ATOMIC DIFFUSION IN SILICON

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We present a unified description of atomic diffusion processes in silicon, based on the results of parameter-free total-energy calculations. A consistent interpretation of both low- and high-temperature data is provided without the need to invoke a change in the nature of intrinsic defects as a function of temperature. The self-interstitial has negative-U properties and can migrate athermally via the Bourgoin-Corbett mechanism along several paths. Both vacancies and self-interstitials mediate self-diffusion with activation energies within the range of observed values. Both intrinsic defects also mediate the diffusion of impurities such as Al and P, but the detailed mechanisms are considerably more complex than those of self-diffusion.

I. INTRODUCTION

Atomic diffusion is an important solid-state process that is poorly understood in semiconductors, especially Si.[1,2] We distinguish two general types of atomic diffusion: Diffusion of atoms that normally occupy substitutional sites (e.g., Si atoms in Si, i.e., self-diffusion, and substitutional impurities such as P, Al, etc.), and diffusion of atoms which either normally occupy interstitial sites or have been dislodged from normal lattice sites by electron irradiation or some other means. Self-diffusion and substitutional-impurity diffusion are generally believed to be mediated by thermally created intrinsic defects such as vacancies, self-interstitials, etc., but no consensus has been achieved so far about either the nature of these defects or the details of the diffusion mechanisms.

During the last few years, a number of groups have developed and implemented practical methods for parameter-free calculations of the key quantities that underlie the interpretation of diffusion data, namely equilibrium configurations of defects, lattice relaxation, formation and migration energies, barrier changes caused by carrier capture, etc.[3-10] Results of these calculations have led to new insights regarding atomic migration and diffusion processes in Si, detailed answers to long-standing questions, and the reconciliation of seemingly inconsistent data. In this paper, we will review briefly the relevant experimental data and the interpretations proposed prior to the advent of parameter-free calculations, describe the new advances achieved with the use of parameter-free calculations (published or received in preprint form prior to this conference), and report new results regarding the high-temperature diffusion of dopant impurities in Si. We, thus, arrive at a unified description of high-temperature self-diffusion and impurity diffusion, and the low-temperature migration of interstitial atoms.

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II. BRIEF REVIEW OF EXPERIMENTAL DATA

At low temperatures (<70 K), experimental data are available for vacancies and self-interstitials created by electron irradiation.[11] Vacancies created in this way have been identified and their migration barriers have been found to be small, 0.2 to 0.3 eV, depending on the charge state. Self-interstitials, on the other hand, have not been detected directly, but experimental data on p-type Si at very low temperatures (~4 K) strongly suggest that self-interstitials migrate athermally.[11] Bourgoin and Corbett[12] suggested that athermal migration may proceed by successive capture of an electron and a hole, which can provide the energy to overcome a small barrier, but the path for such migration could not be determined. Semiempirical calculations[13] considered two paths, shown in Fig. 1 as TH (involving the tetrahedral and hexagonal sites) and BS (involving the bond-centered and split configurations), and concluded that the latter is far more likely to support athermal migration.

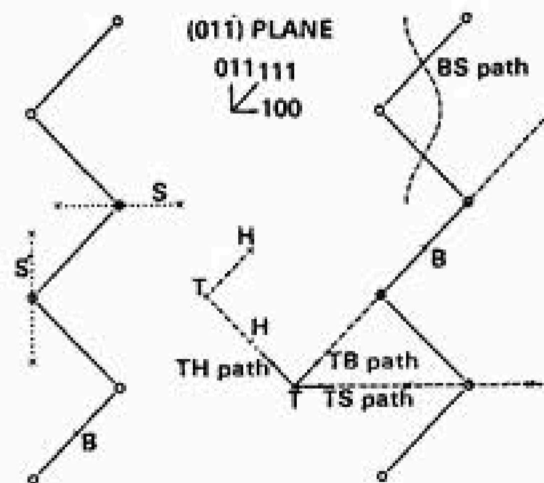

Fig. 1. Interstitial sites and paths shown schematically in one of the (110) planes. Lattice relaxations are not shown.

