found by an improved time-resolved degradation experiment measured with quasi-steady-state photoconductance technique. The experiment reveals that  $U_{gen}$  reaches almost its maximum value if  $\Delta n$  only lies above some threshold value, which is already reached for an illumination with 1 mW/cm<sup>2</sup> on a 0.86 Ωcm Cz-sample. For the process of defect annihilation, an isothermal annealing experiment reveals that it is thermally activated with an energy barrier  $E_{barr} = 1.32 \pm 0.05$  eV, determined for the first time. The last part of the study is dedicated to the electronic structure of the defect. From temperature-dependent lifetime spectroscopy (TDLS) an upper limit of 0.41 eV is found for the energy level of the Cz-defect in its active state. If the TDLS-result of this work is combined with the energy range determined by Schmidt et al. from injection dependent lifetime spectroscopy, the energy level of the defect in its active state can be further localized in the lower band half at  $E_V + 0.35...0.41$  eV.

**Keywords:** Czochralski - 1: Silicon - 2: Defects - 3.

### 1. INTRODUCTION

It is well known that carrier lifetime in standard boron-doped Czochralski-grown silicon (Cz-Si) is strongly reduced under illumination or forward bias leading to a significant loss in solar cell efficiency. This process can fully be reversed by an annealing step at around 200°C. Although this degradation phenomenon was already discovered in 1972 [1], only recently a couple of studies have revealed that the underlying metastable defect is correlated with the boron and oxygen concentration of the Cz-Si material [2,3]. From lifetime spectroscopic measurements Schmidt et al. [4] determined an energy range between  $E_V + 0.35$  eV and  $E_C - 0.45$  eV for the energy level of the defect in its active state  $A$  while Rein et al. [5] found an energy level below 0.1 eV from either band edge for the defect in its passive state  $P$ . These findings explain the strong difference in the recombination activity observed for the defect in state  $A$  and  $P$ . Nevertheless, the exact electronic structure is still unknown. In order to facilitate a further localization of the energy level in state  $A$ , different Cz-materials are analysed in this study by means of temperature-dependent lifetime spectroscopy (TDLS). Concerning the physical mechanism underlying the defect transformation, hitherto only few things are known. Based on qualitative observations, recombination-enhanced defect reaction (REDR) has been proposed as mechanism for defect formation [6]. To give deeper insight in the physical mechanism, the kinetics of defect formation and annihilation are analysed *quantitatively* in the present work.

### 2. NORMALIZED DEFECT CONCENTRATION

To investigate the kinetics of defect transformation by means of lifetime measurements, the defect concentration has to be determined from the measured carrier lifetimes. Let us denote the initial effective lifetime after an anneal at 200°C  $\tau_0$ , the stable effective lifetime after an illumination with AM1.5 for at least 24 h  $\tau_s$ , and the effective lifetime in an arbitrary illumination state  $\tau(t)$  with  $\tau(t) \in [\tau_s, \tau_0]$ . Assuming that (i) the metastable Cz-defect is completely deacti-

vated after the anneal step and completely activated after the illumination step and that (ii) all additional recombination channels are not affected by the anneal/illumination cycle, a normalised defect concentration  $N_i^*(t)$  in an arbitrary illumination state can be determined by

$$N_i^*(t) := \frac{1}{\tau(t)} - \frac{1}{\tau_0} = \left( \frac{1}{\tau_{Cz}(t)} + \frac{1}{\tau_{res}} \right) - \frac{1}{\tau_{res}} = N_i(t) \cdot f(\sigma_n, \sigma_p, E_i; \Delta n, T) \quad (1)$$

where  $N_i(t)$  is the concentration of the Cz-specific defect activated in the current illumination state,  $1/\tau_{Cz}(t)$  is the corresponding SRH-recombination rate and  $1/\tau_{res}$  the recombination rate of all other recombination channels, including surface recombination as well as SRH-recombination at other defects possibly contained in the bulk. The maximum defect concentration results is got for  $\tau(t) = \tau_0$ .

It should be emphasised that although effective lifetimes are measured in the following experiments, the plotted lifetime differences are only affected by SRH-recombination at the Cz-specific defect in its active state. A fundamental prerequisite for the complete elimination of all other recombination channels from the lifetime difference defined in Eq. (1) is that the effective lifetimes in both states are measured at the same injection level  $\Delta n$  and the same temperature  $T$  since the recombination rates of most recombination channels strongly depend on both.

