Diffusion without Vacancies or Interstitials: A New Concerted Exchange Mechanism

K. C. Pandey

IBM Thomas J. Watson Research Center, Yorktown Heights, New York 10598

We present a novel concerted exchange mechanism for the diffusion of substitutional atoms in semi-conductors that does not involve any defects. For self-diffusion in Si we show that this mechanism is energetically favorable and is able to account for a number of experimental observations. Implication for the diffusion of substitutional dopants is discussed.

From the very beginning of diffusion studies it has been assumed, and today is universally accepted,[1] that atomic diffusion in semidonductors is mediated by defects (vacancies or interstitials, depending on the material). In Si, all recent theoretical studies[2,3] of diffusion have been limited to the defect mechanisms and, in spite of years of effort, no clear agreement on the nature of diffusion has emerged and many experimental observations remain unexplained.

In this Letter we present a novel concerted exchange (CE) mechanism[4] for the diffusion of substitutional atoms in Si that does not involve any defects and suggest that this might be the dominant mechanism by which substitutional atoms diffuse in semiconductors. The CE mechanism is "intrinsic" and thus more basic in nature, and it is likely to be of very general validity.

As the most important support for the CE mechanism we present extensive first-principle total-energy calculations for the self-diffusion in Si, which show that the CE mechanism is energetically competitive with, or favored over, both the vacancy and interstitial mechanisms. As additional support for the CE mechanism we show that by using this mechanism we can qualitatively, in simple physical terms, account for a number of long-debated experimental observations[1] in Si: (1) Group-III and -V dopants diffuse faster than group-IV dopants, (2) self-diffusion has a very large entropy, and (3) self-diffusion shows a non-Arrhenius temperature dependence.

The basic physical consideration that naturally leads to our CE mechanism is that the atoms move through a set of configurations in such a way that, for energetic reasons, at any stage the number of broken bonds as well as distortions are kept at a minimum. Figure 1 illustrates our CE path for the diffusion of the black atom (B) to the gray-atom (G) site. The CE path can best be described in terms of two rotations: a rotation of the B and G atoms about their bond center in the plane of paper (θ) and an independent rotation about the original bond (ϕ). Initially atoms move in the $\phi = 0$ plane (all angles and energies measured relative to the ideal configuration). As θ increases to $\sim 30°$, two bonds (B-6 and G-5) are broken. At $\theta \sim 60°$, part of the exchange has

been accomplished; i.e., G-6 and B-5 bonds have been made. In this configuration, there are no broken bonds (the bond angles are, however, severely distorted). For larger θ, G-6 and B-5 bonds are unduly compressed. In our CE path this compression is avoided by a rotation of B and G atoms, from this point on, in a plane parallel to
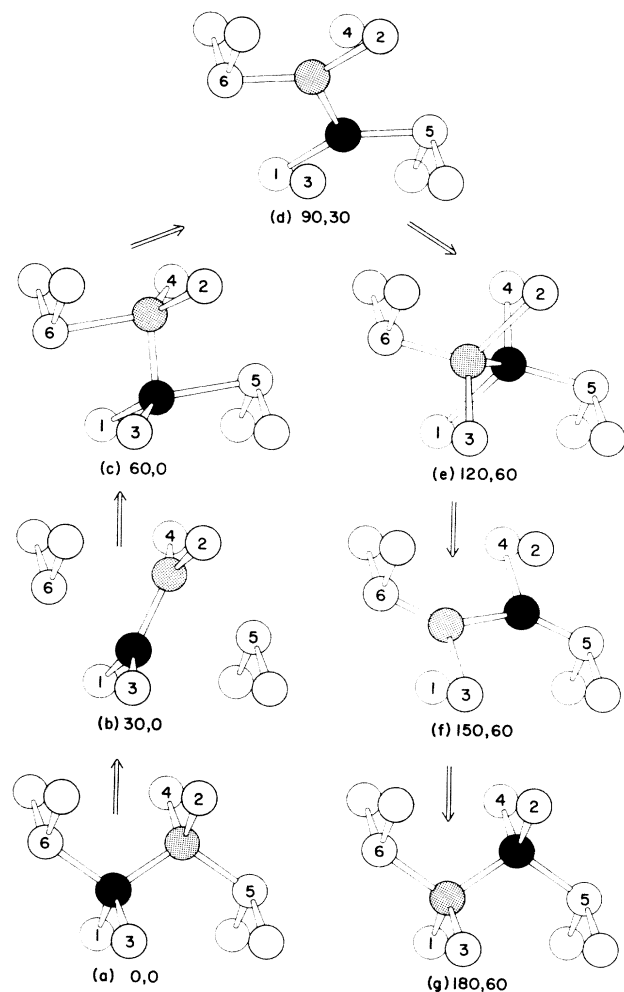

