Mechanisms of Equilibrium and Nonequilibrium Diffusion of Dopants in Silicon

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We have developed a theory of impurity diffusion in silicon under equilibrium and nonequilibrium concentrations of point defects. The results of first-principles calculations of several key quantities are combined with this theory and compared to experimental data. We find that vacancies and self-interstitials mediate the equilibrium diffusion of B, P, and As with comparable activation energies, but interstitials are dominant. Sb diffusion, on the other hand, is mediated primarily by vacancies. We also find that the direct-exchange mechanism plays only a minor role for all dopants studied.

The microscopic mechanisms of dopant-impurity diffusion in Si are of intrinsic scientific interest and also form the cornerstones of modeling programs for the design and fabrication of devices. Despite extensive research on the subject, there exists no general consensus regarding the relative contributions of the various mechanisms. For example, some authors analyze or numerically fit experimental data and conclude that phosphorus (P) diffusion is primarily assisted by vacancies,[1] whereas others conclude that P diffusion is mediated in part or primarily by self-interstitials.[2,3] More recently, Pandey[4] extrapolated his results for self-diffusion and suggested that the concerted exchange (CE), which requires no intrinsic defects, may be the dominant mechanism for dopant-impurity diffusion. Dopant diffusion experiments under injection of excess concentrations of point defects have offered promise for unraveling these controversies.[2,3] However, theories underlying the interpretation of such experiments are unsatisfactory, relying for the most part on assumptions whose validity is uncertain.[5]

In this Letter, we present the main results of an extensive theoretical investigation of the energetics of diffusion for several dopant impurities (B, P, As, and Sb) in Si under both equilibrium and nonequilibrium conditions. In the first part, we report the theoretical activation energies for equilibrium diffusion and compare with available experimental data. In the second part, we present a systematic theory of impurity diffusion under injection of excess point defects. In particular, we derive expressions for the activation energies of diffusion and predict the expected form for the diffusion coefficient. Combining available experimental data with our theoretical results allows us to draw a number of definitive conclusions. We conclude that B, P, and As all have substantial self-interstitial diffusion components, that Sb is primarily assisted by vacancies, and that the exchange mechanism plays only a minor role in substitutional-dopant diffusion.

In the calculations we use density-functional theory,[6] the local-density approximation, and norm-conserving pseudopotentials.[7] The supercell method is used to solve

the relevant Schrödinger equation following the methodology of Ref. 8. Convergence with respect to all variables has been carefully studied. In particular, it was found necessary to use plane waves up to a kinetic energy of 20 Ry for the wave functions and potentials (plane waves above 10 Ry are included in second-order Löwdin perturbation theory), up to 32-atom supercells, and up to three special k points in the irreducible wedge of the Brillouin zone.[9] Unless otherwise stated, relaxation of the surrounding Si network was calculated for every location of the impurity or defect. We estimate our total error to be less than 1 eV, depending upon the particular impurity and the particular atomic configuration. The majority of the error comes from the local-density-approximation uncertainty in the defect- and impurity-related levels in the energy gap. Nevertheless, this scheme has a proven reliability in calculating a number of properties of semiconductors.

The diffusion coefficient D is a sum of contributions of the form

$$D_j = C_j d_j / C_{X_s}, \tag{1}$$

where C_j is the concentration of the defect j whose long-range migration effects diffusion of the substitutional dopant, d_j is the corresponding diffusivity, and C_{X_s} is the concentration of substitutional impurities. For the CE mechanism, the pertinent defect is the substitutional impurity itself, whereas for defect-mediated diffusion, this species needs to be identified (e.g., it can be either the isolated vacancy, the impurity-vacancy pair, etc.). In all cases, under equilibrium conditions, D_j can also be written in the Arrhenius form