An equation for the factor  $f$  in Eq. (1) can be directly derived from general SRH-theory, although  $f$  cannot be determined quantitatively since the electron capture cross section  $\sigma_n$  of the defect is unknown. As  $f$  does not only depend on the defect parameters  $\sigma_n$ ,  $\sigma_p$  and  $E_i$  but also on the measurement conditions  $\Delta n$  and  $T$ , an analysis of the time dependence of  $N_i^*(t)$  requires the same  $\Delta n$  and  $T$  for all  $N_i^*$ . This principle was considered in all dynamic experiments carried out in the present work.

To avoid screening of bulk recombination by surface recombination, all samples were passivated with SiN<sub>x</sub>

(processed at 375°C), which leads to extremely low S-values below 10 cm/s [7].

### 3. MECHANISM OF DEFECT FORMATION

Since the transformation of the Cz-specific defect from the passive state  $P$  to the active state  $A$  is not photon- but excess carrier-induced [8,9], recombination-enhanced defect reaction (REDR) was proposed as a possible mechanism [6]. In REDR-theory [10,11] the energy necessary for a transformation of a defect from state  $I$  to state  $II$  is obtained from the energy gained by the recombination process over defect  $I$ . In the case of the Cz-specific defect the energy for the transformation from state  $P$  to state  $A$  should be delivered by the recombination at the metastable defect in state  $P$ . The densities of the defect in active and passive state,  $N_{IA}$  and  $N_{IP}$ , respectively, should then follow an exponential law [11]

$$N_{IA}(t) \propto N_{IP}(0) \{1 - \exp(-t/\tau_{gen})\} \quad (2)$$

where  $\tau_{gen}$  is the time constant describing the activation process. For the corresponding defect generation rate  $U_{gen}$  REDR-theory predicts [11]:

$$U_{gen} = 1/\tau_{gen} = \Pi R_n \quad (3)$$

where  $R_n$  is the recombination rate of one single defect  $P$  and  $\Pi$  the probability of the transformation process.

Applicability of REDR-theory was supported by two observations: First, the time-dependence of the defect generation process measured on Cz-samples over a wide resistivity range was in good agreement with the time-dependent behaviour predicted in Eq. (2) [2]. And second, the observed strong increase of  $U_{gen}$  with increasing doping level also fitted in REDR-theory, as it is well known from SRH-theory that the recombination activity  $R_n$  of shallow levels as the one of the Cz-specific defect in state  $P$  is strongly doping dependent.

#### 3.1. Doping dependence of the defect generation rate

To check if REDR really is the mechanism responsible for defect formation in Cz-Si, we analysed the doping dependence of the defect generation rate quantitatively. For the recombination rate  $R_p$  via a shallow level ( $n_i \gg p_0$  or  $p_i \gg p_0$ ) the following expression can be derived from general SRH-theory [12] assuming a p-type semiconductor ( $p_0 \gg n_0$ ) under low level injection (LLI) ( $\Delta n \ll p_0$ ):

$$R_n := R_p / N_{IP} = g(E_p, \sigma_{np}, \sigma_{pp}) \Delta n p_0 \quad (4)$$

As the factor  $g$  only depends on the energy level  $E_p$  and the capture cross sections  $\sigma_{np}$  and  $\sigma_{pp}$  of the defect in state  $P$ , the recombination rate  $R_n$  increases linearly with doping concentration  $N_A = p_0$  and excess carrier density  $\Delta n$ . According to Eq. (3), this *linear* dependence on the doping concentration  $N_A$  and the excess carrier density  $\Delta n$  should also be expected for the defect generation rate  $U_{gen}$ .

A fit to our experimental data published in [6] leads to a doping dependence of  $U_{gen}$  with power 1.5. But a closer look at the experimental details makes it obvious that these data are not suitable for a quantitative analysis, as two systematic errors could not be avoided by the experimental setup. On the one hand the lifetime measurements were performed at fixed bias light intensity. As the lifetime level decreases by more than one order of magnitude from the start to the end of degradation, the injection level corresponding to the fixed bias intensity decreases monotonically by the same extent. This leads to an additional decrease of

the measured carrier lifetime since the injection dependence of carrier lifetime in Cz-Si exhibits the typical SRH-increase for a deep defect. On the other hand the lifetime measurements were performed with the microwave-detected photoconductance decay technique (MW-PCD) [13] leading to differential lifetimes  $\tau_{eff,diff}$  instead of absolute (physical) lifetimes  $\tau_{eff}$  [14]. Due to the typical SRH-increase of the injection-dependent carrier lifetime in Cz-Si, the physical recombination lifetime  $\tau_{eff}$  is overestimated by the measured  $\tau_{eff,diff}$ , which leads to a further decrease of the measured carrier lifetime.