FIG. 1. The concerted exchange mechanism for diffusion.

$\theta = \phi$ (or equivalently $\theta = -\phi$). From symmetry, $\theta = 90°$, $\phi = 30°$ is the midpoint of the exchange process, where again only two bonds (G-4 and B-3) are broken. In the downhill path, B and G atoms continue to move in the plane parallel to $\theta = \phi$ until $\theta = 120°$, $\phi = 60°$. Thereafter G and B atoms move in the $\phi = 60°$ plane, completing the exchange. From symmetry, configurations (e), (f), and (g) are identical to (c), (b), and (a), respectively. In the CE mechanism, bonds are broken and made in succession, and at no time during the entire CE path are more than two bonds broken (compared with six in an arbitrary rotation). In our CE mechanism, atoms move in three distinct planes and there are six independent ways in which two given atoms could be exchanged.

To show that the CE path is a unique and low-energy path by which exchange would take place, we have carried out extensive first-principles self-consistent total-energy calculations based on norm-conserving pseudopotentials in the repeated-cell geometry within the local-density formalism.[5] This scheme is well proven and has recently been applied successfully to calculations on defects.[2] The calculations are similar to those of Ref. 2. We have, however, made significant technical improvements that make our calculations more accurate: the use of a larger cell of 54 atoms (on an fcc lattice), the use of eight sampling points in the irreducible part of the Brillouin zone of the supercell, and, most important, a more complete basis set of plane waves with an energy cutoff $E_c = 7-9$ Ry. In all calculations charge neutrality is assumed (i.e., the Fermi level is determined by the levels introduced in the band gap during the exchange process). Thus our calculations simulate diffusion in an intrinsic crystal.

To get an overview of the energies involved in the exchange process, first we consider the ideal CE where only θ and ϕ are varied and with the bulk value for the B—G bond length. For these calculations $E_c = 7$ Ry was used. Calculations were carried out for 75 configurations. The
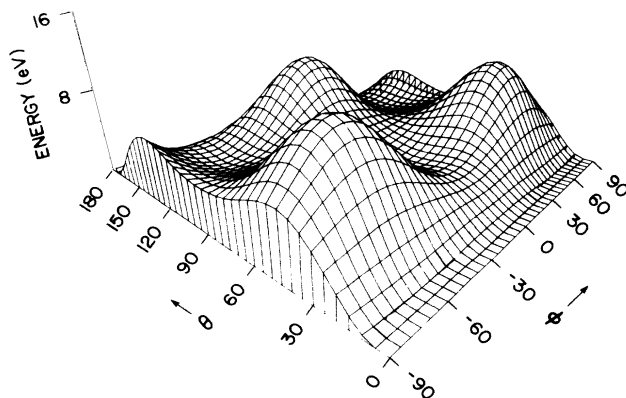
resulting total-energy surface (Fig. 2) shows that the CE path illustrated in Fig. 1 is indeed the lowest energy path for an exchange of atoms—that for small θ exchange proceeds in the $\phi = 0$ plane and only for $\theta \sim 60°$ the system starts feeling the hill in the rear and is forced to go diagonally parallel to the $\theta = \phi$ or $\theta = -\phi$ plane. The hills are 11 eV high. Thus a simple rotation, or any rotation other than the CE, would be energetically very unfavorable. The energy along the CE path of Fig. 1 is shown in Fig. 3. Figures 2 and 3 show that $\theta = 90°$, $\phi = 30°$ is the saddle point of the total-energy surface and it determines the activation barrier. The activation barrier for the ideal CE is 5.4 eV (Fig. 3). This value represents an upper bound for the actual activation barrier because several effects that lower the barrier have been left out from the ideal CE.

