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Investigation of a New Metastable Defect in Boron-Doped Cz-Si

By

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A radiation-induced defect state in oxygen-rich Si:B exhibiting charge-dependent characteristics is studied by deep level transient spectroscopy (DLTS). A model invoking multistability is presented to account for most of the aspects of its behaviour. At temperatures larger than $T = 120$ K the defect displays bistable behaviour having two charge-state-controlled configurations. However, as the temperature decreases during the downwards DLTS scanning mode, the stable configuration is transformed to metastable ones at $T < 120$ K due to changes in both the formation free energy and the entropy of the various defect configurations. A rough configurational coordinate diagram is suggested in order to explain this behaviour. A microscopic description of the structure is also attempted.

Ein strahlungsinduzierter Defektzustand in sauerstoffreichem Si:B mit ladungsabhängiger Charakteristik wird mittels DLTS untersucht. Ein Modell mit mehreren stabilen Zuständen wird vorgeschlagen, um die meisten Aspekte seines Verhaltens zu berücksichtigen. Oberhalb 120 K zeigt der Defekt Bistabilität mit zwei ladungszustandkontrollierten Konfigurationen. Indem in der nach unten gerichteten DLTS-Scanningmode die Temperatur abnimmt, wird die stabile Konfiguration infolge von Änderungen sowohl der freien Bildungsenthalpie als auch der Entropie der verschiedenen Defektkonfigurationen in metastabile umgewandelt. Ein Konfigurationskoordinatendiagramm zur Erklärung dieses Verhaltens wird vorgeschlagen. Ebenfalls wird eine mikroskopische Beschreibung der Struktur versucht.

1. Introduction

A large volume of research findings has been gathered in the last few years indicating that some defects in semiconductors possess more than one structural configurations. Such defects in Si are among others the Fe–acceptor pairs [1], the B–V pair [2,3], the C_i–C_s centre [4, 5], the C_i–P_s defect [6, 7], and the thermal donors [8]. Examples from other semiconductors include the DX centre [9] in $Al_xGa_{1-x}As$ and $GaAs_xP_{1-x}$, the EL_2 defect [10] in GaAs, the M centre [11] in irradiated n-InP, and the MFe centre [12] in InP:Fe.

The DLTS technique has been proved very valuable in studying alternate structures of metastable defects. In general, each structure has its own electronic states which give rise to corresponding DLTS peaks. The appearance of a specific defect configuration is achieved by preparing the defect in the proper charge state by electrical or optical excitation followed by (a fast) cooling to low temperature [13].

In this work a defect exhibiting multistable behaviour is studied. Entropy changes in the configurational space are mainly considered to account for sudden transformations of the defect between various configurations at low temperatures.

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2. Experimental Details

Schottky diodes were prepared by evaporation of aluminium on carefully cleaned, boron-doped, Czochralski-grown prepolished Si wafers. This was done in a high-vacuum evaporator at a pressure of 10^{-4} Pa. Irradiation was performed in-situ at 80 K with 1.5 MeV electrons to a constant dose of a about 2×10^6 electrons/cm^2. Measurements were taken by using a standard DLTS experimental set-up [14], with increasing/decreasing temperature at a constant heating/cooling rate of 0.15 K/s, in the range 80 to 220 K.

3. Experimental Results and Discussion

Fig. 1 presents the DLTS spectrum in the temperature range below 220 K. This spectrum was received after annealing out of the vacancies by heating up the specimens at 220 K for 30 min. It contains four traps specified as H (0.13), H (0.29), H (0.34), and H (0.38). In this notation H stands for holes and the number in brackets denotes the energy depths of the