To eliminate these systematic errors, we repeated the time-resolved degradation experiment on Cz-materials in a doping range from  $6.1 \times 10^{15}$  to  $3.9 \times 10^{16} \text{ cm}^{-3}$  with the quasi-steady-state photoconductance technique (QSSPC) using a WCT-100 system from Sinton Consulting [15]. The use of QSSPC-technique allows on the one hand for a direct measurement of the physical recombination parameters and on the other hand for a lifetime measurement at fixed injection level. To investigate the kinetics of defect formation, the samples were annealed at 425°C for 10 min ( $t=0$ ) and then degraded under  $50 \text{ mW/cm}^2$  illumination while being measured continuously with the flash-lamp of the QSSPC-system. During the QSSPC-measurements the halogen lamps used as degradation light were switched off. The temperature of the stage was controlled with a PT100-thermosensor and could be held at  $33.25 \pm 0.75^\circ\text{C}$  due to cooling by an adjustable  $\text{N}_2$ -flow. A fixed temperature turned out to be important since the sensitivity of the Hf-circuit of the WTC-system changes with temperature.

Figure 1 shows a time-resolved series of subsequent QSSPC-lifetime curves measured during degradation. The systematic error that results from a measurement at fixed bias intensity (as discussed above) is visualised by the open symbols in Fig. 1: If lifetime is measured at fixed bias intensity (open circles: 1 sun), an additional lifetime decrease due to the reduction of the injection level is superposed to the lifetime decrease due to the activation of the Cz-specific defect (open triangles). Thus, an isolated measurement of the lifetime decrease due to the defect formation requires a measurement at fixed injection level as realised in the present work.

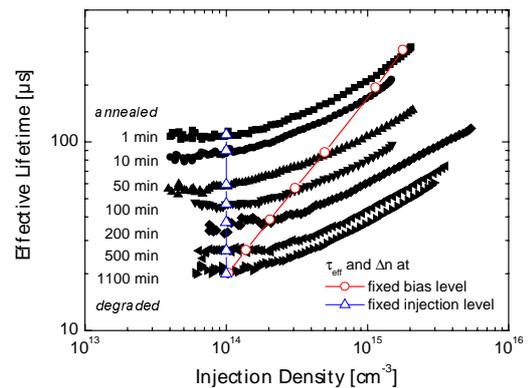


FIG. 1 Time-dependent decrease of QSSPC-lifetime curves measured on a Cz-Si sample under  $50 \text{ mW/cm}^2$  illumination after an anneal at 425°C for 10 min ( $t=0$ ). The illumination times are given on the left.

Figure 2 shows the lifetime curves extracted at three different injection levels from the series of subsequent QSSPC-curves in Fig. 1 and plotted versus illumination time (solid symbols). For comparison, the lifetime curve

extracted at 1 sun intensity is displayed as well (open circles). The overestimation of lifetime degradation becomes obvious.

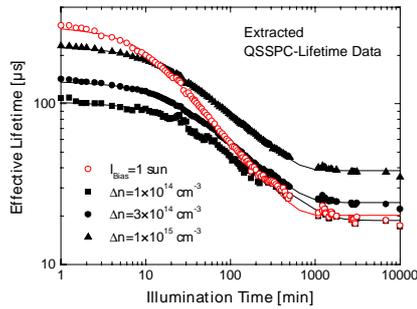


FIG. 2 Time-dependent lifetime decrease of a Cz-silicon sample under 50 mW/cm<sup>2</sup> illumination after an anneal at 425°C for 20 min ( $t=0$ ). Lifetime data are extracted at three fixed injection levels and at fixed bias intensity, respectively.

