A Fourfold Coordinated Point Defect in Silicon

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Vacancies, interstitials, and Frenkel pairs are considered to be the basic point defects in silicon. We challenge this point of view by presenting density functional calculations that show that there is a stable point defect in silicon that has fourfold coordination and is lower in energy than the traditional defects.

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Because of their technological importance, point defects in silicon are among the best studied physical systems. The experimental examination of point defects buried in bulk is difficult and evidence for the various defects usually indirect. Simulations of defects in silicon have been performed at various levels of sophistication ranging from fast force fields to accurate density functional calculations. The generally accepted viewpoint from all these studies is that vacancies and self-interstitials are the basic point defects in silicon.

The stability of crystalline silicon comes from the fact that each silicon atom can accommodate its four valence electrons in four covalent bonds with its four neighbors. The traditional point defects in silicon, the vacancy and the various interstitials, are obtained by taking out or adding atoms to the crystal and thus all destroy fourfold coordination. A relatively high defect formation energy for these defects is the consequence. In addition there is a point defect that conserves the number of particles, the Frenkel pair, consisting of a vacancy and an interstitial. If the vacancy and the interstitial are close, the formation energy of a Frenkel pair is less than the sum of an isolated vacancy and interstitial (Table I). Nevertheless, the formation energy is still considerable since again bonds are broken. Figure 1 shows a defect configuration that has, in contrast to all other point defects, perfect fourfold coordination and will therefore be called fourfold coordinated defect (FFCD) [2].

Using state of the art plane wave density functional theory (DFT) calculations, we will now present evidence that the formation energy of the FFCD of 2.4 eV is lower than the formation energy of all other known point defects both in intrinsic and doped silicon. Even though several calculations of this type were published for the traditional defects, we have decided to repeat them for several reasons. (a) All these calculations take advantage of error cancellations to obtain energy differences that are more precise than the total energies themselves. This cancellation is obviously best if all the total energies that are compared are calculated with exactly the same method. (b) Most DFT calculations used the basic local density approximation (LDA), whereas we used more precise general gradient approximations (GGA) [3]. (c) As was recently

shown [4], cells of at least 216 atoms are required for a reasonable convergence. Most published calculations were done with smaller cells. Because of this large cell size, we could use only the gamma point for the electronic structure part. (d) We constructed very accurate pseudopotentials [5] based on atomic calculations with the same density functional as used in our target calculation, and we afforded a very large plane wave basis set (25 Ry for the LDA and 35 Ry for the GGA calculations). (e) The point defect formation energies in doped silicon were until now obtained in an approximate way by combining density functional total energy results with the concept of a chemical potential that varies as a function of doping across the experimental band gap of 1.12 eV of silicon [6,7]. We have modeled the effect of doping in a coherent way for both *n*- and *p*-type doped silicon by including explicitly two doping atoms (aluminum and phosphor) in our 216 atom supercell. This procedure leads, of course, to high doping concentrations for any reasonable size of our computational cell, but by treating coherently and accurately the extreme cases of high and zero doping we can expect the numbers for more moderate doping concentrations to lie in between these results.

Table I shows all the total energy results. We have included in our compilation all defects that have been classified as being low in energy in previous calculations [6–9], i.e., the split (110) *X* interstitial, the hexagonal *H* interstitial, and the vacancy. In addition, we have included a low energy Frenkel pair. In agreement with recent calculation by Needs [10,11], we found that both the tetrahedral interstitial and the caged interstitial [12] are higher in energy and metastable. They are therefore

TABLE I. The GGA formation energy in eV of the point defects described in the text and depicted in Figs. 1 and 2. For comparison, the LDA values are given in parentheses for intrinsic silicon.

	p-type	Intrinsic	*n*-type
FFCD	2.45	2.42 (2.34)	2.39
Frenkel	5.65	4.32 (4.26)	5.77
X interstitial	3.33	3.31 (2.88)	2.98
H interstitial	2.80	3.31 (2.87)	3.12
Vacancy	3.01	3.17 (3.56)	3.14

