Pair Diffusion and Kick-out: Contributions to Diffusion of Boron in Silicon

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Diffusion of boron in silicon has great technological relevance to microelectronic processing. Despite considerable effort spanning over many years, the dominant mechanism for this diffusion remains strongly debated, together with the values of key activation energies. Some evidence indicates that the principal mobile species is a B-Si complex (so-called "pair diffusion"), whereas other evidence points to a lone boron interstitial ("kick-out"). An attempt to resolve the question is made by formulating a comprehensive kinetic model that incorporates both mechanisms. Rate parameters for the elementary steps are estimated systematically, based on literature reports or physical arguments. In the frequent cases where reports conflict, maximum likelihood estimation is employed to determine the best value, and multivariate statistics to quantify its accuracy. A Monte Carlo technique is used to show that kick-out very likely dominates pair diffusion in both implanted Si *and unimplanted silicon.* © 2004 American Institute of Chemical Engineers *AIChE J,* 50: 3248–3256, 2004

Introduction

Transient enhanced diffusion (TED) of ion-implanted boron in silicon for microelectronic device production has attracted a great deal of study.[1,13] With the continuing shrinkage of device dimensions, detailed modeling of TED has become increasingly important for designing suitable post-implant annealing processes. The state of such modeling is far from satisfactory, however, especially for *a priori* predictive purposes rather than mere correlation. One reason is that many elementary kinetic steps contribute to the experimental observable—typically a dopant depth profile obtained by secondary ion mass spectroscopy (SIMS). Although the profiles can serve as the touchstone for evaluating overall kinetic schemes, reliable deduction of the expressions and constants must take place independently.

Such independent determinations have proven problematic. For example, experimental results have been used to justify diffusion coefficients for the *Si* self-interstitial that vary by more than ten-orders of magnitude at typical processing temperatures.[12] Experiments have been hampered because the mobile species include many point and extended defects that exist at low concentrations and are difficult to observe. Calculations based on density functional theory (DFT) have also proven problematic for several reasons. Most quantum calculations are valid only at 0 K, but mechanisms can change at higher temperatures. For example, diffusion in *Si* at processing temperatures appears to be governed by collective atomic motions that do not operate at lower temperatures.[43] Moreover, DFT calculations typically ignore entropic effects, some of which can change pre-exponential factors by many orders of magnitude.[44] Finally, DFT in the local density approximation is a ground-state theory and predicts bulk band gaps very poorly. By implication, deep electronic levels associated with point defects incur similar errors.[49, 50] In light of these problems, rationally defensible procedures for estimating rate parameters must be accepted in place of certain truth about their forms and values.

This article applies the statistical methods of maximum likelihood parameter estimation together with Monte Carlo analysis to help resolve an important controversy regarding the mechanism of boron diffusion in TED. The controversy concerns the relative roles of "kick-out" vs. "pair diffusion" (or

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"interstitialcy") mechanisms. The problem is approached by first formulating a reaction-diffusion network incorporating both mechanisms and deriving appropriate rate expressions. To handle conflicting literature reports regarding the values for the rate parameters, maximum likelihood parameter estimation is employed. Finally, the relative contributions are compared of the two mechanisms employing a Monte Carlo analysis, based on these estimates. The significance of this article is considered to lie as much in the systematic method of approach as in the mechanistic conclusions it draws.

History of the Question

Most early work on boron diffusion explained the phenomenon in terms of a "pair diffusion" mechanism, in which a boron and a silicon atom diffuse together as a bound complex.[29, 30, 34] Evidence for this view came mainly from surface oxidation experiments in which *Si* interstitials that were injected into the bulk enhanced boron diffusion.[13] *Si* interstitials are well known to mediate boron motion, and formation of a complex is consistent with this fact. However, the precise nature of the complex and its diffusion path were not clearly specified, and the evidence then available did not exclude other possible mechanisms.

For example, diffusion in solids often takes place via a "kick-out" mechanism.[32] Applied to this case, kick-out envisions boron motion to begin when a free *Si* interstitial encounters a substitutional B atom and exchanges with it, leaving the boron in an interstitial position. The boron then moves rapidly in the interstices until it exchanges with another *Si* atom in the host lattice, thereby becoming substitutional and regenerating interstitial *Si*. Around 1990, experimental work by Cowern et al.[10, 11] bolstered by DFT calculations of Nichols et al.[33] concluded that kick-out offers a better description of boron motion than pair diffusion as then conceived. In the experimental work, the shapes, temperature dependence, and surface oxidation dependence of SIMS profiles provided three independent lines of evidence for this conclusion. The computational work supported this view by indicating that the activation barrier for interstitial diffusion is modest.

This view was held throughout most of the 1990s by many workers interested in solid-state diffusion,[51, 52] but there existed a good deal of parallel effort that did not take account of this view.[18, 20, 45] Then in 1999, there appeared simultaneously two DFT-based reports that led to an explicit debate regarding the dominant mechanism. Windl et al.[49] used two variants of the nudged elastic band method (NEBM) in concert with a monopole correction for charged systems to obtain barriers between 39 and 68 kJ/mol (0.4 and 0.7 eV) for pair diffusion. Sadigh et al.[37] used two somewhat different methods to calculate barriers of 66 and 71 kJ/mol (0.68 and 0.73 eV). Since that time, Allipi et al.[2, 3] have reported a barrier of 68 kJ/mol (0.7 eV), in substantial agreement with the 1999 work. This estimate is sufficiently close to that for producing interstitial boron by kick-out (~97 kJ/mol or 1 eV) that, depending on the preexponential factors and other aspects of the kinetic network, the rates for the two mechanisms could be of the same order of magnitude at the high-temperatures (~1,000°C) characteristic of device processing. Presently, the relative importance of pair diffusion and kick-out remains unresolved.

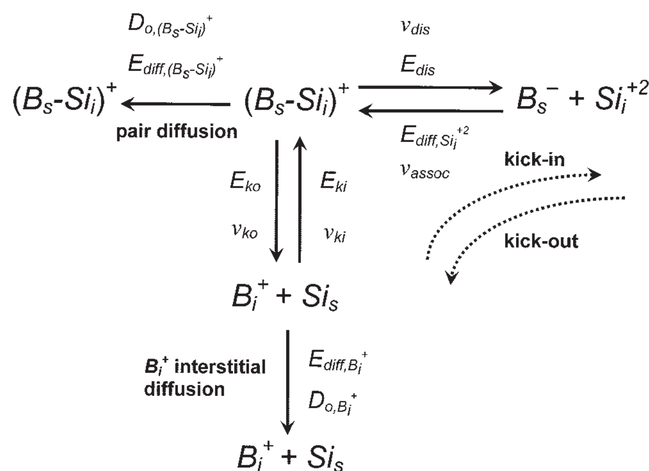

Figure 1. Composite reaction network incorporating the kick-out and pair diffusion mechanisms.

