MICROSCOPIC THEORY OF SELF-DIFFUSION AND IMPURITY DIFFUSION IN SILICON

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Summary

We review briefly our recent calculations of formation and migration energies of vacancies and self-interstitials which led to the following: The self-interstitial can migrate athermally, in agreement with data, along several paths. The observed high-temperature self-diffusion activation energy can be accounted for in terms of both the vacancy and interstitial mechanisms, without the need to invoke a change in the nature of intrinsic defects as a function of temperature. In addition, we report new results on the energetics of dopant impurities (Al and P). We find that the diffusion mechanism of these impurities involves both vacancies and self-interstitials and is considerably more complex than the corresponding self-diffusion mechanisms.

in Proceedings of the 13th International Conference on Defects in Semiconductors
San Diego 1985,
Journal of Electronic Materials **14a**, 269-275 (1985).

The mechanisms of atomic diffusion in Si have been the subject of major controversies over the last 15 years. Many of these controversies arose because experimental measurements of some of the key quantities have not been possible. In contrast, many conclusions were drawn on the basis of indirect evidence whose interpretation depended strongly on assumptions made about related phenomena(1). In addition, reliable theoretical calculations of the key quantities were not available.

It is generally believed that, at high temperatures, atomic diffusion is mediated by thermally created intrinsic defects (vacancies, self-interstitials, etc.). Thus, the main quantities of interest are formation and migration energies and entropies of intrinsic defects. For example, if only one defect species mediates self-diffusion, the self-diffusion coefficient D_o is given by

$$D_{SD} = D_o \exp\left(- Q_{SD}/kT\right), \tag{1}$$

where Q_{SD}, the self-diffusion activation energy, is given by

$$Q_{SD} = H_F + H_M, \tag{2}$$

where H_F and H_M are the formation and migration enthalpies, respectively, of the defect. The preexponential D_o is proportional to $\exp(S_F+S_M)$, where S_F and S_M are the formation and migration entropies, respectively, of the defect in units of k, the Boltzman constant. In such a mechanism, self-diffusion proceeds as follows: A marked Si atom (e.g., a radioactive isotope) occupying a normal atomic site waits until a thermally created defect (e.g., vacancy or self-interstitial) comes to a nearby site and helps it make a step to a new atomic site. The defect then goes on its way and the marked atom waits for another defect to come along. The same mechanism in principle operates for substitutional impurities. It is straightforward to conclude that, if that were the case, the activation energy for impurity diffusion in Si would be the same as that of self-diffusion. Self-diffusion activation energies extracted from different experiments range between 4.1 and 5.1 eV, whereas shallow-impurity activation energies are typically smaller, ranging between 3.5 and 4.2 eV (Refs. 1 and 2).

Over the years, the main debate has been over the identity of the defects mediating diffusion. There have been advocates of vacancies, divacancies, "extended" vacancies, "extended" interstitials, etc. The suggestion that the defects mediating diffusion are "extended", i.e., an amorphous region containing either less or more atoms than normal, was motivated by the observation that the preexponential of the self-diffusion coefficient in Si is substantially larger than corresponding values in simple metals(1). Such extended defects would have a large number of equivalent configurations and, thus, large formation entropy. No motional models for such defects have, however, been proposed.

Low-temperature experiments have provided valuable information about the migration energies of vacancies and self-interstitials by creating these defects by electron irradiation(3). It was found that vacancies have a migration enthalpy of about 0.2 to 0.3 eV, depending on the charge state, whereas self-interstitials migrate completely athermally. No reliable experimental information was available for formation enthalpies, however. Simple theoretical estimates suggested formation enthalpies of order 2-3 eV for the vacancy (quoted in Ref. 2) and of order 1 eV (quoted in Ref. 2) or 10 eV (Ref. 4) for the self-interstitial. Thus, no consistent description of low- and high-temperature data emerged. The general belief has been that formation and migration enthalpies depend strongly on

temperature or the defects actually change from simple defects at low temperatures to "extended" defects at high temperatures with very different formation and migration enthalpies.

We recently published(5) the first parameter-free calculations of formation and migration energies of vacancies and self-interstitials in Si in terms of which we provided a detailed description of self-diffusion and reconciled the seemingly inconsistent low- and high-temperature data. In this paper, we update our theoretical results on the vacancy and self-interstitial formation enthalpies and review our main results regarding the low-temperature migration properties of the self-interstitial and high-temperature self-diffusion. We also report new results on impurities which allow us to provide a unified description of atomic diffusion in Si at both low and high temperatures.

