Fractional contributions of microscopic diffusion mechanisms for common dopants and self-diffusion in silicon

Ant Ural, a) Peter B. Griffin, and James D. Plummer
Department of Electrical Engineering, Stanford University, Stanford, California 94305

(Received 2 October 1998; accepted for publication 29 January 1999)

An identical set of thermal oxidation and nitridation experiments has been performed for four common dopants and self-diffusion in Si. Selectively perturbing the equilibrium point-defect concentrations by these surface reactions is a powerful tool for identifying the relative importance of the various atomic-scale diffusion mechanisms. We obtain bounds on the fractional contributions of the self-interstitial, vacancy, and concerted exchange mechanisms for arsenic, boron, phosphorus, antimony, and self-diffusion in Si at temperatures of 1100 and 1000 °C. These bounds are found by simultaneously solving a system of equations making only very conservative assumptions. The validity of common approximations found in previous work and their effects on the results are also analyzed in detail. We find that B and P diffuse by a self-interstitial mechanism, whereas Sb diffusion is almost exclusively vacancy mediated. As and self-diffusion, on the other hand, exhibit evidence for a dual vacancy-interstitial mechanism with the possibility of some concerted exchange component. © 1999 American Institute of Physics. [S0021-8979(99)05109-9]

I. INTRODUCTION

Diffusion of substitutional dopants in Si can be mediated on the atomic scale by either native point defects, namely self-interstitials and vacancies, or by a direct exchange mechanism which occurs in their absence.1−6 Theoretical calculations have predicted that concerted exchange, in which two adjacent substitutional atoms switch positions, is such a possible direct mechanism.7 The relative contribution of each of these three mechanisms for a given dopant is a fundamental property reflecting the complicated many-body energetics occurring on the atomic scale. It is also of significant practical importance for semiconductor devices, since most fabrication processes such as oxidation and ion-implantation perturb the equilibrium point-defect concentrations. The manner in which these perturbations affect the diffusion of a given dopant depends on what fraction of its diffusion is mediated by the perturbed point defect. As a result, an identical process may affect the diffusivity of each dopant in a significantly different manner.

In this article, we take advantage of this fact to determine bounds on the self-interstitial (I), vacancy (V), and concerted exchange (CE) mediated fractions of diffusion for four common dopants (As, B, P, and Sb) and self-diffusion in Si. We use two well-studied surface reactions, thermal oxidation and nitridation, to selectively perturb the equilibrium point-defect concentrations. Although the details of these surface reactions are not fully understood, it has been well established that thermal oxidation injects self-interstitials, whereas nitridation results in vacancy injection into the bulk.8 The complementary nature of these two processes enables us to draw conclusions about the relative importance of each microscopic diffusion mechanism for each dopant. This idea has been utilized in the past in similar experiments.4,8–12 Our experiments offer improvement in a variety of ways. First of all, we perform an extensive set of identical oxidation and nitridation experiments at two temperatures for four dopants and self-diffusion, and solve the resulting system of equations simultaneously. We carry out this solution numerically rather than using analytic arguments as commonly done previously.9−12 In addition, we use secondary ion mass spectrometry (SIMS) to obtain the diffusion profiles, whereas some of the earlier work used spreading resistance analysis, which has a much poorer depth resolution.3,9,10 Furthermore, we do not initially make any assumptions about the point-defect injection levels or mechanisms that result from oxidation and nitridation, nor about the fractional contributions of various diffusion mechanisms for any of the dopants. One of the most significant improvements is that we include the possibility of a CE mechanism in our analysis of As and self-diffusion, which previous studies have almost always ignored without convincing arguments. After solving for this general case, we also analyze the consequences of making some of the assumptions commonly found in the literature. The conclusions we arrive at for B, P, and Sb agree well with previous results.4,9−12 The self-diffusion results, which have been recently published,13 show clear evidence of a dual vacancy-interstitial mechanism. The most important outcome of this work is that the inconsistency observed previously in the oxidation and nitridation data for As4,9,14 is resolved. We find that As diffusion can be analyzed within the same framework as the other dopants, and that it diffuses via a dual vacancy-interstitial mechanism, with the possibility of a CE component.