The largest contribution to the lowering of the barrier comes from atomic relaxations. Because the calculations are prohibitive, we have been able to compute the relaxation effects only for the saddle point. Based on the structural similarity, relaxation effects at nearby configurations are expected to be similar. Consequently, it is unlikely that atomic relaxations will alter the topology of the total-energy surface from that of the ideal CE. At the saddle point, all 54 atoms in the cell were relaxed in response to the Hellman-Feynman forces acting until the forces vanished. This relaxation leads to a large energy gain of 0.75 eV (Fig. 4). Part of this gain is due to the elastic-strain relief and a part is due to the π bonding[6] between B and G atoms (as evidenced by the B—G bond contraction), which becomes possible on relaxation.

The other two factors that further reduce the barrier have their origin in the computational scheme. The first of these is the completeness of the basis set (determined by E_c). We find that as the basis is made more complete

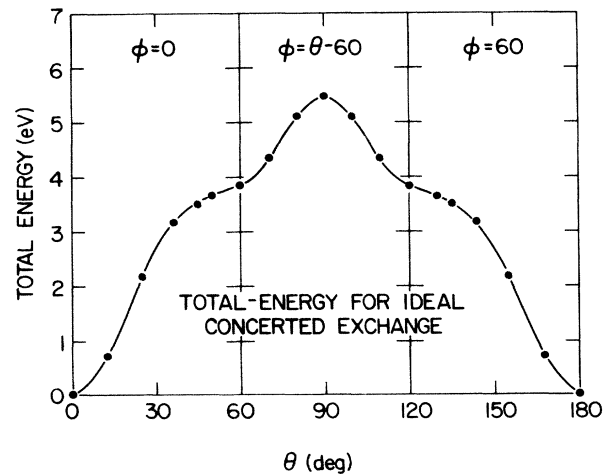FIG. 2. The total-energy surface for the ideal concerted exchange.

FIG. 3. The total energy for the ideal concerted exchange along the path shown in Fig. 1.
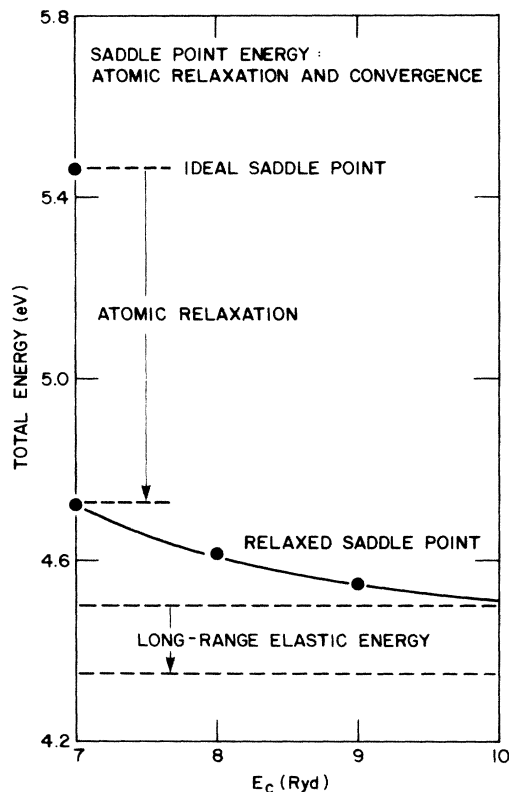
FIG. 4. The total energy for the saddle-point configuration. Effects of atomic relaxation and basis-set convergence are shown (see text).