Our calculations were performed using a self-consistent Green's-function scheme for total energies of defects(6) within the local-density approximation of density functional theory(7). The scheme is based on the Green's-matrix formulation of Williams, Feibelman and Lang(8) which is particularly suitable when atoms are displaced from lattice sites. We use norm-conserving pseudopotentials(9). to treat core effects. Long-range lattice relaxation is included via the Keating model(10). The scheme is parameter-free and allows us to obtain total energies of defects with the same accuracy as perfect-crystal and surface calculations.

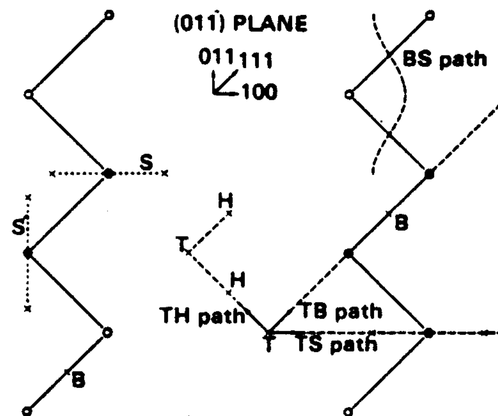

Fig. 1. Interstitial sites and paths shown schematically in one of the (110) planes. Lattice relaxations are not shown.

Before we discuss our results on atomic diffusion, we review briefly previous theoretical results about the migration properties of the self-interstitial in Si. Early semiempirical calculations(11) had suggested that the bond-centered (B) and split-interstitial (S) configurations (see Fig. 1) had the lowest energy and that the BS path was likely to support athermal migration. More recent semiempirical calculations(12) led to the suggestion that the HS path may support athermal migration in p-type material. In 1982, Pantelides et al.(13) reported parameter-free calculations of the energy-level structure of the self-interstitial at the T site (Fig. 1) and combined them with other arguments to suggest that the TH path is the more likely candidate for athermal migration. This suggestion was corroborated by the calculations of Baraff et al.(14) who found that electron capture lowers the TH barrier substantially. Definitive evidence was first obtained by Bar-Yam and Joannopoulos(15) who calculated the actual barrier along TH and found that

capture of two electrons allows the interstitial to overcome this barrier athermally. They also found that the B and S configurations are unstable against decay in the channels and concluded that the BS path does not support athermal migration. They did not discuss any other paths involving the sites studied.

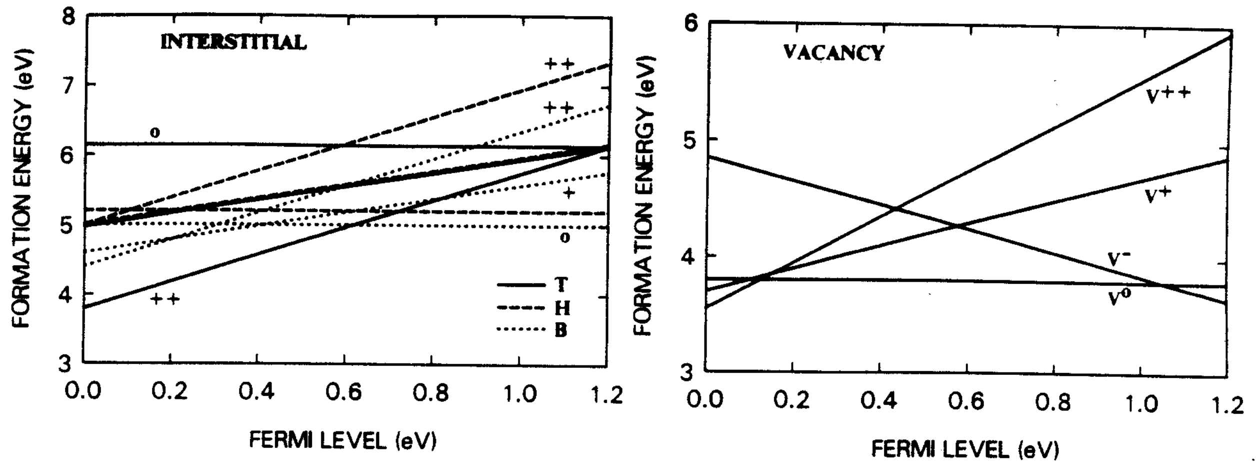

Fig. 2. Formation enthalpies of the self-interstitial (three charge states of three configurations) and the vacancy (four charge states), as in Ref. 5, updated by calculations using more flexible basis sets.

We now review our results and conclusions(5) for the self-interstitials (I). We investigated the various configurations illustrated in Fig. 1 and sought to determine the configuration with the lowest enthalpy. Our results revealed a remarkable richness in the structure and the possible migration paths of the self-interstitial. The formation enthalpies for various charge states of the self-interstitial in the T, H and B configurations are shown in Fig. 2a as functions of the Fermi-level position (E_F) in the gap. The formation enthalpy of the split interstitial (S), for which it was not possible to obtain a fully optimised result, lies somewhat higher in energy (approximately 1 eV above the B configuration) and it is not shown in the figure. Fig. 2a reveals that very different interstitial configurations involving different lattice relaxations have roughly the same formation enthalpies of about 4 to 6 eV. The figure also reveals that the stable charge state is either I^{++} or I^{o}, depending on the value of E_F, but never I^{+}. In other words, the self-interstitial is a negative-U center(5).