In what follows, unless otherwise stated, the word "equilibrium" refers to a condition where thermal equilibrium concentrations of point defects prevail, and "nonequilibrium" indicates that these concentrations have been perturbed by an external excitation.

a)Electronic mail: antural@leland.stanford.edu
II. EXPERIMENTAL PROCEDURE

Five structures were fabricated for this experiment, one for each dopant. For the As, P, and Sb structures, a 15 nm screen oxide was grown thermally on 5–10 Ω-cm (100) CZ silicon wafers, followed by ion implantation of As, P, and Sb at 110 keV to a dose of $1 \times 10^{14} \text{cm}^{-2}$, at 70 keV to a dose of $2 \times 10^{14} \text{cm}^{-2}$, and at 140 keV to a dose of $1 \times 10^{14} \text{cm}^{-2}$, respectively. The tilt angle was 7° with no rotation of the wafers. Following implantation, a drive-in inert anneal at 1100°C was performed for 5 h, and an intrinsic silicon surface layer was grown epitaxially by chemical vapor deposition (CVD). For As and Sb, this surface layer was roughly 400 nm, whereas for faster diffusing P, 800 nm. The B structure was fabricated by CVD growth of a 1000 nm intrinsic Si layer, followed by a roughly 350 nm boron doped surface layer. In all structures, the peak concentrations of the dopants were kept at around a few $10^{18} \text{cm}^{-3}$, avoiding complications that could arise from extrinsic doping effects. Finally, the Si isotope structure was grown by CVD with a surface layer of roughly 300 nm containing the three stable isotopes of silicon in their natural relative abundances, and a buried layer heavily depleted in $29^{\text{Si}}$ and $30^{\text{Si}}$. For example, $30^{\text{Si}}$, the isotope used to monitor self-diffusion, was reduced from a natural abundance of 3.10% at the surface to 0.002% at the buried layer. This transition was graded due to Si autodoping effects during predeposition cleaning.

These five structures, one for each dopant, were then annealed in a furnace in inert (100% Ar), nitridizing (100% NH$_3$), and oxidizing (100% O$_2$) ambients at 1100 and 1000°C for 1 and 5 h, respectively. The average oxide thickness grown was 126.5 and 163.4 nm for the 1100 and 1000°C for 1 and 5 h, respectively. Measurement of nitride grown was 126.5 and 163.4 nm for the 1100 and 1000 °C dry oxidations, respectively. Measurement of nitride thicknesses revealed an average value of 3.6 and 3.1 nm, respectively. The average oxide thickness revealed an average value of 3.6 and 3.1 nm, respectively. Measurement of nitride grown was 126.5 and 163.4 nm for the 1100 and 1000 °C dry oxidations, respectively. Measurement of nitride thicknesses revealed an average value of 3.6 and 3.1 nm, respectively. The average oxide thickness revealed an average value of 3.6 and 3.1 nm, respectively.

The six resulting diffusion profiles, along with the as-grown profile for each dopant were obtained by SIMS. SIMS analysis for As, P, and Sb were performed on a Cameca-3f instrument with a 14.5 keV Cs$^+$ primary beam at a sputtering rate of 40, 20, and 8 Å/s, respectively. The B and $30^{\text{Si}}$ profiles were analyzed on a Cameca-4f instrument with an 8 keV O$_2^+$ primary beam at a sputtering rate of 35 and 5 Å/s, respectively. A high mass resolution greater than 3500 was used for $30^{\text{Si}}$ to distinguish it from $29^{\text{Si}}$–H.

The diffusion coefficient for each case was extracted by taking the as-grown profile, and using Tsuprem-4, a process simulator, to numerically diffuse it until a match was achieved with the SIMS profile after annealing. The best fit was determined by minimizing the root-mean-square error. Furnace ramp up and down effects were properly taken into account. The solution of Fick’s law provided a single diffusion coefficient for each case.

Diffusivity enhancements or retardations were computed for each oxidation or nitridation experiment by normalizing the extracted nonequilibrium diffusion coefficient by the corresponding value obtained from the inert anneal. Using these enhancement and retardation values, bounds for the fractional contributions of the three diffusion mechanisms for each dopant were found using AMPL, a mathematical programming tool.

