

Vacancy aggregates in silicon

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The properties of vacancy aggregates in crystalline silicon are studied using density-functional-based molecular-dynamics simulations in large periodic supercells as well as approximate *ab initio* and *ab initio* Hartree Fock in molecular clusters. The stability and properties of aggregates of up to seven vacancies are discussed. The central results deal with the remarkable properties of the ring hexavacancy. Theory predicts it to be very stable, trigonal, planar, electrically inactive, and virtually invisible by photoluminescence and infrared-absorption spectroscopy. However, it could be Raman active. This defect is most likely a gettering center and the nucleus or precursor of a range of extended defects. Further, it suggests that the history of the sample may play an important role. [S0163-1829(97)02740-9]

I. INTRODUCTION

Vacancies and self-interstitials are the two basic intrinsic defects in silicon.¹⁻³ They are both rapid diffusers. The isolated self-interstitial has never been directly observed, but forms pairs with a range of impurities and plays important (though unidentified) roles in processes such as the formation of oxygen-related thermal donors.⁴ Vacancies are better understood than self-interstitials.³ The isolated vacancy and a number of complexes containing vacancies have been observed experimentally and discussed theoretically.

If one host atom is removed from the Si crystal, the four dangling bonds form an a_1 and t_2 states in T_d symmetry. The former lies in the valence band and the latter midgap. The vacancy has negative- U properties,⁵ and the only stable states have zero spin. In the case of V^{2+} , the t_2 levels are empty and the symmetry can remain tetrahedral. V^0 and V^{2-} are orbital triplets in T_d symmetry and therefore Jahn-Teller unstable. They distort to tetragonal symmetry, and substantial reconstruction takes place.⁶

Vacancies are rapid diffusers, with activation energies³ of 0.45 eV for V^0 , 0.32 eV for V^{2+} , and 0.18 eV for V^{2-} . A recent molecular-dynamics⁷ study of the neutral vacancy shows that it will hop in very short times at high temperatures. In the present study, we focus on the clustering of neutral vacancies.

Recent studies⁸ of the concentration of vacancies bulk Si (using Pt diffusion experiments) show that it is quite low even at temperatures of the order of 800 °C, with concentrations less than 10^{14} cm⁻³. However, above-equilibrium concentrations of vacancies are (believed to be) generated during a variety of processes such as ion implantation, electron or neutron irradiation, ion-beam milling, wet and dry etching,⁹ laser annealing, deposition of Al contacts, or exposure to various plasmas (hydrogenation, nitridization). The damage-inducing processes are normally followed by high-temperature anneals to “heal” the damage, as measured by electrical and optical means.

During such treatments, vacancies and self-interstitials may recombine, diffuse out of the material, interact with im-

purities, and/or form pairs or larger complexes. For example, a series of four vacancy-hydrogen complexes have been identified theoretically^{6,7,10} and experimentally.¹⁰ Vacancies form pairs¹⁻³ with acceptors (B, Al, Ga), donors (P, As, Sb), and other impurities (C, Ge, etc.). They also interact with each other and form divacancies, which themselves diffuse¹³ above ~ 250 °C with an activation energy of about 1.3 eV. Divacancies also interact with impurities. For example, V_2O_n complexes have been reported,¹⁴ and the divacancy has recently been proposed¹⁵ to be the center responsible for the 1018 meV photoluminescence (PL) band.¹⁶

Photothermal ionization spectroscopy (PTIS)^{17,18} studies show that electrically and optically inactive defects remain in neutron-irradiated material after high-temperature anneals. These defects can be electrically activated by hydrogenation. Similar activation of otherwise invisible defects has been shown to occur in Li-drifting experiments¹⁹ in the case of D defects. Positron annihilation spectroscopy²⁰ (PAS) studies show that a wide range of vacancy aggregates are created by damage-inducing treatments. Theoretical assignments for various positron lifetimes have been proposed²¹ but there is no experimental confirmation of most assignments.

Finally, Raman studies²² of ion-implanted Si have shown that a yet unidentified Raman line at about 90 cm⁻¹ intensifies as the implantation dose is increased. The properties of the spectrum are consistent with this line being caused by a defect cluster with a size of the order of 10 Å.

In the present paper, we report the results of systematic theoretical studies of vacancy aggregates (up to seven) in crystalline silicon. The key result is the prediction²³ that the trigonal and planar ring hexavacancy (V_6) is remarkably stable and essentially invisible to most electrical [deep-level transient spectroscopy (DLTS)] and optical [PL and Fourier transform infrared absorption (FTIR)] methods, although it could be Raman active. However, it is a large void in the crystal, and therefore should be a gettering center. It is also a plausible candidate as the nucleus or precursor of a number of extended defects, including H-related platelets²⁴⁻²⁶ and prismatic dislocations or dislocation loops.²⁷

Our results were obtained using a variety of theoretical

techniques to make sure that the predictions are independent of the methodology and of the way the host crystal is approximated. The methodologies are discussed in Sec. II, the results in Sec. III, and Sec. IV concludes the paper with a summary and some speculations.