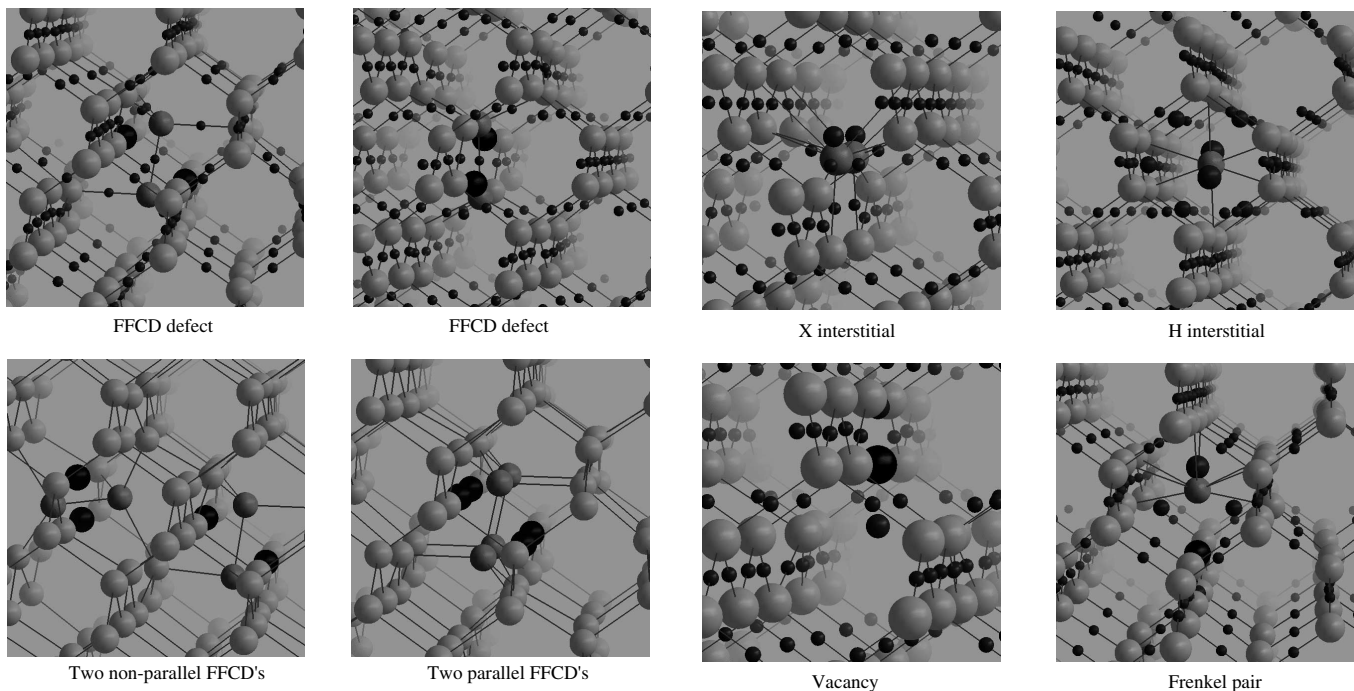   0031-9007/02/88(23)/235501(4)$20.00

FIG. 1.   Two views of the FFCD defect (upper part) and two FFCD pairs (lower part) [1]. The defects are obtained by moving atoms from the initial positions denoted by black spheres into the final dark grey positions. The centers of the Wannier functions are indicated by the small black spheres for the single FFCD but omitted for the two pairs. The formation of the FFCD is easily understandable from the upper left panel. There, the upper dark grey atom originates from the upper black position to the left. The swinging movement needed for this displacement does not break the bonds with the upper neighbors, but with the lower ones. A corresponding swing is needed for the lower defect atom. In the final position two new bonds can be formed so that in the end all atoms are again fourfold coordinated [1].

not included in the compilation. The energies in Table I do not contain an additional lowering of the energy that is obtained in an infinite crystal by a long range elastic field, which is suppressed in our finite cell. We have calculated this extra elastic energy for a few configurations and found it to be negligible, namely, less than 0.05 eV. Because of the negative U character of the traditional vacancies and interstitials that was postulated with the help of DFT calculations [13,14] and confirmed experimentally [15], the lowest energies are obtained by closed shell configurations. Consequently, all calculations were performed without spin polarization.