General Kinetic Model

The following paragraphs lay out an overall kinetic scheme for boron diffusion in silicon, develop appropriate rate expressions for the elementary steps, and assign numerical values to the rate parameters according to maximum likelihood estimation.

Overall kinetic scheme

An overall reaction network that contains all of the elementary steps for both kick-out and pair diffusion appears in Figure 1. The scheme is shown for heavily doped *p*-type material, which is the focus of technological interest. In such material, boron exists as B_i^+[16, 33] interstitial silicon as Si^{+2}[16, 33], and the substitutional boron-interstitial complex as $(B_s\text{-}Si_i)^+$.[16, 29, 49, 51, 52] The $(B_s\text{-}Si_i)^+$ complex plays the most central role in this scheme. Once formed, this complex can diffuse, dissociate into substitutional boron and interstitial silicon, or undergo kick-out to yield interstitial boron that subsequently diffuses. The relative balance among these various pathways determines the relative importance of kick-out vs. pair diffusion.

Rate expressions

Table 1 shows a summary of the rate expressions for the various elementary steps in a consistent and systematic way. The two mobile species involving boron are B_i^+ and $(B_s\text{-}Si_i)^+$. The hopping diffusivities of these species can be represented as the product of a site-to-site hop rate r_{hop} and a hop length λ according to

$$D_{hop} = r_{hop}\lambda^2 \tag{1}$$

Since both B_i^+ and $(B_s\text{-}Si_i)^+$ can jump into several types of sites having different geometries and effective hop lengths, we define λ to be an aggregate quantity with suitably weighted contributions from all the relevant configurations. Note that our definition of λ as a site-to-site hopping distance does not correspond to the effective interstitial diffusion length discussed by some workers.[8]

A further point of possible confusion needs clarification at

Table 1. Rate Expressions and Arrhenius Parameters in Elementary Steps for B Diffusion

Reaction	Symbol	Rate Expression	Activation Energy (kJ/mol)	Pre-exponential Factor
$(B_s\text{-}Si_i)^+$ diffusion	$D_{(B_s\text{-}Si_i)^+}$	$D_{o,(B_s\text{-}Si_i)^+}\exp(-E_{diff,(B_s\text{-}Si_i)^+}/kT)$	65 ± 3	1×10^1 m²/s
B_i^+ diffusion	$D_{B_i^+}$	$D_{o,B_i^+}\exp(-E_{diff,B_i^+}/kT)$	36 ± 4	1×10^1 m²/s
Si_i^{+2} diffusion	$D_{Si_i^{+2}}$	$D_{o,Si_i^{+2}}\exp(-E_{diff,Si_i^{+2}}/kT)$	70 ± 3*	1×10^1 m²/s
$(B_s\text{-}Si_i)^+ \rightarrow B_i^+ + Si_s$	r_{ko}	$k_{ko}\exp(-E_{ko}/kT)\,[(B_s\text{-}Si_i)^+]$	101 ± 7	6×10^{12} s^{-1}
$B_i^+ + Si_s \rightarrow (B_s\text{-}Si_i)^+$	r_{ki}	$k_{ki}\exp(-E_{ki}/kT)\,[B_i^+]$	48 ± 10	6×10^{12} s^{-1}
$(B_s\text{-}Si_i)^+ \rightarrow B_s^- + Si_i^{+2}$	r_{dis}	$k_{dis}\exp(-E_{dis}/kT)\,[(B_s\text{-}Si_i)^+]$	57 ± 6*	6×10^{12} s^{-1}
$B_s^- + Si_i^{+2} \rightarrow (B_s\text{-}Si_i)^+$	r_{assoc}	$k_{assoc}\,[B_s^-][Si_i^{+2}]$, where $k_{assoc} = 4\pi a D_{o,Si_i^{+2}}\exp(-E_{diff,Si_i^{+2}}/kT)$	70 ± 3*	3×10^{-4} m³/s

*These estimated standard deviations do not account for bias errors that may be present in the component data.

this stage. It is often the practice in the literature to write diffusion equations in terms of the species most easily observed experimentally: total boron. With care, this practice can be made to work rigorously, as long as the concentration of each kind of mobile species is weighted properly. An example of such a form is[1, 13]

$$D = D^0 + D^+\left(\frac{p}{n_i}\right) + D^{+2}\left(\frac{p}{n_i}\right)^2 \tag{2}$$

where D^0, D^+, and D^{+2} denote hopping diffusivities in intrinsic material of the corresponding charged species, and n_i and p denote carrier concentrations according to the usual conventions. The definition of D in Eq. 2 can lead to confusion about the diffusion mechanism, however, especially when there are large disparities in the diffusion lengths of mobile species or when dopant gradients are large. Such cases often lead to profiles of total boron that are described as "non-Fickian." In fact, the behavior may be entirely Fickian when each mobile species is considered separately. Such problems have been discussed briefly by Cowern et al.[9] although these workers still proceeded to formulate one of their diffusion equations in terms of total boron. We go a step further by entirely avoiding formulations in terms of total boron, opting instead to write mass balances for each individual mobile species B_i^+ or $(B_s\text{-}Si_i)^+$. Adding the results after solution yields the concentration of total boron.

Breakup of the $(B_s\text{-}Si_i)^+$ complex to yield interstitial species occurs by two pathways that are each kinetically first-order in the concentration of $(B_s\text{-}Si_i)^+$. Dissociation to yield free Si_i^{+2} is denoted by the rate r_{dis}, while dissociation via kick-out to yield free B_i^+ is denoted by r_{ko}.

The reverse reaction of kick-in is also fundamentally first-order, depending only on the concentration $[B_i^+]$ because each B_i is completely surrounded by lattice Si atoms with which it can react.

The association reaction between Si_i^{+2} and B_s^- is second-order, however, because B_s^- is by far the minority species in terms of lattice site occupation. Although an activation barrier may exist in principle when these species get close enough to react, the opposite charges on the reactants, and the negative free energy of formation for the complex give reasons to believe that the complex forms with no barrier. A rate expression describing standard diffusion limitation by reactants (see, for example,[24]), therefore, seems warranted

$$r_{assoc} = k_{assoc}[B_s^-][Si_i^{+2}] \tag{3}$$

$$\text{with} \qquad k_{assoc} = 4\pi a D_{assoc} \tag{4}$$

where $D_{assoc} = D_{B_s^-} + D_{Si_i^{+2}}$, with $D_{B_s^-} \ll D_{Si_i^{+2}}$. Here, a represents a reaction distance or "capture radius".