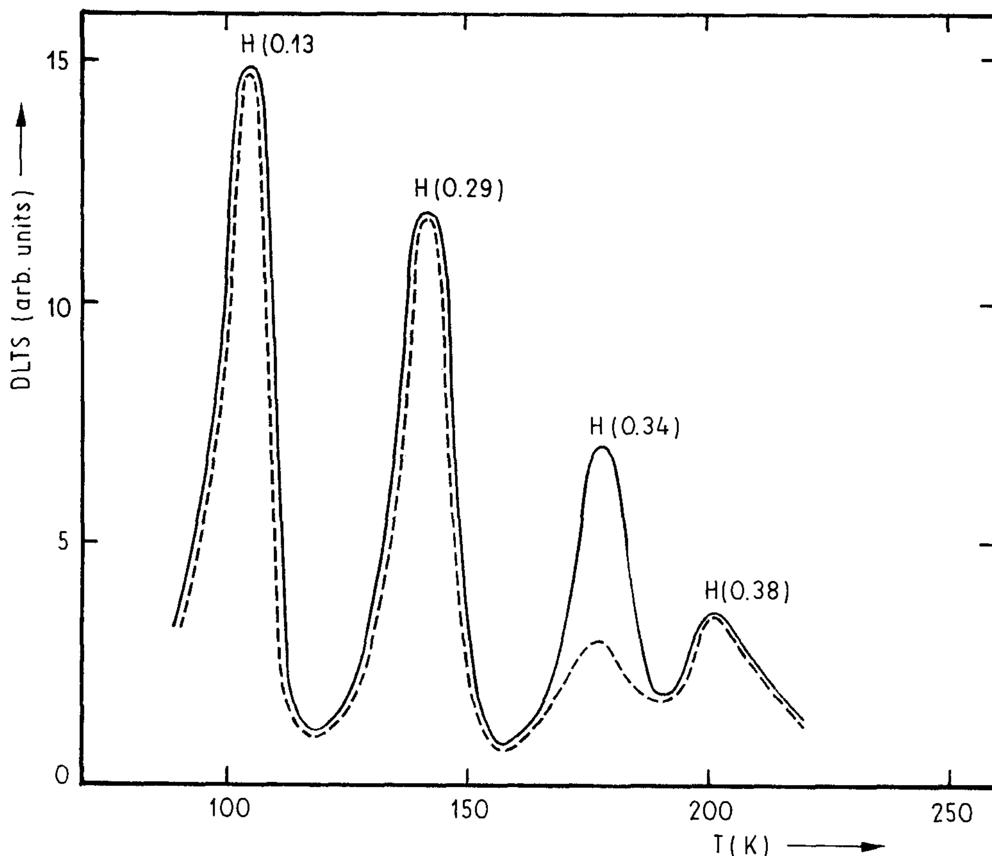


Fig. 1. The DLTS spectrum of Si:B irradiated with electrons at 80 K. The solid curve was received after cooling down from 220 K with bias off and the dashed curve with bias on. The spectra were recorded with the temperature ramped upwards

traps from the valence band edge (in eV). Preliminary discussion on the obtained spectra appeared in [15]. The solid curve shows the observed peaks after a 5 min anneal at 220 K with bias off ($V_R = 0$), quench to 80 K, and then scanning upwards. The dashed curve corresponds to the solid one but with the application of a reverse bias ($V_R = -5$ V) during the 5 min anneal. The cooling-down procedure in both the above cases was done by keeping the same voltage conditions as during the corresponding anneal. Such a procedure allows us to prepare specific charge states of our samples before applying the DLTS. The variation of the peak amplitude of H (0.34) as seen in Fig. 1 (solid and dashed curves) indicates that the corresponding centre may alternate between two different configurations. The changes in the amplitudes of the H (0.34) peak are observed only for slow enough rate windows which allow the detection of the corresponding peak below 195 K. For faster rate windows H (0.34) is always low.

Surprisingly enough, when the temperature is ramped downwards from values above $T \approx 180$ K an additional feature H (Fig. 2) appears in the spectra irrespective of the previous annealing with or without application of a reverse bias. Peak H exhibits the following

