Stable Fourfold Configurations for Small Vacancy Clusters in Silicon from *ab initio* Calculations

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Using density-functional-theory calculations, we have identified new stable configurations for tri-, tetra-, and pentavacancies in silicon. These new configurations consist of combinations of a ring hexavacancy with three, two, or one interstitial atoms, respectively, such that all atoms remain fourfold. As a result, their formation energies are lower by 0.6, 1.0, and 0.6 eV, respectively, than the "part of a hexagonal ring" configurations, believed until now to be the lowest-energy states.

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Vacancies and their clusters are fundamental defects of silicon. Usually, they result from the irradiation of silicon with electrons [1–4], neutrons [5–7], protons [8,9], or ions [10,11], or from plastic deformations [12,13]. However, vacancy clusters can also be present in as-grown crystals [14]. The presence of defects in crystalline semiconductors determines, to a large extent, their electrical and optical properties, making their study of great importance.

Calculations performed using density-functional-theory (DFT) molecular dynamics [15,16], the Hartree-Fock method [15,16], and the DFT tight-binding method [17], among others, predict that the ring hexavacancy should be significantly more stable than other types of vacancy clusters. This can be explained using simple bond counting arguments: The crystal can reconstruct almost perfectly around a hexavacancy, making all atoms remain fourfold. For smaller clusters, the same calculations [15–17] conclude that the most stable configurations occur when atoms are removed sequentially from the hexagonal ring.

The ring hexavacancy is known to be a good trap for various impurities, such as carbon, oxygen, and copper atoms [16]. It is reasonable to expect, therefore, that it may also be an efficient trap for self-interstitials. Exploring this avenue, we demonstrate in this Letter, on the basis of *ab initio* calculations, that penta-, tetra-, and trivacancies in the form of combinations of ring hexavacancies with one, two, or three self-interstitials constitute very stable complexes, with formation energies significantly lower than "part of hexagonal ring" (PHR) configurations. In a sense, this family of defects is a generalization of the "fourfold coordinated point defect" described in [18], which is essentially a combination of a divacancy with two self-interstitials.

The calculations of the energies and relaxed geometries of the vacancy clusters were performed using the Vienna *Ab-initio* Simulation Package (VASP), which employs pseudopotential DFT with the projector augmented-wave method [19,20]. We used a 216-atom supercell, an energy cutoff of 22 Ry, and the local-density approximation for the exchange-correlation functional. Results are reported for Γ-point sampling only of the Brillouin zone, which we found is sufficient to ensure convergence of the relative energies of the defects. One of the standard experimental tools for the study of defects in semiconductors is positron annihilation spectroscopy [21]; we therefore also performed calculations of the positron lifetimes for various vacancy clusters. The positron wave functions and annihilation rates were calculated using the potential and electron density given by the DFT calculations; the effect of electron-positron correlations was taken into account by introducing an additional correlation potential and annihilation enhancement factor according to the interpolation formulas by Boroński and Nieminen [22] with corrections for semiconductors (see review by Puska and Nieminen [23] for details).

Figure 1 presents the proposed fourfold configurations for the penta-, tetra-, and trivacancy in silicon. Figure 1(a) (left) shows the unrelaxed ring hexavacancy, with labels 1 to 12 indicating the 12 atoms each having initially one dangling bond. In the process of relaxation, these 12 atoms form six new bonds with each other (right). However, if one silicon atom is added to the defect, four of the 12 atoms can form new bonds with it while the others pair in the same way as in the case of the simple hexavacancy [Fig. 1(b)]. If two atoms are added, they will satisfy eight of the 12 dangling bonds while four atoms pair [Fig. 1(c)]; and if three atoms are added, all 12 dangling bonds of the hexavacancy are satisfied [Fig. 1(d)]. Thus, these configurations for the penta-, the tetra-, and the trivacancy have *no dangling bonds at all.* As a result, they are expected to be more stable than the PHR configurations where two dangling bonds remain at the ends of the vacancy chain after the lattice has relaxed. Note that, for the tetravacancy, two different configurations are possible: symmetric [Fig. 1(c)], where the first atom is bonded to atoms 1–4 and the second to atoms 7–10, and nonsymmetric, where the second atom is bonded to atoms 5–8. For penta- and trivacancies, all possible configurations are equivalent.

