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MICROSCOPIC THEORY OF ATOMIC DIFFUSION MECHANISMS IN SILICON

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Self-interstitials in Si are known to migrate athermally at very low temperatures (~4 K). In contrast, at high temperatures (1100–1600 K), self-diffusion has an activation energy of ~5 eV. We describe results of self-consistent Green's-function total energy calculations which, for the first time, provide detailed microscopic understanding of the mechanisms underlying these phenomena and reconcile the contrasting low- and high-temperature data.

1. Introduction

Atomic diffusion is a fundamental solid-state process which plays a central role in the design of electronic devices. Yet, in semiconductors, especially Si, atomic-diffusion processes are poorly understood. The most fundamental of these processes is self-diffusion, namely the motion of Si atoms in the Si lattice. In this paper we focus on the question of self-diffusion in Si. We review briefly the key experimental information and then present our recent theoretical results [1] which allow us to resolve several existing puzzles and reconcile seemingly inconsistent data.

At low temperatures, irradiation experiments have given valuable information about atomic motion. High-energy electrons create vacancies which have been identified [2]. The vacancy migration barriers were obtained from thermal annealing studies and found to be small and slightly dependent on the charge state (0.2–0.3 eV) [2]. Self-interstitials, on the other hand, have not been detected directly. Instead, after irradiation of Al-doped Si, interstitial Al was detected by electron paramagnetic resonance (EPR) at roughly the same concentration as vacancies. Analogous effects were seen in Ga- and B-doped Si [2]. The conclusion was that self-interstitials in p-type material are highly mobile, since they are able to find and replace the substitutional impurities. Data suggest that this high mobility persists down to 4 K, so that migration is, for all practical purposes, athermal.

At high temperatures (1200–1650 K), self-diffusion measurements using radioactive tracer Si atoms found that the self-diffusion coefficient D is well described by an Arrhenius relationship of the form

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

with Q ranging from 4.1 to 5.1 eV [3–5]. Part of the uncertainty in the value of Q stems from the fact that different types of experiments are used in different temperature regimes. It appears that the high values, closer to 5 eV, are obtained from measurements at relatively high temperatures (1400–1650 K), whereas the smaller values, closer to 4 eV, are obtained from relatively lower temperatures (1200–1400 K) [3–5]. Another notable result of the tracer measurements is that the preexponential D_0 is larger than typical values in metals [3, 4].

Diffusion at high temperatures is generally believed to be mediated by thermally created intrinsic defects. Over the years, there have been advocates of vacancies, divacancies, self-interstitials, etc. [3–5]. No consensus has been achieved, however, because supporting arguments in favor of different mechanisms derive from analysis of indirect experimental observations (e.g. of oxidation-induced stacking faults, gold diffusion, etc.) [3–5] which are also not well understood. Theory has not been particularly

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helpful either, because calculations of the relevant quantities are very difficult. If only one mechanism is active, the diffusion coefficient is given by eq. (1), where

$$Q = H_F + H_M. \tag{2}$$

Here, H_F and H_M are the formation and migration enthalpies, respectively, of the defect mediating self-diffusion. All existing calculations for the vacancy find Q's that are too small (2–3 eV) [3–5]. For the interstitial, existing Q's are either too small (1–3 eV) [3–5] or too large [6]. Similarly, if only one mechanism is active, D_0 is proportional to $\exp(S_F + S_M)$, where S_F and S_M are the formation and migration entropies, respectively. Because D_0 is observed to be large, it has been inferred that the defect or defects mediating self-diffusion must have large formation or migration entropies [3–5].

Before we present our new theoretical results that bear on the issue of self-diffusion, it is useful to inquire what values of individual Q's (i.e., $H_F + H_M$) would be consistent with the experimental observations. It is possible that two or more mechanisms are active simultaneously and the sum of two terms like eq. (1) still appears to have the form of a single exponential in the temperature range of the observations. We have explored this possibility and found that a number of mechanisms with Q's ranging between roughly 4 and 6 eV can give rise to a curve that is consistent with observations. As an illustration, in fig. 1 we show the result of two mechanisms having $Q = 4$ and 6 eV, respectively, and preexponentials in a ratio of 5:1. We see that a slope of 5 eV results for most of the temperature range of interest, except for an upturn toward smaller slopes at low temperatures. A collection of the experimental data suggests that the self-diffusion activation energy Q in Si behaves in just this manner [3].

