Physical atomic kinetic Monte Carlo modeling of Fermi-level effects of species diffusing in silicon

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An accurate physically based Fermi-level modeling approach, amenable to be implemented in an atomistic process simulator, is reported. The atomic kinetic Monte Carlo method is used for point and extended defects, in conjunction with a quasiatomic, continuum approach treatment for carrier densities. The model implements charge reactions and electric bias according to the local Fermi level, pairing and break-up reactions between particles, clustering-related dopant deactivation, and Fermi-level-dependent solubility. We derive expressions that can be used as a bridge between the continuum and the atomistic frameworks. We present the implementation of two common dopants, boron and arsenic, using parameters that are in agreement with both ab initio calculations and experimental results.


I. INTRODUCTION

Current microelectronic technology is facing increasingly complex phenomena related to very high doping, reduced thermal budget (nonequilibrium conditions), and three-dimensional (3D) effects. Such conditions require a deep insight into the underlying physical mechanisms in order to correctly model the material properties. In particular, high-doping concentrations demand a correct description of diffusion under nonequilibrium conditions.1,2 Other charge-related issues are Fermi-level dependent solubility3,4 and clustering-related dopant deactivation.5

Continuum modeling, based on solving partial differential equations (PDE) discretized by the finite element method, has been used since the 1980s, but this method is limited by the number of equations that can be solved without running into convergence instabilities. Moreover, meshing issues and dimensionality make this approach extremely complicated in 3D. The International Roadmap for Semiconductors 2003 (Ref. 6) establishes the “modeling hierarchy from atomistic to continuum” among the difficult challenges that need to be solved before 2010. The atomistic kinetic Monte Carlo (kMC) method,7 has proven to be a powerful approach that allows the inclusion of comprehensive, physically based models without significantly degrading the simulator’s performance. Some semiconductor companies8,9 have already started to develop simulators based on this atomistic kMC approach. Modelling Fermi-level effects is one of the critical steps in developing a comprehensive kMC simulator. Here we will describe a detailed Fermi-level modeling approach specially designed to be included in this methodology, which has been implemented and tested in an atomistic kMC process simulator.10

We first describe in detail the basic physical models and then the particular implementation of point defects and of two representative dopants (boron and arsenic), and finally show a simulation example.

II. PHYSICAL MODELS

In this section we will introduce some concepts not explicitly present in continuum models which will allow us to adapt the formulation of Fermi-level effects in diffusion1 to an atomistic framework.

In our simulation scheme, particles are represented atomistically, with a particular position, species, type (substitutional, interstitial) and charge. Defects are formed by such particles. Electrical equilibrium can be assumed even when particle concentrations are far from equilibrium conditions because the charge reactions are much faster than structural reactions.11 As a consequence, the Fermi level (\(e_F\)) is considered to be well defined and carrier concentrations are treated in a continuum fashion.

A. Concentrations of charged states

Let us consider a particle \(X\) as an example of native point defect (self-interstitials, \(I\), or vacancies, \(V\)) in silicon, which is the focus of our study. They can be in multiple charge states \(X^j\), with \(j=-\infty, -1, 0, +1, +2\).

We denote by \(e(j+1,j)\) the energy level associated to the charge transitions between \(X^{j+1}\) and \(X^j\). Then, the relative concentrations are

\[
\frac{[X^j]}{[X^{j+1}]} = \frac{g_i^j}{g_i^{j+1}} \times \exp\left(\frac{e_F - e(j+1,j)}{kT}\right) \quad (1)
\]

\(g_i^j\) being the degeneracy factor and \(kT\) the thermal energy. We assume the same degeneracy factor for all the charge states.

Our convention is to take the origin of energy levels at the valence-band edge. We can assume that the electric levels of all charged species vary with the temperature proportionally to the band gap width \(E_g\).