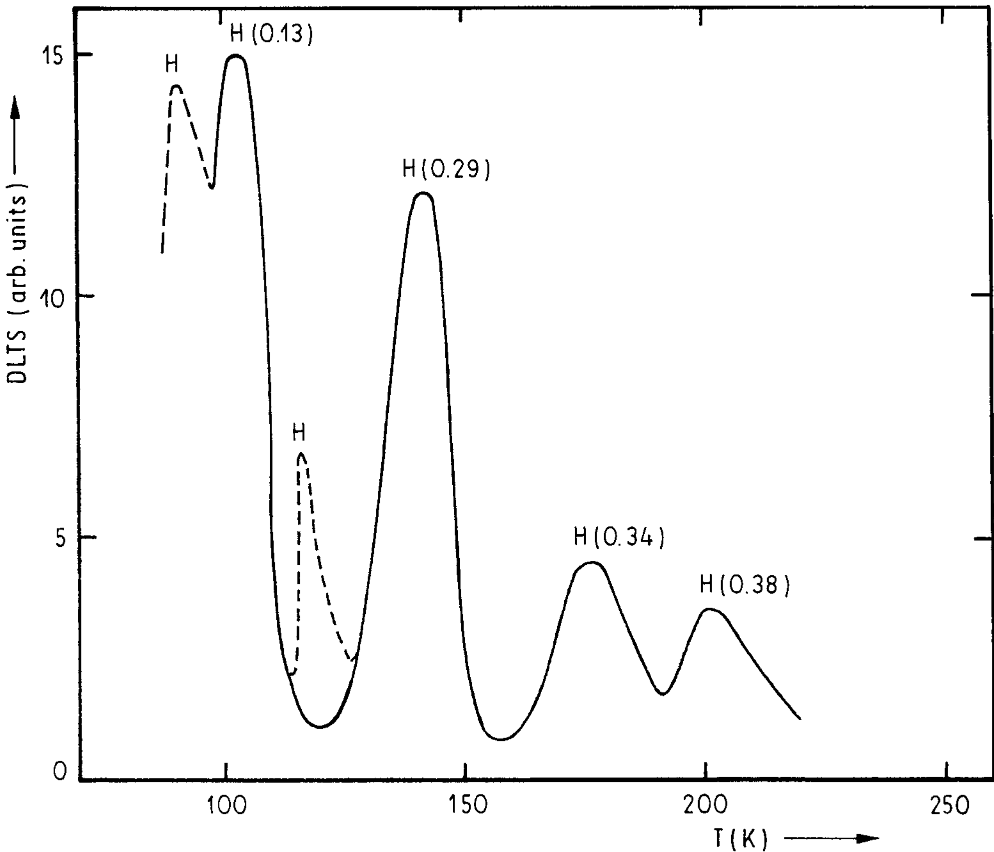


Fig. 2. The DLTS spectrum obtained with the downwards scanning mode from 220 K. The additional feature H initially emerges on the left side of the H (0.13) peak and finally on its right side

systematic behaviour. Initially it appears on the left side of peak H (0.13). After a couple of days, while measurements were always restricted to below $T = 220$ K, H suddenly emerges on the right side of H (0.13) where it finally remains. In this position it appears always in the temperature range just below 120 K, no matter what rate window is operating. It appears always in the downwards scanning mode when beginning from $T > 180$ K and it has the appearance of a peak which is abruptly interrupted during its tracing. For temperatures lower than 120 K peak H disappears, but peak H (0.34) is still low. These changes indicate that a specific relationship exists between the appearance/disappearance of the H peak and the H (0.34) one. When H emerges the amplitude of H (0.34) is low and remains low having an intermediate value between that of the solid and that of the dashed curve in Fig. 1. A precursor report of the results appeared in [15] where H (0.34) and H have been considered as arising from two different defects. However detailed studies and analysis of the data have shown the following:

(i) Peak H (0.34) and feature H are introduced simultaneously in the spectra. Actually, two DLTS scans carried out in the temperature range 80 to 220 K, one upwards, the other downwards, immediately after the irradiation show that the two peaks are initially absent. However, after annealing out the vacancies by heating the sample for 0.5 h at 220 K both peaks appear in the spectra, indicating additionally a possible correlation of a vacancy with the defect structure.

(ii) At first sight, H (0.34) appears to anneal out earlier than H. The fact is that H (0.34) anneals out just above room temperature when a peak H (0.35) of the (C_i–O_i) pair arises in the spectra after the migration of the C_i peak H (0.29). Thus, peak H (0.34) being already low enough is completely masked by the emergence of peak H (0.35). However, careful analysis has shown small charge-dependent changes in the amplitude of the H (0.35) peak indicating the presence of the H (0.34) peak. It is worth noticing that in the latter case H appears always as a faint signal the height of which more or less matches with the small changes in the H (0.35) amplitude. More significantly, these changes seem to disappear together with the disappearance of H from the spectra. Thus the two peaks H and H (0.34) seem to emerge and go out together backing the suggestion that they possess a common origin.

(iii) We should add that, after its appearance in the first downwards scanning, feature H fails to appear again when the temperature is cycled restricted below 180 K, although peak H (0.34) is present in the spectra with small amplitudes. However, this seemingly contradictory behaviour is easily explained by the proposed configurational coordinate diagram discussed below.

These facts strongly indicate that the two peaks should be considered as alternative manifestions of the same metastable defect. Finally it is noted that the appearance of the additional DLTS peak in the downward scanning as compared to the upward scanning, was not observed using floating zone Si instead of the pulled Si.

