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The impact of dopant compensation on the boron–oxygen defect in p- and n-type crystalline silicon

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We review recent results relating to the boron–oxygen defect in compensated crystalline silicon for solar cells. The experimental observations are not easily explained by the standard model for the boron–oxygen defect, which involves substitutional boron. In addition, the proposed presence of boron–phosphorus pairs as a possible explanation for these findings is inconsistent with numerous other results. A recently proposed new model for the defect, based on interstitial boron, appears to resolve these problems. In this paper we attempt to extend this model to the case of boron-containing n-type silicon. The model predicts that the defect will occur in such material, as has been observed experimentally. However, the tentatively predicted impact of the defect on carrier lifetimes in such material does not appear to be consistent with recent experimental results.

1 Introduction Solar-grade silicon is potentially a low cost source of feedstock for the photovoltaic industry. However, these materials contain shallow dopants such as boron, phosphorus and aluminium, meaning that the material is compensated. Recently, there has been considerable interest in the behaviour of the well-known boron–oxygen defect in compensated p-type silicon. This defect is prevalent in solar cells made with boron-doped p-type Cz silicon, and to a lesser degree in p-type multicrystalline silicon [1]. It is activated by the injection of minority carriers, either by illumination or by application of a voltage.

In non-compensated p-type silicon, the concentration of the defect is found to be linearly related to the boron concentration N_A [1]. However, recent results on compensated p-type silicon, which contained significant concentrations of both boron and phosphorus N_D, show that the defect concentration is determined by the net doping, $p_0 = N_A - N_D$, rather than N_A [2]. This has raised questions about the fundamental structure of the boron–oxygen defect [3], and has implications for the impact of this defect in compensated n-type silicon containing boron. This paper reviews the current state of knowledge of the boron–oxygen defect in compensated p-type and n-type silicon, and attempts to explain the experimental observations in terms of a recent new model for the boron–oxygen defect [3].

2 The B–O defect in compensated p-type Si The standard model for the boron–oxygen defect involves an interstitial oxygen dimer O_{2i}, which, under illumination, diffuses and binds with an immobile substitutional B atom, B_s, creating the defect B_sO_{2i} [4]. The relative concentration of the defect, N_i^*, can be determined by carrier lifetime measurements taken before and after activation of the defect [1]. The defect concentration N_t^* has been found to be approximately quadratic in the interstitial oxygen concentration $[O_i]$ and approximately linear in the substitutional boron concentration $[B_s] = N_A$ in standard non-compensated p-type Cz silicon [1].

This model leads to the natural expectation that in compensated p-type silicon, N_t^* should also scale with N_A. However, recent measurements of p-type compensated cell voltages indicated a lower than expected impact of the boron–oxygen defect [5]. This was later confirmed by carrier lifetime measurements, which demonstrated that the defect concentration was determined by the majority hole concentration p_0, rather than the boron concentration N_A [2].

This observation was corroborated by measurements of the rate of formation of the defect. In non-compensated silicon, the defect formation rate R under illumination has been found to be jointly proportional to both N_A and p_0 [2]. In the standard defect model, the dependence on N_A is thought to be due to the requirement for the diffusing dimers to bond with a B_s atom, and so the greater the concentration of B_s atoms, the more rapid the defect formation, in direct analogy to the formation of FeB pairs in p-type silicon [6]. The joint dependence of the defect formation rate on the majority hole concentration p_0 derives from the requirement of the oxygen dimer to capture a free hole in order to facilitate its diffusion in the lattice [7]. In non-compensated silicon, this leads to a formation rate $R \alpha N_A\ p_0 = N_A^2$, and would be expected to result in a formation rate proportional to $N_A\ p_0$ in compensated silicon, assuming that all of the boron is available to form the defect. However, recent measurements of the defect formation rate in compensated p-type Cz silicon have shown that it is proportional to p_0^2. This confirmed previous reports indicating that the formation rate was slower than expected [8].