There exist significant questions about what value a should take. The capture radius may depend on the identities of the atoms involved, as well as their charge states and orientation within the Si lattice[6]. For example, Coulombic attraction between species of opposite charge probably lead to increased values of a, while like charges lead to decreased values. Effects of this sort remain inadequately treated in the literature, so that a has been assigned a variety of values, ranging from the nearest neighbor distance[7, 36] of 0.27 nm to the Si lattice constant[31] (~0.5 nm) to even larger values near 0.7 nm.[6] Because literature reports of a mostly represent assumptions rather than reported values, and because a varies with reaction stoichiometry and other factors, the quantitative methods employed here for assigning a most probable value are not suitable. We instead treat it as a fixed parameter with an assumed value of the Si nearest neighbor distance, 0.27 nm. Other choices are certainly defensible, particularly larger ones in view of the opposite charges on B_s and Si_i that causes them to attract. However, the B_s^- substitutional defect has a weakly bonded charge cloud associated with it that can be described with hydrogenic wavefunctions. This cloud is quite polarizable, and has an effective radius approaching 1 nm.[44] Thus, when a positively charged Si interstitial approaches within this radius, neutralization may take place, which would largely eliminate the electrostatic attraction and reduce the value of a. Effects of this sort are poorly understood, and in any case are unlikely to affect a by more than a factor of about three. Since, the value of a enters into the pre-exponential factor, which is already uncertain by at least this factor as discussed later, the exact choice of a is not crucial. Also, the results presented later are not very sensitive to pre-exponential factors, so this uncertainty does not affect the conclusions to be drawn later.

Rate Parameters

Rigorous parameter estimation

The rate expressions developed in the previous section require rate constants with activation energies and pre-exponential factors. In several cases, the reported literature values vary widely. Both experimental measurements and quantum calcu-

lations have nontrivial uncertainties. Hence, there is no clear way to discern which, if any, of the reported values are correct. Yet some value must be chosen for useful progress to be made. This problem crops up commonly in petroleum reforming and catalysis, atmospheric chemistry, combustion, growth of amorphous materials, and many others involving complicated reaction networks with many elementary steps. In our opinion, the approach to parameter selection sometimes tends to be *ad hoc*.

We approach this problem more rigorously through the application of the statistical technique of maximum likelihood parameter estimation.[5] This approach gives the most likely value for each parameter based on the available literature, and estimates the corresponding uncertainty. The most likely value $\bar{y}$ for a given parameter is obtained by minimizing the objective function[5]

$$\Phi(\bar{y}) = \sum_i w_i(y_i - \bar{y})^2 \tag{5}$$

where y_i denotes the estimate for the parameter drawn from a particular article i in the literature, and w_i is a weighting factor that accounts for the accuracy of y_i. Setting the derivative of $\Phi(\bar{y})$ with respect to $\bar{y}$ equal to zero yields an analytic formula for $\bar{y}$:

$$\bar{y} = \frac{\sum_i w_i y_i}{\sum_i w_i} \tag{6}$$

Computational articles (particularly by DFT) often produce several estimates for a parameter using a family of closely related methods. In such cases, we took y_i as the average of the individual estimates y_{ij}. This procedure tacitly assumes that all estimates reported by a particular laboratory have equal probability.

The weighting factors w_i were computed based on the common assumption[5] that the uncertainty in γ_i can be represented using a normal (Gaussian) distribution. Thus, w_i was set to equal the inverse of the variance σ_i^2, where σ_i is the standard deviation of y_i. We adopted the following procedure for determining σ_i. In experimental studies, we obtained activation energies by linear fits of ln(D) vs. reciprocal temperature (1/T) using an ordinary least-square estimator. Assuming that errors are additive and satisfy standard Gauss-Markov assumptions (that is, that the errors are uncorrelated, have zero-mean, and have constant variance), σ_i obeys[5]

$$\sigma_i = \sqrt{\frac{\min_{b_1 b_0} \sum(Y_k - b_1 X_k - b_0)^2}{(m-2)\sum(X_k - \bar{X})^2}} \tag{7}$$

Here, X_k and Y_k respectively represent $1/T$ and ln(D) for each data point; $\bar{X}$ denotes the mean of X; m denotes the total number of data points, and b_1 and b_0 represent the fitting parameters, that is, the activation energy and the prefactor.

In computational articles offering multiple estimates y_{ij}, the standard deviation was calculated using the formula

$$\sigma_i = \sqrt{\frac{\sum_j (y_{ij} - y_i)^2}{n-1}} \tag{8}$$

where n is the total number of estimates in the article. There were, however, instances where a laboratory published only a single computational estimate. In these cases σ_i was taken to be the average of the standard deviations from other laboratories using similar computational methods.

The uncertainty in the most likely value $\bar{y}$ was quantified as a standard deviation given by

$$\bar{\sigma} = \frac{1}{\sqrt{\sum_i \frac{1}{\sigma_i^2}}} \tag{9}$$

Parameter estimates given below are reported in the form of $\bar{y} \pm \bar{\sigma}$.

Activation energies

For diffusion of the $(B_s\text{-}Si_i)^+$ pair, we are aware of three reports in the literature, based on quantum calculations. The work of Windl et al.[49] used a single DFT method in two approximations (local density and generalized gradient) to arrive at values between 39 and 68 kJ/mol (0.4 and 0.7 eV). Sadigh et al.[37] employed a different DFT method in the same two approximations to arrive at 66 and 71 kJ/mol (0.68 and 0.73 eV). Recently, Alippi et al.[2, 3] used a DFT-based, tight-binding molecular dynamics method to obtain 64 kJ/mol (0.66 eV). On the basis of these results, the maximum likelihood method yields 65 ± 3 kJ/mol (0.67 ± 0.03 eV) for $(B_s\text{-}Si_i)^+$ pair diffusion.