At high temperatures (1100-1650 K), experiments using radioactive Si isotopes as tracers 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.[1,2] In addition, D_0 was found to be substantially larger than corresponding values in metals.[1,2]

If there is a dominant intrinsic defect mediating self-diffusion, Eq. (1) holds and the activation energy Q is given by

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

where H_F and H_M are the formation and migration enthalpies of the defect. In addition, D_0 is proportional to $\exp(S_F+S_M)$, where S_F and S_M are the formation and migration entropies of the defect. If several defects are active, D is given by a sum of terms such as Eq.(1).

As we just saw, migration energies for vacancies and interstitials were measured at very low temperatures and found to be quite small (0-0.3 eV). These values suggest that, if either of these defects mediates self-diffusion, its formation energy must be large,[11] of order 5 eV. The formation and migration energies of vacancies and self-interstitials have not, however, been determined unambiguously in the self-diffusion temperature regime.

Instead, a number of indirect observations led to the general belief that, whatever the intrinsic defect mediating self-diffusion, its formation and migration energies are of the same order of magnitude (2-3 eV). This belief was corroborated by semiempirical estimates of about 2.5 eV for the vacancy formation energy.[1,2]

The observed large entropy of self-diffusion led to the suggestion that the defect or defects mediating self-diffusion are either "extended" vacancies or "extended" interstitials,[1,2] i.e., amorphous regions containing one less or one more atom. No motional models for such "extended" defects have been proposed, but the suggestion[14] that such amorphous regions might move with an activation energy of about 2.5 eV (equal to the activation energy for the motion of an amorphous-crystalline interface) further strengthened the notion that formation and migration energies are comparable at high temperatures.

The field of impurity diffusion is too broad to cover thoroughly. We, therefore, restrict our attention to group-III and group-V dopants which normally occupy substitutional sites. At low temperatures ($<$100 K), after electron irradiation, some of these impurities (e.g., Al, B) have been studied at interstitial sites and their activation energy for migration (of order 1 eV) has been found to become even smaller upon injection of excess carriers.[15,16] At high temperatures ($>$1000 K), the diffusion activation energy of these impurities has been measured to be between 3 and 4 eV, i.e., approximately 1 eV smaller than the activation energy of self-diffusion. As in the case of self-diffusion, the main debate has been over the nature of the intrinsic defect mediating diffusion without much attention paid to motional models. Indirect observations have been interpreted to suggest one or the other defect.[1,2]

The polarization over whether vacancies or self-interstitials mediate self-diffusion and impurity diffusion in Si continues quite strong, even though the belief that both probably contribute, perhaps at different temperature regimes, seems to be gaining ground.[1,2]

III. RECENT ADVANCES BASED ON THEORY

1. Self-Interstitial Migration at Low Temperatures.

In 1982, parameter-free calculations of the energy-level structure of the Si self-interstitial (I) at the tetrahedral site led Pantelides, Ivanov, Scheffler and Vigneron[17] to challenge the long-standing result that Bourgoin-Corbett-type athermal migration proceeds along the BS path and to present arguments in favor of the TH path. Independent results by Baraff, Schluter and Allan[4] supported this suggestion: These authors concluded that capture of two electrons by a self-interstitial would lower the TH barrier by about 2 eV, but the initial barrier was not calculated. Definitive evidence for the TH path and against the BS path was provided by Bar-Yam and Joannopoulos[7] who reported the first parameter-free total-energy calculations for the four relevant sites (T, H, B, and S) and for other points along the TH path. They found that, for the TH path, the initial barrier for I^{++} is about 1.4 eV and that capture of two electrons enables the interstitial atom to overcome this barrier athermally. They also found that the B and S configurations are completely unstable against decay into the channels and concluded that the BS path is not realizable. They did not discuss any other paths involving the four sites for which calculations were carried out.

Car, Kelly, Oshiyama, and Pantelides[8] subsequently reported independent parameter-free total-energy calculations[18] for the same four sites (T, H, B and S) and concluded that the self-interstitial has a very rich structure and that the four high-symmetry configurations

