

BORON-OXYGEN-RELATED RECOMBINATION CENTERS IN COMPENSATED SILICONBianca Lim¹, An Liu², Fiacre Rougeux², Daniel Macdonald², Karsten Bothe¹, and Jan Schmidt¹¹Institute for Solar Energy Research Hamelin (ISFH)

Am Ohrberg 1, D-31860 Emmerthal, Germany

²School of Engineering, College of Engineering and Computer Science, The Australian National University
Canberra ACT 0200, Australia

ABSTRACT: The impact of boron-oxygen-related recombination centers as well as their defect kinetics have been intensely studied in boron-doped oxygen-rich *p*-type crystalline silicon. Experimental data for the defect in simultaneously boron- and phosphorus-doped compensated *p*- and *n*-type silicon, however, is sparse. In this study, we present time-resolved carrier lifetime measurements on Czochralski-grown silicon (Cz-Si) doped with both boron and phosphorus under illumination at 30°C (defect generation). We confirm a linear dependence of the normalized defect concentration N_t^* on the net doping concentration p_0 as well as a proportionality between the defect generation rate R_{gen} and the square of the net doping concentration p_0^2 in compensated *p*-type Cz-Si. In addition, the defect generation in compensated *n*-type Cz-Si is found to proceed on a similar time scale as the defect generation in (compensated) *p*-type Cz-Si. However, the shape of the carrier lifetime reduction during defect generation in compensated *n*-type silicon differs considerably from that in (compensated) *p*-type Cz-Si. The defect annihilation in compensated *n*-type Cz-Si is found to take up to 1000 times longer than in (compensated) *p*-type Cz-Si.

Keywords: Czochralski silicon, boron, phosphorus, lifetime, recombination, defects

1 INTRODUCTION

Light-induced degradation (LID) of the carrier lifetime in oxygen-rich boron-doped crystalline silicon due to the formation of boron-oxygen-related recombination centers is a well-known and intensely studied phenomenon [1-6]. In B-doped Czochralski-grown silicon with sufficiently low metal concentrations, the boron-oxygen-related defect has been found to ultimately limit the carrier lifetime [5]. As a consequence, this defect also plays an important role for solar cells fabricated on such material, since it limits the open-circuit voltage and accordingly the energy conversion efficiency. The recombination center can be annihilated by a short anneal in the dark, leading to a recovery of the carrier lifetime [1,2]. However, subsequent illumination results in renewed generation of the defect and accordingly in renewed degradation of the lifetime.

While most of the previous work has focused on (exclusively) boron-doped *p*-type silicon, light-induced degradation has also been observed in B-doped *n*-type silicon, which was overcompensated through the formation of thermal donors [7]. Very recently, LID was observed in *n*-type Czochralski-grown silicon, which was doped with both boron and phosphorus [8].

In this work, we present time-resolved studies of both defect generation under illumination and defect annihilation in the dark at 200°C in boron- and phosphorus-doped *p*- and *n*-type Cz-Si with varying net doping concentrations p_0 and n_0 , respectively.

We confirm recent reports that the normalized defect concentration N_t^* increases linearly with the net doping concentration p_0 and present data which supports recent findings that the defect generation rate R_{gen} in

compensated *p*-type Cz-Si scales with the square of the net doping concentration p_0^2 (instead of the product of net doping and total boron concentration $p_0 \times N_A$).

Comparing compensated *p*- and *n*-type Cz-Si, the defect generation is found to proceed in similar time intervals, while the evolution of the lifetime during defect generation differs considerably in both cases. The defect annihilation, on the other hand, is found to take significantly longer in *n*-type silicon when compared to *p*-type silicon of similar net doping.