III. THEORY

Before we proceed to the results of the experiments, we need to derive the equations used to find the fractional contributions of the various mechanisms from diffusivity enhancement or retardation data. First, we need to note that the diffusivity coefficient, $D_A^\text{eq}$, for a dopant $A$ under both equilibrium and nonequilibrium conditions is given by

$$D_A^\text{eq} = \sum_X d_A \frac{C_{AX}^\text{eq}}{C_A^\text{eq}}. \quad (1)$$

where $A$, in our case, is As, B, P, Sb, or Si, and X is the mechanism of diffusion ($X = I$, $V$, or CE). $C_{AX}^\text{eq}$ and $d_A$ are the concentration and diffusivity, respectively, of the defect $AX$ whose migration determines the $X$ mechanism mediated diffusion of species $A$. For example, this migrating defect could be a dopant-defect pair, an interstitial dopant, or a single native point defect. $C_A^\text{eq}$ is the total concentration of the substituitional dopant $A$. For P diffusion, for instance, theoretical calculations have predicted that the phosphorus-interstitial (P$_I$) and phosphorus-vacancy pair (PV) are the relevant defects which determine P diffusion by an I and V mediated mechanism, respectively. For the CE mechanism, the corresponding defect is the substitutional phosphorus (P$_s$) itself. To simplify the analysis, it is customary to define the $X$ mechanism mediated fraction of $A$ diffusion under equilibrium as

$$f_{AX} = \frac{d_A C_{AX}^\text{eq} / C_A^\text{eq}}{D_A^\text{eq}}. \quad (2)$$

Here, the superscript eq denotes equilibrium conditions. Combining Eqs. (1) and (2), we can write the diffusivity ratio that occurs under nonequilibrium conditions as

$$\frac{D_A}{D_A^\text{eq}} = f_{AI} C_{AI}^\text{eq} + f_{AV} C_{AV}^\text{eq} + f_{ACE}. \quad (3)$$

The only approximation made in Eq. (3) is that there is only one migrating defect $AX$ which contributes to the $X$ mediated diffusion of $A$. We will come back to this point at the end of the discussion. The ratio of the diffusivity coefficient under oxidation to that under inert annealing gives one equation of the form Eq. (3) for each dopant. A similar equation can be written down for nitridation. As a result, five dopants annealed under identical conditions lead to ten equations with 30 unknowns, since for each dopant there are six unknowns: $f_{AI}, f_{ACE}, C_{AI}^\text{eq}, C_{AV}^\text{eq}, C_{AI}^\text{eq}/C_{AV}^\text{eq}$, $C_{AI}^\text{eq}/C_{AV}^\text{eq}$, and $C_{AV}^\text{eq}/C_{AV}^\text{eq}$. The last four unknowns listed are the migrating defect perturbation levels where the superscripts ox, nit, and eq denote oxidation, nitridation, and equilibrium (inert anneal) conditions, respectively. The normalization condition $f_{AI} + f_{AV} + f_{ACE} = 1$ eliminates $f_{AV}$ for each dopant. With that many unknowns, it is virtually impossible to arrive at any non-trivial bounds on the fractional contributions of different diffusion mechanisms. The problem is greatly simplified if a relation is found between the concentration of the migrating defect, $C_{AX}$, and that of the corresponding native
point defect $C_X$. The complete set of equations governing the interactions between these two species are

$$I + A_s \leftrightarrow AI,$$  
(4)

$$V + AI \leftrightarrow A_s,$$  
(5)

$$V + A_s \leftrightarrow AV,$$  
(6)

$$I + AV \leftrightarrow A_s,$$  
(7)

$$I + V \leftrightarrow Si,$$  
(8)

where $A_s$ is the substitutional dopant $A$, and $Si$ in Eq. (8) represents bulk $Si$. Using this set of equations, expressions for the time rate of change of defect concentrations can be obtained. Assuming the concentrations have no spatial dependence, the expression for the migrating defect $AI$ is