In order to determine the defect generation rate  $U_{gen}$  for the different  $\tau(t)$ -curves, we plotted the quantity  $1/\tau_d - 1/\tau(t)$  since this quantity is determined with better accuracy than the usual  $N_{td}(t)$ . For  $1/\tau_d - 1/\tau(t)$ , which describes that part of the concentration of the defect in state A remaining for activation, i.e.  $N_{ip}(0) - N_{td}(t)$ , REDR predicts a mono-exponential decay to zero with the same time constant as in Eq. (2):

$$1/\tau_d - 1/\tau(t) = N_{ip}(0) \exp(-t/\tau_{gen}) \quad (5)$$

While some samples show the expected mono-exponential decay, the modeling of the entire decay curve of other samples requires a double-exponential fit. The slight deviation of the mono-exponential decay can be explained e.g. by REDR-theory: As lifetime changes by more than one order of magnitude between the annealed and the fully degraded state, the carrier density generated by the constant light intensity of the degradation lamps decreases by the same extent. According to Eq. (4), the consequence is a reduction of the recombination rate  $R_n$  via the passive defect which leads to a reduced defect generation rate  $U_{gen}$  and results in a slower decay of  $1/\tau_d - 1/\tau(t)$ . As it is not possible to avoid this effect in the experiment, we took it into account for the data evaluation: as the first half of decay curves was always free of such superposed effects, we fitted this part of all  $1/\tau_d - 1/\tau(t)$  curves mono-exponentially. Additionally, we fitted all (non-exponential) curves double-exponentially in the whole time range and identified the shorter of the two time constants with  $\tau_{gen}$ .

Exponent $\alpha$ $U_{gen} \propto (N_A)^\alpha$	$1/\tau_d - 1/\tau$ Fit mono-exp.	$1/\tau_d - 1/\tau$ Fit double-exp.	$1/\tau_d - 1/\tau$ Fit combined
$1 \cdot 10^{14} \text{ cm}^{-3}$	$2.03 \pm 0.14$	$2.02 \pm 0.20$	<b><math>1.99 \pm 0.12</math></b>
$3 \cdot 10^{14} \text{ cm}^{-3}$	$1.95 \pm 0.07$	$1.94 \pm 0.11$	<b><math>1.99 \pm 0.09</math></b>
$1 \cdot 10^{15} \text{ cm}^{-3}$	$1.79 \pm 0.04$	$1.93 \pm 0.12$	<b><math>2.02 \pm 0.09</math></b>
$\Delta n$ -Average	<b><math>1.92 \pm 0.12</math></b>	<b><math>1.97 \pm 0.05</math></b>	<b><math>2.00 \pm 0.02</math></b>

TAB. 1 Influence of the model used to fit the  $1/\tau_d - 1/\tau(t)$  curves on the doping dependence of  $U_{gen}$ .

By plotting the defect generation rates  $U_{gen} \propto N_A^\alpha$  in double logarithmic scale versus the doping concentration  $N_A$  of the samples, the exponent  $\alpha$  for the doping dependence of  $U_{gen}$  results from a linear fit to the data. In

order to estimate the influence of the fitting model on the exponent  $\alpha$ , we fitted the  $U_{gen}$  vs.  $N_A$  data for all three injection levels and both fitting models of  $1/\tau_d - 1/\tau(t)$ . The results are displayed in Tab. 1. Furthermore, we combined both fitting models by determining  $U_{gen}$  for each  $1/\tau_d - 1/\tau(t)$  curve from the better of the two fits. The results are labeled as ‘combined’ fit in Tab. 1. Finally, we averaged for each sample and each fitting model the  $U_{gen}$ -values to the three different  $\Delta n$ -values. The three resulting averaged  $U_{gen}(N_A)$ -datasets are plotted in Fig. 3. As it can be seen from Fig. 3, the slopes of all three curves are very similar leading to exponents  $\alpha$  all close to 2. From the data based on the ‘combined’ exponential  $1/\tau_d - 1/\tau(t)$ -fit the doping dependence of the defect generation rate is determined to be given by  $\alpha = 2.00 \pm 0.02$ . This result clearly contradicts the REDR-theory which predicts a linear doping dependence of  $U_{gen}$ .

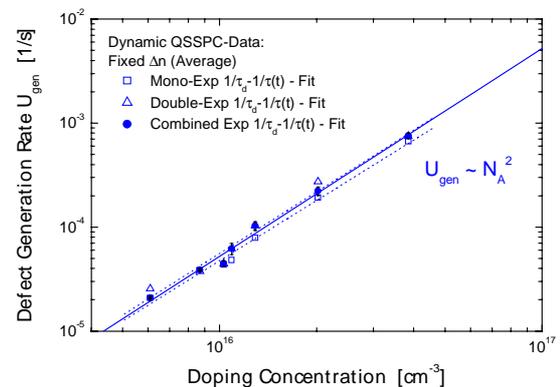


FIG. 3 Defect generation rates  $U_{gen}$  for different boron-doped Cz-Si materials determined from the fits to the  $1/\tau_d - 1/\tau(t)$  curves measured at fixed injection level using QSSPC. The quadratic dependence clearly contradicts the REDR-theory as model for the defect formation process.