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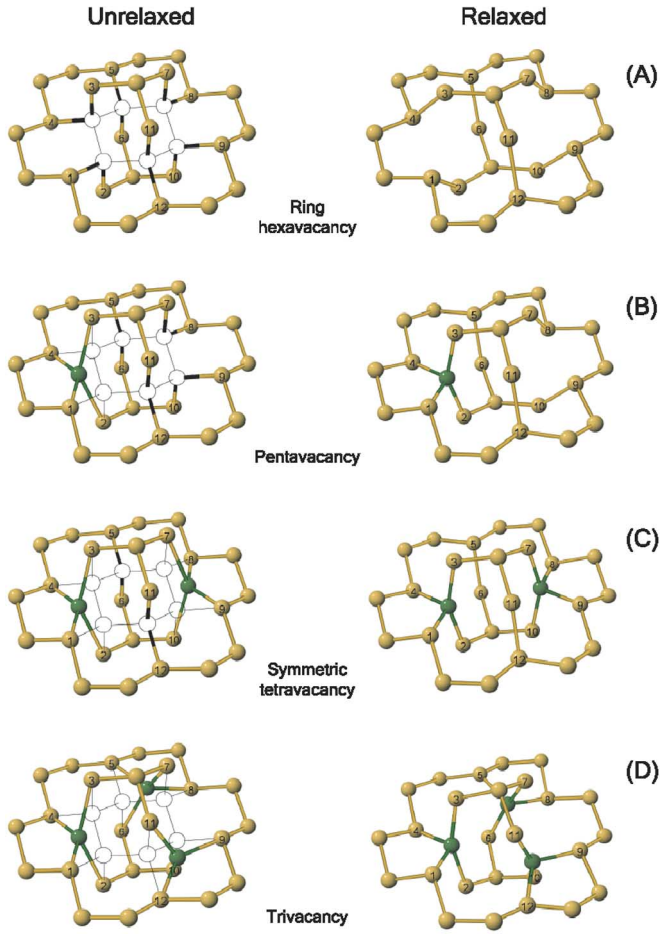

FIG. 1 (color online). Initial (left) and relaxed (right) geometries for the ring hexavacancy (a), and for the pentavacancy (b), the symmetric tetravacancy (c), and the trivacancy (d) in the fourfold configurations (combinations of a hexavacancy with one, two, or three self-interstitials, respectively). The self-interstitials added to the hexavacancy are shown in dark green. The open circles indicate the positions of the atoms removed from the lattice to form the starting-point ring hexavacancy.

The expectation that the fourfold configurations described above are more stable than the usual PHR configurations is verified by computing the formation energies. In our calculations, each additional atom is initially placed at the geometrical center of its group of four future neighbors (see Fig. 1). The system is then relaxed using the conjugate-gradient algorithm. For comparison, we have also performed calculations for the PHR configurations and for the chain tetravacancy.

The calculated formation energies are presented in Table I, where we also give the symmetry groups of the fourfold defects. The formation energies for the tri-, tetra-, and pentavacancies in the fourfold configurations are indeed lower than those for the PHR configurations, by 0.6, 1.0, and 0.6 eV, respectively. It should be mentioned that, in contrast to [15,17], we find the chain tetravacancy to have lower energy than the PHR configuration. However, both our calculations and [15,17] show a very small energy difference between the two configurations so they can be considered equally stable.

As mentioned earlier, these results were obtained using only the Γ point to sample the Brillouin zone. In order to check for convergence, we have also performed some calculations using a $2 \times 2 \times 2$ Monkhors-Pack grid. We find that the formation energies change by at most 0.5 eV, while the relative energies given above change by no more than a few percent and are thus converged with respect to $\mathbf{k}$-point sampling. Full convergence of the formation energies is numerically intensive and would not alter our conclusions.

Figure 2 shows the calculated binding energy, i.e., the energy necessary to remove one vacancy from a cluster, $V_n \rightarrow V_{n-1} + V$. For the PHR configurations, our calculations are in good agreement with the results of Staab *et al.* [17]: We also find the absolute value of the binding energy to be minimal for the trivacancy, and to increase with the size of the cluster for $3 \leq N_v \leq 6$. For the fourfold configurations, now, our calculations show the binding energy to be approximately the same for all defect sizes. For $4 \leq N_v \leq 6$, this result can be explained by the structure of the defects: Additional atoms attach to the hexavacancy more or less independently, and thus approximately the same energy is necessary to remove the first, second, or last atom.

TABLE I. Calculated formation energies for various configurations of vacancy clusters (N_v = number of vacancies), in eV per defect. In the PHR configurations, atoms are removed sequentially from the hexagonal ring; the fourfold configurations are shown in Fig. 1. For the latter, the symmetry groups are also given.

	Formation energy		
N_v	PHR configurations	Fourfold configurations	Group for fourfold configurations
1	3.51		
2	5.01		
3	6.80	6.20	D_3
4	8.26 (chain)	7.26 (sym)	C_{2h}
	8.35 (PHR)	7.35 (nonsym)	C_{1h}
5	9.07	8.42	C_2
6	9.41		D_{3d}

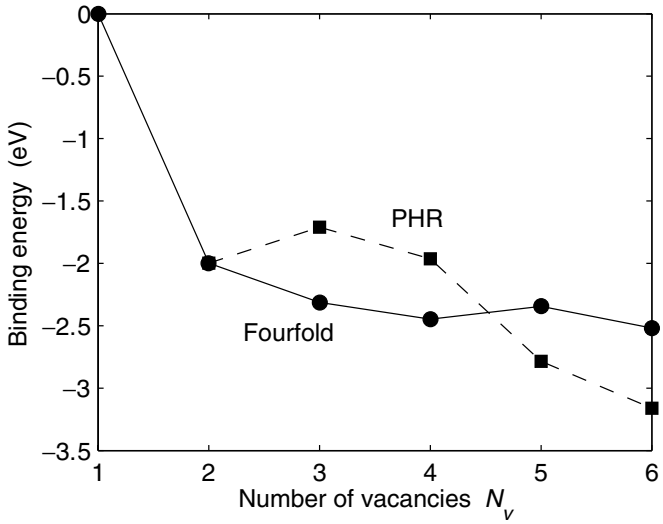

FIG. 2. Binding energy for vacancy clusters as a function of size, $V_n \rightarrow V_{n-1} + V$. The dashed line corresponds to PHR configurations and the solid line to fourfold configurations (see Fig. 1).