$$\frac{\partial C_{AI}}{\partial t} = k_{4f}C_A C_{AI} - k_{3r} C_{AI} - k_{5f} C_{AI} C_{AI} + k_{5r} C_{AI}$$  
(9)

where $k$’s denote the reaction rate constants with the first index in the subscript referring to the number of the reaction equation given above. The second index, on the other hand, indicates whether the rate constant is that of the forward ($f$) or reverse ($r$) reaction. An expression for the nonequilibrium perturbation level $C_{AI}/C_{AI}^eq$ under steady-state conditions can be found by setting the right side of Eq. (9) to zero and dividing by the corresponding equation found under equilibrium:

$$\frac{C_{AI}}{C_{AI}^eq} = \frac{k_{4f} C_A C_{AI} + k_{5r} C_{AI} (k_{4f} + k_{5f} C_{V}^eq)}{k_{4f} C_A C_{AI} + k_{5r} C_{AI} (k_{4r} + k_{5f} C_{V}^eq)}$$

This general form can be simplified under certain special cases. If the reactions represented by Eqs. (4) and (5) are individually at local chemical equilibrium both under equilibrium and nonequilibrium concentrations of point defects, Eq. (10) reduces to

$$C_{AI}/C_{AI}^eq = C_{V}/C_{I}^eq.$$  
(11)

This follows from taking the ratio of the two relations obtained from the chemical equilibrium requirement on the reaction in Eq. (4):

$$\frac{C_{AI}}{C_A C_{AI}} = \frac{k_{4f}}{k_{4r}}$$  
and

$$\frac{C_{AI}^eq}{C_{AI}^eq} = \frac{k_{4f}}{k_{4r}}.$$  
(12)

By obtaining an analogous ratio from reaction Eq. (5), it also follows that in this case,

$$C_I C_{V} = C_I^eq C_{V}^eq.$$  
(13)

Another special case is if the reaction in Eq. (5) is insignificant compared to Eq. (4), in which case Eq. (10) simplifies again to Eq. (11). If, on the other hand, Eq. (4) is insignificant and Eq. (5) is dominant, the correct simplification becomes $C_{AI}/C_{AI}^eq = C_{V}/C_{I}^eq$. In general, $C_{AI}/C_{AI}^eq$ lies somewhere between these two values.

A similar analysis can be performed for the migrating defect $AV$. If the reactions in Eqs. (6) and (7) are individually at local chemical equilibrium,

$$C_{AV}/C_{AV}^eq = C_{V}/C_{V}^eq.$$  
(14)

In the second special case, if Eq. (6) is the only dominant reaction, Eq. (14) is again the correct simplification. If, on the other hand, Eq. (6) is insignificant compared to Eq. (7), $C_{AV}/C_{AV}^eq = C_{V}/C_{I}^eq$.

Theoretical calculations suggest that reactions represented by Eqs. (4) and (6) are energetically much more favorable compared to Eqs. (5) and (7), respectively. Furthermore, it has been pointed out recently that interactions between migrating and native point defects such as those given in Eqs. (4)–(7) individually reach local chemical equilibrium on a time scale much smaller than that typical in diffusion experiments. Based on these considerations, a reasonable approximation to Eq. (3) can be obtained by substituting Eqs. (11) and (14),

$$D_A = \frac{D_A^eq}{C_I} = f_{AE} C_I + f_{AV} C_V + f_{ACE}.$$  
(15)

This equation is the form that has been widely used in the literature often without the exchange term, $f_{ACE}$.

As mentioned before, Eq. (3) will have additional terms if more than one defect species contributes to the $X$ mediated diffusion of $A$. However, Eq. (15) will still be valid, if each of these defect species is at local chemical equilibrium with the corresponding native point defect.