2 EXPERIMENTAL DETAILS

In this work, we use samples from two compensated Czochralski-grown silicon ingots, which were doped with both boron and phosphorus. In Ingot A, the boron and phosphorus concentrations added to the melt were $[B]_{\text{melt}} = [P]_{\text{melt}} = 3 \times 10^{16} \text{ cm}^{-3}$. As a result, the transition from *p*- to *n*-type conductivity is located at about 98% relative distance from the seed end. The interstitial oxygen concentration $[O_i]$, as determined via Fourier transform infrared spectroscopy, decreases with increasing distance from the seed end, from $[O_i] = (10 \pm 2) \times 10^{17} \text{ cm}^{-3}$ to $[O_i] = (7 \pm 1) \times 10^{17} \text{ cm}^{-3}$. In Ingot B, the boron concentration added to the melt was $[B]_{\text{melt}} = 6 \times 10^{16} \text{ cm}^{-3}$ while the phosphorus concentration added to the melt was $[P]_{\text{melt}} = 9 \times 10^{16} \text{ cm}^{-3}$. The transition from *p*- to *n*-type conductivity is located at about 25% ingot height. The resistivity of the *p*-type samples from Ingot A ranges from 1.4 to 5.1 Ωcm, while the investigated *n*-type sample from Ingot B has a resistivity of 1.05 Ωcm.

For lifetime measurements, the samples were damage-

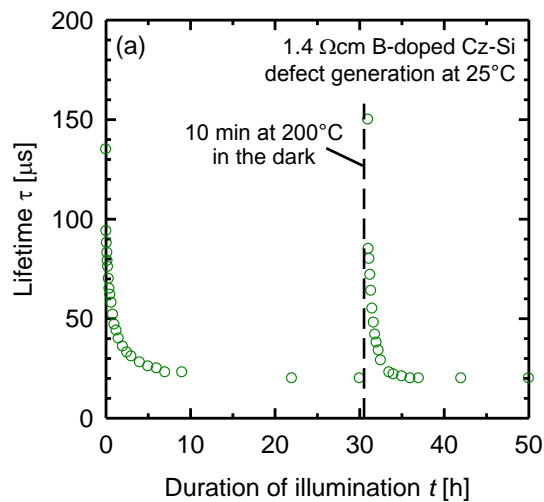


Figure 1: Light-induced degradation at 25°C of the carrier lifetime in 1.4 Ωcm boron-doped Cz-Si. The lifetime can be fully recovered by a 10 min anneal at 200°C, as indicated by the dashed line. However, renewed illumination also results in renewed degradation.

etched and RCA-cleaned. Subsequently, the samples underwent a phosphorus diffusion (50 min at 847°C) to remove any fast-diffusing metal impurities. The resulting n^+ -layers on both sides were removed by a short etch in KOH before passivation by plasma-enhanced chemical vapor-deposited silicon nitride [9].

Lifetime measurements were performed at 29°C using the quasi-steady-state photoconductance decay technique (QSSPC) [10]. The carrier lifetime τ was extracted at a fixed injection level of $\Delta n = 0.1 \times n_0$ (or p_0), if not stated otherwise. Note that the QSSPC technique requires knowledge on the majority- and minority-carrier mobility sum $\mu_{\text{maj}} + \mu_{\text{min}}$. Since the default mobility model for the QSSPC analysis is based on a parameterization of measurements done on non-compensated silicon, it is not expected to be fully applicable to the compensated samples studied in this work. Consequently, we measured both μ_{maj} and μ_{min} for each wafer and subsequently used the obtained values in the analysis [11].

3 RESULTS AND DISCUSSION

In Fig. 1, an example of light-induced degradation of the carrier lifetime in a 1.4 Ωcm boron-doped Cz-Si sample is shown. Initially, the sample has a lifetime of 130 μs but under illumination at 25°C, the lifetime decreases to 20 μs in the course of 20 hours. The degradation is fully reversible by a 10 minute anneal at 200°C in darkness, as indicated by the dashed line, however, subsequent illumination results in renewed degradation.

To determine the rate of the defect generation R_{gen} , the lifetime data τ is converted to a normalized defect