For diffusion of B_i^+, there exist two experimental and three quantum-based reports. Watkins employed annealing studies with electron paramagnetic resonance (EPR) to obtain a value of 58 kJ/mol (0.6 eV).[47] However, this number is actually transposed from other EPR measurements concerning spin alignment reported in the article. Our own least-squares fit of the data shown in Figure 10 of Watkins' article yields a value of 43 kJ/mol (0.45 eV). More recently, Collart et al.[8] studied room-temperature diffusion of B after low-energy implants in *Si*. By combining the results of their work with those of Cowern et al.,[10, 11] Collart et al. derived a value of 39 kJ/mol (0.4 eV). Using DFT calculations, Zhu et al. offered an estimate of 29 kJ/mol (0.3 eV).[52] However, this number represents only a difference in formation energy between the initial and final states of hopping, which is not necessarily the same as a true transition-state barrier. Also, the calculation concerns neutral B_i, while in p-doped material the boron interstitial is likely to be positively charged. It is unknown to what extent charge affects the activation energy, but we choose here to incorporate the results for neutral and charged species on the same basis. Zhu reported 19 kJ/mol (0.2 eV) in a different set of calculations.[51] This result, however, also pertains to a formation energy difference rather than a true barrier. The text of the article does not clearly specify the charge state of B_i. On the basis of these results, the maximum likelihood method yields 36 ± 4 kJ/mol (0.37 ± 0.04 eV) for B_i^+ diffusion.

For Si_i diffusion, we are aware of two experimental and numerous quantum-based reports. Disconcertingly, the values exhibit an enormous variance. In experimental work using deep level transient spectroscopy, Hallen et al.[17] monitored the disappearance of proton-beam-generated point defects below

room temperature. With the assumption that the disappearance was limited by Si_i diffusion, these workers assigned a corresponding activation barrier of 6.3 ± 1.4 kJ/mol (0.065 ± 0.015 eV). The low value was tentatively attributed to enhancements resulting from the irradiation procedure. Wijaranakula reported a large activation energy of 180 kJ/mol (1.86 eV),[48] based on experiments where oxygen donors were used to trace Si interstitial motion. Neither experimental study indicated the charge state of the Si_i. Numerous computational estimates exist for neutral Si_i diffusion, obtained by DFT, tight-binding, and quantum-based molecular dynamics methods. Most work treats diffusion of the neutral interstitial, although there are reports for Si_i^+ and Si_i^{+2}. As with the experimental work, the values exhibit an enormous variance. The range cannot be explained by either computational method or choice of charge state. In early work, Nichols et al.[33] employed DFT in the local density approximation (LDA) to obtain a barrier of 39 kJ/mol (0.4 eV) for hopping of Si_i^0. More recently, Leung et al.[27, 28] used roughly similar methods to obtain a range of barriers of 3 to 14 kJ/mol (0.03 to 0.15 eV) in LDA and 17 to 19 kJ/mol (0.18 to 0.20 eV) in the generalized gradient approximation (GGA) for Si_i^0, with the results depending on diffusion path. Lee et al.[26] reported a range of 14 to 17 kJ/mol (0.15 to 0.18 eV) in LDA for Si_i^0, depending on path. They reported corresponding values of 45 to 57 kJ/mol (0.47 to 0.59 eV) for Si_i^+, and a lower bound of 97 kJ/mol (1.0 eV) for Si_i^{+2}. These workers suggested that the charge state most responsible for diffusion depends on Fermi energy E_F, and, by implication, that the diffusion barrier also varies. For example, the barrier is predicted to begin at 97 kJ/mol (1.0 eV) for Fermi energies E_F below 18 kJ/mol (0.19 eV) above the valence band maximum (where Si_i^{+2} diffusion dominates). The barrier then drops to 45 kJ/mol (0.47 eV) for $18 < E_F < 24$ kJ/mol ($0.19 < E_F < 0.25$ eV) where Si_i^+ dominates, and drops further to 14 kJ/mol (0.15 eV) where Si_i^0 dominates. These workers also postulated a charge-assisted hopping mechanism in which the interstitial is neutral in the initial and final states, but converts to Si_i^{+2} in the transition state. The barrier for such motion was calculated to be less than 5 kJ/mol (0.05 eV). In a similar manner, Zhu et al.[52] reported a barrier of 135 kJ/mol (1.4 eV) for Si_i^0, which decreases to 87 and 68 kJ/mol (0.9 and 0.7 eV) if charge exchange is permitted in the transition state of +1 and +2, respectively. Some of these last numbers are quite high. A high barrier of 132 kJ/mol (1.37 eV) for Si_i^0 has also been reported by Tang et al.[40] from tight-binding molecular dynamics simulations for neutral Si. Gilmer et al.[15] employed a classical MD simulation to obtain an intermediate result of 87 kJ/mol (0.9 eV). It is unknown to what extent charge affects the activation energy, but as with B_i^+ we choose to incorporate the results for neutral and charged species on the same basis.

Use of the maximum likelihood method required a bit of judgment in this case. Simple application of the algorithm described above for assigning the weighting factors w_i leads to a barrier of 16 kJ/mol (0.17 eV). This value is suspect for several reasons. First, it relies too heavily on the report of 6.2 kJ/mol (0.065 eV) from Hallen et al. The standard deviation of 1.4 kJ/mol (0.015 eV) for this number, roughly 25% of the actual value, is reasonable on a relative scale but is an order of magnitude smaller than all the other standard deviations employed for Si_i. In consequence, the result of Hallen et al. takes on a value for w_i more than an order of magnitude larger than all other reports, greatly skewing the mean value. The report itself is suspect for several reasons. The data analysis relies on several assumptions that are difficult to verify. The temperature range of measurement differs greatly from that of TED, opening the possibility of mechanism change. The number is smaller than experimental and computational results for B_i, which seems incongruous because the larger size of and greater potential for coordination of Si_i relative to B_i suggests that the barrier for Si_i should be larger. For these reasons, we adjusted w_i for the report of Hallen et al. to equal the mean for that of all other reports for Si_i. On this basis, the maximum likelihood method yields 70 ± 3 kJ/mol (0.72 ± 0.03 eV) for Si_i^{+2} diffusion.

For the kick-out reaction that yields B_i^+ from the $(B_s\text{-}Si_i)^+$ complex, we are aware of two quantum-based reports. Zhu et al. report a value of 97 kJ/mol (1.0 eV)[52], although the calculation pertains to neutral charge states for both the complex and the interstitial. Zhu subsequently gives 106 kJ/mol (1.1 eV)[51] in a calculation for $(B_s\text{-}Si_i)^+$. The charge state of the boron interstitial is, however, not clearly specified. On the basis of these results, the maximum likelihood method yields 101 ± 7 kJ/mol (1.05 ± 0.07 eV) for E_{ko}.

For the kick-in (that is, reverse) reaction that yields $(B_s\text{-}Si_i)^+$ from B_i^+, two of the available reports originate from the two articles discussed earlier, and are subject to the same issues regarding charge state identity. Zhu et al. reports 0.6 eV for kick-in involving neutral species,[52] while Zhu report 39 kJ/mol (0.4 eV) for $(B_s\text{-}Si_i)^+$ and an indefinitely charged boron interstitial.[51] Tarnow[41] offers a "lower bound" on the barrier of 52 kJ/mol (0.54 eV) for $(B_s\text{-}Si_i)^+$. On the basis of these results, the maximum likelihood method yields 48 ± 9 kJ/mol (0.5 ± 0.1 eV) for E_{ki}.