### IV. RESULTS AND DISCUSSION

Figure 1 shows the measured SIMS profiles and simulation fits of the 1000 °C, 5 h anneals for As, B, P, Sb, and $^{28}Si$ under inert, nitridizing, and oxidizing ambients. Corresponding plots for the 1100 °C anneals exhibit the same general trends. The simulation results fit the experimental data well in all cases. The extracted equilibrium (inert ambient) diffusion coefficients, listed in Table I, agree well with previous work for all dopants. It is evident from Figs. 1(b) and 1(c) that $B$ and $P$ diffusion are retarded during nitridation and enhanced during oxidation. The opposite is true for $Sb$. These results qualitatively show that $B$ and $P$ diffuse mainly by a self-interstitial mechanism, whereas $Sb$ diffusion is vacancy mediated. On the other hand, Figs. 1(a) and 1(e) clearly show that As and self-diffusion are enhanced by both vacancy and interstitial injection. This gives the first hint that these dopants have non-negligible vacancy and self-interstitial components of diffusion. Indeed, if either one of the point-defect mechanisms were solely dominant, a retardation in diffusivity would have been observed when the opposite type of defect is injected. On the other hand, if the exchange mechanism were dominant, perturbing the point-defect concentrations would not have any effect on the diffusivity.

More quantitative information about the fractional contribution of each of the three mechanisms can be obtained by representing the results as an underdetermined system of ten equations of the form Eq. (15) with 14 unknowns. This is a major reduction in the number of unknowns compared to that resulting from Eq. (3). Still further reduction is possible since theoretical calculations have predicted that the activation energy of CE is much larger than that of the point defect.
mechanisms for B, P, and Sb, making its contribution negligible for these dopants. Therefore, excluding the CE fraction in Eq. (15) for these dopants, we arrive at a system of ten equations with 11 unknowns. These unknowns are $f_{BI}, f_{PI}, f_{SBI}, f_{ASBI}, f_{SI}, f_{SI}, \frac{C_{I}}{C_{eq}}^{ox}, \frac{C_{I}}{C_{eq}}^{ox}, C_{I}^{nit}/C_{eq}^{nit}$, and $C_{V}^{nit}/C_{eq}^{nit}$. The last four unknowns listed are the point defect perturbation levels where the superscripts have the same meaning as before. Five out of the ten equations, one for each dopant, are obtained from the oxidation experiments, whereas the remaining five come from nitridation data. The measured diffusivity ratios, each of which appear on the left hand side of one of the equations in the system are tabulated in Table II at the temperatures 1100 and 1000 °C. A ratio greater than one implies a diffusivity enhancement, whereas smaller than one indicates retardation. In reality, the point defect concentrations during oxidation and nitridation, and therefore the diffusivity ratios are all functions of time. Although not explicit in the formulas, the quantities measured at the end of the experiment are thus time and space averaged values.

We numerically solved the above mentioned system of ten equations using the following conservative bounds on the nonequilibrium point defect ratios:
TABLE II. Diffusivity enhancements or retardations for arsenic, boron, phosphorus, antimony, and 30Si under nonequilibrium point defect conditions caused by oxidation and nitridation. Anneals were performed at 1100 °C for 1 h and 1000 °C for 5 h.

<table>
<thead>
<tr>
<th></th>
<th>Oxidation</th>
<th>Nitridation</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1100 °C</td>
<td>1000 °C</td>
</tr>
<tr>
<td></td>
<td>1100 °C</td>
<td>1000 °C</td>
</tr>
<tr>
<td>Arsenic</td>
<td>1.33</td>
<td>2.20</td>
</tr>
<tr>
<td>Boron</td>
<td>3.07</td>
<td>4.70</td>
</tr>
<tr>
<td>Phosphorus</td>
<td>2.51</td>
<td>3.84</td>
</tr>
<tr>
<td>Antimony</td>
<td>0.391</td>
<td>0.266</td>
</tr>
<tr>
<td>30Silicon</td>
<td>1.60</td>
<td>2.73</td>
</tr>
</tbody>
</table>