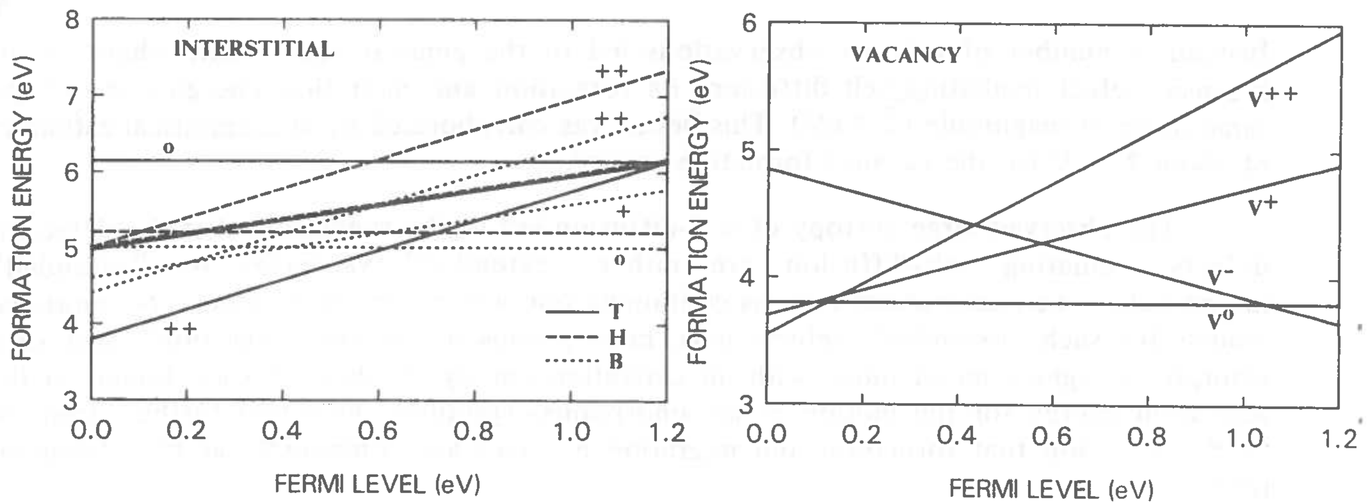

Fig. 2. Formation enthalpies for the Si self-interstitial at three different configurations and three different charge states as a function of the position of the Fermi level in the energy gap. Shown also are the formation enthalpies of the vacancy in four charge states. From Ref. 8, updated here by calculations using more flexible basis sets.

define several paths that may support athermal migration. They noted that, in order to determine which path or paths actually support athermal migration, it was necessary to determine the equilibrium site and charge state and then consider paths emanating from it. By examining the formation energies of the four configurations in three charge states (++, + and neutral), they concluded that the self-interstitial, just like the vacancy,[19] has the remarkable negative-U property: For all positions of the Fermi level in the energy gap, the stable charge state is either ++ (at the T site) or neutral (at the B or H site), never + (Fig. 2). Thus, migration paths must involve the T site in p-type Si and the B or H site in n-type Si (the B and H sites are degenerate within the uncertainty of the calculation). Car et al.[8] also pointed out that there can be two kinds of paths: **Simple paths,** such as the TH or BS paths, considered by all earlier theories, which involve motion of only one atom, but also what were called **interstitialcy paths,** which involve constant interchange between the interstitial Si atom and Si atoms at normal atomic sites. Such paths are, for example, the TS path which involves two-atom exchanges and the TB path which involves three-atom exchanges. The total-energy curves for the TH,[20] TB and the combined TBTH paths are shown in Fig. 3. These curves and similar curves for the TS path demonstrate that athermal migration according to the Bourgoin-Corbett mechanism occurs along these paths. They also reflect another feature of the self-interstitial noted in Ref. 8: Upon capture of one or two electrons at the T site, a Jahn-Teller instability sets in because of the triply degenerate level occupied by the extra electron(s). As a result, the total-energy curves have a linear slope indicating that athermal migration induced by electron capture is further driven by a Jahn-Teller instability. The actual curves in Fig. 3 were drawn by using a simple theory that allows the calculation of total-energy curves between high-symmetry points.[21] That theory added new insights about the conditions that need to be satisfied in order to have athermal migration, but space does not allow us to review those conclusions in detail.