Dissociation of the $(B_s\text{-}Si_i)^+$ complex yields B_s^- and Si_i^{+2} in material with significant p-doping.[16, 51] The available reports for this reaction all derive from quantum calculations, and all concern differences in formation energies rather than true transition state barriers. Zhu gives 21 kJ/mol (0.22 eV) for E_{dis}[51], while Hakala et al. give 23 kJ/mol (0.24 eV).[16] These authors did not, however, apply a correction for artifacts of charging that tend to crop up in DFT calculations. The magnitude of this correction is quite large; Windl et al.[49] cite values of 15 and 62 kJ/mol (0.16 and 0.64 eV) for singly and doubly charged species, respectively. The best method of correction has been the subject of debate—while Windl et al. employ a monopole correction based on a Madelung-style computation[23], other workers have argued for aligning the energy levels of the deepest core states.[53] Windl et al.[49] and Sadigh et al.[37] applied a monopole correction. Both laboratories applied local density and generalized gradient approximations to arrive at separate estimates for E_{dis}. Windl et al. list E_{dis} at 97 and 77 kJ/mol (1.0 and 0.8) eV by these respective methods, while Sadigh et al. list values of 87 and 100 kJ/mol (0.9 and 1.03 eV). Since the calculations from within each laboratory differ only by the DFT approximations they use, we average the results into aggregate numbers of 87 ± 9 kJ/mol (0.9 ± 0.1 eV) for Windl et al. and 94 ± 9 kJ/mol (0.97 ± 0.09 eV) for Sadigh et al. These aggregates are considerably higher than the values given by Zhu and Hakala et al. mainly because of the monopole correction applied in the former cases. Hakala et al. in fact cite the former works in the conclusions to their article, indicating that application of the monopole correction produced results

within 19 kJ/mol (0.2 eV) of those of Windl et al. However, Hakala et al. still cite their lower number of 23 kJ/mol (0.24 eV) in the abstract and main text, implicitly indicating that a correction of this magnitude may not be warranted. On the basis of these various results, the maximum likelihood method yields 57 ± 6 kJ/mol (0.59 ± 0.06 eV) for E_{dis}.

The reverse reaction to dissociation is the association of B_s^- and Si_i^{+2} to form the $(B_s\text{-}Si_i)^+$ complex. Inspection of the diffusion-limited rate expression in Table 1 shows that the activation energy E_{assoc} is simply the activation energy for Si_i^{+2} diffusion, which was discussed earlier.

Pre-exponential factors

Theoretical treatments of boron diffusion have paid scant attention to prefactors, focusing instead on activation energies. Thus, the model of Figure 1 requires a significant number of *a priori* estimates for prefactors. In general, simple kinetic models for elementary reactions view rate constants as the mathematical product of an attempt frequency and a Boltzmann factor describing what fraction of reactants is likely to traverse the energy barrier on a single attempt. In a solid having a distribution of phonon frequencies, a single aggregate attempt frequency for atomic motion is difficult to define. One commonly used possibility for approximation purposes is the Debye frequency, which for *Si* is about $6 \times 10^{12}\ s^{-1}$. However, it is well known from other branches of kinetics that such a simple picture often does a poor job of estimating prefactors. For example, a survey[46] of prefactors for gas desorption from semiconductor surfaces shows that, while the average value indeed lies near $10^{13}\ s^{-1}$, only 10 % of individual cases fall within an order of magnitude of this range. The story is roughly similar for hopping diffusion on semiconductors (see, for example,[38]). Clearly the use of *a priori* estimation of prefactors requires caution. Nevertheless, progress in diffusion modeling requires that rationally defensible estimates be made.

For B_i^+ exchange (in both directions) with $(B_s\text{-}Si_i)^+$ and for $(B_s\text{-}Si_i)^+$ dissociation, the Debye-frequency estimate can be used without further modification. For hopping diffusion, however, the pre-exponential factor D_o is proportional to the attempt frequency ν and hop length λ according to[22]

$$D_o = \nu\lambda^2 \tag{10}$$

Insertion of the Debye frequency into Eq. 12 together with a hop length λ of 0.27 nm yields a value for D_o near 1×10^{-3} cm^2/s. This value agrees exactly with that reported from quantum based molecular dynamics simulations by Allipi et al.[2,3] for B diffusion. For the association reaction of Si_i^{+2} with B_s^- to form $(B_s\text{-}Si_i)^+$, Eq. 6 yields a pre-exponential factor for the rate constant k_{assoc} equal to 3×10^{-10} cm^3/s.

Predictions of the Model

The pair diffusion mechanism for boron diffusion requires the existence of an intact complex $(B_s\text{-}Si_i)^+$, while the kick-out mechanism relies on B_i^+. Comparing, the relative importance of the two mechanisms, therefore, requires comparing the rates of overall mass transport by the two species. As suggested by Eq. 2 this overall rate is proportional to not only the hopping diffusivity, but also the concentration of each species. It is, therefore, useful to define a mass-transport ratio *R* as follows

$$R \equiv \frac{[B_i^+]D_{B_i^+}}{[(B_s\text{-}Si_i)^+]D_{(B_s\text{-}Si_i)^+}} \tag{11}$$

When $R > 1$, mass transport by kick-out dominates; pair diffusion dominates for $R < 1$.

We have already developed expressions for the diffusivities in Eq 11; the more difficult problem is estimating the concentrations. These concentrations depend through $[Si_i^{+2}]$ on a host of other rate processes taking place within the solid—most notably interstitial cluster formation in TED. The quantity $[B_i^+]$ is also tied to the formation of boron-interstitial clusters (BICs).[35] Thus, the dominant mechanism is likely to depend on processing history of the material, spatial location in a diffusion gradient, temperature, doping concentration, and other factors. At best, we can examine only some plausible scenarios here.

