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Pressure effects on self-diffusion in silicon

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The effects of hydrostatic pressure on the energetics of self-diffusion in silicon are investigated via parameter-free total-energy calculations. The three microscopic mechanisms, vacancy, interstitial, and concerted exchange, which have very similar activation energies in Si, exhibit different pressure dependences. The results suggest that a set of experiments carried out at different pressures can unravel their relative contributions by a comparison to the present results. In addition, it is shown that in contrast to the (111) surface, the nearest neighbors of the Si vacancy relax inwards, rather than outwards.

Self-diffusion in silicon has been the subject of extensive experimental and theoretical studies. Various microscopic mechanisms have been considered, but no consensus has yet been achieved regarding their relative importance. Experimentally, the measured activation enthalpy varies from 4.1 to 5.1 eV (Ref. 1) depending on the measurement technique and temperature range. Due to the nature of the bonding in silicon, it was initially thought that native defects mediate self-diffusion. In addition, it was shown experimentally that the concentration of native defects is small, and therefore the contributions of complex defects, e.g., divacancies, are negligible.[2] Theoretical studies[3,4] obtained very similar activation enthalpies for the vacancy and interstitial mechanisms, as well as proposed a new one, namely that of concerted exchange.[5] All three mechanisms have activation energies in the experimentally observed range. Therefore, due to both experimental uncertainties and theoretical approximations, it has not been possible to determine the relative contributions of these mechanisms to the self-diffusion process. In this paper we present the results of parameter-free total-energy calculations of the effects of hydrostatic pressure on the energetics of these mechanisms. Although the three mechanisms have very similar activation enthalpies at zero pressure, the response to external pressure of each mechanism is qualitatively different, making the determination of their relative contributions possible.

The use of pressure as a probe to investigate diffusive processes in solids is not new. Several results for metals and ionic compounds were reported over twenty years ago.[6] In semiconductors, however, the first results of pressure effects on self-diffusion in germanium[1] and silicon,[7] and on diffusion of As in silicon,[8] have appeared only recently.

In the high-temperature regime the self-diffusion coefficient can be written as

$$D_{\mathrm{sd}} = D_0 \exp(-\Delta H_{\mathrm{sd}}/kT) , \tag{1}$$

where ΔH_{sd} denotes the activation enthalpy. The prefactor D_0 in (1) is proportional to $\exp(\Delta S_{\mathrm{sd}}/k)$, where ΔS_{sd} is the activation entropy. For diffusion involving defects, the activation enthalpy is the sum of the formation enthalpy ΔH_f and the migration enthalpy ΔH_m.

We will now analyze the process whereby a native defect is created in a crystal and the effect of an external pressure on its formation energy. When a vacancy is created in a dislocation-free crystal, one atom leaves a lattice site and migrates to the surface. Therefore, the volume of the crystal increases by one atomic volume. The formation of an interstitial is the reverse process: One atom leaves the surface by migrating into the crystal, decreasing the total volume by one atomic volume. Therefore, when an external pressure is applied, the work associated with the change in volume also has to be considered in order to determine the formation enthalpy of the defect under pressure. Thus, the formation enthalpy as a function of pressure is[9]

$$\Delta H_f = \Delta E_f + P\Delta V_0 + T(\alpha/\kappa_T)\Delta V_P , \tag{2}$$

where ΔE_f is the internal energy necessary to create the defect (including the interaction with the surface) at constant volume (constant lattice parameter) corresponding to the pressure P, and ΔV_0 is equal to plus or minus one atomic volume at the pressure P for the vacancy and the interstitial formation, respectively. The last term in (2) is due to the difference between the formation entropy at constant volume and the formation entropy at constant pressure, where T is the absolute temperature, α is the coefficient of thermal expansion, κ_T is the isothermal compressibility, and ΔV_P is the change in the volume of the crystal at constant pressure. In Si, even at high temperatures, the contribution of the last term in (2) is of the order of 10^{-2} eV, and therefore negligible when compared to the first two terms (see below).

