# First-Principles Calculations of Self-Diffusion Constants in Silicon

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We report the first parameter-free calculations of self-diffusion constants in silicon. We have computed diffusion constants for the defect-mediated mechanisms using the local-density approximation in combination with *ab initio* molecular-dynamics simulations and obtained the diffusion constant for the concerted exchange mechanism from earlier results by Pandey and Kaxiras. We obtain diffusion constants in the range of the experimental values, with the self-interstitial mechanism dominating over the contribution of the other mechanisms.

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Self-diffusion in silicon has been the subject of intense debate for several decades. Experimental data [1-4] exhibit an Arrhenius behavior

$$D(T)=D_0\exp(-Q/k_BT)\,, \tag{1}$$

with an activation energy $Q$ in the range 4-5 eV and a preexponential $D_0$ that is much larger than typical values for metals. For many years, the debate focused on whether self-diffusion is mediated primarily or exclusively by vacancies ($V$) or self-interstitials ($I$). More recently, the concerted exchange mechanism ($X$) has been suggested as a new contender [5]; experimentally it has not been possible to determine unambiguously the relative importance of the various mechanisms. Theory [5-7] has focused so far on predicting the activation energies $Q$ for the various mechanisms. More recently, the entropy of diffusion, the key quantity in $D_0$, has been calculated for the exchange mechanism [8]. For an unambiguous theoretical determination of the relative importance of the competing mechanisms, however, one has to calculate the complete self-diffusion constants for all of them.

In this paper, we determine for the first time the self-diffusion constants of the two defect-mediated mechanisms from parameter-free, state-of-the-art total-energy calculations. We bring to bear the full power of the Car-Parrinello technique [9], which allows the accurate determination of lattice rearrangements of the point defects and the monitoring of their diffusive motion in real time. The diffusion constant for the exchange mechanism can be determined directly from the activation energy and diffusion entropy calculated earlier by Pandey and Kaxiras [8]. We find that the interstitial-mediated mechanism dominates self-diffusion close to the melting point of silicon. The diffusion constant of the vacancy mechanism is approximately 3 orders of magnitude smaller and that of the exchange mechanism is 4 orders of magnitude smaller.

The diffusion constants of the defect-mediated mechanisms, $D_I$ and $D_V$, can be decomposed into a product of the concentration of native defects ($C_I$ and $C_V$) that are available for self-diffusion, normalized by the concentration of lattice sites $C_s$, and the diffusivities ($d_I$ and $d_V$) of silicon atoms in the presence of one such native defect, which are a measure of the speed of diffusion. The total diffusion constant $D$ arising from all three mechanisms is

$$D=\frac{C_I}{C_s}d_I+\frac{C_V}{C_s}d_V+D_X\,, \tag{2}$$

where $C_s=5\times10^{22}\ \mathrm{cm}^{-3}$ is the concentration of lattice sites in the silicon crystal and $D_X$ denotes the diffusion constant for the exchange mechanism. The concentration of a native defect can be written as

$$C(T)=C_s\exp\left(-\frac{E_f-TS_f}{k_BT}\right). \tag{3}$$

The formation energy $E_f$ is the energy required to create a native defect, and the formation entropy $S_f$ is related to the phase space volume accessible to the defect.

We have calculated energies, entropies, and diffusivities using the density-functional theory in the local-density approximation [10,11], which is the most common framework for state-of-the-art electronic structure calculations. We employ first-principles norm-conserving pseudopotentials [12] together with the Car-Parrinello [9] method, which allows us to determine fully relaxed defect structures and to simulate the dynamics of the defect migration [13]. All calculations have been done with the defects in their neutral charge state and in a constant volume ensemble. Preliminary results have been reported in a conference proceedings [14].

