Silicon self-diffusion constants by tight-binding molecular dynamics

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The thermodynamic integration method has been incorporated into the tight-binding molecular-dynamics scheme to compute formation free energies of native point defects in bulk silicon. By combining previous simulated diffusivity data with present free-energy estimates, we present a thorough quantum-mechanical picture of self-diffusion in silicon that is both consistent with the state-of-the-art experimental data and able to predict separately the vacancy and self-interstitial contributions.

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Self-diffusion in silicon has been the subject of intense research since it rules many fundamental materials phenomena, such as equilibrium and nonequilibrium properties of native defects and processes of matter transport. It also underlies the microstructural evolution of bulk silicon under many technologically-relevant processes, such as Czochralski crystal growth or ion implantation. It is nowadays well established that the self-diffusion coefficient \( D_{SD} \) follows an Arrhenius equation

\[
D_{SD}(T) = D_0 \exp\left( -\frac{E^d}{k_B T} \right),
\]

over a wide range of temperatures.\(^1\) Recent experimental measurements of self-diffusion in isotope heterostructures\(^2\) have shown a temperature dependence accurately described over many orders of magnitude by an activation energy of migration \( E^d = 4.75 \pm 0.04 \) eV and by a preexponential factor \( D_0 = 530^{+250}_{-170} \) cm\(^2\) s\(^{-1}\).

Although the global picture is clear, there is still uncertainty about the relative contributions to \( D_{SD} \) due to the various elementary mechanisms of diffusion. As a matter of fact, self-diffusion is influenced by vacancy (V) and self-interstitial (I) migration, as well as by the direct exchange of two Si atoms, occurring between two neighboring lattice sites.\(^3\) This latter mechanism, however, is usually disregarded since no experimental evidence has been found for it,\(^2\) and its contribution to \( D_{SD} \) has been theoretically predicted to be negligibly small.\(^4\) Accordingly, the self-diffusion coefficient can be cast in the form\(^2\)

\[
D_{SD}(T) = f_I C_I^{eq}(T) d_I(T) + f_V C_V^{eq}(T) d_V(T),
\]

where \( C_I^{eq}(T) \) and \( C_V^{eq}(T) \) represent, respectively, the (normalized) equilibrium concentration of V’s and I’s defects, while \( d_I(T) \) and \( d_V(T) \) indicate the corresponding diffusivities. The \( f_I \) and \( f_V \) terms represent the autocorrelation factors for native defect migration trajectories and are well known for the diamond lattice.\(^5\) The open problem, therefore, consists of providing separately an estimation of \( C_I^{eq} \) and \( C_V^{eq} \), \( d_I \) and \( d_V \) and their explicit dependences upon temperature.

By means of metal diffusion experiments\(^6\) it has been possible to characterize the I-contribution to self-diffusion as

\[
C_I^{eq}(T) d_I(T) = 2980 \exp\left( -4.95 \frac{\text{eV}}{k_B T} \right) \text{cm}^2 \text{s}^{-1},
\]

which, combined with the above result for the total \( D_{SD}(T) \), allows to evaluate the V contribution as

\[
C_V^{eq}(T) d_V(T) = 0.92 \exp\left( -4.14 \frac{\text{eV}}{k_B T} \right) \text{cm}^2 \text{s}^{-1}.
\]

Other experimental data\(^1\) have been published, according to which the above diffusion constants should be

\[
C_I^{eq}(T) d_I(T) = 914 \exp\left( -4.84 \frac{\text{eV}}{k_B T} \right) \text{cm}^2 \text{s}^{-1},
\]

and

\[
C_V^{eq}(T) d_V(T) = 0.6 \exp\left( -4.03 \frac{\text{eV}}{k_B T} \right) \text{cm}^2 \text{s}^{-1}.
\]

Both data sets predict a self-diffusion dominated by self-interstitial (vacancy) mobility at a high (low) temperature. However, the crossover temperature for the dominating mechanism is different: 890 °C and 1000–1100 °C, for Eqs. (3), (4) and (5), respectively.

As for theory, a thorough study of self-diffusion requires accurate free-energy calculations (aimed at predicting temperature-dependent equilibrium concentrations) and extensive diffusivity simulations (aimed at computing migration and diffusion prefactors) both for I and V defects. Once the formation free energies \( F_{I,V} = E_{I,V}^\text{f} + TS_{I,V}^\text{f} \), as well as migration energies \( E_{I,V}^\text{m} \) and diffusivity prefactors \( d_{I,V}^0 \) are known, Eq. (2) can be recast in the form

\[
D_{SD}(T) = d_0 \exp\left( -\frac{E_{I}^\text{f} - TS_{I}^\text{f}}{k_B T} \right) \exp\left( -E_{I}^\text{m}/k_B T \right) + d_0 \exp\left( -\frac{E_{V}^\text{f} - TS_{V}^\text{f}}{k_B T} \right) \exp\left( -E_{V}^\text{m}/k_B T \right),
\]

so that a direct theory vs experiment comparison is possible.