For the concerted exchange mechanism[5] the activation energy is given by the difference between the total energies of the saddle point for the exchange and the perfect crystal. Since the concerted exchange mechanism does not involve any exchange of atoms with the surface of the crystal, the pressure dependence of the activation enthalpy is equal to that of the activation energy.

In the calculations we used a norm-conserving nonlocal pseudopotential,[10] and the electronic wave function was expanded in a plane-wave basis set. The pressure was simulated by changing the atomic volume of the crystal, and the relationship between the volume and the pressure was obtained from the Murnaghan's equation of state.[11] The supercell approximation was used to treat defects and

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distortions in the crystalline lattice[4] and all the results presented below were obtained using a 32-atom unit cell. Convergence studies using a 16-atom unit cell showed that small changes (about 5%) occur in the magnitude of the energies as the size of the unit cell is increased. This is to be expected since the dispersion in the defect levels decreases when the unit cell is enlarged. However, the changes in the calculated pressure effects were negligible. The basis set included plane waves up to 6.0 Ry directly, while plane waves up to 12.0 Ry were included through Löwdin's perturbation theory. The convergence of the main results was checked by enlarging the cutoffs to 8 and 16 Ry, respectively. Only small changes in the magnitude of the energies were observed.

Theoretical studies[3,4] have shown that interstitial defects in Si can appear in various configurations. It has been shown previously[3,4] that the activation enthalpy of the interstitial mechanism is largely determined by the formation enthalpies of the various interstitial configurations. In this work we focus on two specific configurations: tetrahedral (I_T) and bond centered (I_B), both of which participate in a crucial path for self-diffusion via interstitials at high temperatures. This path, often called *interstitialcy* in the literature, is very important because it involves exchange with atoms on lattice sites.[3] Figures 1(a) and 1(b) show the pressure dependence of the formation energy ΔE_f and formation enthalpy ΔH_f of the tetrahedral and bond-centered interstitials, respectively, in their neutral charge states. In both cases the formation energy increases with pressure. However, the term $P\Delta V_0$ (negative in this case) is dominant and the formation enthalpy decreases with pressure. Since the neutral interstitial in the bond-centered configuration is the saddle point of this path,[3,4] the activation enthalpy for self-diffusion via interstitials decreases with an increasing pressure. In Fig. 1(c) we display the formation energy and the formation enthalpy as a function of pressure for the neutral vacancy V. Although the formation energy decreases with pressure, its variation is overcome by the $P\Delta V_0$ term (positive in this case) and the resultant formation enthalpy increases with pressure. Since the migration barrier for vacancy diffusion in Si is small (0.45 eV, Ref. 12), the pressure dependence of the vacancy mechanism is mainly determined by the variation of its formation enthalpy with pressure. Figure 1(d) shows the pressure dependence of the ideal saddle point of the concerted exchange mechanism. It exhibits a very weak dependence on pressure, decreasing by only 0.12 eV in the range from 0 to 115 kbar. Since large atomic relaxations alter substantially the energy of the ideal saddle point,[5] we have investigated via gradient techniques the effect of pressure on this relaxation. At zero pressure we obtain a relaxation energy of 0.68 eV, which agrees very well with the 0.75 eV value quoted in Ref. 5. For the maximum pressure the relaxation energy is 0.62 eV, which shows that the effect of pressure on the relaxation energy is very small.