The concentration of neutral native point defects (\(P^0\) or \(V^0\) in equilibrium conditions, denoted as \([X^0]^n\), is controlled by its formation energy, \(E_f[X^0]\), that is independent of \(e_F\). From Eq. (1) one can derive the concentration of charged states and their formation energies. The total point defect concentration as a function of \(e_F\) will be primarily determined by the charge state with lower \(E_f\). For \(e_F=e(j+1,j)\) the formation energies of \(X^{j+1}\) and \(X^j\) are the same and therefore...
for all the charge states, \([X^{+1}] = [X^+]\). Since there are no explicit assumptions of equilibrium in Eq. (1) it is still valid out of equilibrium, and then the supersaturation, defined as \(S_X = [X]/[X]^+\), is the same for all the charge states,

\[ [X^0]/[X^+]^+ = S_X. \]

### B. Defect diffusivities

In atomistic kMC, defect diffusivity is related to the random walk of migrating defects. The point defect migration frequency \(\nu_m\) for a given charge state \(j\) of a particle \(X\) is

\[ \nu_m(X^j) = \nu_{m,0}(X^j)\exp(-E_m(X^j)/kT) \]

\(\nu_{m,0}\) being the migration prefactor and \(E_m\) the migration energy. Accordingly, in three dimensions,

\[ D(X^j) = \lambda^2\nu_m(X^j)/6, \]

where \(\lambda\) is the jump distance. We have chosen \(\lambda\) to be equal to the second neighbors distance in the silicon lattice (0.384 nm). The transport capacity due to diffusion will be \(DC(X) = \Sigma_j D(X^j)\). Under equilibrium conditions the products \(D(X^j)/[X^+]^+\) are going to have an activation energy of \(E_{diff}(X^j) = E_m(X^j) + E_f(X^j)\), denoted as diffusion energy. The transport capacity will be dominated by the charge state with lower \(E_{diff}\).

### C. Electric drift

Figure 1 shows electric drift as a natural consequence of the local dependence of the formation energies of charged particles. Within the kMC framework, the relation between the migration frequency in the positive and negative directions along the \(x\) axis for a point defect with charge \(jq\) is

\[ \frac{\nu_{m,+x}}{\nu_{m,-x}} = \exp\left(-\frac{\lambda}{kT} \frac{dE}{dx}\right) = \exp\left(-\frac{jqE_x\lambda}{kT}\right), \]

where \(E_x\) is the electric field and \(q\) is the absolute value of the electron charge. The last equality assumes constant band gap. From Eq. (4) one can derive the \(x\) component of drift velocity to be equal to

\[ v_x = \lambda(\nu_{m,+x} - \nu_{m,-x})/6 \]

which, in a first order approximation, becomes the Einstein relation \(v_x = jqDE_x/(kT)\).

### D. Point-defect reactions

Reactions between particles take place in kMC when particles are within the capture radius of each other. In our model two different reactions are implemented, pairing with impurities \(A\) and break up,

\[ X^j + A^k \rightleftharpoons AX^{j+k} \]

conserving the charge, and reactions of equilibrium between different charge states,

\[ X^{j+1} + e^- \rightleftharpoons X^j. \]

The pairing reactions between repulsive species are forbidden. For the break up reactions, due to the charge conservation, \(\nu_{bk}\) does not depend on \(e_F\). Equations (5) together with Eq. (6) are enough to take into account the different break up paths because we assume that the equilibrium between different charge states is instantaneous.

In the present model clusters are assumed to be neutral and only neutral particles are emitted and captured. Once the neutral particle has been emitted as a point defect, it can change its charge state according to the local Fermi level. It would be easy to implement extended defects charge states in kMC, but reliable values for physical parameters (either from calculations or experiments) would be needed.

### E. Solubility

The solubility of charged species depends on \(e_F\). For the case of a dopant \(A^j\), the solubility limit is given by

\[ [A^j]_{\text{max}}(T) = [A^j]_{\text{intrinsic}}(T) \times \exp\left(\frac{e_F - e_{F_j}^*}{kT}\right), \]

where

\[ [A^j]_{\text{intrinsic}} = \left(\frac{[A^j]_{\text{max}}}{n_i}\right)^2. \]

is the solubility in intrinsic conditions \((e_F=e_i)\) and \([A^j]_{\text{max}}\) the solubility when \([A^j]_{\text{max}} > n_i\). Equation (7) is a consequence of the fact that the formation energy of charged defects depends on \(e_F\). In an atomistic framework expression (7) can be fulfilled by trapping and emitting only neutral particles of the type \(AX^0\) with an emission rate independent of \(e_F\).

