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LETTER TO THE EDITOR

Nature and diffusion of the self-interstitial in silicon

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Abstract. We exploit self-consistent, semi-empirical molecular orbital calculations (CNDO) for large silicon clusters to characterise self-interstitials. Hexagonal (I^+) and split ⟨100⟩ forms (I^- and probably I^0) are favoured among the several forms investigated. Possible extended high-temperature forms are not discussed. Our results imply Bourgoin–Corbett athermal diffusion in p-Si and low-activation energy classical motion in n-Si; local excitation enhanced motion is possible, though not verified, but local heating is unlikely. Results agree well with experiment, both for Si and in understanding the different behaviour of silicon and diamond. The energetic advantage of the split form predicted is also supported by the observed split impurity interstitials and unidentified defects, related to the self-interstitial, observed in structures similar to the split ⟨100⟩ form.

The self-interstitial in silicon is a tantalising defect. It is one of the basic intrinsic defects, and one whose involvement is important in many solid-state processes from below 1 K to near the melting point of Si (for reviews see Watkins 1964, 1967, 1975 and Seeger *et al* 1979). Yet there are no confirmed, direct observations of the self-interstitial. Several centres seen in spin resonance, internal friction or channelling might be isolated interstitials, but the consensus at present is that these are probably merely related centres. Evidence for the properties of this elusive defect relies on indirect, sometimes controversial, analyses and on the rates, natures and ranges of occurrence of solid state reactions. Our present calculations allow us to rationalise much of the lower-temperature data in a way which is consistent with corresponding but distinct results (both theoretical and experimental) for diamond.

The experimental situation is one of considerable controversy. We may summarise the results concisely as follows. At the lowest temperatures (0.5–20 K), in p-Si only, replacement reactions occur which displace substitutional impurities X_s into interstitial sites, the silicon interstitial moving to the vacated lattice site, i.e. $Si_i + X_s \rightarrow X_i$. The long-range motion of the interstitial appears to be athermal, driven by the ionisation produced at the same time as the defect. Replacement processes are observed for X = B, Al; at higher temperatures, similar processes seem to occur for C and Ga. However, Ge is not displaced to an interstitial site. At intermediate temperatures (50–900 K) there are signs of interstitial motion in n-Si, though no evidence for athermal motion. Various studies give low motion energies in the range 0.4 eV (Watkins 1967) to 0.08 eV (Brown and Fathy 1981). At higher temperatures still (above 900 K) evidence is from the

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formation of swirl defects and from diffusion studies. In the present Letter we shall not discuss this high-temperature regime, though it is important to realise that the models most seriously considered for interstitials at these temperatures (if they are indeed responsible for observed behaviour) have high entropy and probably low symmetry.

Even this brief survey of the complex and incompletely understood data indicates that any useful calculation should consider charge states I^+, I^0, I^- at least. Similarly, those experiments which give structural information dictate that we consider a range of different geometries too. Internal friction, spin resonance and channelling suggest predominantly split-interstitial and related geometries for what appear to be self-interstitials or self-interstitial complexes. In a split $\langle hkl \rangle$ geometry, two atoms, oriented along $\langle hkl \rangle$, replace a single host atom. The geometry can allow effective rebonding without large distortion terms. Impurity interstitials also suggest a variety of sites: C_i^+ and B_i^- have the $\langle 100 \rangle$ split form; B_i^0 and O_i show tilted structures; B_i^+ appears either hexagonal or bond-centred. Only simple closed-shell (possibly with a weakly-bound carrier) interstitials, e.g. Al^{2+} or Li^0, together with some of the transition metal impurities (V, Cr, Mn, Fe) occupy the simple tetrahedral sites. Thus, in addition to the range of charge states, any useful theory will need to examine a range of possible geometries, many with low symmetry for which relaxation of neighbouring atomic positions is important. Experiment makes it manifestly clear (and our calculations confirm this point) that theories which concentrate solely on the 'obvious' unrelaxed tetrahedral and hexagonal sites contain little of the important physics.

The several implications of the experimental data determine our choice of theoretical method. A first requirement, to establish energetically favoured geometries, means we shall need to calculate total energies. Sums of one-electron eigenvalues are unacceptable because they are well known to mislead (Larkins 1971), notably for bond-centre sites, where the errors of double-counting and omitted nuclear–nuclear interactions combine. Secondly, the method should work for the complex geometries and low symmetries of the models we consider (tetrahedral; hexagonal; split $\langle 100 \rangle$; split $\langle 110 \rangle$; split $\langle 111 \rangle$; bond centre; more complex 'diffuse' models are currently being considered at the same level) and for various charge states. Thirdly, the method should be rapid, and ideally it should be self-consistent to include any rebonding satisfactorily.