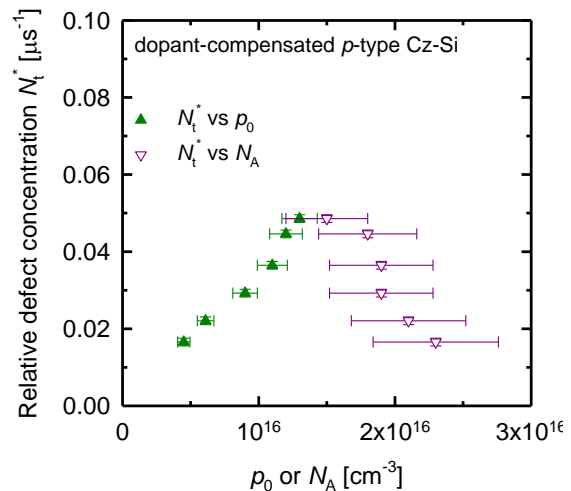


Figure 2: Normalized defect concentration N_t^* in dopant-compensated p -type Cz-Si plotted versus the net doping concentration p_0 (triangles up) and the total boron concentration N_A (triangles down). We observe an increase of N_t^* with increasing p_0 but a decrease of N_t^* with increasing N_A . Given that in exclusively B-doped Cz-Si, N_t^* was found to increase with $p_0 = N_A$, a decrease of N_t^* with increasing N_A in compensated Cz-Si is highly unlikely. Thus, these results strongly indicate that N_t^* actually depends on p_0 and not on N_A .

concentration N_t^* , according to $N_t^*(t) \equiv \tau^{-1}(t) - \tau_0^{-1}$, where t is the duration of illumination and τ_0 is the lifetime after complete defect annihilation. The dependence of N_t^* on t can then be described by an exponential rise to maximum function of the form $N_t^*(t) = N_{t,\text{max}} [1 - \exp(-R_{\text{gen}} t)]$, where $N_{t,\text{max}}$ is the final defect concentration.

In exclusively boron-doped Cz-Si, the normalized defect concentration N_t^* was found to increase linearly with the boron concentration N_A [2,4,5,6]. This finding has been explained by a defect model where the recombination center is composed of a substitutional boron atom B_s and an interstitial oxygen dimer O_{2i} to form a recombination-active B_sO_{2i} complex [4,12,13]. In a recent study on B- and P-doped compensated p -type Cz-Si, however, we provided preliminary evidence that N_t^* actually depends on p_0 and not on N_A , although the data base in this study was quite small (only 2 data points) [14]. To verify these recent findings on a wider data base, Fig. 2 shows the normalized defect concentration N_t^* measured in the compensated p -type samples from Ingot A plotted versus both p_0 (triangles up) and N_A (triangles down).

Conveniently, the net doping concentration p_0 and the total boron concentration N_A in our Ingot A exhibit opposing trends: p_0 decreases with increasing distance from the seed end, while N_A increases with increasing distance from the seed end. As a result, we observe an increase of N_t^* with increasing p_0 but a decrease of N_t^* with increasing N_A . However, it should be noted that (in non-compensated p -type Cz-Si) the defect concentration

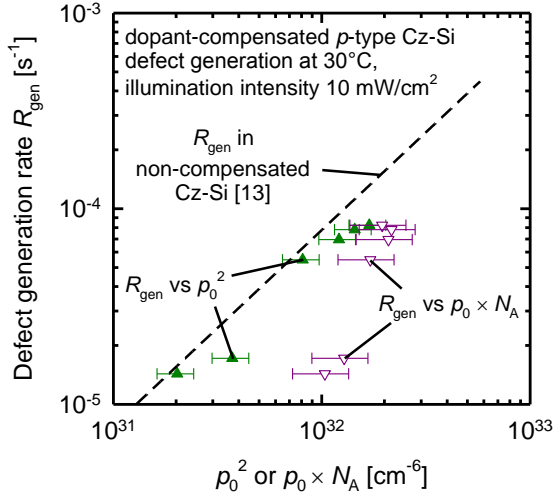


Figure 3: Defect generation R_{gen} determined in dopant-compensated p -type Cz-Si plotted versus the square of net doping concentration p_0^2 (triangles up) and the product of the net doping and the total boron concentration $p_0 \times N_A$ (triangles down). The dashed line is a fit to existing data of R_{gen} in non-compensated Cz-Si, where $p_0 = N_A$ [13]. The agreement between compensated and non-compensated material is much better when R_{gen} is plotted versus p_0^2 than for the case where R_{gen} is plotted versus $p_0 \times N_A$.

N_t^* has also been found to depend quadratically on the interstitial oxygen concentration $[O_i]$ [2,4,5,6].