### III. POINT DEFECTS: INTERSTITIALS AND VACANCIES

#### A. Vacancies

The charge levels for vacancies \((V^{++}, V^+, V^0, V^-)\), are well characterized and they are represented in Fig. 2. The dependence of the formation energies with \(e_F\) for charged vacancies using the values of Table I are displayed in Fig. 3(a) (dashed lines). Thick dashed lines correspond to the most stable charge state (lower formation energy and higher concentration) that depends on the Fermi level. As it can be seen \(V^0\) is a metastable state, i.e., it is not the minimum \(E_f\) for any value of \(e_F\). \([V^0]^+\), that is constant with \(e_F\), is dominant for \(p\)-doped materials and of the same order as
[V$^-$] for intrinsic silicon. The solid lines are the diffusion energies. $E_m$ is different for each charged species, but we assume it does not depend on $e_F$.

The parameters displayed in Table I and represented in Fig. 3(a) have been chosen to correctly fit the vacancy transport capacity reported in Ref. 14 as well as the charge levels of Refs. 1 and 13. The Arrhenius plot for vacancy transport capacity with the contribution of different charge states is represented in Fig. 4(a).

**B. Interstitials**

The charge levels of silicon self-interstitials ($I^-, I^0, I^+$, $I^{++}$), are not conclusively established. Theoretical calculations indicate that $I^+$ is metastable but with a very low migration energy and controls interstitial diffusion for $p$-doped and intrinsic materials. However, experiments show that in intrinsic silicon, diffusion is dominated by $I^0$. The charge states of silicon self-interstitials ($I^-, I^0, I^+$) are also shown. Other parameters used in this work are, for boron, $E_m=1.0$ eV and we have assumed the same value for the other charge states. These parameters fit experimental data for interstitial diffusivity in intrinsic silicon.

![Fig. 2. Electronic levels for V, I, B, AsV, and AsI.](image)

![Fig. 3. Formation energies ($E_f$, dashed lines) and diffusion energies ($E_{diff}$= $E_f$+$E_m$, solid lines) of charged Silicon vacancy (a) and self-interstitial (b) as a function of Fermi level ($e_F$) using the parameter set of Table I. $E_f$ is measured from the valence band edge. (Band-gap energy is $E_g=1.17$ eV for $T=0$ K). Minimum values of $E_f$ and $E_{diff}$ are drawn with thick lines. $E_{diff}$ corresponds to the diffusion energy for intrinsic silicon ($e_F=e_F$). Open circles indicate the energy crossings corresponding to charge levels.](image)

TABLE I. Parameters used for charged states of silicon vacancy (V$^0$), silicon self-interstitial (I$^0$), interstitial boron (B$^i$), and vacancy and interstitial arsenic (AsV$^0$/AsI$^0$). $D_m$ is the diffusivity prefactor [Eq. (3)], $E_m$ the migration energy, and $e_f$ the charge level measured from the valence band edge. For $T$ $\neq$ 0, we assume that $e_f$ scales with band gap energy. (Ref. 12). Prefactors for equilibrium concentrations and formation energies of I$^0$ and V$^0$ are also shown. Other parameters used in this work are, for boron, $D_{b0}(B^i_0)=0.4$ cm$^2$ s$^{-1}$, $E_{b0}(B^i_0)=0.1$ eV; and for arsenic, $D_{ak0}(AsV^0)=1 \times 10^{-3}$ cm$^2$ s$^{-1}$, $E_{ak0}(AsV^0)=1$ and $D_{ak0}(AsI^0)=5 \times 10^{-3}$ cm$^2$ s$^{-1}$, $E_{ak0}(AsI^0)=0.1$ eV. $D_{b0,0}$ is the break-up prefactor expressed in diffusivity units $[=\lambda^2/6\nu_{b0,0}]$. $D_{b0}$ and $E_b(T)$ can be obtained from Eqs. (11) and (12). The point defect capture volume is $2\lambda^3$.