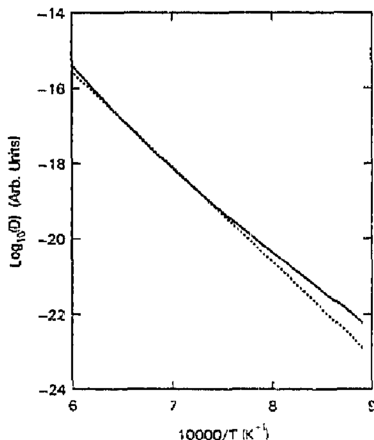

Fig. 1. Logarithmic plot of $D_{eff} = D_1 \exp(-Q_1/kT) + D_2 \exp(-Q_2/kT)$ with $Q_1 = 4$ eV and $Q_2 = 6$ eV and $D_2 : D_1 = 5:1$ (solid line), compared with a plot of $D = D_0 \exp(-Q/kT)$ with $Q = 5$ eV (dashed line) demonstrating that two terms may appear as a single exponential in a given temperature range.

2. Theory

Green's-function methods were shown in the last six years [7, 8] to be very powerful in treating isolated point defects in infinite host crystals, without the limitations imposed by cluster or supercell approximations. Until recently, it was possible to calculate only the charge densities, single-particle energy levels and wavefunctions. We have now extended this development to allow the calculation of total energies for various atomic arrangements [9]. We use density functional theory and the local-density approximation with norm-conserving pseudopotentials [10]. We reproduced the single-particle energy levels obtained by earlier Green's-function calculations [7, 8] and carried out a series of tests specifically designed to check the accuracy of the total-energy results [11]. The main result of technical significance is that, for accurate total-energy calculations, it is necessary to retain basis orbitals on considerably more shells of atoms than is needed if one is only interested in single-particle energy levels. For example, for the relaxed vacancy, it was necessary to retain orbitals on 46 atoms (five shells of atoms around the central site), which corresponds to having orbitals on the

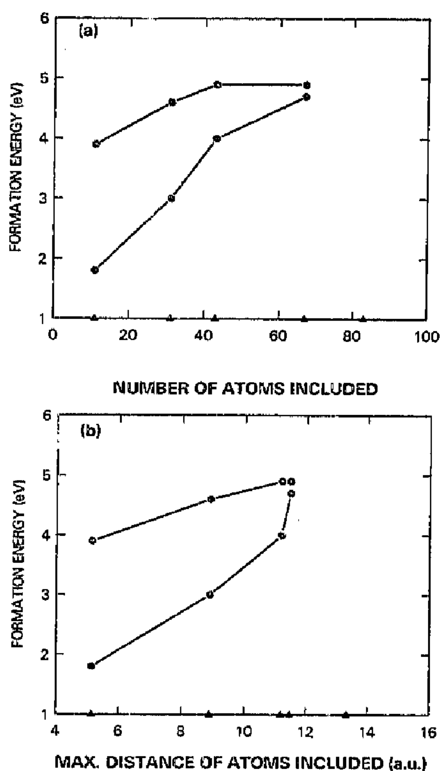

Fig. 2. Calculated formation enthalpy for a self-interstitial in Si at the tetrahedral site as a function of (a) the number of atoms and (b) the radial distance of atoms on which basis orbitals are retained. In each case, the two curves correspond to two different expressions for the total energy, as discussed in ref. 11. The triangles mark complete shells of atoms.

first and second neighbors of each displaced atom. For the self-interstitial at the tetrahedral site, without any lattice relaxation, the convergence rate is shown in fig. 2, where the upper curve refers to the total-energy calculated using the eigenvalue expression and the lower curve to the total-energy obtained with the kinetic-energy expression [11].

All the total-energy results described in this paper were obtained by allowing the nearest neighbors to relax to their optimum position. Long-range lattice relaxation was included by the semiempirical Keating model [12, 13]. The overall uncertainty in the calculations ranges from 0.5 to 1 eV and arises primarily from limitations imposed by computer capacity.

3. Results

The main results of our calculations are described in ref. 1. We summarize them here and discuss briefly how they relate to the experimental data mentioned in the Introduction. Our results for the formation enthalpy of the vacancy (V) are shown in fig. 3a. This figure reflects the well-known negative-U properties of the vacancy, namely that V^+ is not the equilibrium charge state for any Fermi-level position [13, 14]. Fig. 3a looks somewhat different from the figures in Ref. 12, because it incorporates the fact that the formation energy of a neutral vacancy does not depend on the Fermi energy, since no electron transfer to or from it occurs. For our purposes here, the most significant result is that