Undefected material in thermal equilibrium

For undefected, unimplanted *Si*, let us suppose that clustering, surface, and extended defect effects are insignificant. That is, interstitials of both *B* and *Si* are created only from lattice sites—leaving behind corresponding vacancies. A full quantitative description of the equilibrium between vacancies, and either *Si* or B_i is still lacking because of controversy over vacancy formation energies.[13, 39, 42] However, as a crude estimate, let us assume that at 1,000 °C, $[Si_i^{+2}]$ is on the order of 10^{19} m^{-3} as given by Harrison.[19] Let us also assume that $[B_i^+]$ has a similar magnitude—its lower mole fraction being roughly compensated by its lower formation energy. Finally, let $[B_s^-] = 10^{24}$ m^{-3}, a typical modest doping concentration. We must now estimate $[(B_s\text{-}Si_i)^+]$ to permit evaluation of *R*. A quasi-steady state mass balance on this complex yields

$$0 = r_{ki} - r_{ko} + r_{assoc} - r_{dis} = k_{ki}[B_i^+] - k_{ko}[(B_s\text{-}Si_i)^+] + k_{assoc}[B_s^-][Si_i^{+2}] - k_{dis}[(B_s\text{-}Si_i)^+] \tag{12}$$

Rearrangement yields

$$[(B_s\text{-}Si_i)^+] = \frac{k_{ki}[B_i^+] + k_{assoc}[B_s^-][Si_i^{+2}]}{k_{ko} + k_{dis}} \tag{13}$$

Substituting Eq. 13 into Eq. 11 yields an expression for *R* that can be evaluated easily. However, the activation energies embedded within *R* have ranges $\bar{\sigma}$ as specified in Table 1. These ranges implicitly describe probability distributions; hence, the ratio *R* is also characterized by a probability distribution function. The distribution function describing *R* represents a complicated composite of the distributions for the constituent parameters. Monte Carlo simulations can be used in obtaining the composite,[4] and that method was employed here. Monte Carlo simulations propagate the distributions of the activation energies by generating a large number of samples that represent the distribution of *R* rather than direct computation of the density function. We calculated *R* using 10^6 sets of activation energies produced with a random number generator. The sets were

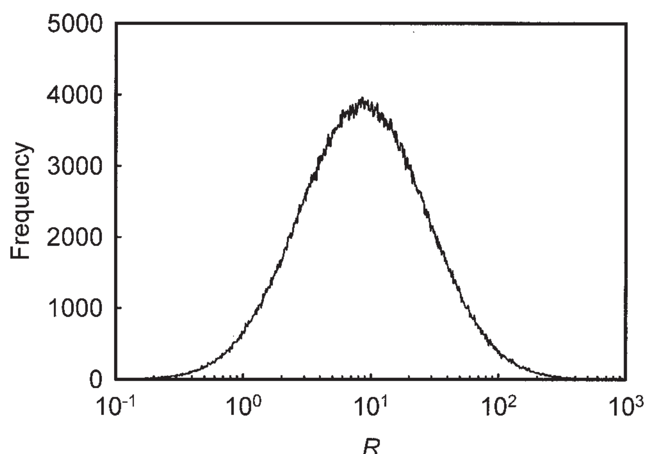

Figure 2. Probability distribution of the diffusivity ratio *R* for undefected material in thermal equilibrium.

Results come from Monte Carlo analysis as described in the text. In only 3% of the cases does R dip below unity. The mean value (not evident on the logarithmic scale) is 16, which is larger than the peak value at approx. 9.

chosen such that each activation energy obeyed the $\bar{y} \pm \bar{\sigma}$ relation given in Table 1, according to a normal (Gaussian) distribution.[4] The resulting 10^6 samples of R represent the composite distribution, which can be visualized conveniently with a histogram.

Figure 2 shows the resulting composite distribution for R. The mean value is roughly 16, and the probability that R falls below unity is only 3%. A value for R at 16 indicates that the relative contributions to overall diffusion flux from pair diffusion and interstitial mechanisms are 6 and 94%, respectively at 1,000°C. These contributions do not change dramatically as the temperature varies in this general range, because the activation energies (and, therefore, temperature dependences) of the key elementary steps are modest. We conclude that, relative to the evidence summarized in Table 1, it is probable that interstitial diffusion dominates boron diffusion under the near-equilibrium conditions we have considered.

The following heuristic rationalization may be offered for this conclusion. Under these conditions, k_{dis} in the denominator of Eq. 13 dominates k_{ko} by two-orders of magnitude, due to the smaller activation energy for cluster dissociation. In the numerator, the kick-in term dominates that for complex association by roughly four orders of magnitude. With the kick-in term dominating, R reduces to the following simplified form

$$R = \frac{k_{dis} D_{B_i^+}}{k_{ki} D_{(B_s - Si_i)^+}} \tag{14}$$

Thus, $(B_s\text{-}Si_i)^+$ complexes form mainly by kick-in of B_i^+ and disappear mainly by dissociation to Si_i^{+2}. As long as conditions are such that $[Si_i^{+2}] \approx [B_i^+]$, the rather weak temperature-dependences of the terms in Eq. 13, permit this conclusion to hold over all temperatures of practical interest down to slightly above room temperature.

Note that the properties of the distribution in Figure 2 (and Figure 3 later) depend on the estimated standard deviations in Table 1. These estimates are correct under the common assumption employed here that the uncertainties in the activation energies obey a Gaussian distribution. However, this assumption yields unrealistically narrow standard deviation estimates when some of the component data contain significant bias errors due to methodological deficiencies. A typical signature for such bias errors appears when the standard deviations for results from individual laboratories do not overlap. A good example in this case is the dissociation energy E_{dis} for the complex $(B_s\text{-}Si_i)^+$, where laboratories report values centering near 20 and 90 kJ/mol (0.2 and 0.9 eV) depending on whether the monopole correction was applied in the calculations, but the standard deviations for each laboratory are no more than about 10 kJ/mol (0.1 eV). A similar example in Table 1 is the activation energy $E_{diff,\, Si_i^{+2}}$ for silicon interstitial diffusion. Bias errors distort the shape of the uncertainty distribution for the parameter into a shape that is not Gaussian. Since, the nature and magnitude of the bias errors are not known *a priori*, there is no satisfactory way to account for them except to assess the sensitivity of the results in Figures 2 and 3 to the standard deviations. We have found that the distributions in the figures are insensitive to the standard deviations in $E_{diff,\, Si_i^{+2}}$, but are sensitive to the dissociation energy E_{dis}. This finding should motivate additional studies to better determine E_{dis}, which would increase the confidence in the assessment of the relative importance of pair diffusion and kick-out.

Implanted material

Equation 13 is useful for analyzing boron-implanted material, although clustering and declustering kinetics make *a priori* estimates of Si_i and B_i more difficult than in the previous case. Process simulators can aid in this purpose, although the results must be used with more circumspection because of uncertainties in cluster kinetics and because simulators employ the very kinetics we have been discussing to arrive at their results. Nevertheless, we will assume that the results are at least roughly correct, and will then search for contradictions to these assumptions in the conclusions.