<table>
<thead>
<tr>
<th>Species</th>
<th>$E_f$ (eV)</th>
<th>$E_m$ (eV)</th>
<th>$e_f(T=0)$ (eV)</th>
<th>$D_{m,0} \times 10^{-3}$ (cm$^2$ s$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>V$^-$</td>
<td>3.85</td>
<td>1.0</td>
<td>1.06</td>
<td>5</td>
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<tr>
<td>V$^0$</td>
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<td>0.2</td>
<td>0.13</td>
<td>1</td>
</tr>
<tr>
<td>V$^{++}$</td>
<td>1.4</td>
<td>1.3</td>
<td>1.1</td>
<td>1</td>
</tr>
<tr>
<td>V$^+$</td>
<td>1.7</td>
<td>1.3</td>
<td>1.1</td>
<td>1</td>
</tr>
<tr>
<td>I$^-$</td>
<td>1.0</td>
<td>1.0</td>
<td>1.0</td>
<td>1</td>
</tr>
<tr>
<td>I$^0$</td>
<td>1.0</td>
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<tr>
<td>I$^+$</td>
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<td>1.0</td>
<td>1.0</td>
<td>1</td>
</tr>
<tr>
<td>I$^{++}$</td>
<td>1.0</td>
<td>1.0</td>
<td>1.0</td>
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</tr>
</tbody>
</table>

FIG. 2. Electronic levels for V, I, B, AsV, and AsI.
interstitial transport capacity. The experimental points (symbols) have been extracted from Refs. 19 and 20. The lines have been calculated using the parameters displayed in Table I.

IV. PAIR POINT DEFECTS: BORON AND ARSENIC

Once the point defects, I and V, have been introduced, we will focus our study on the diffusion of dopants. Substitutional impurities are assumed to be immobile. Let us consider now the cases in which the migrating defect can be seen as the pair AX, where A is an impurity and X is either an I or a V. We will describe first the diffusion of boron using Bi and later the case for arsenic with AsV and AsI.

A. Boron

It is commonly accepted that B migrates mainly due to interstitial mechanism, via $B_i$ (either as an interstitial $B_i$ or a $B_i$ pair), rather than via $V$-mediated mechanism.

The known charged states of $B_i$ are $B_i^-$, $B_i^0$, and $B_i^+$. The three states are included in our model, although the inclusion of $B_i^+ \pm$ will only show up for systems far from equilibrium.

FIG. 4. Arrhenius plots for the relative transport capacity ($DC/V\text{Si}$) for (a) V and (b) I in intrinsic conditions. The parameters are set to fit the experimental data for I (Refs. 19 and 20) and V (Ref. 14).

FIG. 5. Potential energy diagram showing the formation and migration energies for $B_i^-$ and $P^\circ$, and the $B_i^+$ binding and break-up energies.

The pairing, break up and charge reactions related to $B_i$ are represented by the reactions

$$P^\circ + B^- \leftrightarrow B_i^- \quad \uparrow \downarrow \uparrow \downarrow$$

$$I^+ + B^- \leftrightarrow B_i^0 \pm$$

In the following, we assume that substitutional boron is always immobile and ionized ($B_i^+$). In Eq. (9) horizontal reactions (pairing and break-up) conserve the charge while vertical reactions establish the electrical equilibrium. The rate of the horizontal reactions will not depend on the Fermi level. Direct break-up of $B_i^+$ is not included because $I^{++}$ is not implemented. The charge level values for $B_i$ are listed in Table I and illustrated in Fig. 2. These values have been measured by electrical characterization.