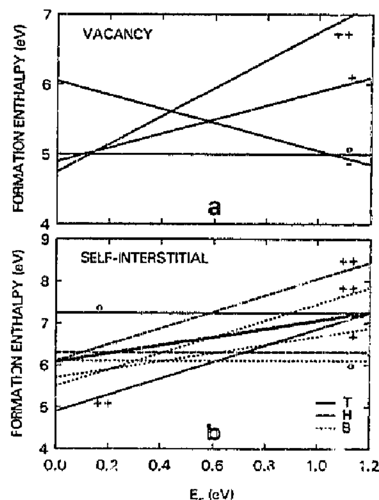

Fig. 3. Calculated formation enthalpies of various charge states of (a) the vacancy; and (b) the self-interstitial at three different sites (see fig. 4) in Si.

the formation enthalpy is large, of order 5 eV for all charge states [15]. This is a rather novel result and provides a natural connection with the low-temperature annealing data according to which the vacancy migration energy is small, 0.2–0.3 eV. Using this migration energy (computer capacity did not allow us to obtain a reliable theoretical migration energy), the resulting Q for self-diffusion is within the experimental range. In contrast, earlier estimates of Q for the vacancy were small (of order 2–3 eV), leading to the need to postulate a much larger migration enthalpy at high temperatures. The large values of the vacancy formation enthalpies resulting from our calculations may raise concern about the resulting concentrations, if comparisons are to be made with estimates extracted from quenching experiments [16]. However, concentrations depend on both formation enthalpy and formation entropy. Lannoo and Allan [17] recently carried out semi-empirical calculations of the vacancy formation entropy and found that it can be quite large. We should point out, however, that we are unable at present to calculate the formation enthalpy of rebonded models of the vacancy in the spirit of rebonding known to occur on surfaces [18]. Rebonded or 'extended' vacancies may have smaller formation enthalpies and larger migration enthalpies with a net Q still of order 5 eV. If that were to occur, both simple and rebonded vacancies would mediate self-diffusion.

Our results for the self-interstitial (I) reveal a very rich structure. In search of the equilibrium configuration, we investigated several sites, illustrated schematically in fig. 4. Our results for three sites are shown in fig. 3b. We see that the self-interstitial, just like the vacancy, exhibits *negative-U* properties in the sense that I^{+} is not the equilibrium charge state for any Fermi-level position. Note, however, that the negative-U property is now accomplished by motion of the interstitial to different sites as the charge state changes. Such charge-state instabilities underlie athermal migration according to the Bourgoin–Corbett mechanism [19]. In this particular case, in p-type Si, the equilibrium site is the T site, where the interstitial is in the 2^{+} charge state and has an empty localized state of T_2 symmetry at

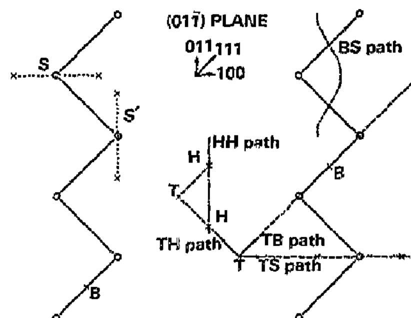

Fig. 4. Schematic definitions of several configurations of the self-interstitial in Si. T: Tetrahedral site; H: Hexagonal site; B: Bond-centered site; S: (100) split configuration; S': (110) split configuration. In the calculations, the lattice around the interstitial is allowed to relax. Several paths are defined by the sites involved: TH is a path in the low-density channels, as is the HH path. The TBTH path combines three high-symmetry sites and corresponds to motion along a (111) direction involving continuous exchange with atoms at lattice sites. The TS path corresponds to motion along a (100) direction, also involving continuous exchange with atoms at lattice sites. The BS path is a simple path with the extra atom winding through the bonds as proposed in ref. 23. Other possible paths, not shown, are TS' and BS', both of which are interstitialcy paths.

just about the conduction-band edge. Capture of one or two extra electrons makes the center unstable against Jahn–Teller distortions. Motion away from the T site results in a splitting of the T_2 state, lowering of one component into the gap, and a linear gain in energy. On the basis of this notion, we constructed a theory of carrier-capture-enhanced and athermal migration which allows us to draw total-energy curves between high-symmetry sites and to determine when athermal migration is possible [20]. We found that athermal migration is just barely possible along the TH path (fig. 4), which was proposed in ref. 21 and supported by ref. 22. Athermal migration is possible along the TB and TBTH paths (fig. 4), and likely along the TS path (fig. 4). The total-energy curves for the TH, TB and TBTH paths are shown in fig. 5. Athermal migration is not, however, possible along the BS path as proposed in ref. 23. We were unable to