By applying a simple theory which is described in detail in Ref. 16, we obtain the variation of the total energy for the different charge-states of the self-interstitial along various paths connecting the high-symmetry configurations, as shown in Fig. 1. Note that the linear drop in the energy of I^{+} and I^{o} near the T sites is a result of Jahn-Teller instability that sets in after I^{++}(T) captures one or two electrons. We distinguish two types of paths(5): **Simple paths,** such as the TH and the BS paths, do not involve exchange with atoms at lattice sites. **Interstitialcy paths,** such as the TB or the TS paths, involve exchange with atoms at lattice sites. The calculated total energy of the self-interstitial along the TH, the TB, and the combined TBTH paths is shown in Fig. 3 for different Fermi-level positions and different charge-states. We see that, in addition to the TH path(12-14), the TB, TBTH, and possibly the TS(5) paths support athermal migration via the Bourgoin-Corbett mechanism(17) and explain the experimental results in irradiated p-type Si at low temperatures(2). More recently, Bar-Yam and Joannopoulos(18) gave a detailed description of their work on the TH path and

subsequently reported(19) extensive studies of the barriers along the TB, TS, and a path involving a novel configuration akin to the (110) split interstitial. All paths were found to support athermal migration in the presence of excess electrons and holes, and the negative-U character(5) of the self-interstitial was preserved.

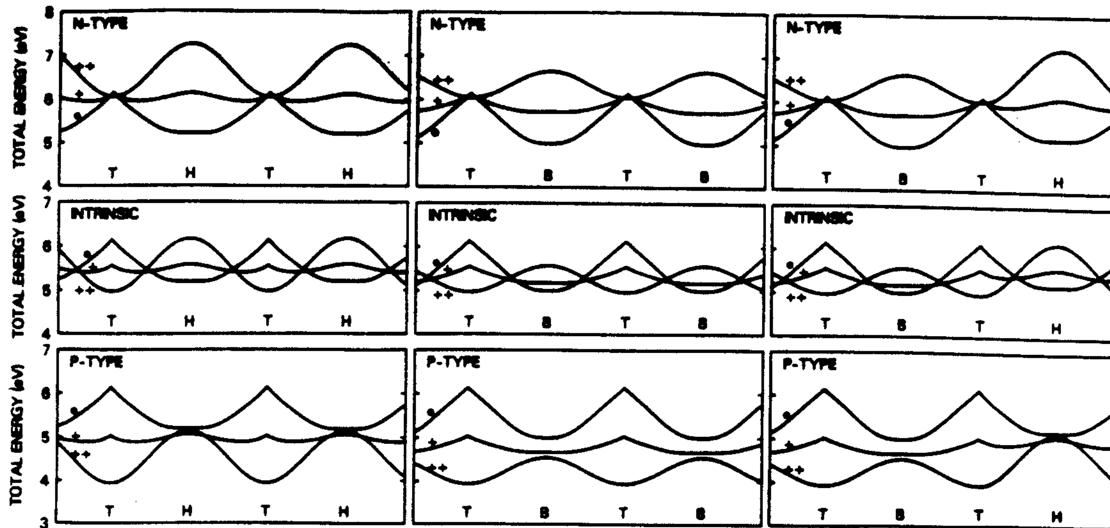

Fig. 3. The total energies of I^{++}, I^{+}, and I^{0} along three different paths, as in Ref. 5, except for the updated values (Fig. 2) above.

We turn now to the high-temperature regime where diffusion is activated by intrinsic defects that are produced thermally. We note that interstitialcy paths, as defined above, are necessary for self-diffusion. In the self-diffusion temperature range, E_F remains at roughly midgap for most doping levels so that the relevant activation energy for the TB path in Fig. 3 is ~5.4 eV, i.e., within the range of values extracted from experiment(1). Within the theoretical error bar, the TS path also contributes to self-diffusion with roughly the same Q. Finally, we note that interstitial diffusion via simple paths also has roughly the same activation energy as the TB and TS paths, and thus augments self-diffusion. The important conclusion is that many different configurations of the self-interstitial with varying degrees of lattice distortions contribute to self-diffusion with roughly the same activation energy, suggesting a high activation entropy, in agreement with the experimental findings(1).