In order to identify a possible formation mechanism for the fourfold vacancy clusters (other than the capture of self-interstitials by an earlier-formed hexavacancy), we calculated, using the nudged elastic band method [24], the transition barrier between the PHR and the fourfold pentavacancy. In this transition, an atom originally bonded to only two neighbors [atoms 1 and 2 in Fig. 1(a), for example] moves to the interstitial position to form two new bonds [with atoms 3 and 4 [Fig. 1(b)]]. Our calculations show that the barrier for this transition is very low, about 0.02–0.03 eV. Thus, the PHR pentavacancy should quickly move to the fourfold configuration. In a similar way, a fourfold tetravacancy can easily be formed from two parallel second-nearest-neighbor divacancies by moving two twofold atoms to the interstitial positions. Likewise, a possible initial configuration for the formation of the fourfold trivacancy is three second-nearest-neighbor vacancies in the hexagonal ring.

Table II presents the calculated positron lifetimes for the different vacancy clusters. The calculations were performed for both relaxed and unrelaxed geometries. For the unrelaxed PHR configurations, our lifetimes are in perfect agreement with the results of Staab *et al.* [17]. For the relaxed PHR states, we find close agreement for larger clusters, whereas for $N_v \leq 3$ our calculations give values larger by 10–15 ps. A possible explanation for the (small) differences is some variations of the relaxed geometries due to the use of different methods of calculation.

TABLE II. Calculated positron lifetime (in ps) for the unrelaxed and relaxed (in brackets) geometries of the same vacancy clusters as in Table I.

N_v	PHR configurations	Fourfold configurations
1	252 (226)	
2	296 (255)	
3	329 (290)	321 (258)
4	343 (291) (chain)	342 (292) (sym)
	340 (294) (PHR)	347 (298) (nonsym)
5	354 (301)	363 (312)
6	376 (316)	

It is generally believed that the lifetimes calculated for unrelaxed geometries correspond more closely to experiment because positron-induced outward relaxation compensates for the usual inward relaxation around vacancy clusters [17,25]. However, in the case of the ring hexavacancy, such calculations overestimate the lifetime by about 20 ps [25]. Moreover, it is not clear what "unrelaxed geometries" means for the fourfold configurations. In our calculations, we simply take this as the initial configuration where the interstitial atoms are placed at the geometrical centers of their groups of neighbors. One can see from Fig. 1 that the additional atoms really move towards the defect center from their initial positions in the process of relaxation, which makes our choice reasonable. Obviously, calculations performed for the geometries relaxed with respect to both electronic and positronic forces are necessary to get reliable values of the lifetimes for the fourfold configurations. Nevertheless, the numbers shown in Table II provide reasonable estimates.

We have performed electronic structure calculations and found that, similar to the simple ring hexavacancy [15,16], fourfold vacancy clusters have no energy levels in the band gap. As a result, they should be optically inactive, making their direct observation difficult. That being said, there is experimental evidence, mostly from positron annihilation spectroscopy, that the fourfold configurations are likely states of these defects. In particular, Motoko-Kwete *et al.* [3] reported a positron lifetime value of 350 ps, consistent with both fourfold and PHR configurations. However, they observe the defects to be more stable at high temperature than the usual tetravacancies. This result has been explained by the presence of impurities in the material. Our calculations suggest that the defects actually are the fourfold configurations reported in this Letter. Also, the formation of fourfold trivacancies provides a natural explanation to the experimental results of Poirier *et al.* [9]; these authors have observed that, in the process of divacancy annealing at $T = 250\,^{\circ}\mathrm{C}$, the infrared absorption, which is associated with divacancies, decreases with time, while positron lifetime and trapping rate remain unchanged. According to Table II, the difference between positron lifetimes for fourfold trivacancies and divacancies is rather small, certainly within the uncertainty arising from the computational method (see above). Since fourfold trivacancies are invisible to infrared spectroscopy, the "coalescence" of divacancies into fourfold trivacancies resolves the apparent contradiction reported in [9].

In summary, we propose new fourfold configurations for tri-, tetra-, and pentavacancies in silicon. Our DFT

calculations show that they have formation energies lower by 0.6, 1.0, and 0.6 eV, respectively, than the PHR configurations, generally believed to be the stable states of these defects. We have identified a possible formation mechanism for the fourfold vacancy clusters and performed preliminary calculations for positron lifetimes associated with them.

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