The pulse-width variation method was employed to measure the capture cross-section σ of the H (0.34) peak. To this end, after cooling with bias off, a slow enough rate window was used ($1\ s^{-1}$) to trace H (0.34) at a temperature adequately smaller than 195 K where configurational conversions occur as discussed below. The determined value $\sigma = 8 \times 10^{-19}\ cm^2$ is relatively small indicating that the transition during hole capture is between two charge states, the positive, C^+, and the neutral, C^0, charge state of the centre.

The bias-dependent decay and regeneration of the H (0.34) peak as described by the solid and dashed curves of Fig. 1 could be easily explained within the framework of a model involving a bistable defect with two charge-state-related metastable configurations. However,

the results of Fig. 2 and, more specifically, the strange appearance and behaviour of feature H complicate the situation.

Recently, Hamilton et al. [16] (HPP) reported defect metastabilities detected in electron-irradiated floating-zone Si. As the metastabilities they observed did not indicate any changes in their charge state, they proposed according to earlier theoretical developments [17] that these phenomena manifest entropy variations in the configuration space and they were able to give a macroscopic explanation of their DLTS spectra.

In this paper, we will show that our DLTS spectra can equally well be explained according to the arguments of the HPP theory. Based on the macroscopic explanation of the HPP theory we will discuss a possible microscopic description based on short-range order and randomness. In concluding, our decription indicates that a possible short-range order may be responsible for the observed anomalies in the DLTS spectra. This short-range order may induce large changes in the formation entropy of a defect configuration which, however, cannot be separated from the corresponding changes in the formation enthalpy.

The HPP theory anticipates that stable defect configurations imply a minimum in the Gibbs free energy of formation, G, of the defect. The variation of G with a configuration parameter, Q, as shown in Fig. 3, indicates regions where stable or metastable defect configurations may exist. This implies that it is not only the formation enthalpy (formation energy), H, of the defects which will determine the kind of the defect stability but it is also the formation entropy, S, which plays a dominant role. Thus according to the HPP theory, critical temperatures T_c exist at which the changes in the formation entropy and the formation enthalpy determine transition regions between various metastable configurations of the defect.

In the present case, like in the HPP theory, we can associate our experimental findings with variations of the Gibbs free energy of formation along a configuration parameter. Thus, we can argue that annealing the sample with bias off results in free hole capturing into the level leaving the defect in its positive charge state (C^+). In this charge state the defect can exist in three configurations: A stable, B_1 and B_2 metastable (curve C^+ in Fig. 3). Cooling down the sample, the defects freeze in configuration A which gives rise to a strong peak H (0.34) in the spectra. Annealing the sample with bias on leaves the level empty of holes setting the defect in the neutral charge state (C^0) (curve C^0 in Fig. 3). In this charge state, configurations A and B_1 have similar values of Gibbs free energy and therefore both of them could be populated. This explains why H (0.34) still remains in the spectra but with low amplitudes. In configuration B_1 the defect tends to give a peak in the spectra which appears around 120 K. However, in this temperature range the energy barrier between B_1 and B_2 is totally eliminated and the defect automatically passes to B_2. The DLTS system suddenly begins sensing configuration B_2 instead of B_1. Thus, the emergence of peak H is suddenly interrupted. This explains the strange appearance and shape of feature H. H is the unfinished signature in the spectrum of the defect state in configuration B_1.

In the framework of the presented model it is also obvious why peak H does not appear when scanning upwards immediately after its tracing at $T < 120$ K in the downward scanning mode, i.e. simply because the defect is now in configuration B_2, which does not possess this state. If we begin scanning downwards before the temperature surpasses 180 K, peak H also fails to appear in the spectra since the defect continues to remain in configuration B_2. B_2 is assigned to the defect configuration which is not observed in DLTS, and which the defect is transformed to when the temperature becomes less than $T = 120$ K. Its presence is justified from the fact that the H (0.34) peak remains low after the disappearance of the H