The fact that it is the net doping p_0, rather than the boron concentration N_A, which determines both the defect concentration and formation rate, can be explained in two possible ways. Firstly, if the standard model for the boron–oxygen defect is correct, then the results imply that not all of the boron in compensated silicon is available to form the defect. This has led to the proposal of B–P pairs being present in the material [2, 5, 9, 10]. Secondly, it is possible to conceive alternative models for the boron–oxygen defect that do not have a direct involvement of B_s. Such models have been proposed before, for example in Ref. [11] involving interstitial boron, B_i. This idea has recently been developed by Voronkov and Falster [3], who have shown that a model based on B_i can explain the observed dependences of the defect parameters on p_0, rather than N_A.

3 The B–P pair model Pizzini and Calligarich [9] and Krühler et al. [10] observed that the recombination activity in compensated p-type Cz silicon solar cells appeared to be determined by the net doping rather than the boron concentration, leading them to consider the possible presence of B–P pairs. This idea was revived recently by Kopecek et al. [5] who observed that the impact of the boron–oxygen defect on compensated p-type solar cell voltages appeared to be lower than expected based on the boron concentrations. The proposed B–P pairs would presumably form during ingot cooling, and prohibit the oxygen dimer binding with the B_s, thus meaning that only the uncompensated boron atoms, with concentration $p_0 = N_A - N_D$, are available to form the defect, neatly explaining the observed dependence of the defect concentration and formation rate on p_0 [2].

Indeed, such B–P pairs have been observed in compensated silicon before, but only in material with much higher dopant concentrations, around $10^{20}\,cm^{-3}$ (see for example Ref. [12]), and even then only as a small fraction of the total dopant concentration, as pointed out recently by Voronkov and Falster [3]. This makes it unlikely that B–P pairs represent a significant fraction of the dopants in the more lowly doped material typical of solar cells. In addition, the presence of B–P pairs is not consistent with measurements of the majority carrier mobility in compensated silicon, which could be modelled much more accurately when assuming the dopants were all isolated, rather than paired [13]. They are also not consistent with carrier lifetimes measured in Fe-implanted compensated wafers, in which the lifetimes were as expected for FeB pairs, revealing no evidence of other levels such as Fe–B–P complexes, which should exist if B–P pairs were present [14]. Other indirect evidence against the presence of B–P pairs was presented by Lim et al. [15], based on the fact that the deactivation of the defect was found to depend on N_A, rather than p_0.

Finally, another implication of the B–P pair model is that the defect should be absent in compensated n-type silicon, since all of the B is bound to P, and hence cannot form the defect. However, very recently, the defect has indeed been observed in boron–phosphorus compensated n-type Cz silicon [16]. Combined, these considerations make the B–P pair model implausible. It is therefore necessary to consider alternative models for the boron–oxygen defect in order to explain the observations that the defect concentration and the formation rate are determined by p_0, rather than N_A.

4 The B_iO_{2i} model Such a new model has been proposed recently by Voronkov and Falster [3]. In this model, the defect is comprised of interstitial boron B_i rather than substitutional boron B_s. The B_i atoms are thought to be generated by the kick-out mechanism, via silicon self-interstitials formed during the creation of oxygen precipitates during ingot cooling. B_i is known to have two levels in the band gap, a donor level 0/+ at $E_C - 0.13\,eV$, and an acceptor level −/0 at $E_C - 0.37\,eV$ [17]. This means that in intrinsic or p-type silicon, the donor level dominates, and B_i is positively charged in thermal equilibrium. Note that the diffusivity of B_i^+ is much higher than B_s^- (approximately 3×10^{-19} [18] compared to $6 \times 10^{-27}\,cm^2/s$ [19] at 400 °C). At moderate temperatures during ingot cooling, the dissolved B_i^+ ions are constantly exchanging with large, neutral clusters of B_i, according to the reaction:

$$B_i^+(\text{dissolved}) \leftrightarrow B_i(\text{cluster}) + h^+,$$

The law of mass action then implies that the concentration $[B_i^+]$ is proportional to the hole concentration $[h^+]$. As a p-type ingot cools and passes the intrinsic point (around 400 °C for a $10^{16}\,cm^{-3}$ doped ingot), the hole concentration becomes equal to the net doping p_0, and so $[B_i^+]$ is proportional to p_0. At lower temperatures, the exchange with the clusters ceases, and $[B_i^+]$ becomes fixed. According to Voronkov's model, the B_i^+ ions bond with species such as O_{2i}, O_i and B_s, and these complexes become frozen in at room temperature. The B_iO_{2i} defect then represents the latent form of the well-known boron–oxygen defect, which is

subsequently activated under illumination. This contrasts to the standard model, in which the activation is caused by diffusion of the dimer and subsequent bonding with the B_s.

A crucial point in Voronkov's model is that the B_i concentration is driven by p_0, rather than N_A in the case of B_s. This occurs because a hole is required to remove a B_i from the clusters. This directly leads to the defect concentration being determined by p_0, as observed experimentally. This is likely to be true for any boron–oxygen defect model involving B_i instead of B_s, irrespective of the subsequent details of the interactions of B_i with the oxygen dimers, which are quite complex in Voronkov's model. Indeed, it is possible to conceive a 'hybrid' model, in which the defect formation mechanism follows the standard model, except with B_i replacing B_s. In this case, the B_i and dimer are initially isolated, and the p_0^2 dependence of the formation rate follows naturally from the dependence of $[B_i]$ on p_0, combined with the requirement for the dimer to capture a hole in order to diffuse. A complication arises with this hybrid model however, since, as noted above, at room temperature, the B_i^+ ions will be almost entirely bound with species such as O_i, C_S, B_S and others. Hence such a hybrid model would require the diffusing dimer to somehow exchange places with the species already bound with the B_i^+ ions. Whether a plausible mechanism exists at room temperature for such an interchange is unclear.

Finally, one might expect that the exchange with the B clusters would cause the final $[B_i^+]$ to be sensitive to the ingot cooling rate. However, the fact that many different Cz ingots follow quite closely the same empirical dependence on p_0 and $[O_i]$ suggests otherwise. This is perhaps not surprising considering the minimal requirement for exchange to maintain thermal equilibrium in the p-type case, as discussed below. Also note that while a previous study [20] found no apparent impact of silicon interstitials on the defect formation, it is possible that the interstitial concentrations in that work were too low to replicate the effect of the oxide precipitates.

5 The B_iO_{2i} model in compensated n-type Si It is interesting to consider the expected behaviour of the new B_iO_{2i} model in boron-containing compensated n-type silicon, a potential low-cost material for high efficiency solar cells. This section tentatively attempts to extend the model to this case, although numerous assumptions are required, and several poorly known parameters, such as the freeze-in temperature for the B_i ions, play a key role, and relatively small changes in their values can reverse the expected outcomes. Nevertheless, we attempt to do so, even if only to outline some of the key principles for this interesting case.

Following the argument above, during ingot cooling at higher temperatures, the material is intrinsic, the B_i defect is positively charged, and its concentration is proportional to $p_0 = n_i$. As the ingot cools below the intrinsic temperature, the material becomes n-type. The charge state of the B_i defect then depends on how strongly doped the n-type material is. B_i has been shown to be a negative-U defect [17], meaning that the charge state changes directly from positive to negative as the Fermi level rises past an 'effective level' between the donor and acceptor levels, bypassing the neutral state. The position of the effective level is equal to the average of the donor and acceptor levels, and lies at $E_C - 0.26\,\text{eV}$. At room temperature, this energy level corresponds to a net doping concentration n_0 of approximately $10^{15}\,\text{cm}^{-3}$. However, at room temperature, the B_i concentration is already frozen in. The relevant temperature for determining the charge state of the B_i ions is therefore the 'freeze-in' temperature, below which the exchange with the B_i clusters ceases. This temperature is probably in the range of 200–300 °C [3]. An energy level of $E_C - 0.26\,\text{eV}$ corresponds to a net dopant concentration n_0 of around $10^{17}\,\text{cm}^{-3}$ at 200 °C and $4 \times 10^{17}\,\text{cm}^{-3}$ at 300 °C. Assuming a freeze-in temperature of 200 °C, if the net doping n_0 in the sample is above $10^{17}\,\text{cm}^{-3}$, the B_i will be negatively charged, if below, positively charged. In compensated solar-grade silicon the latter case will generally prevail, except when very heavily doped material is used, or if the freeze-in temperature is below 200 °C. The freeze-in temperature itself will depend on the density of boron clusters.