In the present set of samples, $[O_i]$ decreases with increasing distance from the seed end of the ingot and accordingly with increasing N_A . As a result, one might expect an increase of N_t^* due to the increase of N_A and simultaneously a decrease of N_t^* due to the decrease of $[O_i]$. The interstitial oxygen concentration in Ingot A decreases from $[O_i] = (10 \pm 2) \times 10^{17} \text{ cm}^{-3}$ to $[O_i] = (7 \pm 1) \times 10^{17} \text{ cm}^{-3}$. This decrease accounts for a decrease of N_t^* by a factor of 2. However, we observe a decrease in the defect concentration by a factor of 3. Given that the decrease of N_t^* due to the decrease of $[O_i]$ would also be counteracted by the increase due to the increasing boron concentration N_A , the observed decrease cannot be fully attributed to this effect.

Given that in all studies on exclusively B-doped Cz-Si an increase of N_t^* with increasing $N_A = p_0$ was observed, an opposing trend in compensated Cz-Si is difficult to explain. On the other hand, an increase of N_t^* with increasing p_0 is in excellent agreement with previous experimental data on both compensated and non-compensated Cz-Si. However, these findings do call for a reassessment of the B_sO_{2i} defect model [4,13].

Figure 3 depicts the measured values of R_{gen} for the p -type Cz-Si samples as a function of the square of the net doping p_0^2 (triangles up) and as a function of the product of net doping and total boron concentration $p_0 \times N_A$ (triangles down), respectively, on a double-logarithmic scale. We plot R_{gen} versus p_0^2 as well as $p_0 \times N_A$ because

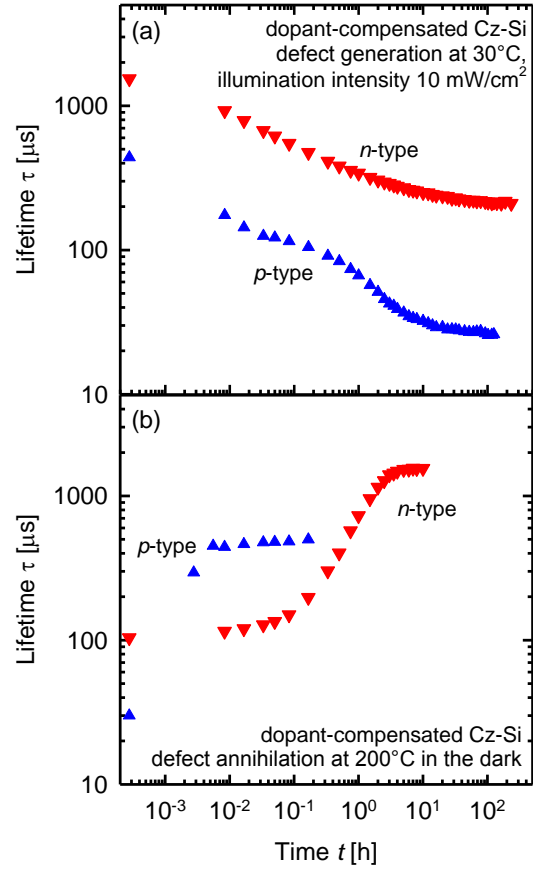


Figure 4: Typical time dependence of the carrier lifetime τ in compensated p - and n -type Cz-Si under (a) 10 mW/cm² illumination at 30°C and (b) at 200°C in the dark. Both the defect generation and the defect annihilation take 2 to 3 orders of magnitude longer in n -type Cz-Si than in p -type Cz-Si of comparable net doping and comparable total boron concentrations.

in the B_sO_{2i} defect model the defect generation rate R_{gen} depends on $p_0 \times N_A$ (which, in non-compensated Cz-Si, equals $p_0^2 = N_A^2$ and agrees with experimental data on non-compensated B-doped p -type Cz-Si [3,6,15]). However, our recent measurements on two compensated Cz-Si samples suggested that the defect generation rate R_{gen} in compensated p -type Cz-Si actually scales with p_0^2 rather than with $p_0 \times N_A$ [14]. With regard to this question, Fig. 3 shows both dependencies.

Figure 3 also depicts a fit to existing experimental data of R_{gen} in non-compensated p -type Cz-Si (dashed line) [12]. As can be seen from Fig. 3, the present data is in good agreement with this fit when R_{gen} is plotted versus p_0^2 , while we observe considerable deviation if R_{gen} is plotted versus $p_0 \times N_A$. This supports our recent findings that the defect generation rate in p -type Cz-Si actually depends on p_0^2 rather than on $p_0 \times N_A$ [14]. We will discuss the consequences of our experimental results concerning the defect model in more detail in Section 4.