We have chosen the self-consistent, semi-empirical molecular orbital method, known as CNDO, as implemented in the Harwell MOSES code (Harker and Lyon 1979). This approach fulfils the requirements described above and has been used with success for similar calculations. These include vacancies (Mainwood 1978) and interstitials (Mainwood *et al* 1978) in diamond, as well as hydrogen in diamond and silicon (Mainwood and Stoneham 1983). The main approximations involve the rewriting of matrix elements in terms of three types of empirical parameters: an orbital exponent ξ_i for the outer s and p orbitals, an electronegativity E_i for the same orbitals, and a 'bonding' parameter β. These parameters were fixed previously by Harker and Larkins (1979) so as to fit the observed lattice parameter, cohesive energy and valence band width for the perfect crystal. We have used their values ($\xi_{3s} = \xi_{3p} = 1.54\,a_0^{-1}$; $E_{3s} = 6.3$ eV, $E_{3p} = 4.5$ eV; $\beta = 6.4$ eV) without alteration. We emphasise that these parameters completely define the method: no experimental data are introduced later (e.g. bandgap or promotion energy) as is occasionally found. Two main limitations should be borne in mind. First, the method uses a restricted basis (3s and 3p orbitals only) with parameters determined primarily by valence band electrons. Features associated with the conduction band should be interpreted cautiously. Secondly, we use a cluster method, using a large number of silicons (typically 29 or 32) with their dangling surface bonds saturated by 'pseudo-silicons', essentially re-parametrised 'hydrogens' with parameters which mimic single hybrid silicon orbitals. It is very important to try a range of cluster sizes and geometries, so as to ascertain whether any features are sensitive. Clearly, our approach makes a number of approximations; given our results, however, which identify important cases, one could use more powerful methods on selected geometries and charge states.

Our important results are these.

(i) The split ⟨100⟩ and hexagonal forms are always the most stable of the simple forms. We have not assessed yet the extended forms proposed for high temperatures.

(ii) The split form becomes increasingly stable for the more negative interstitials, i.e. I^- is clearly favoured as a split ⟨100⟩ form and I^+ as the hexagonal form. Exactly where the change occurs, i.e. which form I^0 adopts, is less clear, partly because of some cluster-size dependence (table 1) and partly because lattice relaxation is important. Making the assumption that our limited lattice relaxation has underestimated the very significant relaxation energies, I^0 is probably split ⟨100⟩.

Table 1. Stability of the split ⟨100⟩ form relative to the hexagonal split interstitial. Results are in eV, with a positive sign corresponding to the split ⟨100⟩ form lowest. Cluster sizes show (number of Si atoms)/(number of saturating pseudo-silicons). Since clusters have different forms (the 29/36 cluster is centred on a host atom site and the 32/42 on a bond-centre site) these results, by themselves, should not be used to extrapolate to other cluster sizes.

	I^+	I^0	I^-
29/36	−0.90	0.35	1.4
32/42	−2.2	−0.95	−0.01

(iii) All three charge states I^+, I^0 and I^- are bound. Since we are comparing a variety of clusters in various charge states, we should not use one-electron levels to decide stability. Instead we use self-consistent total energies of comparable clusters to show that the loss of an electron from I^- to the lowest state of a perfect cluster, initially neutral, is endothermic, as is the gain of an electron by I^+ from a perfect cluster, initially neutral.

(iv) The harmonic translational motion of the split ⟨100⟩ interstitials is characterised by approximate effective frequencies of 81% (I^+), 80% (I^0) and 87% (I^-) of the Raman frequency ($9.8 \times 10^{13}\ s^{-1}$).

These results point to several important conclusions, which we shall discuss in more detail in a separate paper. First, we can understand the interstitial mobility in p-Si. A Bourgoin–Corbett (1972) mechanism is possible, involving alternate electron and hole capture ($I^+ + e \rightarrow I^0$; $I^0 + h \rightarrow I^+$) with changes of geometry from split ⟨100⟩ to hexagonal and vice versa. Secondly, we can see why this mechanism does not occur in n-Si, where I^0 and I^- will dominate and where both share the split ⟨100⟩ geometry. Thirdly, we can understand the different behaviour in diamond and silicon. In diamond, the split ⟨100⟩ form is favoured for all charge states, so the Bourgoin–Corbett mechanism cannot operate. Instead, the most important mechanism in diamond appears to be a low activation energy, classical, process whose energy was successfully predicted by a theory like ours (Mainwood *et al* 1978). We anticipate, but have not demonstrated, a similar low activation energy in Si, probably comparable to that observed. Fourthly, we can exclude 'local heating' mechanisms of enhanced diffusion, since the reaction coordinate is not a local mode, nor even approximately so (see the discussion by Stoneham 1981;

the important point is that ω_{eff} lies in a region of high phonon density of states). 'Local excitation' mechanisms may occur, but we have not yet investigated excited states to test this; previous work on the diamond interstitial suggested such processes are possible. Finally, the relative stability of split ⟨100⟩ forms goes some way to understanding why interstitial complexes (whether impurity or intrinsic) can often be described in terms of split interstitial components and rarely, if ever, as involving tetrahedral interstitials.

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