$$D_j^* = D_{j,0}^* \exp(-Q_j^*/kT), \tag{2}$$

where $D_{j,0}^*$ is the preexponential which contains a variety of factors, Q_j^* is the activation energy, k is the Boltzmann's constant, and T is the temperature. The asterisk denotes equilibrium quantities. For the CE mechanism, Q_j^* is the energy needed to place a pair of atoms (the impurity atom and one of its nearest-neighbor Si atoms) at the saddle point of the exchange path. For defect-
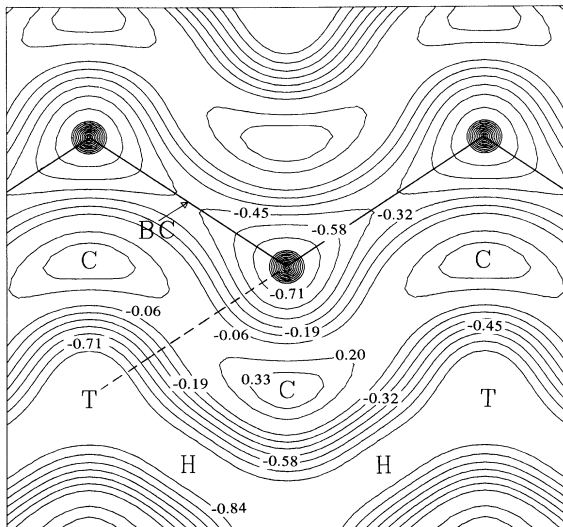
FIG. 1. Total-energy contour plot depicting the migration of a neutral B interstitial through the Si crystal. The labeled sites are T (tetrahedral), H (hexagonal), BC (bond center), and C (at the center of a rhombus formed by three adjacent Si atoms and the nearest T). The energy difference between contours is 0.13 eV. The dashed line is the kick-out pathway.

FIG. 2. The calculated activation energies under equilibrium conditions for vacancy-mediated (V), interstitial-mediated (I), and concerted-exchange (CE) mechanisms for Si self-diffusion and various impurities. The boxed areas are a selected range of experimental results from Ref. 13. The self-diffusion CE activation energy is from Ref. 4.

mediated mechanisms, Q_j^* is the sum of the formation and migration energies for the diffusing species.

For defect-mediated mechanisms, the first task of theory is to determine which defect or complex leads to diffusion with the smallest Q_j. For vacancy-mediated (V-mediated) diffusion, we find that the relevant diffusing species is the vacancy for B and the impurity-vacancy (XV) pair for P, As, and Sb.[10,11] For interstitial-mediated (I-mediated) diffusion, a global total-energy surface was needed in order to determine the precise migration pathways and the diffusing species.[12] A contour plot of such a surface in the (110) diamond-structure crystal plane for a neutral B interstitial (B_i) is shown in Fig. 1. We find that the energetically preferred diffusion pathway in all cases is the kick-out process,[10,11] so that the diffusing species is the interstitial impurity atom.

The determination of Q_j^* for the CE mechanism necessitates mapping out the entire exchange path and identifying the lowest-energy saddle point. Pandey carried out such a task in the case of self-diffusion (Si-Si exchange), but the reoptimization of the entire path for impurity-Si exchange is an unduly demanding computational task. For our purposes, it was adequate to obtain an upper bound for the saddle-point energy.[11]

The calculated activation energies for V-, I-, and CE-mediated mechanisms for substitutional B, P, As, and Sb diffusion under equilibrium conditions are shown graphically in Fig. 2. A selected range of experimental values are shown as well.[13] For comparison, we also show the corresponding activation energies for self-diffusion.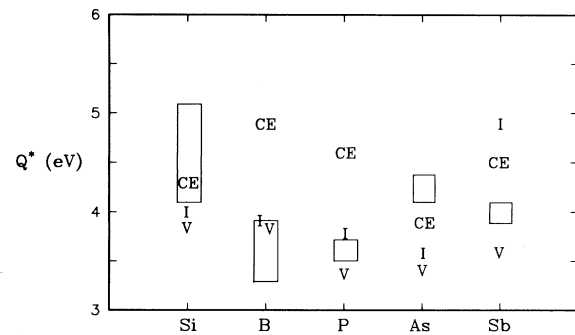 In all cases, the activation energies are those for neutral species. Species of different charge states have been found to contribute with only slightly different activation energies at the temperatures of interest.[10] We note that for B, P, and As, the V- and I-assisted-mechanism activation energies are the same within the accuracy of the calculation (0.4 eV is the maximum difference). Because the theoretical CE activation energies are only upper bounds, we view them as comparable to those of defect-mediated mechanisms. Only in the case of Sb does the large difference between activation energies allow us to conclude that the V-assisted mechanism dominates, in agreement with conclusions drawn from experimental data.[3] In summary, our calculated activation energies, being in the same range as experimental values, confirm the reliability of our theoretical methods but do not establish the relative importance of the various mechanisms, with the exception of Sb. For such a task, it would be necessary to determine the values of the respective preexponentials, which is currently unfeasible. Nevertheless, we show in the remainder of this paper that theoretical calculations combined with experiments involving injection of excess point defects allow a number of important definitive conclusions to be made.