Figure 4 depicts the typical time t dependence of the lifetime τ during (a) defect generation (i.e., light-induced degradation) and (b) defect annihilation in a p - (triangles

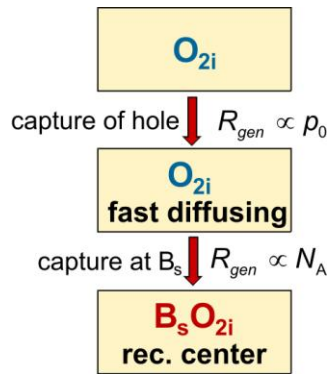


Figure 4: Schematic of the B_sO_{2i} defect model proposed in [13].

up) and n -type sample (triangles down) on a double-logarithmic scale. The samples have a similar net doping of $n_0 = p_0 = 1.0 \times 10^{16} \text{ cm}^{-3}$. The defect generation was performed at a light-intensity of 10 mW/cm^2 and a temperature of 30°C while the defect annihilation was performed at 200°C in the dark. Complete defect generation in both the p - and the n -type sample takes approximately 50 h, however, the shape of the reduction of the lifetime over time in the two samples differs considerably. On the other hand, defect annihilation in the n -type sample takes about 1000 times as long as in the p -type sample. This finding is in agreement with a recent publication, where the defect annihilation at 215°C in the dark was reported to take more than 3.5 h in a compensated n -type Cz-Si sample [8].

4 DEFECT MODELS

In non-compensated boron-doped Cz-Si, the defect concentration N_t^* shows a proportional increase with the total boron concentration N_A and a quadratic increase with the interstitial oxygen concentration $[O_i]$ [2,4,5,6]. In addition, the defect generation rate R_{gen} was found to be proportional to N_A^2 [3,6,15]. These results led to the development of a defect model where the recombination center is composed of one substitutional boron atom B_s and an interstitial oxygen dimer O_{2i} [4,12,13]. The defect concentration N_t^* is naturally proportional to N_A in this model. Additionally, the defect kinetics of the B_sO_{2i} model predict a proportionality of R_{gen} on the product of the hole concentration and the total boron concentration $p_0 \times N_A$. The dependence on p_0 follows from the requirement of the oxygen dimer to catch a hole to speed up the O_{2i} diffusivity while the dependence on N_A is a consequence of the oxygen dimers bonding with a B_s atom [13]. This model was found to be in excellent agreement with the experimental data measured on non-compensated p -type Cz-Si, since in exclusively B-doped Cz-Si $p_0 \times N_A = N_A^2$.

However, in compensated silicon, where the net doping concentration p_0 differs from the total boron

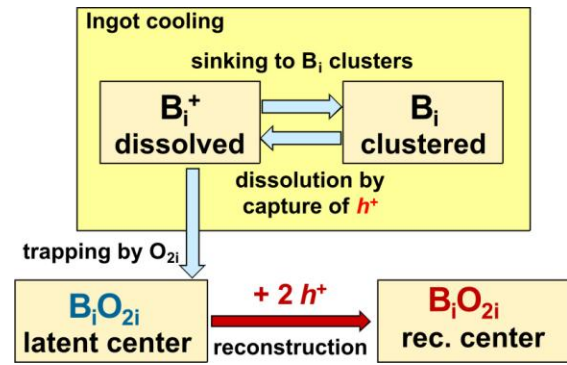
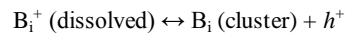


Figure 5: Schematic of the B_iO_{2i} defect model proposed in [16].

concentration N_A , initial results suggest that N_t^* actually depends on p_0 (and not on N_A) and that R_{gen} actually depends on p_0^2 and not on $p_0 \times N_A$ [14]. These findings are confirmed in the present study on the base of a much wider data set. As a result, the B_sO_{2i} model needs to be reassessed.