the barrier decreases. For the relaxed saddle-point configuration (based on $E_c = 7$ Ry) we have calculated the barrier for two additional values of $E_c = 8$ and 9 Ry (Fig. 4). A simple extrapolation using these three points shows that the converged value of the barrier height, corresponding to a very large E_c, is 4.5 eV (Fig. 4). The second factor that further lowers the barrier is the relaxation of atoms that lie outside the 54-atom cell. To estimate this barrier lowering, we have used the Keating model,[7] which is justified here because these atomic relaxations are small. This relaxation leads to an additional barrier lowering of 0.17 eV (Fig. 4). Thus, our best estimate for the activation barrier for diffusion via the CE mechanism is 4.3 eV. We expect the actual barrier to be somewhat lower because atoms were not allowed to relax further as E_c was increased from 7 to 9 Ry.

Now we compare our results with experimental data on Si self-diffusion and with previous theoretical studies. Experiments indicate[1] that the activation energy for diffusion varies from 4.1 eV at 1100 K to 5.1 eV at 1500 K. This variation need not be due entirely to temperature, because there is considerable scatter in the data. Experiments also show[1] that the prefactor is large, corresponding to an entropy of $10k$ or more. The entropy also seems to increase with temperature. Our calculations for the CE mechanism and calculations based on vacancies

and interstitials by others,[2,3] both give activation barriers in agreement with experiment. Thus, based on energy considerations alone, the relative contributions of different mechanisms cannot be evaluated and other factors must be considered. Quantitative calculation of the entropy is extremely tedious and there is only one calculation of a rather preliminary nature which indicates that the entropy for the interstitial mechanism is small.[8] The CE mechanism is likely to have a large entropy because it involves large displacements of more than fifty atoms and also because there are six independent ways in which two atoms can be exchanged. By contrast, in diffusion via vacancies, only four to six atoms are displaced appreciably, and there is only one known way in which vacancies can move from one site to the other.

Kinetic factors favor the CE mechanism. This is because the defect mechanisms implicitly assume that vacancies or interstitials are created singly, which is possible only at free surfaces or at dislocations. They also assume a thermodynamical equilibrium distribution of defects. Thus, during rapid annealing the bulk of a crystal will be deficient in defects. In such cases only the CE mechanism can be operative.

We now discuss two experiments which provide additional support for the CE mechanism. First, we consider the diffusion of a group-III or -V dopant in Si. These dopants diffuse faster than a group-IV dopant.[9] Our CE mechanism provides a simple physical explanation for this in terms of the bonding configuration at the saddle point where the dopant and host atoms are both threefold coordinated. This bonding configuration is energetically more favorable when the dopant is a group-III or -V atom than when it is a group-IV atom, because both group-III and -V atoms have a stronger tendency to form three bonds. Since the energy of the saddle-point configuration determines the barrier height, faster diffusion of group-III and -V dopants follows.

Next we consider the temperature dependence of the activation barrier and entropy for the self-diffusion in Si. It is generally thought that this temperature dependence arises because different diffusion mechanisms are operative in the low- and high-temperature regimes.[1] Based on simple qualitative arguments, the CE mechanism provides a possible alternative explanation for this temperature dependence. In the CE mechanism, the 0-K activation barrier is just the energy of the relaxed saddle-point configuration (ground state). With the introduction of atomic vibrations, the saddle-point energy must increase because the geometrical configuration is no longer the ground-state configuration. For configurations around the saddle point, a smaller increase in the energy is expected because these are not the minimum energy configurations. As a result, the total-energy surface near the saddle point rises and flattens as temperature increases, and thereby both the barrier and entropy increase. The large relaxation energy in our model indicates that this effect could be large.

In conclusion, we have presented an alternative mechanism by which substitutional atoms might diffuse in semiconductors. For Si self-diffusion, we have shown that this mechanism is energetically as good as or better than the defect mechanisms. In simple physical terms, our mechanism accounts for several experimental observations. This mechanism might be responsible for the formation of antisite and antistructure defects in III–V compounds. A similar mechanism might even apply in the case of the relatively open-structured bcc metals, where diffusion is not always well explained by the defect mechanisms.

