

## Microscopic Theory of Atomic Diffusion Mechanisms in Silicon

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We report self-consistent Green's-function *total-energy* calculations which provide, for the first time, a firm theoretical framework for understanding the microscopic mechanisms of atomic diffusion in Si. We find that the self-interstitial has *negative-U* properties, roughly the same formation energy at several sites, small migration barriers, and charge-state instabilities that allow athermal migration along several paths. We also find that *both* vacancies and interstitials mediate self-diffusion and reconcile contrasting low- and high-temperature data.

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Atomic diffusion is an important solid-state process that is poorly understood in semiconductors, especially Si. The most fundamental type of diffusion is self-diffusion, e.g., the motion of Si atoms in the Si lattice. At very low temperatures (1–4 K), Si atoms dislodged from lattice sites by electron irradiation are known to migrate *athermally* with high mobility.<sup>1</sup> The path and mechanism for this athermal migration have not been determined because neither experiment nor theory has been able to identify the equilibrium site of a Si interstitial. At high temperatures (1100–1650 K), the self-diffusion coefficient  $D$  is well described by an Arrhenius relation

$$D = D_0 \exp(-Q/kT), \quad (1)$$

with  $Q$  ranging from 4.1 to 5.1 eV.<sup>2,3</sup> Such diffusion is mediated by thermally created intrinsic defects. No consensus has been achieved about the nature of these defects, however, because arguments in favor or against each model (vacancies, divacancies, interstitials, "extended" vacancies, "extended" interstitials, or combinations of these) usually stem from indirect evidence. If only one defect is active, Eq. (1) holds and

$$Q = H_F + H_M, \quad (2)$$

where  $H_F$  and  $H_M$  are the formation and migration enthalpies of the defect. If several defects are active,  $D$  is given by a sum of terms such as Eq. (1). By allowing several defects to be active with a range of preexponentials, we find that the observed curves can be reproduced if individual  $Q$ 's range from 4 to about 6 eV. Thus, theory can contribute to this difficult problem by determining which defects have  $Q$ 's in that range. However, all calculations so far yielded  $Q$ 's which are much smaller, of order 2–3.5 eV, and have, therefore, generally been dismissed as unreliable.<sup>3,4</sup> In addition, it has not been possible to reconcile the low- and high-tem-

perature data.

In this paper, we report total-energy calculations of vacancies and self-interstitials in Si. We find a very rich structure for the self-interstitial: Its formation energy is roughly the same at several sites which involve no, moderate, or large lattice relaxation, and migration barriers are small along a variety of paths. In addition, different charge states have different stable sites, which leads to athermal migration by the successive capture of electrons and holes. We also find that *both* vacancies and interstitials contribute to high-temperature self-diffusion with activation energies in the range of observed values, and are able to reconcile the contrasting low- and high-temperature data.

First, we remark briefly on the calculations. We use density-functional theory, the local-density approximation for exchange and correlation,<sup>5</sup> and norm-conserving pseudopotentials.<sup>6</sup> We implemented the Green's function formulation of Williams, Feibelman, and Lang,<sup>7</sup> which is particularly suitable when atoms are displaced from lattice sites. We reproduced earlier<sup>8–10</sup> Green's-function results for energy levels and found that, for accurate *total-energy* calculations, basis orbitals on considerably more atoms are needed.<sup>11</sup> In each of the cases reported below, relaxation of the nearest neighbors is included in a self-consistent way. Long-range lattice relaxation is included via the Keating model.<sup>12,13</sup> All absolute total energies reported here have an uncertainty ranging from 0.5 to 1.0 eV, which is primarily a result of limitations imposed by computer capacity.