From the first reaction in Eq. (9) the number of broken $B_i^-$ per unit of volume and time will be $[B_i^-] \nu_b(B_i^-)$ and the number of new formed $B_i^-$ is not binding and break-up actions $[B_i^0] \nu_m(P^\circ)$ consequence, in local equilibrium conditions,

$$\frac{[B_i^-]}{[B^-]} = \frac{\nu_m(P^\circ)}{\nu_b(B_i^-)} \nu_{\text{capt}},$$

$\nu_{\text{capt}}$ being the effective capture volume for pairing reaction and $\nu_b$ the break-up frequency. The ratio of Eq. (10) is independent of $e_F$ because the charges of $B_i^+$ and $B_i^-$ are the same. In contrast, $[B_i^0]/[B^-]$ and $[B_i^+]/[B^-]$ are Fermi-level dependent. The activation energies of the $[B_i^0]/[B^-]$ fractions are represented as formation energies in Fig. 6.

The activation energy for $B_i^-$ break-up will be $E_b(B_i^-)$ and the activation energy for $B_i^0$ break-up will be $E_b(P^\circ)$ (see Fig. 5), $E_b$ denoting the binding energy. Considering energy conservation in reactions of Eq. (9) we obtain

$$E_b(B_i^-) = E_b(B_i^-) + e_F(0,-) - e_F(+,0)$$

and the activation energy for $B_i^0$ break-up will be $E_b(P^\circ) + e_m(P^\circ)$. Electronic levels scale with $E_b$, introducing a slight $T$ dependence in $E_b(B_i^-)$. From equilibrium conditions it can be also derived that the break-up prefactors, $\nu_b, \nu_m$, must fulfill
FIG. 6. Dashed lines, energy to form a $B_i'$ from a $B^- [E_i(B_i')]$ as a function of Fermi level using the values of Table I. Solid lines, activation energy of the contribution of $B_i'$ for the effective Boron diffusivity in equilibrium conditions, $E_{\text{diff}}$ [see Eq. (13)]. Migration energies $[E_m(B_i')]$ are the differences between solid and dashed lines. Black dot indicates the value of $E^*_{\text{diff}}$. The other notations correspond to Fig. 3.

$$v_{\text{het}}(B_i')/v_{\text{het}}(B^-) = \frac{\nu_m(1)}{\nu_m(0)}.$$  \hspace{3.5cm} (12)

Boron effective diffusivity $D(B)$ is given by the sum of the contribution of all mobile species

$$D(B) = D(B_i') \frac{[B^-]}{[B^-]} + D(B_i'^0) \frac{[B_i'^0]}{[B^-]} + D(B_i'^+) \frac{[B_i'^+]}{[B^-]}.$$  \hspace{3cm} (13)

The diffusion energy value for boron under intrinsic conditions in Fig. 6 ($E^*_{\text{diff}}$) will be similar to the activation energy of the Arrhenius plot of equilibrium boron diffusivity. The small differences can be attributed to the charge states and the modification of the charge levels with temperature. The activation energies of the terms in the previous equation [usually known as “defect-assisted diffusion energies” or just “diffusion energies,” $E_{\text{diff}}(B_i')$] are represented in Fig. 6. From this figure it can be seen that $B_i'^0$ is a metastable state (as $e_{B_i'} > e_{B_i'^0}$) but is the main contributor for boron diffusion in a wide range of $e_F$ and in consequence $D(B) \propto p/n_i$ (Ref. 2). According to Fig. 6 the effective migration energy of a $B_i$ for $e_F = e_i$ is $E_{\text{diff}}(B_i'^0) - E_{\text{diff}}(B_i') = 0.6$ eV, in agreement with the experimental observation. It is also noticeable, that one can have $D_{pp}$ with no $I^+$. Actually, $D(B)$ does not depend on the charge states of $I$, but on those of $B_i$.

The parameters listed in Table I and used in Fig. 6 have been chosen to fit the Arrhenius plot of equilibrium boron diffusivity, $D(B)$, reported in Ref. 24. In particular, the binding energy of $B_i'$ and migration energy of $B_i'^0$ have been taken to fit the boron diffusivity Arrhenius plot, and the migration energies for $B_i'^-$ and $B_i'^+$ are in agreement with the picture derived from ab initio calculations and the experimental $D'(B)$ for $n$ type silicon.