More restrictive bounds can be obtained by making approximations relating the perturbation levels of point defects during oxidation and nitridation. In the bulk, sufficiently away from the surface, I and V recombine thermally to form substitutional silicon atoms and are generated from them via Eq. (8). This process involves the creation and annihilation of I and V simultaneously, so their concentrations remain dependent. In addition, I and V can be singly created or annihilated at the surface independent of each other. Therefore, if the steady-state recombination and generation of I and V in the bulk is dominant over surface generation and recombination, we expect the relation of Eq. (13) to hold. In general, however, this relation is not satisfied. A detailed solution of the relevant continuity equations\(^1\) as well as experiments on short-time oxidation and nitridation\(^1\) have concluded that, in general,

$$1 \geq \frac{C_{v}^{\text{equiv}}}{C_{v}^{\text{eff}}} \geq \frac{C_{I}^{\text{eq}}}{C_{I}^{\text{eff}}} \text{ and } 1 \geq \frac{C_{v}^{\text{equiv}}}{C_{v}^{\text{eff}}} \geq \frac{C_{v}^{\text{equiv}}}{C_{v}^{\text{eff}}}.$$  \hspace{1cm} (17)$$

The system of equations resulting from the data was solved again using the constraints given by Eq. (17) instead of the more relaxed ones represented by Eq. (16). The results for the fractional contributions are tabulated in the second

TABLE III. Bounds on fractional contributions of I, V, and CE mechanisms of diffusion for As, B, P, Sb, and self-diffusion in Si obtained from 1100 °C 1 h anneals. The first column gives the solutions for the most general case, and the approximations made in the successive columns are noted in the headings.

<table>
<thead>
<tr>
<th></th>
<th>CE included</th>
<th>CE included</th>
<th>CE included</th>
<th>No CE</th>
<th>No CE</th>
<th>No CE</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$0 \leq C_{I}^{eq}/C_{V}^{eq} \leq 1$</td>
<td>$0 \leq C_{I}^{eq}/C_{V}^{eq} \leq 1$</td>
<td>$0 \leq C_{I}^{eq}/C_{V}^{eq} \leq 1$</td>
<td>$0 \leq C_{I}^{eq}/C_{V}^{eq} \leq 1$</td>
<td>$0 \leq C_{I}^{eq}/C_{V}^{eq} \leq 1$</td>
<td>$0 \leq C_{I}^{eq}/C_{V}^{eq} \leq 1$</td>
</tr>
<tr>
<td>$f_{BI}$</td>
<td>0.84–1.00</td>
<td>0.94–1.00</td>
<td>0.94–0.99</td>
<td>0.86–1.00</td>
<td>0.98–1.00</td>
<td>0.98–0.99</td>
</tr>
<tr>
<td>$f_{PI}$</td>
<td>0.86–1.00</td>
<td>0.96–1.00</td>
<td>0.96–1.00</td>
<td>0.86–1.00</td>
<td>0.98–1.00</td>
<td>0.98–1.00</td>
</tr>
<tr>
<td>$f_{SBI}$</td>
<td>0–0.16</td>
<td>0–0.03</td>
<td>0–0.03</td>
<td>0–0.14</td>
<td>0–0.01</td>
<td>0–0.01</td>
</tr>
<tr>
<td>$f_{SIV}$</td>
<td>0.24–0.65</td>
<td>0.26–0.60</td>
<td>0.26–0.59</td>
<td>0.51–0.65</td>
<td>0.59–0.60</td>
<td>0.59</td>
</tr>
<tr>
<td>$f_{SCE}$</td>
<td>0.06–0.62</td>
<td>0.06–0.62</td>
<td>0.06–0.62</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>$f_{SV}$</td>
<td>0.09–0.49</td>
<td>0.10–0.41</td>
<td>0.11–0.41</td>
<td>0.35–0.49</td>
<td>0.40–0.41</td>
<td>0.41</td>
</tr>
<tr>
<td>$f_{I}$</td>
<td>0.15–0.54</td>
<td>0.17–0.47</td>
<td>0.17–0.47</td>
<td>0.36–0.54</td>
<td>0.42–0.47</td>
<td>0.42–0.47</td>
</tr>
<tr>
<td>$f_{AV}$</td>
<td>0.18–0.64</td>
<td>0.21–0.58</td>
<td>0.21–0.58</td>
<td>0.46–0.64</td>
<td>0.53–0.58</td>
<td>0.53–0.58</td>
</tr>
<tr>
<td>$f_{C}$</td>
<td>2.73–3.18</td>
<td>2.73–2.88</td>
<td>2.75–2.88</td>
<td>2.73–3.13</td>
<td>2.73–2.77</td>
<td>2.75–2.77</td>
</tr>
<tr>
<td>$f_{C}$</td>
<td>0.434–0.348</td>
<td>0.348–0.343</td>
<td>0.348–0.363</td>
<td>0–0.388</td>
<td>0.361–0.388</td>
<td>0.361–0.363</td>
</tr>
<tr>
<td>$f_{C}$</td>
<td>2.83–4.13</td>
<td>2.83–3.64</td>
<td>2.83–3.64</td>
<td>2.83–3.24</td>
<td>2.83–2.86</td>
<td>2.83–2.86</td>
</tr>
<tr>
<td>$f_{C}$</td>
<td>0.395</td>
<td>0.274–0.395</td>
<td>0.274–0.353</td>
<td>0–0.395</td>
<td>0.350–0.390</td>
<td>0.350–0.353</td>
</tr>
</tbody>
</table>
columns of Tables III and IV for the 1100 and 1000 °C anneals, respectively. It is clear that the range of acceptable values becomes a subset of the most general case when more restrictive constraints on the point-defect perturbation levels are used. Hence, the general conclusions drawn from the first columns of the same tables still remain valid.