Our group has previously employed[21] the process simulator

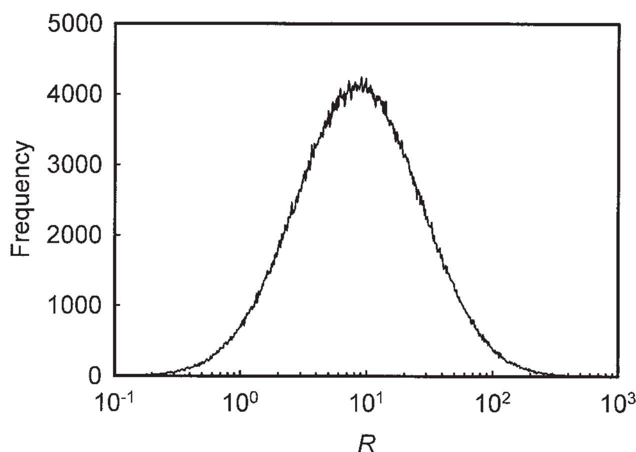

Figure 3. Probability distribution of the diffusivity ratio *R* implanted *Si*.

In only 3% of the cases does R dip below unity. The mean value (not evident on the logarithmic scale) is 14, which is larger than the peak value at approx. 8.

FLOOPS of the University of Florida.[25] Typically implant energies on the order of 0.5 keV and doses near 10^{15} cm^{-2} lead to $[B_s] \sim 1 \times 10^{26}$ m^{-3}, the boron solid solubility level at 1,000 °C.[13] Under these conditions, $[Si_i] \sim 5 \times 10^{20}$ m^{-3}, and $(B_i) \sim 6 \times 10^{18}$ m^{-3}. The composite probability distribution for R was determined using these numbers as described earlier. Figure 3 shows that R is approximately 14, close to the value obtained for undefected Si, and the probability that R falls below unity is again only 3%. The interstitial diffusion contributes 93% of the overall diffusion flux relative to pair diffusion at 1,000°C. These contributions do not change dramatically as the temperature varies in this general range because the activation energies (and, therefore, temperature dependences) of the key elementary steps are modest. We conclude that, relative to the evidence summarized in Table 1, it is probable that interstitial diffusion dominates boron diffusion under the TED conditions we have described.

The following heuristic rationalization may be offered for this conclusion. In Eq. 13 the revised assumptions for B_s, Si_i, and B_i affect only the terms in the numerator. The kick-in term still dominates complex association by one order of magnitude. Eq. 14 is, therefore, still valid, leading to essentially the same results in the Monte Carlo simulation.

Conclusion

Despite considerable uncertainty in the rate parameters for some of the elementary steps in the reaction network that describes boron diffusion, the forgoing analysis proved capable of arriving at conclusions that are firm enough for practical modeling. Key aspects of this analysis were (1) formulating a rigorous kinetic model including pre-exponential factors (which are often neglected in published work), and (2) avoiding protracted debates about the relative merits of various published parameter values by using a maximum likelihood parameter estimation technique. These methods allow estimation of the most likely parameters with the corresponding uncertainties described in terms of normal distribution functions. Such a procedure does not guarantee a correct answer, but at least it provides a rationally defensible way to make progress.

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Literature Cited

1. Agarwal A, Pelaz L, Vuong HH, eds. *Silicon Front-End Processing - Physics & Technology of Dopant-Defect Interactions II*. Warrendale, PA: Materials Research Society; 2000; No. 610.
2. Alippi P, Colombo L, Ruggerone P. Energetics and diffusivity of atomic boron in silicon by density-functional-based tight-binding simulations. *Comp. Materials Sci.* 2001;22:44-48.
3. Alippi P, Colombo L, Ruggerone P, Sieck A, Seifert G, Frauenheim T. Atomic-scale characterization of boron diffusion in silicon. *Phys. Rev. B.* 2001;64:075207.
4. Bard Y. *Nonlinear Parameter Estimation*. New York: Academic Press; 1974.
5. Beck JV, Arnold KJ. *Parameter Estimation in Engineering and Science*. New York: Wiley; 1977.
6. Bunea MM, Fastenko P, Dunham ST. Atomistic simulations of damage evolution in silicon. In: Gossmann H-J, Haynes T, Larsen AN, Law M, Odanaka S, eds. *Si Front-End Processing - Physics and Technology of Dopant-Defect Interactions.* Vol 568. Pittsburgh, PA: MRS Proceedings; 1999:135.
7. Chakravarthi S, Dunham ST. A simple continuum model for boron clustering based on atomistic calculations. *J. of Appl. Physics.* 2001; 89:3650-3655.
8. Collart EJH, Weemers K, Cowern NEB et al. Low energy boron implantation in silicon and room temperature diffusion. *Nuclear Instruments and Methods in Physics Research Section B.* 1998;139:98-107.
9. Cowern NEB, Janssen KTF, van de Walle GFA, Gravesteijn DJ. Impurity diffusion via an intermediate species: The B-Si system. *Phys. Rev. Lett.* 1990;65:2434-2437.
10. Cowern NEB, van de Walle GFA, Gravesteijn DJ, Vriezema CJ. Experiments on atomic-scale mechanisms of diffusion. *Phys. Rev. Lett.* 1991;67:212-215.
11. Cowern NEB, van de Walle GFA, Zalm PC, Oostra DJ. Reactions of point defects and dopant atoms in silicon. *Phys. Rev. Lett.* 1992;69: 116-119.
12. Eaglesham D. Dopants, defects and diffusion. *Physics World.* 1995;8: 41-45.
13. Fair RB. *Rapid Thermal Processing: Science and Technology*. Boston, MA: Academic Press; 1993.
14. Fukata N, Kasuya A, Suezawa M. Vacancy formation energy of silicon determined by a new quenching method. *Japanese J. of Appl. Physics.* 2001;40:L854–L856.
15. Gilmer GH, de la Rubia TD, Stock DM, Jaraiz M. Diffusion and interactions of point defects in silicon: Molecular dynamics simulations. *Nuclear Instruments and Methods in Physics Research Section B.* 1995;102:247-255.
16. Hakala M, Puska MJ, Nieminen RM. First-principles calculations of interstitial boron in silicon. *Phys. Rev. B.* 2000;61:8155-8161.
17. Hallen A, Keskitalo N, Josyula L, Svensson BG. Migration energy for the silicon self-interstitial. *J. of Appl. Physics.* 1999;86:214-216.
18. Hane M, Matsumoto H. A model for boron short time annealing after ion implantation. *IEEE Trans. on Electron Devices.* 1993;40:1215-1222.
19. Harrison WA. Diffusion and carrier recombination by interstitials in silicon. *Phys. Rev. B.* 1998;57:9727-9735.
20. Heinrich M, Budil M, Pötzl HW. Simulation of transient boron diffusion during rapid thermal annealing in silicon. *J. of Appl. Physics.* 1991;69:8133-8138.
21. Jung MYL, Seebauer EG. New physics for modeling transient enhanced diffusion in RTP. *Proc. of the Rapid Thermal and Other Short-Time Processing Technologies II.* Vol 2000-9. Toronto, Canada: ECS; 2000:15-20.
22. Kittel C. *Introduction to Solid State Physics*. 7th ed. New York: Wiley; 1996:543.
23. Kresse G, Furthmüller J. *VASP the Guide*. Vienna, Austria: Vienna University of Technology; 1999.
24. Laidler KJ. *Chemical Kinetics*. 3rd ed. New York: Harper & Row; 1987:212.
25. *Florida Object Oriented Process Simulator (FLOOPS) 2000* [computer program]. University of Florida, Gainesville, FL.; 2000.
26. Lee W-C, Lee S-G, Chang KJ. First-principles study of self-interstitial diffusion mechanisms in silicon. *J. of Physics: Condensed Matter.* 1998;10:995-1002.
27. Leung W-K, Needs RJ, Rajagopal G, Itoh S, Ihara S. Calculations of silicon self-interstitial defects. *Phys. Rev. Lett.* 1999;83:2351-2354.
28. Leung W-K, Needs RJ, Rajagopal G, Itoh S, Ihara S. Quantum monte carlo study of silicon self-interstitial defects. *VLSI Design.* 2001;13: 229-235.
29. Morehead FF, Lever RF. Enhanced "tail" diffusion of phosphorus and boron in silicon: Self-interstitial phenomena. *Appl. Physics Lett.* 1986; 48:151-153.
30. Mulvaney BJ, Richardson WB. Model for defect-impurity pair diffusion in silicon. *Appl. Physics Lett.* 1987;51:1439-1441.
31. Mulvaney BJ, Richardson WB. The effect of concentration-dependent defect recombination reactions on phosphorus diffusion in silicon. *J. of Appl. Physics.* 1990;67:3197-3199.
32. Murch GE, Nowich AS. *Diffusion in Crystalline Solids*. Orlando, FL: Academic Press; 1984.
33. Nichols CS, van de Walle GFA, Pantelides ST. Mechanisms of dopant impurity diffusion in silicon. *Phys. Rev. B.* 1989;40:5484-5496.