*Calculation of formation energies.*—The formation energies of the native defects have been calculated previously by several authors. However, the values they obtained show a wide spread from 3.5 to 4.0 eV for the vacancy. We have recalculated these values using larger supercells and a more rigorous treatment of atomic relaxations than previously possible. Furthermore, we calculate the formation energies here for both interstitials and vacancies with exactly the same level of accuracy.

In order to obtain the formation energies of the native defects, we first determined their structure. This has been done by minimizing the total energy with respect to all atomic coordinates. In order to assure that the minimum energy has been found, we quenched the system several times during a molecular-dynamics run at a temperature close to the melting point of silicon. The structure of the vacancy is well understood [15,16]. In the neutral charge state it undergoes a Jahn-Teller distortion by forming two pairs out of the four dangling bonds of the vacancy. The self-interstitial has a more complicated structure [6]: a pair of silicon atoms, oriented in the $\langle 110 \rangle$ direction, that occupies a single lattice site. We found zero temperature formation energies $E_f$ of 3.3 eV for the self-interstitial and of 4.1 eV for the vacancy [17].

*Calculation of formation entropies.*—The entropy of formation is the sum of the configurational entropy and the vibrational entropy. The configurational entropy follows from simple geometrical arguments: It is related to the number of ways in which the native defect can be incorporated at one particular lattice site. There are three possible arrangements for the vacancy and six for the self-interstitial, resulting in configurational entropies of $1.1k_B$ and $1.8k_B$, respectively.

More difficult to calculate, and obtained here for the first time, are the vibrational entropies for the two native defects in silicon. The vibrational entropy is a measure of how tightly the native defect is constrained in its equilibrium structure. We have calculated the vibrational entropy in the so-called local harmonic approximation that has been suggested and tested recently by Najafabadi, LeSar, and Srolovitz [18]. This approximation allows one to calculate the entropy as a sum of local (atomic) contributions. Each local contribution is obtained from the curvature of the total energy as a function of the position of a single atom, while the positions of the remaining atoms are kept unchanged. The curvature of the total energy is obtained from twelve distortions for each atom along a starburst mesh. We have included three shells of lattice sites surrounding the defect. We find that the contribution from the local entropies is already converged beyond the second neighbor shell. The vibrational entropies are distributed over a large number of atoms. For the vacancy the first four atoms forming the first shell contribute $0.68k_B$ each; the second shell (twelve atoms) contributes $1.12k_B$. Similarly, the two atoms forming the split interstitial contribute $0.88k_B$ each. The first, second, and third nearest neighbor shells contribute $1.4k_B$, $0.56k_B$ and $0.18k_B$, respectively.

The total entropies of formation, including configurational and vibrational parts, are $6k_B$ for the self-interstitial and $5k_B$ for the vacancy. The resulting concentrations amount to $10^{12}$–$10^{13}$ self-interstitials and $10^8$–$10^9$ vacancies per cm$^3$ at 1000 °C. Even at the melting point we find vacancies about 3 orders of magnitude less frequently than self-interstitials.

*Calculation of the diffusivities.*—The last unknown is the diffusivity of silicon atoms in the presence of one native defect. Diffusivities can also be broken up into energy and entropy contributions. However, because of the complicated structure of the native defects, in particular that of the self-interstitial, we have used the most unbiased approach possible, namely, a direct simulation of the atomic motion via molecular dynamics.

Even though the concentration of defects in our supercell calculation is very high, our simulation corresponds to that of isolated defects. Since in our calculation neighboring defects are correlated by periodic boundary conditions, they have a minimum distance of about 10 Å. At this distance interactions between the periodic images are small so that the motion of isolated defects is observed. During the simulation, the temperature was held constant by a Nosé thermostat [19]. We have used temperatures of 1500 K for the self-interstitial and of 1200, 1400, and 1600 K for the vacancy. After sufficient equilibration of each sample at these temperatures, we have performed simulations up to 20 psec, which corresponds to about 350 phonon oscillations.