### 3.2. Injection dependence of the defect generation rate

As a second test for the applicability of the REDR-theory, we investigated the influence of light intensity on the defect generation rate. We measured the dynamic lifetime degradation on the same Cz-sample three times choosing illumination intensities of 1, 10 and 100 mW/cm<sup>2</sup> for the degradation light. To estimate the difference in the defect generation rate that should be expected from REDR, the injection density  $\Delta n(I_{deg})$  induced by the degradation light has to be estimated. Theoretically,  $\Delta n(I_{deg})$  is given by:  $\Delta n(I_{deg}) = G \tau \propto I_{deg} \tau$ , where  $G$  is the generation rate due to illumination and  $\tau$  the effective carrier lifetime at the injection density  $\Delta n(I_{deg})$ . As the injection-dependent lifetime curves of Cz-Si increase with increasing  $\Delta n$  (in the annealed and the degraded state as shown e.g. in [4]), the relative difference between the  $\Delta n(I_{deg})$ -values can only be equal or higher than the relative difference of the corresponding intensities  $I_{deg}$ . From this, it can be concluded that a linear fit to the  $U_{gen}$ -data plotted versus  $I_{deg}$  instead of  $\Delta n(I_{deg})$  leads to an upper limit for the exponent  $\beta$  describing the  $\Delta n$ -dependence of  $U_{gen}$ .

The averaged  $U_{gen}$ -values extracted by a mono- and a double-exponential fit from the three  $1/\tau_d - 1/\tau(t)$ -curves at fixed injection level (see Sec. 3.1) are displayed in Fig. 4. While REDR predicts a linear  $\Delta n$ -dependence of  $U_{gen}$  ( $\beta=1$ ) (see Eq. (3) and (4)), the experimentally observed  $\Delta n$ -dependence of  $U_{gen}$  is much weaker being described by

an exponent  $\beta < 0.063$ . In contrast to the REDR-theory, defect activation seems to occur with nearly maximum generation rate  $U_{gen}$  if  $\Delta n$  only lies above some threshold value. From our experiments an upper limit of  $10^{13} \text{ cm}^{-3}$  could be determined for this threshold carrier density. This result is in good agreement with experiments on solar cells presented on this conference [16].

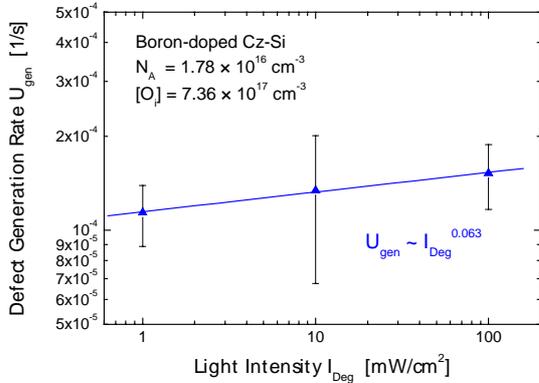


FIG. 4 Defect generation rate in one boron-doped Cz-Si-material for different intensities of the used degradation light. The weak dependence clearly contradicts the REDR-theory as model for the defect formation process.

Thus, both experiments clearly indicate that the physical mechanism underlying the defect transformation *cannot* be described by REDR although several qualitative observations led to this assumption in previous studies. Another mechanism that might explain these new findings could be a simple charging process. But to establish such a new model for defect transformation, further investigations have to be performed.

#### 4. MECHANISM OF DEFECT ANNIHILATION

In the second part of the study, we examined the kinetics of defect annihilation. As the transformation of the defect from state *A* to state *P* occurs above a threshold temperature [17], defect annihilation seems to be thermally activated. If the annihilation process is formulated as decay process, a continuous annealing-step at temperature *T* should lead to a mono-exponential decrease of the defect concentration  $N_i(t)$  given by:

$$N_i(T, t) = N_i(T, 0) \cdot \exp(-R_{ann}(T) \cdot t) \quad (6)$$

The thermal activation of this decay process is introduced into Eq. (6) by assuming an annihilation rate  $R_{ann}(T)$  that increases exponentially with temperature:

$$R_{ann}(T) = R_{ann}(T \rightarrow \infty) \cdot \exp\left(-\frac{E_{barr}}{kT}\right) \quad (7)$$

Thus, the kinetics of defect annihilation is controlled by an activation energy  $E_{barr}$ . As the annihilation process depends on time *and* temperature,  $E_{barr}$  can be determined from two experiments: (i) from an *isothermal* experiment observing the time-dependent decay of  $N_i(t)$  at a constant temperature  $T_{iso}$  and (ii) from an *isochronal* experiment observing the temperature-dependent decay  $N_i(T)$  for a constant annealing time  $t_{iso}$  at each temperature.