Assuming then that the B_i ions are positively charged, as for the p-type case, the concentration $[B_i^+]$ would be proportional to p_0, due, once again, to the requirement to capture a hole in order to exchange with the clusters. In further analogy with the p-type case, the B_i^+ ions could then bond with oxygen dimers, creating the same latent form of the defect. Furthermore, the subsequent active level of the defect would be the same in both p- and n-type silicon, meaning that it would have the same energy level and capture cross-sections.

However, in the case of compensated n-type silicon, p_0 is not simply the net doping $N_A - N_D$, as for the p-type case, but would be the minority hole concentration *at the freeze-in point*, $p_{0-\text{freeze-in}}$. This is given by $p_0 = n_i^2/n$ with all quantities determined at the freeze-in temperature and:

$$n = (N_D - N_A)/2 + \text{sqrt}[(N_D - N_A)^2/2 + n_i^2],$$

where n_i is the intrinsic carrier concentration. This leads to the unusual situation where $p_{0-\text{freeze-in}}$, and hence the boron–oxygen defect concentration, is *inversely* related to the net doping n_0. In other words, a higher net n-type doping n_0 will lead to a lower $p_{0-\text{freeze-in}}$ value, resulting in fewer boron–oxygen defects.

An important cautionary note for the above train of thought relates to the impact of the cooling rate on the freeze-in temperature for the n-type case. In the simpler p-type case, once the material becomes extrinsic, $p_0 = N_A - N_D$, which is entirely temperature independent, meaning that no actual exchange is required in order to maintain equilibrium conditions during cooling. One can then confidently expect that the concentration of B_i^+ will be proportional to p_0 once the exchange with the clusters ceases. However, for the n-type case, p_0 is the *minority* carrier concentration, which depends very strongly on the temperature via the intrinsic

carrier concentration, as discussed above. It is more difficult for thermal equilibrium to be maintained when the quantity in question changes rapidly with temperature, being limited by the rate of exchange with the clusters. The net result would be an increase in the effective freeze-in temperature, in turn resulting in the concentration of isolated B_i^+ being higher than expected. In short, the actual value of the freeze-in temperature could be strongly affected by the cooling rate for the n-type case.

The considerations above reveal that the application of Voronkov's model to the case of compensated n-type silicon is more complicated than for the p-type case. The expected dependence of the defect concentration on p_0 or n_0 depends on the doping level itself, and the freeze-in temperature, which probably also depends strongly on the cooling rate for the n-type case. Nevertheless, the model does predict that the defect will occur in n-type silicon, as opposed to the B–P pair model.

Indeed, lifetime degradation in boron-compensated n-type silicon has been observed experimentally, and attributed to the boron–oxygen defect. Bothe et al. [21], found that the defect occurred in boron-doped n-type oxygen-rich float-zone silicon (6 Ωcm) that was initially overcompensated by thermal donors, but could then be switched to p-type (20 Ωcm) by annihilating the donors at 700 °C. Interestingly, they found that they could fit the injection dependent lifetime curves for both p- and n-type with the Shockley–Read–Hall model by effectively assuming the same defect concentration, energy level and capture cross-section ratio for both cases. This implies that the annihilation of the donors does not significantly affect the dimer concentration, and that the active level of the defect is the same in both polarities. According to Voronkov's model, and the assumptions and reasoning outlined above, the defect concentration in the n-type case might be expected to be proportional to $p_{0-\text{freeze-in}}$, and in the p-type case to p_0 (assuming B_i can exchange with the clusters again during cooling after thermal donor annihilation). Therefore, in this model, there is no reason to assume that the defect concentration should be the same in Bothe's two cases. However, in practice, it turned out that these values were not very different, and so, by coincidence, the B_iO_{2i} model would indeed predict that the defect concentration would be approximately the same.