Excess point defects can be injected into the bulk by surface treatments. For example, evidence has accumulated that oxidation injects self-interstitials whereas nitridation injects vacancies.[2,3,14,15] Under these conditions, the dopant diffusion coefficient in buried impurity layers is either retarded or enhanced. Conclusions derived from such experiments have, however, widely conflicted, largely because they were based on unsatisfactory assumptions. The most serious shortcoming was the implicit assumption that the concentrations of *vacancies* and *self-interstitials* determine the dopant diffusion coefficient. As we made clear earlier in this paper, the relevant concentrations are generally those of either the impurity-vacancy pair (XV) or the interstitial impurity (X_i). The key element of a correct theory of nonequili-

brium diffusion is to recognize that the diffusion coefficient D is still given by a sum of terms of the form of Eq. (1) where the diffusivities d_j have the same values as in equilibrium. It is then the task of theory to determine the correct expressions for all the relevant C_j. We present here the essential elements of such a theory under injection of interstitials (the theory for vacancy injection is completely analogous).

We first determine the effect of excess point defects on the CE mechanism for which D_j is proportional to the concentration of substitutional impurity atoms, C_{X_s}. Point-defect injection occurs at comparatively low levels so that it affects C_{X_s}, and hence D_{CE}, only minimally through the formation of XV pairs or X_i. As a result, if the CE mechanism is the dominant impurity diffusion mechanism, the diffusion coefficient *cannot be retarded by moderate levels of injection.* But this is in contradiction with experimental observation.[2,3] We therefore do not discuss the CE mechanism any further in the following treatment.

We now turn to the effects of defect injection on defect-mediated diffusion and, specifically, on the concentrations of the relevant diffusing species, the XV pair or X_i. For this purpose, it is essential to identify *all* the reactions that govern the defect concentrations. These are as follows:

$$S \rightleftarrows V \text{ and } S \rightleftarrows I, \tag{3}$$

$$I + X_s \rightleftarrows X_i, \tag{4}$$

$$V + X_s \rightleftarrows XV, \tag{5}$$

$$I + XV \rightleftarrows X_s, \tag{6}$$

$$I + V \rightleftarrows \square, \tag{7}$$

$$V + X_i \rightleftarrows X_s. \tag{8}$$

Reactions (3) are written schematically and indicate that a free or internal surface S can produce or absorb both vacancies and interstitials independent of each other. In reaction (7), the symbol $\square$ represents bulk Si.

Starting with the seven reactions given above, one can immediately obtain four expressions of the form

$$\frac{\partial C_j}{\partial t} = \sum_\alpha g_{j\alpha} - \sum_\alpha r_{j\alpha} C_j \tag{9}$$

for each of the four defect species j (V, I, XV, X_i). The terms $g_{j\alpha}$ are generation rates and $r_{j\alpha}$ are recombination frequencies. At steady state, we require $\partial C_j / \partial t = 0$ for all four species. The resulting four equations comprise a complete and exact set which can in principle yield solutions for all relevant concentrations.