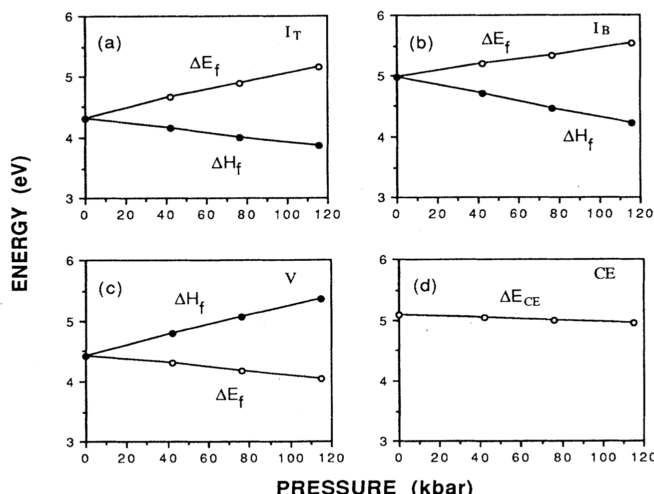

FIG. 1. Pressure effects on the formation energy (ΔE_f) and formation enthalpy (ΔH_f) of (a) the neutral tetrahedral interstitial, (b) the neutral bond-centered interstitial, (c) the neutral vacancy, and (d) the energy of the saddle point in the concerted exchange mechanism (ΔE_{CE}) relative to the ground state of the system.

We have also investigated the effects of pressure on charge states of defects. Figure 2 depicts the pressure dependence of the formation energy and formation enthalpy of the doubly positively charged tetrahedral interstitial (I_T^{2+}) in intrinsic Si. It is clear from Figs. 1(a) and 2 that the formation enthalpy follows the same trends for the neutral and charged states of this interstitial. Similar results were found for the vacancy and the bond-centered interstitial. (See also Table I.)

In the 0–115-kbar pressure range the variation of the energies with pressure is approximately linear. Table I synthesizes our results for pressure effects on the formation enthalpies of defects and the saddle point of the concerted exchange mechanism in terms of linear pressure coefficients. For the charge states of defects the coefficients were calculated for intrinsic Si.

To our knowledge, the experimental studies by Aziz *et al.*[7] of the effects of hydrostatic pressure on self-diffusion in Si are the only ones that have been reported. A tenfold increase in the self-diffusion was observed as the pressure was increased to 35 kbar. However, all the measurements were performed at a fixed temperature of 1000 °C. It is

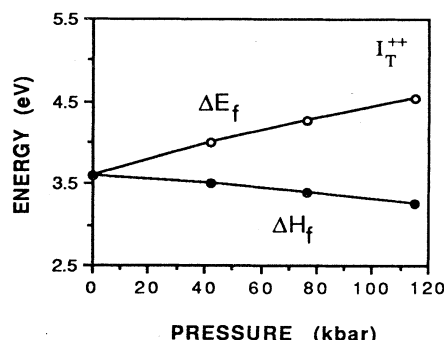

FIG. 2. Pressure effects on the formation energy (ΔE_f) and formation enthalpy (ΔH_f) of the doubly positively charged tetrahedral interstitial.

TABLE I. Linear coefficients of the pressure dependence of formation enthalpy of defects and the saddle point in the concerted exchange mechanism in the low-pressure limit [meV/kbar]. V denotes the vacancy, I_T the tetrahedral interstitial, I_B the bond-centered interstitial, and CE the concerted exchange. The superscripts define the charge state.

V^0	V^{2+}	I_T^0	I_T^{2+}	I_B^0	I_B^+	I_B^{2+}	CE
9.5	7.5	−3.5	−3.0	−7.0	−7.0	−7.0	−0.5

therefore not possible to separate the relative contributions due to variations in the activation entropy and activation enthalpy, respectively, from the overall change in the self-diffusion coefficient. Since a parallel study which investigated both pressure and temperature dependence of diffusion of As in Si (Ref. 8) showed that the prefactor decreases from $10^{4.5}$ cm^2/s to $10^{1.8}$ cm^2/s when the pressure is increased to 30 kbar, significant effects on the prefactor for self-diffusion by changes in pressure cannot be excluded. Such a decrease could be caused by, for example, a change in the diffusion mechanism. Since only the enthalpy variation with pressure was calculated in the present work, the results cannot be directly compared to those of Ref. 7.

A study of nonhydrostatic pressure effects on the diffusion of As and B in Si was carried out by Manda *et al.*[13] They observed no effects up to the yield point of Si (i.e., stresses of the order of 10 bars). Our results show that the activation enthalpy for self-diffusion via any mechanism would have changed by less than 10^{-2} meV at that pressure. Assuming that the changes in activation enthalpies for impurity diffusion with pressure are of similar magnitude, the present results explain the lack of an observable effect in their data.