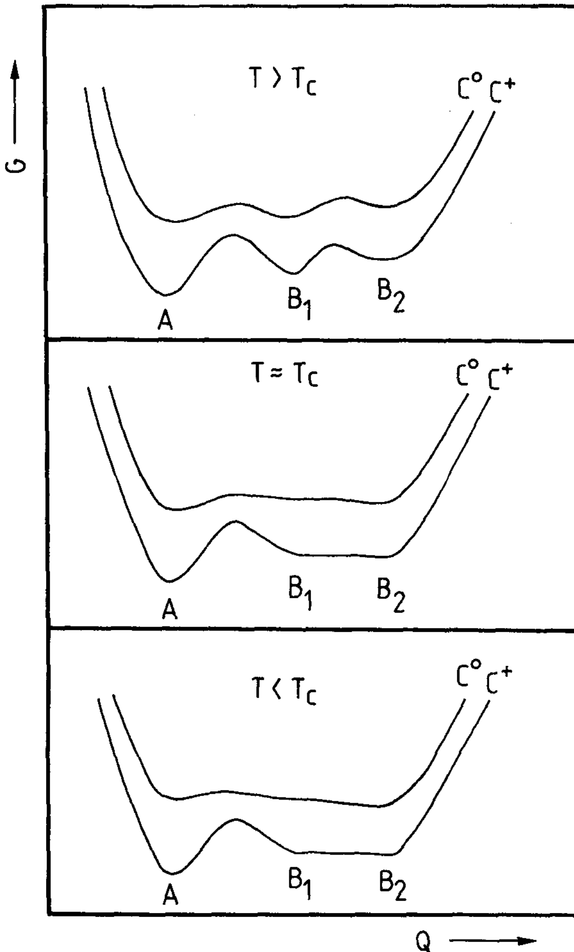


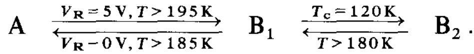
Fig. 3. A rough configurational coordinate diagram for the defect system, Q is the configurational coordinate

peak. Thus annealing with bias on sets the defect in configuration B_1 but quenching to 80 K transforms it to B_2.

Obviously for the inverse transition $B_2 \rightarrow B_1$ to occur an energy account should be settled. The barrier $B_2 \rightarrow B_1$ could be surpassed by heating up the sample at $T > 180$ K as is observed experimentally. In B_2 the defect has either very weak hole capture properties that make it undetectable by DLTS or its levels give DLTS peaks above 180 K where the defect has been converted to B_1 and therefore its signals cannot be traced in our experiments.

Cooling down from 220 K while the DLTS system is operating, the defect is partly in configuration B_1 and partly in configuration A. The defect has the tendency to be in A during the application of the filling pulse and in B_1 when the filling pulse is removed [18]. The conversion from A to B_1 during the cool-down scanning does not take place in the same measure as in the case leading to the dashed curve of Fig. 1. This explains the intermediate height of the H (0.34) peak of Fig. 2. It is evident from the proposed configurational coordinate diagram of Fig. 3 that the defect could convert to the B_2 configuration only in the C^0 charge state for $T < T_c$.

Preliminary studies of the transformation kinetics between the various configurations of the defect have shown that $T_{A \to B_1} = 195$ K and $T_{B_1 \to A} = 185$ K. The transition $B_1 \to B_2$ occurs at $T_{B_1 \to B_2} = 120$ K although $T_{B_2 \to B_1} = 180$ K. The transformations $A \to B_1$, $B_1 \to A$, and $B_2 \to B_1$ are thermally activated although $B_1 \to B_2$ is barrierless. The observed series of intradefect configurational changes could be outlined by the following scheme:



$$A \underset{V_R = 0\,V,\, T > 185\,K}{\overset{V_R = 5\,V,\, T > 195\,K}{\rightleftarrows}} B_1 \underset{T > 180\,K}{\overset{T_c = 120\,K}{\rightleftarrows}} B_2 \,.$$

In the following we will attempt a microscopic explanation of our results based on the macroscopic concepts discussed above. The microscopic picture we prepose is based on the additional observation that floating-zone Si does not exhibit the above-described behaviour in the cool-down scanning mode. This allows us to assume that the H peak and the associated changes in H (0.34) are due to the excess oxygen in pulled Si [15].