It can be seen from the second columns of Tables III and IV that the ranges of point-defect perturbation ratios are fairly narrow, which is an indication that Eq. (13) can be considered a fair approximation for the anneal temperatures and times used in this study. Therefore, even more restrictive bounds on the fractional contributions can be obtained by assuming that Eq. (13) holds exactly. Resolving the system with this more restrictive constraint, we obtain the values listed in the third columns of Tables III and IV for the 1100 and 1000 °C anneals, respectively. Close inspection will show that these results are almost identical to those obtained using the constraints given by Eq. (17).

An interesting feature of the results so far is that, in all cases, the lower bound on the CE fractions of As and Si are zero. For I and V components of these dopants, on the other hand, a nonzero minimum always exists. In other words, although we do not have evidence to rule out the CE component, we cannot prove its existence, either. Therefore, whether the CE mechanism plays any role in dopant diffusion in Si still remains an open question. It is useful, however, to repeat the calculations above, excluding the CE fractions of As and Si, namely \( f_{ACE} \) and \( f_{SICE} \). The fourth, fifth, and sixth columns of Table III tabulate the results obtained without any CE components using the point-defect constraints represented by Eqs. (16), (17), and (13), respectively, for the 1100 °C anneals. The results for the 1000 °C anneals are listed in the corresponding columns of Table IV.

A few comments are in order. To begin with, we have mentioned in the introduction that in previous work, the bounds on the fractional contributions have been calculated analytically. Here, we analyze the B data using this conventional approach as a comparison to our numerical solutions. Assume that dopant \( E \) is enhanced under nitridation, whereas dopant \( R \) is retarded. From the diffusivity ratios for these dopants, assuming no CE contribution, we get the lower bound for the I component of \( R \) diffusion as

\[
 f_{RI} \geq 1 - \frac{D_R^{II}/D_R^{E}}{D_E^{II}/D_E^{E}}, \tag{18}
\]

where nit and eq denote nitridation and equilibrium (inert anneal), respectively. For example, dopant \( R \) could be B, and \( E \) could be Sb. Using the diffusivity ratios from Table II, we get at 1100 °C, \( f_{RI} \geq 0.87 \), and at 1000 °C, \( f_{RI} \geq 0.91 \). These numbers agree closely with those given in the fourth columns of Tables III and IV. In the most general case, when solving for five dopants, including the possibility of a CE component, and allowing for error margins, obtaining such analytical bounds becomes too tedious a task.