For the FFCD, the bond length and angle do not significantly deviate from their bulk values. Whereas the bond length and angle in the bulk are 2.35 Å and 109°, they respectively vary from 2.25 to 2.47 Å and from 97° to 116° for the bonds formed by the two defect atoms. The fourfold coordination is also visible from the fact that the centers of the maximally localized Wannier functions [16], which give the best possible spatial location of an electron, are located practically exactly in the middle of the bonds established by the geometric distance criteria. The spread
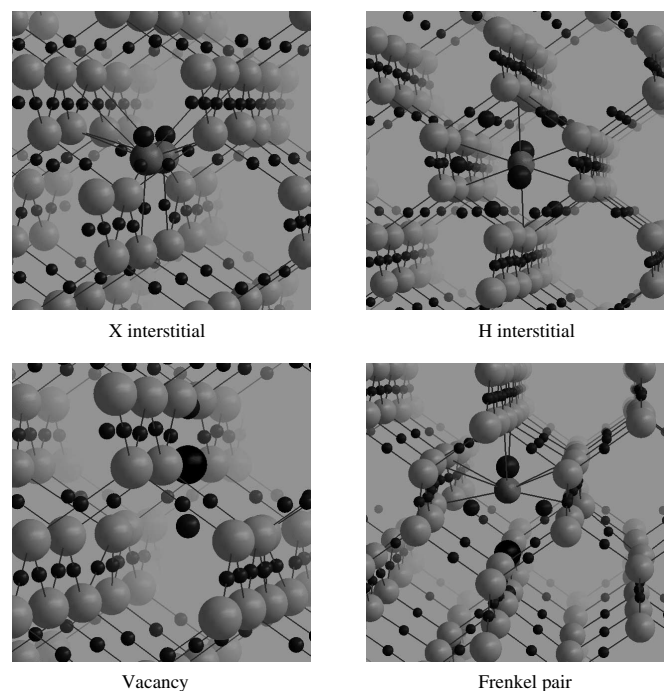

FIG. 2.   Classical point defects in silicon: Dark grey atoms indicate atoms in new positions. For the vacancy and the Frenkel pair, the empty lattice site is shown by a black sphere. The centers of extended Wannier functions are visualized by increasingly bigger dark spheres, Wannier functions with the typical bulk extension by small dark spheres.

of all the Wannier functions is very close to the bulk value of 2.7 a.u. In order to convert the FFCD back into the bulk structure, two bonds have to be broken which leads to a barrier of 0.57 eV.

The fact that the LDA and GGA formation energies are very close is not surprising. The simple covalent bonds are very well described by any reasonable density functional, and we expect an error of less than a tenth of an eV for this configuration. Correlation effects are more important for the broken bonds of the other point defects. Hence, the DFT values are less reliable than in the case of the FFCD. Recent quantum Monte Carlo calculations [11] for interstitials are in better agreement with GGA values than with LDA values. We therefore believe that it is unlikely that the energetical ordering predicted by our GGA calculations does not correspond to reality.