Using the Maxwell-Boltzmann approximation, Eq. (13) is usually written in continuum models as

$$D(B) = \frac{S_I}{N_i} \left[ D_{\chi}(B) + D_P(B) \frac{p}{n_i} + D_{pp}(B) \left( \frac{p}{n_i} \right)^2 \right],$$  \hspace{2.5cm} (14)

$S_I$ being the interstitial supersaturation, and $p$ and $n_i$ the hole concentration and the intrinsic concentration, respectively. The relations between the above diffusivity components $D_{\chi}(B)$, $D_P(B)$, and $D_{pp}(B)$ and the microscopic parameters are therefore

$$D_{\chi}(B) = v_{\text{cap}}D(P)[P] \left[ \frac{\nu_m(B^-)}{\nu_{\text{het}}(B^-)^*} \right],$$

$$D_P(B) = v_{\text{cap}}D(P)[P] \left[ \frac{\nu_m(B_0^0)}{\nu_{\text{het}}(B^-)^*} \right] \times \exp\left[ \left( e_{B_i}(0,+) - e_i \right)/kT \right],$$

$$D_{pp}(B) = v_{\text{cap}}D(P)[P] \left[ \frac{\nu_m(B_i'^0)}{\nu_{\text{het}}(B_i'^+)} \right] \times \exp\left[ \left( e_{B_i}(0,-) + e_i + 2e_i \right)/kT \right],$$  \hspace{3cm} (15)

$e_i$ being the intrinsic level.

These expressions can be used as a bridge between the parameters of continuum simulators and those of a kMC simulator. Nevertheless, the above continuum expression assumes Maxwell-Boltzmann and quasiequilibrium conditions, which are not needed within the kMC approach. We should point out that the above terms only depend on $D(P)$ without dependences on $I^+$ or $I^-$. The ratios $\nu_m(B_i')/\nu_{\text{het}}(B_i'^+)$ mean that the diffusivity of each term can be increased by increasing the migration rate, or decreasing the break-up rate, but increasing or decreasing both leaves the magnitude unchanged. The atomistic meaning is that the $B$ diffusivity does not depend on how fast $B_i$ moves, but on the distance traveled (long hop) by the $B_i$ before breaking up.

For slightly doped material, the dominant diffusing interstitial is $P$, which upon interaction with substitutional boron creates a $B_i'^+$ which in turn switches to $B_i'^+$ very quickly because $B_i'^+$ has the lowest formation energy for these conditions. However, $B_i'^+$ is a slow diffusant that can also switch to $B_i'^0$, which is a fast diffusant and provides the main contribution to the overall boron diffusivity. Notice that the most frequent break-up reaction is for the $B_i'^-$ charge state to fulfill microscopic reversibility of the most frequent pairing reaction.

B. Arsenic

Once boron charged states have been explained, a similar analysis can be done for arsenic, which has both vacancy and interstitial contributions, related to $AsV$ and $As_i$ defects, respectively. Arsenic reactions are

$$P^0 + As^+ \rightleftharpoons As_i^\uparrow\uparrow \rightleftharpoons As_i^0$$  \hspace{3.5cm} (16)

and
where we are also assuming that \( \text{As}^+ \) is immobile and always ionized.

Arsenic diffusion will have all previously mentioned contributions,

\[
D(\text{As}) \approx D(\text{As}V^+) \frac{[\text{As}V^+]}{[\text{As}^+]^0} + D(\text{As})_i \frac{[\text{As}^i]}{[\text{As}^+]} + D(\text{As}V^0) \frac{[\text{As}V^0]}{[\text{As}^+]^0} + D(\text{As}V^-) \frac{[\text{As}V^-]}{[\text{As}^+]^0}
\]

(18)

which, in continuum models is usually reduced to\(^{26}\)

\[
D(\text{As}) = [f_i S_f - (1 - f_i) S_v] \\
\times \left[ D_\chi(\text{As}) + D_M(\text{As})_i \frac{n}{n_i} + D_{MM}(\text{As}) \left( \frac{n}{n_i} \right)^2 \right],
\]

(19)

\( f_i \) being the fraction of interstitial-assisted diffusion.