34. Orlowski M. Unified model for impurity diffusion in silicon. *Appl. Physics Lett.* 1988;53:1323-1325.
35. Pelaz L, Jaraiz M, Gilmer GH et al. B diffusion and clustering in ion implanted Si: The role of B cluster precursors. *Appl. Physics Lett.* 1997;70:2285-2287.
36. Rafferty CS, Gilmer GH, Jaraiz M, Eaglesham D, Gossmann H-J. Simulation of cluster evaporation and transient enhanced diffusion in silicon. *Appl. Physics Lett.* 1996;68:2395-2397.
37. Sadigh B, Lenosky TJ, Theiss SK, Caturla M-J, de la Rubia TD, Foad MA. Mechanism of boron diffusion in silicon: An *ab initio* and kinetic monte carlo study. *Phys. Rev. Lett.* 1999;83:4341-4344.
38. Seebauer EG, Jung MYL. Surface diffusion of adsorbates on metals, alloys, oxides, and semiconductors. In: Bonzel HP, ed. *Landolt-Börnstein Numerical Data and Functional Relationships: Adsorbed Layers on Surfaces.* Vol III/42A. New York: Springer Verlag; 2001.
39. Souza MM, Sunkara Narayanan EM. Self-diffusion in silicon. *Defect & Diffusion Forum.* 1998;153-155:69-80.
40. Tang M, Colombo L, Zhu J, de la Rubia TD. Intrinsic point defects in crystalline silicon: Tight-binding molecular dynamics studies of self-diffusion, interstitial-vacancy recombination, and formation volumes. *Phys. Rev. B.* 1997;55:14279-14289.
41. Tarnow E. Theory of the B interstitial related defect in Si. *Europhysics Letters.* 1991;16:449-454.
42. Van Vechten JA. Divacancy binding enthalpy and contribution of divacancies to self-diffusion in Si. *Phys Rev B.* 1986;33:2674-2689.
43. Van Vechten JA. Activation enthalpy of recombination-enhanced vacancy migration in Si. *Phys. Rev. B-Condensed Matter.* 1988;38:9913-9919.
44. Van Vechten JA, Thurmond CD. Entropy of ionisation and temperature variation of ionisation levels of defects in semiconductors. *Phys. Rev. B (Solid State).* 1976;14:3539-3550.
45. Vandenbossche E., Baccus B. Modeling inactive boron during predeposition processes. *J. of Appl. Physics.* 1993;73:7322-7330.
46. Wang Z, Seebauer EG. Estimating pre-exponential factors for desorption from semiconductors: Consequences for *a priori* process modeling. *Appl. Surface Sci.* 2001;181:111-120.
47. Watkins GD. Defects in irradiated silicon: EPR and electron-nuclear double resonance of interstitial boron. *Phys. Rev. B.* 1975;12:5824-5839.
48. Wijaranakula W. An experimental estimation of silicon interstitial diffusivity. *J. of Appl. Physics.* 1990;67:7624-7627.
49. Windl W, Bunea MM, Stumpf R, Dunham ST, Masquelier MP. First-principles study of boron diffusion in silicon. *Phys. Rev. Lett.* 1999;83:4345-4348.
50. Windl W, Sankey OF, Menendez J. Theory of strain and electronic structure of $Si_{1-y}C_y$ and $Si_{1-x-y}Ge_xC_y$ alloys. *Phys. l Rev. B.* 1998;57: 2431-2442.
51. Zhu J. *Ab initio* pseudopotential calculations of dopant diffusion in Si. *Computational Mat. Sci.* 1998;12:309-318.
52. Zhu J, de la Rubia TD, Yang LH, Mailhiot C, Gilmer GH. *Ab initio* pseudopotential calculations of B diffusion and pairing in Si. *Phys. Rev. B.* 1996;54:4741-4747.
53. Zywietz A, Furthmüller J, Bechstedt F. Vacancies in SiC: Influence of Jahn-Teller distrotions, spin effects, and crystal structure. *Phys. Rev. B.* 1999;59:15166-15180.

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