Shortly thereafter, Bar-Yam and Joannopoulos published a detailed account of their work on the TH path,[22] followed[23] by extensive investigations of the barriers along the TH, TB, and TS paths, and also along a path through the T site and a site which is akin to the (110) split interstitial (S' in Fig. 1), which they termed the "exchange configuration" X. They studied several points along these paths and concluded that athermal migration is possible along all of them. They also concluded that, even after considering the X site, the

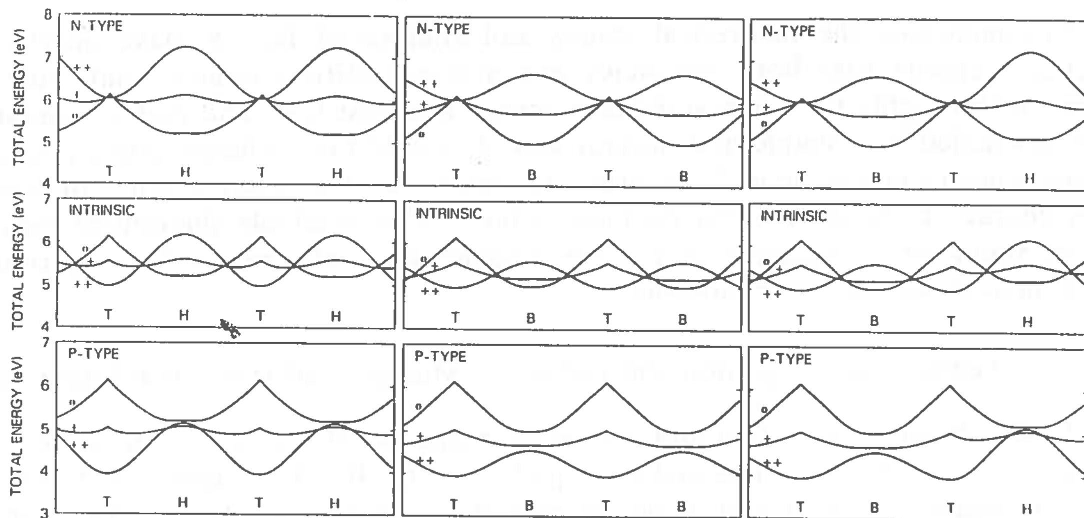

Fig. 3. The total energy of a self-interstitial (I^{++}, I^{+}, and I^{0}) along three different paths as reported in Ref. 8, except for the updated absolute values of the formation energies (Fig. 2 above). The curves illustrate that athermal migration is possible by capture of one and/or two electrons.

negative-U property of the self-interstitial[8] persists. In addition, they concluded that the X site may support a negatively-charged state, but could not trace its migration properties.

The net conclusion of all the above is that the self-interstitial has a most remarkable property: Its energy is roughly the same at a surprizingly large number of sites and configurations. Some of these (e.g., T) involve no lattice relaxation, some (e.g. H) involve moderate lattice relaxation, whereas others (e.g., B, S) involve substantial lattice relaxation. As a result, migration barriers along both simple and interstitialcy paths are quite small and can be overcome athermally by carrier capture.[24]

2. Self-Diffusion at High Temperatures

In addition to the low-temperature athermal migration of self-interstitials, Car et al.[8] used the results of total-energy calculations as a framework within which to understand high-temperature self-diffusion. They reported the first parameter-free values for the formation enthalpies of both self-interstitials and vacancies (they also reported migration enthalpies for the self-interstitial, but not for the vacancy). Updated values for these quantities can be read off Figs. 2 and 3.[25] When the Fermi level is in the midgap region, the self-diffusion activation energy for the vacancy mechanism is 4.1-5.0 eV. For the interstitialcy mechanisms, allowing for charge-state changes along the migration path leads to an activation energy of 5.3 eV. Without charge-state changes, I^{++} and I^{+} have an activation energy of about 5.5 eV. The uncertainties in these numbers are estimated to be of order 0.5 eV. The main conclusion is as stated in Ref. 8: Both the vacancy and the self-interstitial have formation enthalpies which are large, of order 4 to 5 eV. The consequences of this new result are quite far-reaching:[8] It implies that the low-temperature data regarding migration energies and the high-temperature data regarding the self-diffusion activation energy can be accounted for in a natural way without the need to invoke a dramatic change in the nature of the intrinsic defects.[1] The observed large entropies and their possible variation with temperature still need to be understood in detail, but there are

estimates[26] and other arguments[8,23] pointing to substantial entropies for both vacancies and interstitials.

In conclusion, the theoretical results and analysis of Ref. 8, have provided strong theoretical support that both vacancies and self-interstitials indeed contribute to self-diffusion with roughly the same activation energy and that low- and high-temperature data can be reconciled in a simple and natural way. It would take reliable entropy calculations, including ionization entropies,[27] in order to determine the relative contributions of the various charge states of the two intrinsic defects. The available theoretical results have, however, significant consequences for the interpretation of many other experiments. No detailed analysis has yet been published.