Using the fact that the Helmholtz free energy evaluated at constant volume[9] (lattice constant) is equal to the Gibbs free energy at constant pressure, the formation volume of the vacancy is 15 $Å^3$ at the low-pressure limit and $T=0$ K [cf. Fig. 1(c)]. Two effects contribute to the formation volume: (i) crystal expansion due to the migration of an atom from the inside of the crystal to the surface when the vacancy is created; (ii) relaxation of the crystal following the formation of the vacancy. The first effect contributes one atomic volume to the formation volume, i.e., 20 $Å^3$. Because the internal energy of vacancy formation decreases with pressure [see Fig. 1(c)], the relaxation volume is negative (-5 $Å^3$). Considering local relaxations, it is well known from the elasticity theory that the variation in the volume of the crystal is basically determined by the local changes in the volume of the region surrounding the defect. The present calculations show that the nearest neighbors to the vacancy relax radially inwards by 2.8% of a bond length, which represents a reduction of 4.9 $Å^3$ in the volume of the region surrounding the vacancy. This inwards relaxation of the nearest neighbors is somewhat counterintuitive, since an outwards relaxation would be expected by analogy to the Si(111) surface.[14] It is the result of the interactions of the dangling bonds of the vacancy across the vacancy cavity. The present result agrees with a more recent calculation,[15] which also found an inwards relaxation of the nearest neighbors of the vacancy.

Recently, Ref. 16 analyzed the experimental results[17] for the activation volume for the annealing of E centers (V-P pairs) in Si with the simultaneous formation of A centers (V-O pairs). The experimental results suggest that the formation volume of the E center is 10 $Å^3$. The formation volume of an isolated vacancy should be of similar magnitude. In Ref. 16, it was assumed that the positive sign of the formation volume was a consequence of an outward local relaxation of the nearest neighbors of a vacancy, which causes an increase in the volume of the crystal. This was in agreement with some of the previous theoretical predictions.[14] Furthermore, in order to obtain an outward relaxation, it was assumed that due to the open structure of the Si lattice a vacancy-interstitial pair (Frenkel pair) was formed when the vacancy is created, instead of the interstitial migrating to the surface of the crystal.[17] However, since interstitials in Si migrate athermally during irradiation and are mobile even at very low temperatures,[18] vacancy-interstitial pairs are unlikely to occur in the equilibrium regime. In addition, since the experiment was performed at 360 K, the contribution of the formation entropy of the neutral vacancy[19] to the Gibbs free energy is at most 0.3 eV, which is small when compared to the formation energy. Therefore, since an atom placed on the surface represents a positive contribution of 20 $Å^3$, the experimental result can only be understood by a negative relaxation volume of the crystal following the formation of the vacancy.

In conclusion, the present results show that studies of the effects of pressure elucidate the nature and predominance of microscopic mechanisms that mediate self-diffusion in Si. The activation enthalpy of each proposed mechanism changes in a very distinct way as pressure is applied to the crystal. It increases for the vacancy mechanism, decreases for the interstitial mechanism, and remains practically constant for the concerted exchange mechanism. The different behavior in each case allows for the identification of a possible dominant mechanism in each temperature range by a comparison of experimental data with the results of the present calculations. In the case that more than one mechanism contributes substantially in a certain temperature range, an enhancement of the non-Arrhenius temperature dependence with increasing pressure should be observed, since the activation enthalpy of each mechanism varies at a different rate with pressure. Note that for this to occur, the activation enthalpies for these mechanisms must be within a few kT's from each other. Further experimental work cover-

ing a larger range of temperatures and pressures is necessary in order to determine the relative contributions of the various self-diffusion mechanisms in Si. In addition, the present calculations predict an inwards relaxation of the vacancy surrounding the lattice and consequently a negative relaxation volume of the crystal following the creation of the vacancy.

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