(More precisely, in the p-type case, the thermal donors are annihilated, only boron remains, and the resistivity may be converted to $p_0 = N_A = 6.7 \times 10^{14}\,\text{cm}^{-3}$. Using this N_A value for the n-type case, and with an additional $N_D = 1.45 \times 10^{15}\,\text{cm}^{-3}$ of thermal single donors or $N_D = 1.06 \times 10^{15}\,\text{cm}^{-3}$ of thermal double donors, gives a resistivity of 6 Ωcm according to Klaassen's mobility model [22], yielding a net doping close to $n_0 = 7.8 \times 10^{14}\,\text{cm}^{-3}$. At an assumed freeze-in temperature of 250 °C, this leads $p_{0-\text{freeze-in}} = 4 \times 10^{14}\,\text{cm}^{-3}$, quite close to the p_0 value for the p-type case).

Very recent results presented by Schutz-Kuchly et al. [16], also demonstrate that the B–O defect occurs in boron-compensated n-type silicon. In this case the n-type dopant was phosphorus, rather than thermal donors. Note that this result again contradicts the B–P pair model, which requires the defect to be absent in such boron–phosphorus compensated n-type material. Using an expression from Bothe et al. [1], Schutz-Kuchly calculated the expected final degraded lifetime in their n-type wafers. This calculation assumed that the known energy level and capture cross-section ratio for p-type silicon are also valid for n-type silicon, which seems reasonable based on Bothe's previous results, and on the B_iO_{2i} model discussed above. They used their measured values of $[B] = 1.6 \times 10^{17}\,\text{cm}^{-3}$ and $[O_i]$ as input parameters in Bothe's expression. This yielded an expected lifetime of 5.4 μs for the degraded lifetime in the n-type wafer, somewhat lower than the measured value of 12 μs. However, according to the tentative model discussed above for n-type silicon, [B] should be replaced by $p_{0-\text{freeze-in}}$ (approximately $10^{13}\,\text{cm}^{-3}$ for a freeze-in temperature of 250 °C) in Bothe's expression, which would lead to a lifetime well above 1 ms. Thus the model as outlined above for n-type silicon is evidently inconsistent with the extent of the lifetime degradation observed by Schutz-Kuchly. Note that those lifetimes were measured at much higher injection levels than are usually applied for boron–oxygen defect concentration measurements, meaning that they may have been affected by additional recombination channels such as Auger recombination, leading to a reduction in the measured lifetime. However, this is very unlikely to explain the magnitude of the discrepancy with the model above.

Finally, we may also speculate about the defect formation rate in compensated n-type silicon. It is difficult to predict this in Voronkov's model, since the transformation from the latent state to the passive state requires the capture of carriers, the polarity of which depends on the relative positions of the Fermi level and the energy levels of the numerous latent, transient and active states of the defect [3]. However, under the hybrid model described above, in which the B_i and diffusing dimer bond during defect formation, we might speculate that the formation rate under illumination should depend on Δp, from the diffusion requirements of the oxygen dimer (as well as depending jointly on the concentration of B_i, whatever it is determined by). In general, this would lead to a significantly reduced formation rate in n-type silicon, since under normal illumination conditions, Δp in n-type wafers is much less than p_0 in typical p-type wafers.