*Vacancies.*—In Fig. 1(a), we display our results for the formation enthalpy<sup>14</sup> of four charge states of the vacancy ( $V$ ) as a function of the Fermi-level position  $E_F$  in the gap. The formation enthalpy of  $V^0$  does not depend on  $E_F$  because no electron transfer to or from it occurs. Figure 1(a) reflects the well-known negative- $U$  properties of the vacan-

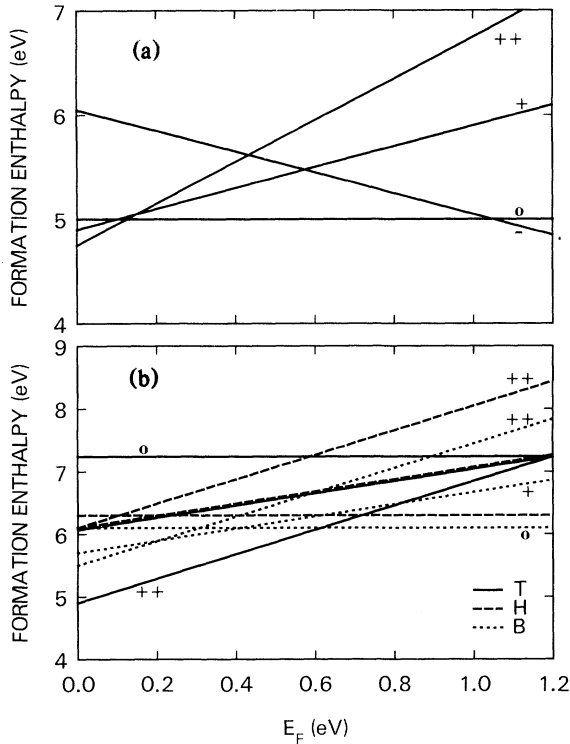


FIG. 1. Formation enthalpies of various charge states of (a) the vacancy and (b) the self-interstitial as a function of the Fermi-level position in the gap.

cy,<sup>13</sup> i.e.,  $V^+$  is not the equilibrium state for any  $E_F$ .

In the self-diffusion temperature range,  $E_F$  remains at roughly midgap for most doping levels so that the relevant formation enthalpies<sup>15</sup> for the four charge states range from 5 to 6 eV. We combine these values with migration enthalpies measured by Watkins (0.2–0.3 eV)<sup>1,16</sup> and obtain  $Q^*$ s which are within the observed range of 4–6 eV. We conclude that all charge states of the vacancy contribute to self-diffusion.

**Self-interstitials.**—In Fig. 2, we illustrate several configurations of the self-interstitial ( $I$ ) (see also Refs. 1–4). The central problem is the determination of the configuration with the lowest formation enthalpy and the barriers for migration along various paths.

**Equilibrium configuration.**—We have investigated the tetrahedral ( $T$ ), hexagonal ( $H$ ), bond-centered ( $B$ ), and split ( $S$ ) interstitial configurations. Nearest-neighbor relaxation is negligible for the  $T$  site, moderate for the  $H$  site ( $\sim 0.2$  a.u.), and large for the  $B$  site ( $\sim 2.2$  a.u.). It is also large for the  $S$  site, for which it was not feasible to obtain a fully optimized result. Other configurations of even

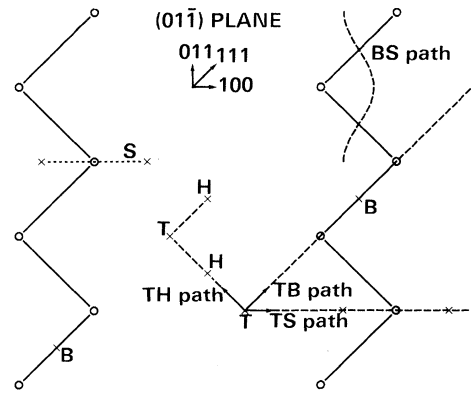


FIG. 2. Schematic definitions of various forms of the interstitial and migration paths in Si:  $T$ , tetrahedral;  $H$ , hexagonal;  $B$ , bond-centered;  $S$ , split interstitial. In the calculations, the nearest neighbors are allowed to relax (see text). The  $TBTH$  path corresponds to motion in the  $[111]$  direction and the  $TS$  path corresponds to motion along the  $[100]$  direction.