At present, quantitative free-energy calculations are still rare, due to the considerable computational demands of finite-temperature simulations: an accurate simulation including high-temperature anharmonic effects, as well as reliable quantum-mechanical description of the bond dynamics involved in defect formation and migration, is in fact a very demanding task. A model potential molecular dynamics (MD) simulation, based on the Stillinger-Weber (SW) potential, has been presented by Sinno et al.\(^8\) Although the proposed numbers define a self-contained picture, the overall reliability is questionable, due to the limitation of the SW
was defined as \( f \). In turn, the TBMD Si sample. The ensemble average \( H \) state obtained by integrating constant-temperature simulations on a 64 \( \times \) 64 cell. The net force \( f \) acting on the \( a \) th atom was defined as \( f_a = \lambda f_{a}^{TBMD} + (1 - \lambda) f_{a}^{Inst}. \) At each state—defined by a given value of \( \lambda \)—the lattice was first carefully equilibrated with runs long up to 16 ps (one time step corresponding to 1 fs) and finally averaged over several more ps. The thermodynamical integration was performed over 16 \( \lambda \) points. Our benchmarks (performed on 216 \( \pm 1 \) atoms and/or \( \lambda = 5 \) points) proved that it is more important to include a higher number of \( \lambda \) points in the TI evaluation than to enlarge the size of the simulation box. We estimate the present energy integrals given in Eq. (8) to be converged to within \( \sim 10^{-4} \) eV. All free-energy calculations were performed at four different temperatures: 300, 500, 1000, and 1400 K.

The formation entropy \( S_f^I \) for the self-interstitial defect was found almost constant with temperature, the average value being \( S_f^I = 11.2 k_B \). First-principles calculations performed in the local harmonic approximation predict a value of \( S_f^I - 6 k_B \), which, however, increases up to \( S_f^I - 10 k_B \) when including anharmonic terms through TI calculations. The case of a vacancy is more complicated. As a matter of fact, due to the high mobility of such a defect, during the equilibration + observation runs, the defect was mobile, thus adding a sizeable contribution of migration entropy in the TI free energy calculations. This is confirmed by the fact that the computed value of \( S_f^V \) varied in the range 10.2–11.7 \( k_B \) in the selected temperature interval, with an average value of \( S_f^V \sim 10.8 k_B \). In fact, the migration contribution is already effectively included in TBMD simulations aimed at measuring \( d_V^0 \). To prevent the double counting of this term, we performed short observation runs, taking care to select only those simulations where \( V \) diffusion actually did not take place. The convergence error thus included in our ensemble averages results in an entropy overestimation of \( \sim 2 k_B \). In conclusion, we estimate an average formation (i.e., configurational + vibrational) entropy of \( S_f^I \sim 8.8 k_B \). Our TBMD results for \( S_f^I \) and \( S_f^V \) are in good qualitative agreement with first-principles calculations by Blochl et al.\(^9,13\) in the sense that the difference in the entropies of formation for \( I \)'s and \( V \)'s is of the order of \( 1 \sim 2 k_B \) in both studies, which predict a larger formation entropy for the interstitial.

Diffusivity constants were obtained by using the migration prefactors and energies computed in a previous work\(^10\) by means of the same TBMD scheme adopted here. In particular, we obtain \( d_I^0 = 1.58 \times 10^{-1} \text{ cm}^2 \text{ s}^{-1} \) and \( d_V^0 = 1.18 \times 10^{-4} \text{ cm}^2 \text{ s}^{-1} \), \( E_I^0 = 1.37 \) eV and \( E_V^0 = 0.1 \) eV. As for the formation energies the TBMD results are \( E_f^I = 3.80 \) eV and \( E_f^V = 3.97 \) eV. In this way, we get a self-consistent set of numbers, characterizing the various physical observables relevant to self-diffusion.

The vacancy contribution to self-diffusion predicted by present calculations is reported in Fig. 1. Experimental data by Bracht et al.\(^7\) and Gösele et al.\(^7\) as well as other SW\(^9\) and first-principles\(^9,13\) theoretical results are shown for comparison.

It is apparent that our TBMD investigation is in excellent agreement with state-of-the-art experimental data, providing

![FIG. 1. Vacancy contribution to self-diffusion coefficient.](image)
an overall atomistic picture for \( V \)-mediated self-diffusion much more reliable than model-potential simulations. We believe that the main source of disagreement between the SW and experimental data is due to the very low value of the vacancy formation energy \( E_V^f = 2.5 \text{ eV} \), which unfavorably compares with the 3.8 eV and 3.3–3.7 eV values given by TBMD and first-principles calculations, respectively. 10 The agreement is better for TBMD even when compared with \textit{ab initio} simulations which are principal superior. We guess that this is due to technical details of the calculations, both performed within the same formal framework, but with a different choice for the number of \( \lambda \) points over which operate the TI integration (only three points were used in Ref. 14). Under this respect, the semi-empirical character of TBMD has proved to be an advantage: thanks to the reduced computational workload it is possible to perform TI simulations in a fully-converged regime, still keeping a quantum-mechanical description of atom interactions.

As for self-interstitials, Fig. 2 confirms the predictivity and reliability of the present results. We note that in this case model-potential data are not so bad, while first-principles calculations were performed at one temperature only, so that no estimation for the activation energy of \( I \) diffusion can be obtained.

Finally, we remark that our investigation predicts the \( I \) defects to dominate self-diffusion at high temperatures, as proved experimentally and confirmed by first-principles calculations. Furthermore, the \( V \)-mediated and \( I \)-mediated mechanisms give equal contributions at \( T \approx 1030 \text{ °C} \). This result is again consistent with available experiments. 2,7

In conclusion, we propose the set of TBMD values reported here for the diffusion constants which frequently may individually carry some model-related or method-related error as the more complete and consistent set of values providing a correct global picture for self-diffusion in bulk Si. The degree of reliability of present results is summarized in Fig. 3 where the silicon TBMD total self-diffusion coefficient \( D_{SD} = D_I + D_V \) is compared with state-of-the-art experimental data. 2,7 The present numbers should be, therefore, useful in modeling Si bulk processing.

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