3. Low-Temperature Migration and Enhanced Migration of Interstitial Impurities.

The problem of migration and enhanced migration of interstitial impurities in Si was first studied in terms of parameter-free calculations by Baraff, Schluter and Allan.[4] They studied the motion of interstitial Al whose barrier for migration along the TH path (Fig. 1) in p-type Si had been found to decrease from 1.2 eV to about 0.3 eV upon injection of excess carriers.[15] On the basis of the energy-level structure of Al at the T and H sites, it was concluded that the observed barrier reduction is caused by the capture of an electron by Al^{+} at the T site followed by the capture of a second electron somewhere on the way to the H site. A simple expression involving only the energy levels in the gap at the T and H sites allowed the calculation of the barrier reduction to be about 0.9 eV, in excellent agreement with experiment. Since then, Baraff and Schluter[9] reported total-energy calculations for the two sites and confirmed the earlier results. More recently, Pantelides, Oshiyama, Car, and Kelly[21] showed that barrier reductions caused by carrier capture cannot in principle be determined by knowledge of the properties of the interstitial at only two points along the path, but the assumption made implicitly in Refs. 4 and 9 yields the correct value in the case of Al. The new analysis also led to the recognition that an Auger-like recombination channel exists when two electrons are captured and pointed out the significance of calculating the relative rates of several processes before definite predictions about migration enhancement can be made.

4. High-Temperature Impurity Diffusion

It is straightforward to observe that the activation energy of impurity diffusion would be equal to that of self-diffusion if only the simple vacancy and interstitialcy mechanisms were operative.[28] One possibility to obtain a reduced activation energy, as indicated by the data,[1,2] is to invoke pairing of the substitutional impurity with a vacancy[29] and/or a self-interstitial. If the binding energy of such a pair 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. We have carried out total-energy calculations for the complex consisting of a P or an Al substitutional impurity plus a neighboring vacancy or self-interstitial. In all cases we found a sizeable binding energy for the defect pair. We have therefore investigated two possible motional models for intrinsic defect-impurity pairs. One model is a vacancy-impurity mechanism which was suggested in 1964 by Watkins and Corbett.[29] The substitutional impurity first binds with a vacancy at a neighbouring site. The impurity jumps onto the vacant site and the vacancy then moves around a six-fold ring and moves to the site "in front" of the impurity so that the whole process may then be repeated. The vacancy remains bound to the impurity all along this motion. The migration energy for the vacancy-phosphorus pair (the so-called E center) has been determined experimentally to be ~1 eV[29] (~0.7 eV larger than the

migration enrgy of a single vacancy). Since we obtain a binding energy of ~1.8 eV for the neutral defect pair in intrinsic silicon, we obtain a reduction of ~1.1 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 the next 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 (Fig. 1) to a different T site "behind" the impurity, so as to repeat the whole process with the impurity moving along the chain of normal lattice sites. In this model, the impurity goes through a bond-centered configuration, but never goes into the channel. The impurity-interstitial pair does not dissociate 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 ~1.5 and ~0.5 eV, respectively. We have also investigated the possibility of having thermally generated Si self-interstitials replace substitutional impurity atoms and found that such a process also contributes to 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. Such a conclusion was reached earlier by Antoniadis, Lin, and Dutton,[30] on the basis of experimental data. The resulting diffusion activation energy is smaller than the self-diffusion activation energy by about 1 eV, in agreement with experimental observations.[1,2] A more complete account of our impurity diffusion results will be given in a future publication.

III. CONCLUSIONS

In conclusion, we have given a unified description of the microscopic mechanisms for atomic diffusion in silicon. This description is able to account for the experimental data at low and at high temperatures for both silicon and impurity atoms. It also elucidates the fundamental role played by vacancies and self-interstitials in mediating atomic motion in a crystal like silicon. These ideas, developed on the basis of theory and a few key experiments, must now be used to gain new insights into many other related experiments (quenching data, oxidation-enhanced diffusion, etc.[1,2,30]) which have been invoked many times in attempts to understand the basic processes of self-diffusion and impurity diffusion.[1,2]

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