In the present work, we performed an isothermal annihilation experiment on a boron-doped Cz-Si sample with a bulk resistivity of  $3.1 \text{ } \Omega\text{cm}$ . The lifetime measurements were performed by means of the MW-PCD-method using a MW-PCD-system with integrated cryostat [5]. Before each

annealing cycle the sample was fully degraded which was controlled by a lifetime measurement at room temperature. During ramping-up to the respective temperature  $T_{iso}$  the sample was illuminated with a maximum light intensity of  $300 \text{ mW/cm}^2$ , which allowed for an almost complete suppression of the annihilation process. After having reached the constant temperature  $T_{iso}$ , we switched off the degradation light at  $t=0$  and measured the effective lifetime repeatedly at the annealing temperature  $T_{iso}$ . In order to avoid superposed formation of defects by the measurement light, the sample was measured at minimum bias intensity that only just allowed to exclude trapping effects and was kept in dark in-between subsequent measurements. Thus, the presented data are not affected by the systematic errors discussed in Sec. 3.1. In order to guarantee a precise temperature control, the temperature was measured directly on the sample surface with a Pt100 temperature sensor.

As discussed in Sec. 2, the defect concentration  $N_i^*(t)$  and its time dependence can be determined from lifetimes measured at  $T_{iso}$  (see Eq. (1)):

$$N_i^*(T_{iso}, t) = 1/\tau(T_{iso}, t) - 1/\tau_0(T_{iso}) \quad (8)$$

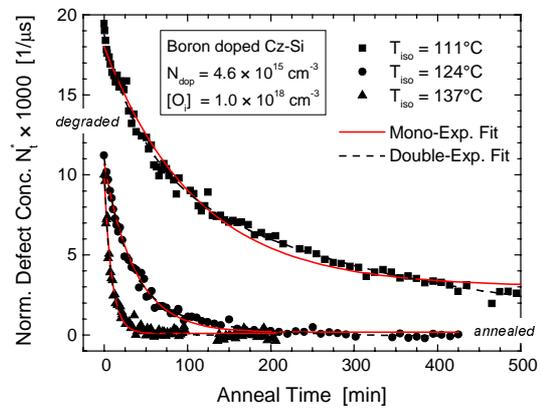


FIG. 5 Isothermal annealing curves of the same Cz-Si-sample measured at different temperatures starting from the fully degraded state ( $t=0$ ). The underlying carrier lifetimes are measured at the corresponding annealing temperatures.

Figure 5 shows the measured decay of  $N_i^*(t)$  for three different annealing temperatures. As predicted by the model in Eq. (6), the time dependence of the decay curves can be described by a mono-exponential fit. As expected, the annihilation process occurs the faster, the higher the annealing temperature is. This is reflected by the time constants  $\tau_{ann}(T_{iso})$  of the mono-exponential decay which range between 110 and 3.7 min for temperatures between  $111^\circ\text{C}$  and  $147^\circ\text{C}$ . It should be stressed that a significant annihilation of the defect in state *A* can already be reached at an annealing temperature around  $110^\circ\text{C}$ .

An Arrhenius-plot of the annihilation rates  $R_{ann}(T_{iso})$  determined from the mono-exponential fits to the  $N_i^*(t, T_{iso})$  curves reveals that the annihilation process is thermally activated (see Fig. 6) with an energy barrier  $E_{barr} = 1.32 \text{ eV}$  determined for the first time. This value lies in a typical range if compared for example with the potential barrier of  $1.2 \text{ eV}$  measured for the thermal dissociation of FeB-pairs [18].

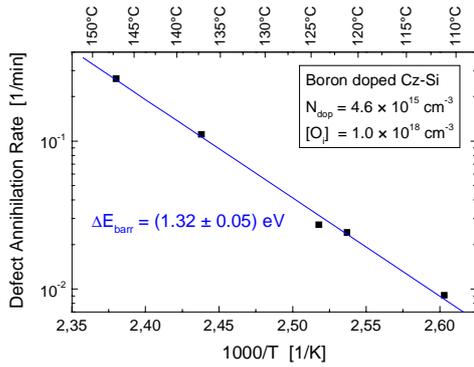


FIG. 6 Arrhenius plot of the defect annihilation rates determined from a mono-exponential fit to the isothermal annealing curves in Fig. 5. The energy barrier  $E_{barr}$  for the thermally activated annihilation process results from a linear fit to the data.