Notice, however, that this continuum description conveys several simplifying assumptions compared to Eq. (18). In the first place, the common assumption that \( D_\chi \) and \( D_M \) fit an Arrhenius plot is only true if the contributions of \( \text{As}V^+ \) and \( \text{As}^i \) have the same activation energy, and the same must be true for the \( \text{As}V^0, \text{As}^0 \) contributions. More importantly, Eq. (19) assumes that the interstitial fraction, \( f_i \), is independent of the Fermi level (i.e., the same for the three charge states), and is also independent of the temperature. These assumptions reduce the range of applicability of Eq. (19). Our parameter set for \( \text{As} \) is reported in Table I. These parameters fit the equilibrium \( \text{As} \) diffusion reported by Ref. 2. The binding energy (1.3 eV) and migration energy used for \( \text{As}V^0 \) compare very well with ab initio calculations.\(^ {27} \) The value of \( e_{\text{As}V^0}(0, -) \) is from Ref. 2. The activation energy of \( f_i \) is the same than the value in Ref. 28.

Figure 7 shows experimental diffusivity (symbols) reported in Ref. 2 for different concentrations and temperatures, compared with our calculated values. We have taken into account the field enhancement factor \( h \).\(^ {1} \)

Figure 8 shows a comparison of profiles obtained with a continuum approach and our atomistic approach. The lines plot the result of solving the one-dimensional (1D) diffusion equation\(^ {1} \)

\[
\frac{\partial C_{\text{As}}}{\partial t} = \frac{\partial}{\partial x} \left( D_{\text{As}} \frac{\partial C_{\text{As}}}{\partial x} \right),
\]

(20)

where \( D_{\text{As}} = h D_{\text{As}}, D_\text{As} \), being the magnitude represented in Eq. (19). We have simulated \( 1.4 \times 10^4 \) s, \( 4.6 \times 10^4 \) s, and \( 10^5 \) s for both intrinsic (dashed lines, \( 10^{19} \) cm\(^{-3} \) As surface concentration) and extrinsic conditions (solid lines, \( 4 \times 10^{19} \) cm\(^{-3} \) As surface concentration). The 1D projection of the obtained 3D atomistic profiles (squares, \( 1.4 \times 10^4 \) s;

\[
\text{As}^0 + \text{As}^+ \rightleftharpoons \text{As}V^+ \\
\uparrow \downarrow \quad \uparrow \downarrow \\
\text{As}^0 + \text{As}^+ \rightleftharpoons \text{As}V^0, \\
\uparrow \downarrow \quad \uparrow \downarrow \\
\text{As}^0 + \text{As}^+ \rightleftharpoons \text{As}V^- \\
\uparrow \downarrow \quad \uparrow \downarrow
\]

FIG. 7. Arsenic diffusion dependence on the temperature and dopant concentration. Symbols, experimental data (Ref. 2). Lines, calculated values (see text).

circles, \( 4.6 \times 10^4 \) s; and triangles, \( 10^5 \) s) are in good agreement with the continuum ones, for the different annealed times at 800 °C. The effect of Fermi level is evident in the obtained boxlike shape profile for extrinsic diffusion. The comparison made in Figs. 7 and 8 validates the parameter translation between atomistic and continuum formulation [Eq. (15) and equivalent for \( \text{As} \)].

V. DOPANT LONG HOPS INVOLVING SEVERAL CHARGE STATES

In systems where diffusion proceeds via an intermediate migrating species the shape of the diffusion profiles of dopants can be substantially different, even though the standard deviations of the profiles are the same.\(^ {29,30} \) This is because the shape is controlled by the value of the long hop distance, \( \Lambda \) (distance traveled by a point-defect pair before breaking up), which is given by\(^ {30,31} \)