Very recently, an alternative defect model was proposed by Voronkov and Falster [16]. In this model, the recombination center is comprised of one interstitial boron atom B_i and an interstitial oxygen dimer O_{2i} . The interstitial boron concentration $[B_i]$ in this model is proposed to be proportional to the net doping concentration p_0 . This dependence follows from the generation of interstitial boron atoms: during ingot cooling, B_i are created via the kick-out mechanism during the creation of oxygen precipitates. Subsequently, the interstitial boron atoms congregate to large clusters. However, at moderate temperatures, B_i^+ atoms (which are positively charged in p -type silicon) can also be released from the neutral clusters after capturing a hole h^+ . As a result, there is a constant exchange between the two states:



Consequently, the concentration of (dissolved) interstitial boron atoms $[B_i^+]$ is proportional to the hole concentration $[h^+]$, which in turn equals the net-doping concentration p_0 (after the ingot temperature passes the intrinsic point). At lower temperature, the exchange between dissolved B_i^+ and B_i clusters eventually ceases and $[B_i^+]$ becomes fixed. In the model of Voronkov and Falster, the interstitial boron atoms B_i^+ then bind with other species such as O_i , O_{2i} and B_s . However, at room temperature, these complexes are all frozen in and the existing B_iO_{2i} complexes are the so-called latent form of the boron-oxygen-related recombination-center.

In this model, the defect concentration N_t^* is proportional to the interstitial boron concentration $[B_i^+]$ which in turn is proportional to the net doping concentration p_0 . Accordingly, this model is capable of explaining the experimental finding of our recent and present work that in compensated silicon N_t^* is proportional to p_0 (and not to N_A).

In addition, the model of Voronkov and Falster

proposes that the latent form of the B_iO_{2i} complex needs to capture two holes in order to transform into the recombination-active form. As a result, the model predicts a quadratic dependence of R_{gen} on p_0^2 , which would be in agreement with both the experimental results on exclusively boron-doped p -type Cz-Si and our recent and present findings on B- and P-doped p -type Cz-Si.

Note however, that the dependence of N_t^* on p_0 (instead of N_A) would also be true for other defect models involving B_i instead of B_s . For example, a combination of the two models also seems conceivable [17]: in this ‘hybrid’ model, the recombination-active complex would be comprised of an interstitial boron atom B_i and an interstitial oxygen dimer O_{2i} , as proposed by Voronkov and Falster. However, B_i and O_{2i} would be initially separated and the defect formation would proceed via the capture of an oxygen dimer at an interstitial boron atom. As a result, N_t^* would be proportional to $[B_i^+]$ and in turn on p_0 , while R_{gen} would be proportional to the product of p_0 (as the dimer again needs a hole to speed up its diffusivity) and $[B_i^+]$, which in turn equals p_0^2 .

Regarding the present results for B-doped compensated n -type Cz-Si, the B_sO_{2i} model predicts a linear dependence of N_t^* on N_A , while the B_iO_{2i} model predicts a linear dependence on the net doping concentration n_0 [17]. Interestingly, in the present study, we observe very similar defect concentrations N_t^* in all n -type wafers, even though both n_0 and N_A vary at least by a factor of 5 within the set of samples. Obviously, more detailed studies are necessary to fully understand the composition and the formation mechanism of the boron-oxygen-related recombination center.

5 CONCLUSIONS

We have presented time-dependent lifetime measurements during light-induced degradation and subsequent lifetime recovery at elevated temperature in the dark in compensated p - and n -type Cz-Si samples doped with both boron and phosphorus. The defect generation has been found to proceed in comparable time intervals in both compensated p - and n -type Cz-Si. However, in compensated n -type Cz-Si, the evolution of the lifetime during defect generation (at constant light intensity and temperature) cannot be described by a simple exponential function (as is the case in B-doped p -type Cz-Si). The reaction speed of the defect annihilation has been found to be reduced by up to three orders of magnitude in compensated n -type Cz-Si when compared to compensated p -type Cz-Si of similar net doping concentration p_0 (and comparable total boron concentration N_A).

In addition, we have determined the normalized defect concentration N_t^* in compensated p -type Cz-Si samples of varying net doping concentrations p_0 and total boron concentrations N_A and observed a proportional increase of N_t^* with increasing p_0 (rather than a proportionality

between N_t^* and N_A). When compared to data obtained on exclusively B-doped p -type Cz-Si, the defect generation rate R_{gen} in compensated p -type Cz-Si showed better agreement when R_{gen} was plotted versus p_0^2 than for the case where R_{gen} was plotted versus $p_0 \times N_A$.