## 5. ELECTRONIC STRUCTURE OF THE DEFECT

Up to now, all known properties of the Cz-defect were determined by means of lifetime spectroscopy (LS) [19] as it was not possible to detect the defect e.g. by deep-level transient spectroscopy (DLTS). While injection-dependent lifetime spectroscopy (IDLs) allowed for a determination of an energy range between  $E_V+0.35$  eV and  $E_C-0.45$  eV for the energy level  $E_A$  of the defect in the active state  $A$  [4], temperature-dependent lifetime spectroscopy (TDLS) faces the problem that the linear Arrhenius-increase of  $\ln(\tau T)$  due to SRH-statistics is superposed by an increase due to defect annihilation, as both effects occur in the same temperature range [5]. Thus, a direct determination of  $E_A$  from TDLS-data has not been possible.

A fundamental prerequisite for a direct determination of  $E_A$  by TDLS is an efficient suppression of defect annihilation. Based on the knowledge about kinetics, an optimized TDLS-procedure called ‘QUICK’ is developed: To reduce defect annihilation to a minimum value, (i) the temperature ramping-up is performed as quick as possible and (ii) the sample is illuminated with a maximum degradation light of  $300 \text{ mW/cm}^2$  in-between subsequent measurements. The efficiency of this procedure is controlled by a reference procedure called ‘SLOW’ where (i) the ramping-up is performed with strongly reduced heating rate and (ii) the sample is kept in the dark except for the lifetime measurements. In both cases the lifetime measurements themselves were performed at the minimum bias intensity, which allowed to exclude trapping effects, thus, allowing for a determination of the low level injection lifetime.

The exemplary TDLS-analysis was performed on the  $3.1 \text{ } \Omega\text{cm}$  Cz-sample used for the determination of  $E_{barr}$ . Prior to the TDLS-measurements, the sample was always fully degraded. The TDLS-curves resulting from both procedures are plotted in Fig. 7.

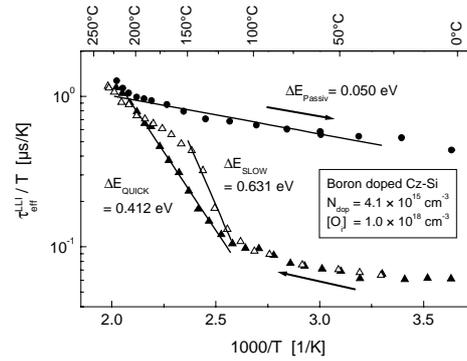


FIG. 7 TDLS-curve of a standard boron-doped Cz-sample measured in different modes (see text).

The time for ramping-up from 90 to  $220^\circ\text{C}$  varies between 35 min in QUICK- and 120 min in SLOW-mode, i.e. almost by a factor of 4. The efficient suppression of defect annihilation in QUICK-mode has been verified from several observations: First, a flatter slope of the Arrhenius-increase is observed in QUICK-mode leading to an energy value  $E_{quick} = 0.412 \pm 0.009$  eV instead of  $E_{slow} = 0.631 \pm 0.057$  eV. Second, a significant lifetime increase from  $565 \text{ } \mu\text{s}$  to  $685 \text{ } \mu\text{s}$  was observed when the degradation light was switched off at the end of the QUICK ramping-up process and the sample was kept at  $220^\circ\text{C}$  for another 30 min. This shows unambiguously that QUICK-mode is able to suppress the annihilation process to some extent even in the upper temperature range. This finding is also reflected in the observed hysteresis between the ramping-up and the ramping-down curves. As the latter was measured on the fully annealed sample kept in the dark during the TDLS-measurement, it represents the TDLS-curve of the passive state (solid circles in Fig. 7). The significant gap between the ramping-up and the ramping-down curves even at temperatures above  $200^\circ\text{C}$  shows that both ramping-up curves are still dominated by the defect in state  $A$  up to  $200^\circ\text{C}$  although a fraction of the active defects is already annihilated. From this, it can be concluded that defect annihilation is sufficiently suppressed in QUICK-mode. Nevertheless, a slight annihilation cannot be completely excluded. Thus, the energy  $E_{quick} = 0.412 \pm 0.009$  eV is (only) an upper limit for the energy level  $E_A$  of the Cz-defect in the active state  $A$ :  $E_A$  cannot be deeper than  $E_{quick}$  from either band edge. Note that a similar QUICK-mode TDLS-curve on a  $1.2 \text{ } \Omega\text{cm}$  Cz-material in Ref. 5 led to the same upper limit, although the effective suppression of defect annihilation has not been controlled that accurately in that experiment. If the TDLS-result of this work is combined with the IDLS-result obtained by Schmidt et al. [4], the energy level in the active state can be further localised in the lower band half at  $E_V + 0.35 \dots 0.41$  eV. For the passive state, the present TDLS-data provide a very shallow level with an activation energy below  $0.1$  eV which confirms the results in Ref. 5.