In order to obtain the diffusivities $d_I, d_V$, we monitored the mean square displacement of all atoms in the cell and evaluated

$$d = \frac{1}{6} \lim_{t \to \infty} \sum_{i=1}^{N} \frac{|R_i(t) - R_i(0)|^2}{t}, \tag{4}$$

where $R_i(t)$ is the position of the $i$th atom at time $t$. It is noteworthy that the diffusivities of the vacancy and the self-interstitial lie in a very similar range. Their magnitudes are of the order of $10^{-4}$ cm$^2$/sec at the temperatures we have investigated. The calculated diffusivity of the interstitial is consistent with experiments by Griffin *et al.* who have established a lower bound between $10^{-7}$ and $10^{-6}$ cm$^2$/sec at 1500 K [20].

The diffusion process for both the vacancy and the interstitial mechanism typically displaces a different atom with each jump, resulting in reasonable statistics even after short simulation times. The statistical error of the diffusivities affects the diffusion constants by less than a factor of 2 and thus is negligible compared to the uncertainty introduced by the free energy of formation. The error bars quoted here take dynamically correlated events observed in the simulations into account.

We have not attempted to extract the energy of migration from simulations at different temperatures. Because of the exponential decrease of the jump frequency with decreasing temperature, such calculations are feasible only in a small high-temperature region. As a result the error bars in the migration energy would be nearly as large as the calculated values themselves.

*Self-diffusion constants.*—We combine concentrations and diffusivities and obtain the self-diffusion constants shown in Fig. 1. Also shown are the diffusion constants for the exchange mechanism obtained from the activation energy (4.3 eV) and the entropy ($3.3k_B$) reported by Pandey and Kaxiras [5,8,21]. The theoretical self-diffusion coefficients for the interstitial mechanism are in excellent agreement with experiment. We find that the self-interstitial mechanism dominates self-diffusion at high temperatures: The vacancy mechanism contributes about 3 orders of magnitude less, while the exchange mechanism contributes 4 orders of magnitude less than the self-interstitial mechanism.

*Discussion.*—The difference of the self-diffusion constants for the defect mechanisms is mainly due to the different formation energies. The entropies of formation and the diffusivities of the defect-mediated mechanisms, on the other hand, are very similar.

Our findings shed new light onto the so-called entropy puzzle. It has been debated whether a simple defect mechanism can explain the large entropy of diffusion, which is of the order of $10k_B$. Starting with the pioneering work of Seeger and Chik [4], it has been suggested that the defects responsible for diffusion at high temperature are extended over several lattice sites, forming disordered zones with large formation entropies. A detailed microscopic model, however, has not been provided. Our findings show that the simple native defects have entropies of formation of the order of $6k_B$. The diffusion entropy also contains the entropy of migration. Our direct simulations do not break the diffusivities into energies and entropies. However, if we assume a migration energy between 0.7 and 1.5 eV for the self-interstitial, both preexponential and exponential factors are in the range of experimental results.

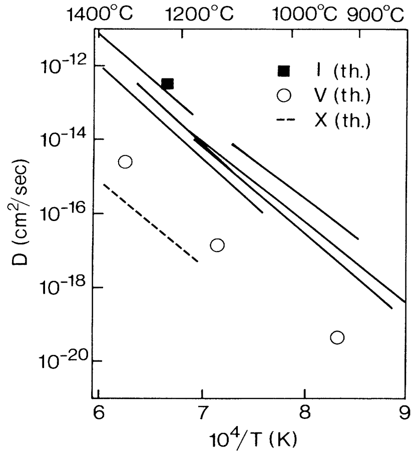

FIG. 1. Calculated self-diffusion coefficients of the three mechanisms contributing to self-diffusion in silicon: the interstitial ($I$), the vacancy ($V$), and the concerted exchange ($X$) mechanism [21]. The experimental self-diffusion coefficients, which are the sum of all three contributions, are represented by lines. The corresponding theoretical number will appear identical to that of the largest contribution ($I$), due to the orders-of-magnitude separation between the individual contributions.