We address now the question whether vacancies also contribute to self-diffusion. The results for the formation enthalpy of four charge states of the vacancy are displayed in Fig. 2b. When the Fermi level is at midgap, the neutral vacancy has the lowest formation energy. If we combine the formation energies of Fig. 2 with the experimentally observed migration energy for the vacancy, i.e. ~0.3 eV (Ref. 2), we obtain activation energies ranging between 4 and 5 eV. As in Ref. 5, we conclude that vacancies also contribute to self-diffusion with activation energies within the range of observed values. The relative contributions of the various charge states of the two defects depend on their respective entropies of formation which cannot be calculated reliably at present.

We note that our results(5) for both the vacancy and the self-interstitial provided, for the first time, a consistent description of both the low- and high-temperature data without having to invoke a change in the nature of intrinsic defects as a function of temperature. At low T, intrinsic defects created by irradiation are very mobile. In particular, self-interstitials may migrate athermally because the barriers are small and can be overcome by carrier capture. At high T,

self-diffusion is limited primarily by the need to create the intrinsic defects that are needed to mediate migration of Si atoms at lattice sites. These results establish that both low- and high-temperature data can be accounted for without the need to invoke a change in character of vacancies and/or self-interstitials, i.e., postulate that these defects assume an "extended" form at high temperatures, as discussed in Ref. 1.

We turn now to the question of substitutional group-III and group-V impurity diffusion. As we noted already, if the vacancy and the interstitialcy mechanisms described above for self-diffusion were also the dominant mechanisms for impurity diffusion, the activation energy for impurity diffusion would be the same as that for self-diffusion. In contrast, experiments reveal that impurity diffusion activation energies are smaller than the self-diffusion activation energy by about 1 to 1.5 eV. We have performed total energy calculations(20) for the complex consisting of a P or a Al substitutional impurity plus a neighboring vacancy or self-interstitial. In all cases we found a sizeable binding energy for the defect pair. If this binding energy is sufficiently large to overcome the possible increase in migration energy due to the fact that a pair rather than a simple defect has to move through the lattice, then the activation energy for impurity diffusion by pair migration will be smaller than that for self-diffusion, as observed. We have therefore investigated two possible motional models for intrinsic defect-impurity pairs.

One model is a vacancy mechanism that was already suggested many years ago by Watkins and Corbett(21). It consists of a vacancy bound to a substitutional impurity at a neighboring lattice site. This vacancy may jump to a different site neighboring the impurity site by moving along a hexagonal ring of the diamond lattice. The vacancy remains bound to the impurity all along this motion. In the final step the vacancy may exchange site with the impurity. The net result of this complex motional mechanism is that the vacancy-impurity pair as a whole has moved by a distance of the order of one bond length, performing an elementary step of the diffusion process. The migration energy for the vacancy-phosphorus pair (the so-called E center) has been determined experimentally to be $\sim$1 eV (Ref. 21). Since we obtain a binding energy of $\sim$1.8 eV for the neutral defect pair in intrinsic silicon, we obtain a reduction of $\sim$1 eV with respect to the vacancy mechanism for self-diffusion. We find similar reductions for the other charge states.

The second motional model for impurity diffusion that we have considered is a new interstitialcy model. The substitutional impurity first binds with a self-interstitial at a T site. The self-interstitial then pushes the impurity to a neighbouring lattice site and takes its place while the impurity pushes the other Si atom into a T site. This new self-interstitial then swings around in the channel to a different T site "behind" the impurity, so as to repeat the whole process with the impurity moving along the chain of normal atomic sites. In this model, the impurity goes through a bond-centered configuration, but never goes into the channel. We note that the impurity-interstitial pair never dissociates completely, so that we can view the entire process as a diffusion of an interstitial-impurity pair, similar to the case of a vacancy-impurity pair discussed above. We have calculated the binding energy of the pair for various configurations (T, B, and H) and, for the two cases of Al and of P in intrinsic silicon, we have found a diffusion activation energy smaller than the self-diffusion activation energy by $\sim$1.5 and $\sim$0.5 eV, respectively. In addition, we have investigated the possibility of having thermally

generated self-interstitials replace substitutional Al atoms and find that such a process also contributes to Al diffusion with a similar activation energy. We conclude that, as in the case of self-diffusion, a vacancy and an interstitialcy mechanism are both acting at the same time to mediate impurity diffusion. This is in agreement with recent experimental findings according to which these impurities diffuse via both vacancies and self-interstitials(22). A more complete account of our impurity diffusion results will be given in a future publication(20).

In conclusion, we have given a unified description of the microscopic mechanisms for atomic diffusion in silicon, which is able to account for the experimental data at low and at high temperatures for both silicon and impurity atoms. This description elucidates the fundamental role played by vacancies and self-interstitials in mediating atomic motion in a crystal like silicon.

Acknowledgement: This work was supported in part by ONR under contract No. N00014-80-C-0679.

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