## CONCLUSION

From a quantitative analysis of the kinetics of defect formation and annihilation in Cz-Silicon, it could be shown that the process of defect formation *cannot* be described with standard REDR-theory as it has been proposed in recent studies. While REDR predicts for the defect generation rate  $U_{gen}$  a *linear* dependence on the doping concentration  $N_A$  and the injection level  $\Delta n$ , a *quadratic* doping and a *vanishing* injection dependence is found in this work. The experiment reveals that  $U_{gen}$  reaches almost its maximum value if  $\Delta n$  only lies above some threshold value,

which is already reached for illumination intensities as low as 1 mW/cm<sup>2</sup>. This is of practical importance as it shows that the upper limit of the cell performance of Cz-Si solar cells can only be measured if the cells are kept completely in the dark after the last annealing step. For the process of defect annihilation, an isothermal annealing experiment reveals that it is thermally activated with an energy barrier  $E_{barr} = 1.32 \pm 0.05$  eV that is determined for the first time. From TDLS-measurements, we finally found an upper limit of 0.41 eV for the energy level of the Cz-defect in its active state. By combining this TDLS-result with the IDLS-result determined by Schmidt et al., the energy level of the defect in its active state can be further localised in the lower band half at  $E_V + 0.35 \dots E_V + 0.41$  eV.

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#### REFERENCES

- [1] H. Fischer and W. Pschunder, *Proc. 10th IEEE PVSC* (Palo Alto, USA, 1973), p. 404-11.
- [2] S. W. Glunz, *et al.*, *Proc. 2nd WC-PVEC* (Vienna, Austria, 1998), p. 1343-1346.
- [3] J. Schmidt, *et al.*, *Proc. 26th IEEE PVSC* (Anaheim, USA, 1997), p. 13-18.
- [4] J. Schmidt *et al.*, *J. Appl. Phys.* **86**, 3175- 80 (1999).
- [5] S. Rein, *et al.*, *Proc. 16th EC-PVSEC* (Glasgow, UK, 2000), p. 1476-81.
- [6] S. W. Glunz, *et al.*, *Proc. 16th EC-PVSEC* (Glasgow, UK, 2000), p. 1070-5.
- [7] H. Maeckel, *et al.*, to be published (2001).
- [8] J. Knobloch, *et al.*, *Proc. 25th IEEE PVSC* (Washington DC, USA, 1996), p. 405-8.
- [9] V. G. Weizer, *et al.*, *J. Appl. Phys.* **50**, 4443-9 (1979).
- [10] L. C. Kimerling, *et al.*, *Proc. 15th Internat. Conf. on Defects in Semiconductors* (Budapest, Hungary, 1988), p. 141-50.
- [11] P. T. Landsberg, *Recombination in Semiconductors* (Cambridge Press, 1991).
- [12] W. Shockley and W.T. Read, *Phys. Rev.* **87**, 835 (1952).
- [13] S. W. Glunz, *et al.*, *Progr. Photovolt.* **4**, 415-24 (1996).
- [14] R. Brendel, *Appl. Phys. A* **60**, 523 (1995).
- [15] R. A. Sinton *et al.*, *Appl. Phys. Lett.* **69**, 2510-12 (1996).
- [16] H. Hashigami, *et al.* (this conference).
- [17] J. Knobloch, *et al.*, *Proc. 13th EC-PVSEC* (Nice, France, 1995), p. 9-12.
- [18] A. A. Istratov, *et al.*, *Appl. Phys. A* **A69**, 13-44 (1999).
- [19] S. Rein, *et al.*, accepted for publ. in *J. Appl. Phys.* (2001).