We would like to thank T. Tan, J. van Vechten, N. Lang, and R. Tromp for helpful discussions. The computations, carried out on an IBM 3090 vector facility, would not have been possible without the help of J. Hollan and R. McNeill.

[1]For a recent review of diffusion in Si, see, e.g., W. Frank et al., in Diffusion in Solids II, edited by A. S. Nowick and G. Murch (Academic, Orlando, FL, 1985).

[2]Y. Bar-Yam and J. D. Joannopoulos, Phys. Rev. Lett. 52, 1129 (1984).

[3]R. Car et al., Phys. Rev. Lett. 52, 1844 (1984).

[4]Based on calculations using empirical potentials, a direct exchange mechanism has been proposed in the past (see Ref. 1, p. 66). To the best of our knowledge, the concerted exchange mechanism of the present Letter has not been proposed earlier and its energetics has not been studied by use of first-principles calculations.

[5]Details of the calculations are the same as in K. C. Pandey, Phys. Rev. Lett. 49, 223 (1982).

[6]K. C. Pandey, Phys. Rev. Lett. 47, 1913 (1981).

[7]P. N. Keating, Phys. Rev. 145, 637 (1966).

[8]Y. Bar-Yam and J. D. Joannopoulos, in Microscopic Identification of Electronic Defects in Semiconductors, edited by N. M. Johnson, S. G. Bishop, and G. D. Watkins, Materials Research Society Symposia Proceedings, Vol 46 (Materials Research Society, Pittsburgh, 1985), p. 123.

[9]A dopant-defect complex has been invoked to explain this effect (Ref. 1, p. 108). However, is is not clear why such a complex helps the diffusion of group-III and -V atoms but not group-IV atoms.
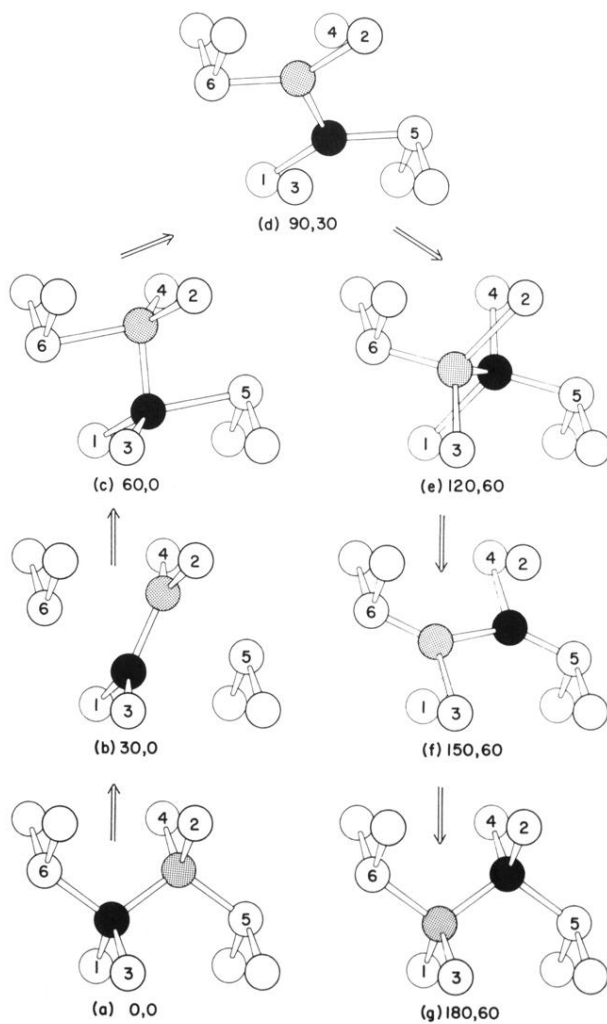
FIG. 1. The concerted exchange mechanism for diffusion.