Irrespective of the charge state of the defect, temperature changes allow either the oxygen concentration to vary around the defect or the number of atoms/ions participating in the defect to undergo substantial structural changes. These introduce local electrostatic and strain field changes at the defect as well as changes in the configurational entropy, σ, of the defect. An estimation of the configurational entropy of the defect may be found by considering the defect as a cluster of a Bethe lattice whose central atom has a (temperature-dependent in general) coordination number Z. If we asume that all species except oxygen participating in the defect act as A-type and oxygen acts as B-type constituent of the defect, we can find the configuration entropy, σ, of such a defect from the equation [19, 20]

$$\sigma = kZ \left[\sum_{i=A,B} x_i \ln x_i - \tfrac{1}{2} \sum_{i,j=A,B} P_{i/j} \ln \left(\tfrac{1}{2} P_{i/j}\right) \right] , \tag{1}$$

where k is the Boltzmann constant, x_A the concentration of the A-species, $x_B = 1 - x_A$, and $P_{i/j}$ denotes the probability a lattice site to be occupied by species i when the neighbouring one is of j-type. The entropy σ represents the number of possible ways one can populate the sites of a cluster (with the conditions $\sum_{i=A,B} x_i = 1$, $\sum_{i,j=A,B} P_{i/j} = 1$) [19]. To the entropy σ one can add entropy changes due to any other structural changes of the defect. The various $P_{i/j}$, i, j, = A or B are explicitly known by giving $P_{A/B}$ and x_A (see, for example, [20]). The variation of entropy σ for various values of x_A, $P_{A/B}$, and given Z are not so large compared to variations due to changes in Z. For Z values between 6 and 12 and for various x_A and $P_{A/B}$ the values of σ predicted by (1) may vary in the range of $2k$ to $9k$ justifying the assumptions of the HPP theory.

According to the above description the change in the entropy which results from the variation of the oxygen concentration of the defects is assumed to be much greater than that due only to structural changes of a defect whose oxygen concentration is not changing with the variation of temperature. On the other hand, the observed relationship between the H (0.34) and H peaks supports our assumption of oxygen-induced changes in the entropy of the defects because it reflects the creation of one type of a defect configuration at the expense of some other one (of the same or a different charge state), a condition that can be justified by oxygen movement.

It is therefore the short-range order correlation ($P_{A/B}$) and the coordination number Z (for certain concentration value x_A) that specify the conditions for a defect configuration. The temperature may specify the local changes in the coordination number Z. Such changes

may be the result of structural changes or/and the capturing of (unbound) oxygen atoms [21]. The large changes in Z which according to (1) are needed in order to account for the desired values of entropy changes made us assume that Z changes are mainly due to the oxygen capturing around the defect rather than to large-scale structural changes.

Within this picture our experimental findings can be interpreted as follows: Thermal annealing at 220 K establishes a thermodynamic equilibrium of various defects of certain oxygen concentration. As the temperature changes, while structural changes take place, oxygen movement is reduced (cool-down mode) or enhanced (upward scanning) with the result that a new type of clustering develops around the defect. These changes (which reflect changes in coordination number Z and $P_{A/B}$) allow changes in the Gibbs energy (enthalpy and entropy changes) of the defect shown in Fig. 3 and exhibited in the DLTS spectra. Abrupt quenching to 80 K freezes the oxygens around their thermodynamically stable configurations. Scanning upwards from 80 K we can trace various defect configurations in different charge states (depending on the annealing voltage V_R). The fact that some configurations are not traced when scanning upwards in temperature (for example feature H of B_1) indicates that the corresponding transformation ($B_2 \rightarrow B_1$) is not barrierless. On the other hand, during the downward scanning we observe also those metastable configurations which by thermal activation become attainable provided that they are traceable with DLTS. However, it appears necessary to start the downward scanning at temperatures greater than 180 K in order to have the H peak exhibited in our DLTS spectra. This condition specifies a temperature for oxygen activation accompanied (or not) by structural activation. Such activations do not alter the charge state of the defect. They change the Gibbs free energy of defect formation and give rise to metastable defect configurations of the particular charge state.

According to the above discussion the variation of G is due to the changes of both the formation entropy of the defect as predicted by (1), and the changes in the formation enthalpy. It is understood that at this stage we cannot go beyond the present model assumptions. We cannot, for example, separate the effect of the electronic changes which accompany the structural changes of the defect from the effect of the entropy changes. Also we cannot exclude possibilities where Si self-interstitials may play a dominant role in capturing oxygen and promote or not its diffusion parameters [21]. Nevertheless the arguments of the present microscopic description indicate that entropy changes should not be underestimated in the consideration of the stability of defects in Si. At the same time we propose a possible microscopic process which, when engaged in extensive numerical work, may justify the present and the HPP descriptions. Finally, it is worth noticing the results of recent calculations [22] for the three-oxygen-atom cluster in silicon. These results, although they refer only to the formation energies of various defect configurations, give strong support to the validity of the microscopic description proposed in the present work.

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