In contrast, the entropy of diffusion for the concerted exchange mechanism, which only contains the entropy of migration, is $3.3k_B$. Even though this may be a lower bound, the defect mechanisms exhibit significantly higher diffusion entropies.

We have carried out an extensive analysis of the error bars of our results. The largest contribution to the diffusion constant is due to the formation energy. The convergence of this quantity has been studied in most detail. The greatest uncertainty comes from the $k$-point sampling; as the number of $k$ points is increased from 8 to 27, the formation energy changes by only 0.09 eV for the self-interstitial and by 0.17 eV for the vacancy. The plane wave convergence error of the formation energies is less than 0.05 eV. Hence, we estimate the absolute convergence error for the energy of formation to be of the order of 0.2 eV or 5%.

It has not been possible to calculate diffusivities and entropies with the most accurate $k$ sampling, and hence a larger relative error is anticipated for those quantities. Entropies and diffusivities can be converted into energies by $F_S = -TS$ and $F_d = -k_B T \ln(d/d_0)$, where $d_0 = l^2 \nu/6$ is given by the bond distance $l$ and the frequency $\nu$ of the optical phonon at $\Gamma$. Since the contributions of vibrational entropy and diffusivity to the free energy (at 1500 K) are much smaller than the formation energy, we expect only a small correction from these terms. Assuming an uncertainty as high as 20%, we arrive at error bars for the free energy of diffusion of 0.1 eV from the vibrational entropy and 0.07 eV from the diffusivity. The statistical error bar of the diffusivities is less than a factor of 2, which translates into an error of 0.09 eV in the free energy of diffusion.

The accuracy of the local harmonic approximation has been tested by performing a fully anharmonic calculation of the formation free energy of the vacancy [22]. At low temperatures (500 K) we find good agreement within the statistical error bars of the anharmonic calculation, which proves the validity of the local harmonic approximation for a material like silicon. At high temperatures (1000 K), however, anharmonicities increase the entropies by $(2\pm1)k_B$ which affects the free energy by 0.26 eV. Similar corrections are expected for the interstitial.

All calculations in this paper have been done for the neutral defects in the electronic ground state. At finite temperatures, excited states and different charge states are also present. The corresponding free energy contribution is

$$F = -k_B T \int_{-\infty}^{\infty} d\epsilon\, \delta D(\epsilon) \ln(1 + e^{-(\epsilon-\mu)/k_B T}),$$

where $\delta D(\epsilon)$ is the vacancy-induced electronic density of states and $\mu$ is the chemical potential, which is assumed to lie at high temperatures in the middle of the gap. We can estimate $\delta D(\epsilon)$ from the experimental ionization energies [23], when the small contributions that are buried in the valence and conduction bands are neglected. It is assumed that the positions of the energy levels relative to the chemical potential do not change with temperature. The resulting correction for the vacancy formation energy is 0.1 eV at 1500 K (compared to 0 K) and the correction for the entropy is $1k_B$. The energy levels of the self-interstitial are not known from experiment and are difficult to establish from theory owing to limitations in the size of the supercell. However, we estimate the electronic contribution to the formation entropy of the self-interstitial to be less than that of the vacancy.

We estimate that the diffusion constants may deviate by approximately 2 or 3 orders of magnitude from our calculated values. Most of the errors in our calculation are of a systematic nature and they behave similarly for both mechanisms. For this reason it is unlikely that they will change the relative contributions of the diffusion mechanisms despite the large error bars on the absolute numbers.

In conclusion, we have calculated for the first time the complete diffusion constants of the two native defect mechanisms, which allows a quantitative comparison of the three primary diffusion mechanisms that contribute to self-diffusion. Our results and analysis suggests that self-diffusion proceeds mainly by an interstitial-mediated mechanism. Our entropies of formation provide a natural explanation for the so-called entropy puzzle.

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