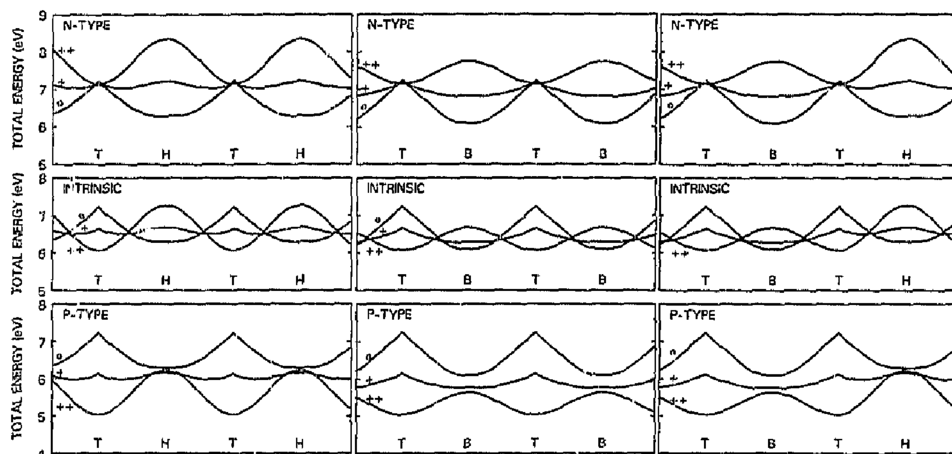

Fig. 5. Total-energy curves for three different charge states of the interstitial along three different paths for three different Fermi levels.

explore the TS′ path because of the low symmetry of the S′ configuration.

According to fig. 5, athermal migration is also possible in intrinsic and n-type material, but the final product of such migration has not been identified [2]. We note, however, that, in n-type material, a Si atom starting at an H site would most likely skip the high-energy T site and move in the channel along a relatively straight path (shown as HH in fig. 5), as envisioned in ref. 21.

Finally, we turn to the high-temperature self-diffusion regime where the Fermi level is, for most doping levels, in the midgap region. Fig. 5 reveals that just about all the charge states exist at several sites with roughly the same formation enthalpy and that migration energies are very small. For self-diffusion, however, one needs paths that involve exchange with atoms at lattice sites, such as the TB, TBTH, TS, and TS′ paths. We have named such paths *interstitialcy paths* since they contribute to self-diffusion via the interstitialcy mechanism. Other paths, such as the TH and BS paths, are referred to as *simple paths.* When combined with interstitialcy paths, simple paths can augment self-diffusion. As fig. 5 reveals, self-interstitials contribute to self-diffusion with effective Q's of order 6–6.5 eV, which, in view of the theoretical uncertainty, overlaps the range of observed values.

As in the case of the vacancy, the large formation energy and small migration energy for the interstitial is quite novel. It provides a natural explanation for the contrasting low- and high-temperature data: At low T (~4 K), self-interstitials are created by irradiation. The small migration barriers are then required for athermal migration. At high temperatures, self-diffusion is limited primarily by the need to create self-interstitials thermally. On the other hand, as in the case of the vacancy, the large formation enthalpy may raise concerns about the net concentration of self-interstitials. In this case, there is no information from quenching measurements, but the large value observed for D_0 suggests large formation and/or migration entropies. Large entropy can arise from the multitude of configurations and charge states of the self-interstitial with roughly the same formation enthalpy. We note that this result is reminiscent of the proposal [3] that the self-interstitial exists in 'extended' forms, a notion that was introduced in order to account for the large preexponential in

terms of configurational entropy. Our calculations provide explicit descriptions of the various configurations of the self-interstitial and also provide detailed motional models, which are lacking in the discussions of 'extended' forms [3]. Again, however, as in the case of the vacancy, our results do not rule out the possibility of more extended and rebonded forms of the self-interstitial, which may have smaller formation enthalpies, larger migration enthalpies, and still contribute to self-diffusion with roughly the same activation energy Q.

4. Conclusions

In this paper we described briefly some of the main results of extensive self-consistent Green's-function total-energy calculations whose objective was to elucidate the microscopic mechanisms of the self-interstitial's low-temperature athermal migration and of high-temperature self-diffusion in Si. These results provide a new set of ideas in terms of which to understand these processes. They have significant consequences for the interpretation of several experiments, including impurity diffusion, oxidation-induced stacking faults, etc. [3]. Such experiments have been interpreted on the basis of qualitative assumptions about formation enthalpies and entropies, including oversimplified assumptions about the energy-level structure of the self-interstitial [3, 24], and various assumptions about other, unrelated phenomena. Conclusions based on such analysis may, as a result, appear in conflict with our results. It is necessary at this point to reexamine the original data and compare them directly with the new quantitative results, unhampered by extraneous assumptions. Such analysis of available experimental data will be reported elsewhere.

Acknowledgement

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