FIG. 8. Arsenic concentration profiles under intrinsic (open symbols and dashed lines) and extrinsic conditions (solid symbols and lines) for 800 °C. Symbols, KMC simulations (squares, \( 1.4 \times 10^4 \) s; circles, \( 4.6 \times 10^4 \) s; triangles, \( 10^5 \) s). Lines calculated for the same conditions within the continuum framework (see text). In order to do an even comparison, Maxwell-Boltzmann statistics have been used in our simulation.
and, finally using Eqs. (3) and (13),

$$\Lambda = \sqrt{\frac{1}{6} \frac{\nu_{v_m}(B_i^+)}{\nu_{bk}(B_i^+)} + \frac{\nu_{v_m}(B_i^-)}{\nu_{bk}(B_i^-)} + \frac{\nu_{v_m}(B_i^0)}{\nu_{bk}(B_i^0)}} - \frac{\nu_{v_m}(P_i^+)}{\nu_{bk}(P_i^+)} + \frac{\nu_{v_m}(P_i^-)}{\nu_{bk}(P_i^-)}}$$

(22)

The last equality assumes that the $I^-$ contribution is negligible. $DC^-(I)$ is the equilibrium transport capacity of interstitials. With the values we are using, $\Lambda \propto \sqrt{p/n}$, for $e_F = e_r$.

The temperature dependence of $\Lambda$ for boron, using the parameters of Table I is displayed in Fig. 9, both for intrinsic and doped silicon, and compared with experimental values for intrinsic materials.$^{29,32}$

It is interesting to note that the concentrations of the different charge states of interstitials (namely $I^+$ and $I^-$) do not directly affect boron diffusivity [see Eqs. (13) and (15)]. This could suggest that, as a simplifying approximation, one can neglect the presence of $I^+$ and $I^-$. However, Eq. (22) shows that, by doing so, an incorrectly large $\Lambda$ value could be obtained for extrinsic materials. In fact, the magnitude of $D(B)$ is governed by the $\nu_{v_m}(B_i^+)[B_i^+]/[B_i^-]$ terms, but how Gaussian the diffusion profile is, depends also on the $\nu_{v_m}(P_i^+)[P_i^-]$ terms.

VI. AN EXAMPLE: BORON PILE UP AND DEPLETION NEAR A PN JUNCTION

One of the reasons for developing the detailed modelling of charge effects presented in this work is that, in the complex processing scenarios which are now common place in advanced semiconductor manufacturing, the dominant mechanisms may not be apparent or, even worse, one can be misled by intuition.

As an example, Fig. 10 shows the results after a 20 h annealing at 750 °C of a uniformly $P$-type doped substrate ($1 \times 10^{18}$ cm$^{-3}$ initial boron concentration) which includes an $N$-type layer ($1 \times 10^{20}$ cm$^{-3}$ arsenic concentration, initially from 0 to 25 nm). During the annealing, $B$ is depleted from the junction into the $N$-type layer and piles up as it enters the $N$ side. However, it is interesting to remark that this apparent electric drift effect was actually associated to a net flux of the neutral $B^0$, maybe against simple intuition. Namely, the gradient of $e_F$ produces a gradient of $[B^0]/[P^+]$, and, in consequence, a diffusion flux of $B^0$ into the $N$ region. Boron pile up at the front of the As-rich region is a result of the lower value of $D(B)$ in $N$-type materials [see Eq. (14)]. The figure clearly shows the same dopant redistribution effect that has been reported by other authors, both theoretically$^{8,33}$ and experimentally$^{34}$.

VII. CONCLUSIONS

In this work an accurate, physically based atomistic modeling of Fermi-level effects of species diffusing in silicon has been presented. This model takes into account the charge reactions and electric bias dependency with Fermi level, pairing and break-up reactions between particles, clustering dopant activation and deactivation and the Fermi-level-dependent solubility. It also includes degenerate Fermi-Dirac
statistics and band-gap narrowing.

The presented model, in particular Eq. (15), establishes a bridge between atomistic kMC and continuum approaches for Fermi-level-dependent diffusivity. These atomistic simulators are expected to play an increasingly relevant role in the forthcoming years due to their ability to directly incorporate ab initio parameters and complex mechanisms.

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