lower symmetry could not be studied with comparable accuracy. In Fig. 1(b) we show the formation enthalpies of the  $T$ ,  $H$ , and  $B$  configurations. The figure reveals that the equilibrium configuration depends on the charge state and  $E_F$ , and that the self-interstitial is a *negative- $U$*  center:  $I^+$  is not the stable charge state for any value of  $E_F$ ; instead, when  $E_F$  is in the lower half of the gap, the stable form is  $I^{++}(T)$ ; when  $E_F$  is in the upper half of the gap, the stable form is  $I^0(B)$ , with  $I^0(H)$  virtually degenerate with it. The  $S$  interstitial [not shown in Fig. 1(b)] lies somewhat higher in energy ( $7 \pm 1$  eV).

**Migration paths.**—We distinguish two types of paths. *Simple paths* are those which do not involve exchange with atoms at lattice sites. For example, the  $TH$  and  $BS$  paths (Fig. 2) are simple. *Interstitialcy paths* involve exchange with atoms at lattice sites. For example, a  $T$  interstitial can move in the  $[100]$  direction toward one of its second neighbors and push that atom into the next channel while taking its place (Fig. 2). We refer to this as the  $TS$  path since the  $S$  configuration is the likely saddle point (Fig. 2). Another interstitialcy path is the  $TB$  path in which a  $T$  interstitial moves in the  $[111]$  direction toward a nearest neighbor, pushes on *two* atoms, and eventually ejects one of them into the next channel.

Paths that are suitable for athermal migration must involve the equilibrium site, i.e., the  $T$  site in  $p$ -type material. Capture of one or two electrons into the  $T_2$  localized state near the conduction-band

edge<sup>9,10</sup> sets in a Jahn-Teller instability. Energy is gained by motion of the interstitial to sites of lower symmetry, which is accompanied by the splitting of the  $T_2$  state and the lowering of one of the components deep into the band gap. Athermal migration is then possible if certain simple criteria are met.<sup>11</sup> We have determined that the  $TH$ ,  $TB$ , and the combined  $TBTH$  paths support Bourgoin-Corbett-type athermal migration. The corresponding total-energy curves are shown in Fig. 3: By capturing one electron, an  $I^{++}(T)$  becomes  $I^+$  and can move to a  $B$  configuration without having to overcome a barrier. At that point, capture of a hole will convert it back to  $I^{++}$ , leading to motion to a  $T$  site, again without having to overcome a barrier. Similar motion along the  $TH$  path, however requires capture of a second electron halfway toward the  $H$  site, etc. The  $TH$  path was proposed in Ref. 9 to be the athermal path in  $p$ -type material and recent calculations<sup>17</sup> concurred. We also note that athermal migration is not possible along the  $BS$  path as proposed in Watkins *et al.*<sup>18</sup> Other paths involving the  $T$  site (e.g.,  $TS$ ) may, however, support athermal migration, but calculations of adequate accuracy are not currently feasible. Finally, Fig. 3 also shows that athermal migration can occur in  $n$ -type Si by hole capture and emission, but the final product of such migration has not been identified.<sup>1</sup>

We turn now to the high-temperature regime. We note that simple migration paths, as defined above, *do not* by themselves constitute self-diffusion since tracer Si atoms at lattice sites are not affected by such migration. This fact has not been

widely recognized in the literature where channel interstitial diffusion is often equated with self-diffusion.<sup>3,4</sup> For self-diffusion, one needs interstitial paths, as defined above. At high temperatures, i.e., for  $E_F$  around midgap, the self-diffusion activation energy  $Q$  is  $\sim 6.5$  eV for all three charge states along the  $TB$  and  $TBTH$  paths (Fig. 3). In view of the theoretical error bar, this value overlaps the range of observed values. Within the theoretical error bar, the  $TS$  path also contributes to self-diffusion with roughly the same  $Q$ . Finally, we note that channel diffusion also has roughly the same activation energy as the  $TB$ ,  $TBTH$ , and  $TS$  paths, and thus augments self-diffusion.