The broken bonds of the other point defects are again best visualized by looking at the centers of the maximally localized Wannier functions in the neighborhood of defects. They are located in empty space regions rather than at positions where geometric criteria would predict bonds. Their spread is also significantly larger than the bulk value. In the case of the vacancy, the two nonbonding Wannier functions have a spread of 3.6 a.u., for the X interstitial 4.1 a.u. and for the H interstitial 4.7 a.u. For the Frenkel pair, there are two nonsymmetric Wannier functions with spreads of 3.5 and 4.4 a.u.
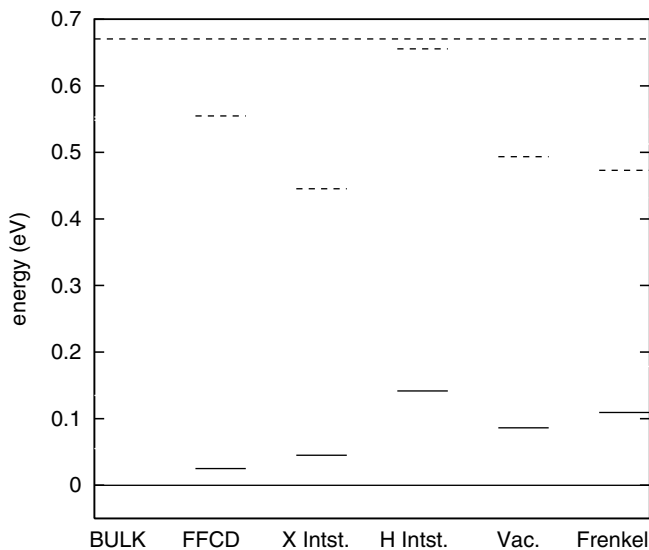
FIG. 3. The HOMO LUMO splitting in intrinsic silicon for the configurations of Table I. The HOMO is denoted by a solid line, the LUMO by a dashed line. The two levels of intrinsic silicon without defects are drawn over the whole interval.

Whereas the classical point defects were all postulated based on simple symmetry considerations, the discovery of the FFCD was made possible by new algorithmic developments. The configurational space was systematically explored by using a modified basin hopping method [17] and an interatomic silicon potential [18]. The most promising configurations were then refined with a plane wave electronic structure code [19] developed by Hutter *et al.* The preconditioned conjugate gradient method [20] was used for the electronic optimization and the DIIS method [21] without any symmetry constraints for the ionic relaxation.

The remarkable fact that the FFCD has not yet been detected experimentally, in spite of its equilibrium concentration which should be many orders of magnitude larger than that of the other defects, is probably due to two factors. First, the experimental search for defects was always guided by theoretical predictions. Second, it is invisible with standard experimental techniques. Because of the perfect fourfold coordination, no unpaired electrons exist, a necessary condition for electronic paramagnetic resonance and electron nuclear double resonance experiments. Deep level transient spectroscopy requires electronic levels within the gap. Given the perfect coordination this seems unlikely. To examine this point further we have calculated the LDA highest occupied molecular orbital (HOMO), lowest unoccupied molecular orbital (LUMO) splitting. Even though it is known that the gap is not well reproduced by DFT, these levels allow for a qualitative interpretation. The results (Fig. 3) show that the FFCD disturbs the band structure indeed much less than the other defects. The FFCD spectrum is also insensitive to the doping level, whereas the other spectra

are strongly influenced via various Jahn Teller distortions [22] because of their orbital degeneracy.

The basic FFCD can serve as a building block for more extended defects. Two simple defects obtained by combining just two FFCD's in two different ways are shown at the bottom of Fig. 1. Their energies of 3.98 eV for the tilted configuration and of 4.17 eV for the parallel configuration are significantly lower than the sum of the energies of two isolated FFCD's. By combining many defects of the FFCD type, amorphous silicon can be obtained [23].

Even though the FFCD does presumably not strongly influence transport properties, it is expected to play an important role in the diffusion properties of silicon. The intermediate (60,0) configuration in the concerted exchange diffusion mechanism [24] is a configuration that is very similar to the FFCD defect.

Note added.— A bond defect with a very similar geometry was shown to be stable in tight binding simulations of bulk silicon [2].

[1] Color versions of all the figures in this Letter are available at the preprint server http://xxx.lanl.gov under cond-mat/0201475.

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