By invoking a series of approximations, analytical expressions for the concentrations can be obtained which manifest the essential physical results.[11] The concentrations of C_{X_i} and C_{XV} *under injection of self-interstitials*

are

$$C_{X_i} = C_{X_i}^* + K_4 C_{X_s} C_I', \tag{10}$$

$$1/C_{XV} = 1/C_{XV}^* + \beta C_I'/C_{X_s} C_V^*, \tag{11}$$

where C_I' denotes the injected interstitial concentration. K_4 is the equilibrium constant of reaction (4) and β is a constant containing the reverse rate constant of reaction (7) divided by the forward rate constant of reaction (6).

Combining Eqs. (1), (10), and (11), the total diffusion coefficient has the form

$$D = D_I + D_V, \tag{12}$$

where

$$D_I = D_I^* + D_I' \tag{13}$$

and

$$1/D_V = 1/D_V^* + 1/D_V', \tag{14}$$

where the subscript I (V) denotes the I- (V-) assisted diffusion component. The primes denote the nonequilibrium contribution to diffusion. D_I' and $1/D_V'$ are proportional to C_I' and $1/C_V'$, respectively, as in the corresponding terms in Eqs. (10) and (11). D_I' and D_V' are activated with activation energies given by

$$Q_I' = E_{inj} - \Delta E + E_m, \tag{15}$$

where E_{inj} is the activation energy of the interstitial injection process, ΔE is the energy difference between X_i and $X_s + I$ as in reaction (4), and E_m is the migration energy of X_i; and

$$Q_V' = (E_{inj} + E_{I\text{-}XV}^{barrier}) - (E_F^V + E_{V\text{-}X_s}^{barrier}) + E_m, \tag{16}$$

where $E_{I\text{-}XV}^{barrier}$ ($E_{V\text{-}X_s}^{barrier}$) is the energy barrier to recombination of interstitials (vacancies) with XV pairs (X_s), E_F^V is the formation energy of vacancies, and E_m is the XV migration energy.

We now discuss three distinct cases. If, under equilibrium, the I component is dominant, interstitial injection leads to an enhanced total diffusion coefficient of the form of Eq. (13), where the activation energy of D' is given by Eq. (15). Hill[16] measured the diffusion coefficients of B, P, and As under interstitial injection and found that they obey Eq. (13). This finding immediately suggests that these impurities diffuse predominantly via an interstitial mechanism. Furthermore, we have calculated the activation energy for these impurities from Eq. (15) using our theoretical values for ΔE and E_m and an experimental value for E_{inj} extracted from Ref. 17. The results, as well as Hill's measured values, are given in Table I. The excellent agreement between two values corroborates the conclusion that these impurities diffuse primarily assisted by interstitials.

On the other hand, if, under equilibrium, the V component is dominant, interstitial injection can lead to either diffusion retardation or enhancement, depending

TABLE I. Activation energies for diffusion mediated exclusively by interstitials under interstitial injection [theory, Eq. (15)] and measured activation enthalpies under oxidation conditions (experiment from Hill, Ref. 16). All quantities are in eV.

Species	Q_I^i (theory)	Q' (experiment)
B	2.6	2.3
P	2.5	2.4
As	2.3	2.3

upon the level of injection. At low levels of injection, the I component remains small while the V component is retarded according to Eq. (14). It is generally believed that Sb diffusion under interstitial injection is such a case,[13] but data are usually reported at a single temperature. We predict that temperature-dependent data would obey Eq. (14) so that a *reciprocal Arrhenius plot* (i.e., $1/D$ vs $1/T$) would be appropriate to extract an activation energy for D_V^i to be compared with Eq. (16). Such data would provide a test of our theory and assess the conclusion that Sb diffuses predominantly by a V mechanism. If interstitial injection were to occur at high levels, the term D_I^i will ultimately overwhelm all other contributions and enhanced diffusion with an activation energy given by Eq. (15) would be observed.

Lastly, if, under equilibrium, the V and I components are comparable, interstitial injection can lead to either a net enhancement or a net retardation, according to Eqs. (12)–(14). Temperature-dependent plots would be rather complex but under certain conditions the new curve will *cross* the corresponding equilibrium curve. Such crossing is a definitive experimental signature of a dual mechanism. Unfortunately, temperature-dependent data of diffusion under vacancy or interstitial injection, though highly desirable, are scarce.

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