Secondly, a recent measurement of Si self-diffusion using isotopically enriched structures over a wide temperature range (855–1388 °C) has yielded Arrhenius behavior

\[
 D(T) = D^0 \exp(-E/k_BT), \tag{19}
\]

with a prefactor \( D^0 \), and a single activation energy, \( E \), of 4.75 eV.\textsuperscript{20} However, a good fit to a single activation energy does not necessarily prove that a single diffusion mechanism is dominant. A hypothetical computation will show that even if self-diffusion has two components, each having the form of Eq. (19) with 1 eV difference in their activation energies, the sum nevertheless exhibits an excellent fit to a single “effective” energy with a correlation factor of 0.99.\textsuperscript{5} In Ref. 20, results from metal diffusion experiments were employed to find Arrhenius equations for self-interstitial and vacancy components of Si self-diffusion. Solving those equations at 1000 °C agrees very closely with our results. Nonequilibrium
experiments have the benefit of obviating the need to use metal diffusion results in determining the relative importance of various diffusion mechanisms.

Another point is that each diffusion mechanism has a dependence on temperature of the form Eq. (19). Hence, the temperature dependence of the bulk steady state conditions for I and V hold, f_{BI} = \frac{D_{ACE}^0 \exp(-E_{ACE}/k_B T)}{\sum_{x=1}^{V,CE} D_{AX}^0 \exp(-E_{AX}/k_B T)}

where $D^0$'s are the pre-exponential terms, and $E$'s are the activation energies as before. Equation (20) has the consequence that the fractional contributions at 1100 and 1000°C cannot be vastly different. A close inspection of Tables III and IV confirms this observation for all the fractions except those of CE. Hence, smaller upper bounds for $f_{SiCE}$ and $f_{ACE}$ at 1100°C can be found by using their respective values at 1000°C. Taking $E_{ASI}$, $E_{ASV}$, and $E_{ACE}$ as 3.4, 3.4, and 3.9 eV, respectively, we get $f_{ACE}(1100°C) \approx 0.44$. Similarly, assuming $E_{SI}$, $E_{SV}$, and $E_{SiCE}$ are 3.8, 3.8, and 4.3 eV, respectively, we get $f_{SiCE}(1100°C) \approx 0.34$. These upper bounds help reduce those obtained in the first three columns of Table III.

Recently, it has been predicted that any substitutional dopant in Si should either be a pure vacancy or self-interstitial diffuser. The result from theoretical atomistic calculations that $E_{BI} = E_{BV} = -2.35$ eV for B was used to reason that the self-interstitial component of diffusion for B is unity to a good approximation. Based on this fact, other dopants were also predicted to have a pure I or V mechanism. However, the corresponding activation energies of each dopant are quite different and such a generalization is misleading. Indeed, our results for As and self-diffusion show proof of a dual-vacancy interstitial mechanism of diffusion, with possibly some CE component. This is clear experimental evidence that not all dopants are pure vacancy or interstitial diffusers.

Finally, it is not inconsistent with the data (last column of Table III) that the CE mechanism has no contribution, that the bulk steady state conditions for I and V hold, $f_{BI}$ and $f_{Pi} \approx 0.98$, $f_{Si} \approx 0.01$, and that self-diffusion is mediated 60% by self-interstitials and 40% by vacancies at 1100°C, whereas As diffusion has an I component of 45% and a V component of 55%.

V. CONCLUSIONS

In conclusion, we have utilized two well-studied surface reactions, thermal oxidation and nitridation, to obtain bounds on the fractional contributions of microscopic diffusion mechanisms for As, B, P, Sb, and self-diffusion in Si at the temperatures of 1000 and 1100°C. These five dopants were annealed under identical conditions, and the resulting set of equations were solved numerically making only very conservative assumptions. The consequences of some of the approximations commonly used in the literature were then assessed in detail.

We find, in agreement with previous work, that B and P diffuse by a self-interstitial mechanism, whereas Sb diffusion is almost exclusively vacancy mediated. On the other hand, As and self-diffusion exhibit evidence for a dual vacancy-interstitial mechanism with the possibility of some concerted exchange component. These results clearly show that As and self-diffusion can be analyzed within the same framework as the other dopants, and no inconsistency, such as that observed previously, is found all the way across the table of solutions regardless of what approximations are used.

ACKNOWLEDGMENT

This work was funded by the Semiconductor Research Corporation.

14. ten atomistic computer code from Avant! Corporation, Fremont, CA.