Our result that the self-diffusion activation energy is due almost entirely to the formation energy is quite novel and provides a natural reconciliation between the contrasting low- and high-temperature data: at low  $T$ , when self-interstitials are created by irradiation, athermal migration is possible 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 self-interstitials and vacancies which are necessary to mediate migration of Si atoms at lattice sites. Our results also have consequences on the interpretation of other experiments, including impurity diffusion.<sup>11</sup>

The most remarkable conclusion is that many different configurations of the self-interstitial with varying degrees of lattice distortions have roughly the same energy. This multitude of configurations is reminiscent of the proposal<sup>2</sup> that the interstitial exists in an "extended" form as an amorphous

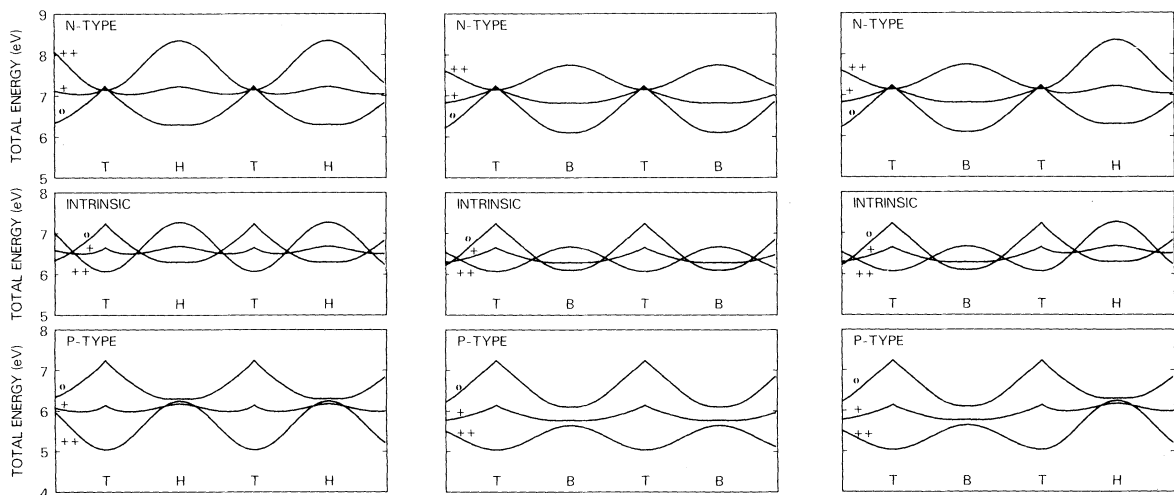


FIG. 3. The total energy of a self-interstitial along the  $TH$ ,  $TB$ , and  $TBTH$  paths (see Fig. 2). Green's function calculations are done only at the high-symmetry sites. The theory that leads to the curves shown will be published elsewhere.

bubble. This proposal was made in order to account for the observed high preexponential factor  $D_0$  since an amorphous bubble can be formed in many ways, leading to high entropy and hence high  $D_0$ . The primary difficulty with the extended interstitial is the lack of a motional model. Our results support the *spirit* of the extended interstitial and actually specify several possible configurations and their migration paths. The observed large entropy follows from both the multiplicity of configurations and the large lattice relaxations accompanying some of these configurations.

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<sup>3</sup>See articles in *Atomic Diffusion in Semiconductors*, edited by D. Shaw (Plenum, New York, 1973).

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<sup>5</sup>For recent reviews see *The Inhomogeneous Electron Gas*, edited by N. H. March and S. Ludqvist (Plenum, New York, 1984). For applications of the theory to perfect crystals and surfaces, see especially the article by A. R. Williams and U. von Barth.

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<sup>14</sup>For a definition of formation enthalpies, see Ref. 2, especially p. 190.

<sup>15</sup>We assume that enthalpies depend weakly on temperature [see, e.g., C. D. Thurmond, *J. Electrochem. Soc.* **122**, 1133 (1975)].

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