As a consequence, similar carrier lifetime limits can be expected in boron-doped compensated p -type silicon and in exclusively B-doped Cz-Si of the same net doping concentration. Accordingly, compensation itself is not expected to further limit the performance of solar cells made on compensated p -type Cz-Si.

In light of the present findings, we have discussed the standard defect model for the boron-oxygen-related recombination center, in which the recombination center is comprised of a substitutional boron atom B_s and an interstitial oxygen dimer O_{2i} , concluding that the experimental results cannot be explained by the B_sO_{2i} model. In addition, we have discussed a recently proposed defect model in which the complex is comprised of an interstitial boron atom B_i and an interstitial oxygen dimer O_{2i} , and concluded that the B_iO_{2i} model is capable of explaining the present experimental results. Still, more experiments are needed to validate the B_iO_{2i} model and in particular the proposed formation kinetics.

ACKNOWLEDGEMENTS

Funding was provided by the State of Lower Saxony. D.M. is supported by an Australian Research Council QEII Fellowship. The authors are grateful to Karl Hesse, Erich Dornberger and Laszlo Fabry from Wacker Chemie AG for kindly providing the silicon wafers and to Denise Kreßner-Kiel from Technische Universität Bergakademie Freiberg for the FTIR measurements.

References

- [1] J. Schmidt, A.G. Aberle, and R. Hezel, Proc. 26th IEEE Photovoltaic Specialists Conference, Anaheim, CA (IEEE New York 1997), p. 13
- [2] S.W. Glunz, S. Rein, W. Warta, J. Knobloch, and W. Wettling, Proc. 2nd World Conference and Exhibition on Photovoltaic Solar Energy Conversion, Vienna, Austria, (WIP, Munich, 1998), p. 1343
- [3] S.W. Glunz, S. Rein, J. Y. Lee, and W. Warta, J. Appl. Phys. **90**, 2397 (2001)
- [4] J. Schmidt and K. Bothe, Phys. Rev. B **69**, 024107 (2004)
- [5] K. Bothe, R. Sinton, and J. Schmidt, Prog. Photovolt: Res. Appl. **13**, 287 (2005)
- [6] K. Bothe and J. Schmidt, J. Appl. Phys. **99**, 013701 (2006)
- [7] Karsten Bothe, Jan Schmidt, and Rudolf Hezel, Proc. 29th IEEE Photovoltaic Specialists Conference, New Orleans, LA, (IEEE New York 2002), p. 194
- [8] T. Schutz-Kuchly, J. Veirman, S. Dubois, and D. R. Hoesling, Appl. Phys. Lett. **96**, 093505 (2010)

- [9] T. Lauinger, J. Schmidt, A.G. Aberle, and R. Hezel, *Appl. Phys. Lett.* **68**, 1232 (1996)
- [10] R. Sinton and A. Cuevas, *Appl. Phys. Lett.* **69**, 2510 (1996)
- [11] B. Lim, F. Rougieux, D. Macdonald, K. Bothe, and J. Schmidt, (submitted to *J. Appl. Phys.*)
- [12] J. Adey, R. Jones, D. W. Palmer, P. R. Briddon, and S. Öberg, *Phys. Rev. Lett.* **93**, 055504 (2004)
- [13] D. W. Palmer, K. Bothe, and J. Schmidt, *Phys. Rev. B* **76**, 035210 (2007)
- [14] D. Macdonald, F. Rougieux, A. Cuevas, B. Lim, J. Schmidt, M. Di Sabatino, and L. J. Geerligs, *J. Appl. Phys.* **105**, 093704 (2009)
- [15] S. Rein, T. Rehl, W. Warta, S. W. Glunz, and G. Willeke, *Proc. 17th European Photovoltaic Solar Energy Conference, Munich, Germany, (WIP, Munich, 2001)*, p. 1555.
- [16] V. V. Voronkov and R. Falster, **107**, 053509 (2010)
- [17] D. Macdonald, A. Liu, F. Rougieux, A. Cuevas, B. Lim and J. Schmidt, (accepted for publication in *phys. stat. sol. c*)