6 Conclusions The concentration and formation rate of the boron–oxygen defect has previously been shown to depend on the net doping p_0 in p-type compensated silicon. However, the proposed presence of B–P pairs to explain these observations is not consistent with a large number of experimental findings. A new model for the defect, based on B_i rather than B_s [3], can explain the dependences on p_0 via the fact that the B_i concentration is determined by the free hole concentration. Here we have attempted to extend this model to the case of boron-compensated n-type silicon. The

model predicts that the defect will indeed occur in n-type silicon, and, with certain tentative assumptions, that its concentration will be determined by the hole concentration at the freeze-in temperature for B_i ions, which is inversely related to the net doping n_0. However, this is found to be inconsistent with reported experimental data for the boron–oxygen defect in n-type silicon. Clearly, more experiments with a large range of net doping values are required to better understand the behaviour of this defect in compensated n-type silicon.

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References

[1] K. Bothe, R. Sinton, and J. Schmidt, Progr. Photovolt.: Res. Appl. **13**, 287 (2005).
[2] D. Macdonald, F. Rougieux, A. Cuevas, B. Lim, J. Schmidt, M. Disabatino, and L. J. Geerligs, J. Appl. Phys. **105**, 093704 (2009).
[3] V. V. Voronkov and R. Falster, J. Appl. Phys. **107**, 053509 (2010).
[4] J. Schmidt and K. Bothe, Phys. Rev. B **69**, 024107 (2004).
[5] R. Kopecek, J. Arumughan, K. Peter, E. A. Good, J. Libal, M. Acciarri, and S. Binetti, Proc. 23rd European Photovoltaic Solar Energy Conference (WIP-Renewable Energies, Munich, 2008), p. 1855.
[6] L. C. Kimerling and J. L. Benton, Physica **116B**, 297 (1983).
[7] D. W. Palmer, K. Bothe, and J. Schmidt, Phys. Rev. B **76**, 035210 (2007).
[8] S. Dubois, N. Enjalbert, and J. P. Garandet, Appl. Phys. Lett. **93**, 103510 (2008).
[9] S. Pizzini and C. Calligarich, J. Electrochem. Soc. **131**, 2128 (1984).
[10] W. Krühler, C. Moser, F. W. Schulze, and H. Aulich, Proc. 8th European Photovoltaic Solar Energy Conference (Kluwer Academic Publishers, Dordrecht, 1988), p. 1181.
[11] J. Schmidt, A. G. Aberle, and R. Hezel, Proc. 26th IEEE Photovoltaic Specialists Conference (IEEE, New York, 1997), p. 13.
[12] V. Tsvetov, W. Allred, and W. G. Spitzer, Appl. Phys. Lett. **10**, 326 (1967).
[13] D. Macdonald, A. Liu, F. Rougieux, A. Cuevas, B. Lim, J. Schmidt, M. D. Sabatino, and L. J. Geerligs, Proc. 24th European Photovoltaic Solar Energy Conference (WIP-Renewable Energies, Munich, Germany, 2009), p. 877.
[14] D. Macdonald and A. Liu, Phys. Status Solidi B **247**, 2218 (2010).
[15] B. Lim, A. Liu, D. Macdonald, K. Bothe, and J. Schmidt, Appl. Phys. Lett. **95**, 232109 (2009).
[16] T. Schutz-Kuchly, J. Veirman, S. Dubois, and D. R. Heslinga, Appl. Phys. Lett. **96**, 093505 (2010).
[17] R. D. Harris, J. L. Newton, and G. D. Watkins, Phys. Rev. B **36**, 1094 (1987).
[18] D. Mathiot and J. C. Pfister, J. Appl. Phys. **55**, 3518 (1984).
[19] J. D. Plummer, M. D. Deal, and P. G. Griffin, Silicon VLSI Technology – Fundamentals, Practice and Modelling (Prentice Hall, Upper Saddle River, New Jersey, 2000), p. 388.
[20] D. Macdonald, P. N. K. Deenapanray, A. Cuevas, S. Diez, and S. W. Glunz, Solid-State Phenom. **108/109**, 497 (2005).
[21] K. Bothe, J. Schmidt, and R. Hezel, Proc. 29th IEEE Photovoltaic Specialists Conference (IEEE, New York, 2002), p. 194.
[22] D. B. M. Klaassen, Solid-State Electron. **35**, 953 (1992).