II. METHODOLOGY

The calculations were performed using two methodologies which differ in the way the Schrödinger equation is solved and the host crystal approximated. (1) Density-functional (DF) based molecular-dynamics (MD) simulations, where the host crystal is represented by periodic supercells containing $64-n$ host atoms ($n = 1, \dots, 7$ is the number of vacancies), and (2) Hartree-Fock (HF) methods in molecular clusters containing $38-n$ host atoms.

The MD simulations were performed with the first-principles pseudoatomic orbital method developed by Sankey and co-workers.^{28,29} The code used for most calculations is based on a version of DF theory which uses the Harris energy functional and the local density approximation. A few fully self-consistent MD calculations were also performed to confirm the key results.

The HF calculations involved the approximate *ab initio* HF method of partial retention of diatomic differential overlap (PRDDO/M).³⁰ It uses minimal basis sets and provides approximate energetics and electronic structures but it predicts reliable geometries and is quite fast. We used these geometries as inputs for single-point *ab initio* HF (Ref. 31) calculations. For the Si atoms, we used Wadt-Hay pseudopotentials³² and split-valence polarized basis sets, in the same clusters. The surface H saturators had a minimal basis set. Each of these calculations requires 10–14 days of CPU time on a dedicated RS6000/375 workstation.

The configurations, energetics, and electronic structures calculated at the HF level can be compared to the ones obtained independently from the DF/MD simulations. This guarantees that the key results are independent of the methodology and the way the host crystal is described. The HF results also give a great deal of chemical data such as Mulliken charges, degrees of bonding,³³ overlap populations, and similar indices which provide information on how the crystal reconstructs. For details about the methodologies, see Ref. 34.

We first used MD simulations to find the possible configurations of aggregates of n vacancies, V_n , with $n = 1, \dots, 6$. We removed all the symmetrically inequivalent sets of n atoms from a 64-atoms supercell and quenched. This procedure forces convergence toward a local minimum of the potential energy and allows a comparison of the (fully relaxed) structures and energies of inequivalent V_n complexes. The time step in the MD calculations was fixed at 2 fs.

Then, the lowest-energy structures of each V_n were reoptimized using gradient techniques with the PRDDO/M method. Because of the large number of degrees of freedom, only the nearest neighbors (NN's) to the various vacancy aggregates were allowed to relax, but with no symmetry constraints. These geometries were used as inputs for the *ab initio* HF calculations.

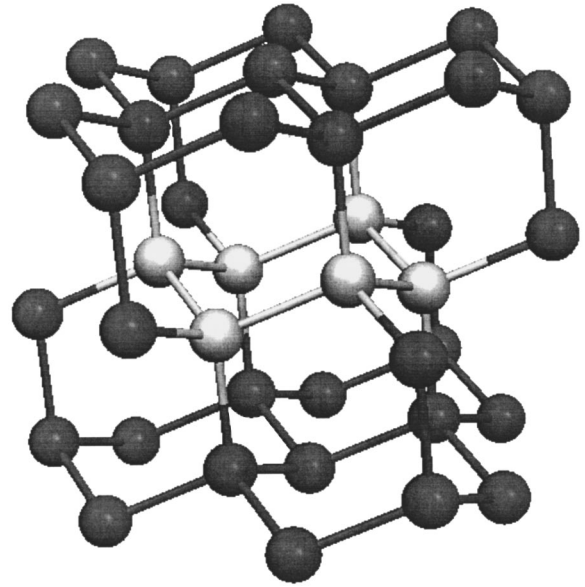


FIG. 1. Hexagonal ring in the diamond lattice. The figure only shows the atoms involved. It represents neither the relaxed hexavacancy nor the cluster or supercell used in the calculations.

III. RESULTS

A. Configurations and energetics

Only one symmetrically inequivalent monovacancy, divacancy, and trivacancy exist. However, there are four ways to remove four adjacent Si atoms from the lattice, 6 to remove five, and 18 to remove six. We optimized the geometry at the MD level for all the possible configurations by removing symmetrically inequivalent Si host atoms and quenching rapidly from 1000 K down to (almost) 0 K. This procedure guarantees that all the lattice relaxations and distortions are included, and provides both the configurations and the energetics.

The lowest-energy configurations of n -vacancy aggregates, with $n = 1, \dots, 6$ correspond to Si atoms successively removed from a hexagonal ring in the crystal. Figure 1 shows such a ring. Figure 2 shows the energy gained by adding an isolated monovacancy to the most stable aggregate of $n-1$ vacancies. In our calculations, this is $\Delta E_n = \{E_n + E_0\} - \{E_{n-1} + E_1\}$. This sets the zero of the energy at $\Delta E_1 = 0$. The formation energy of the vacancy calculated at the MD level is 4.15 eV, a value rather close to that of other authors (3.5–4.1 eV).^{11,12} Note that ΔE_n is minus the dissociation energy of V_n into $V_{n-1} + V_1$. The open circle is minus the experimental binding energy¹³ of the divacancy (1.6 eV). We obtained V_7 by removing a Si atom adjacent to the lowest-energy configuration of V_6 and quenching. The various inequivalent ways of doing this lead to similar energies.

Our calculated formation energies assume that vacancy aggregates grow by the addition of a single vacancy at a time. This is the most likely process since the monovacancy is by far the fastest of the diffusing species involved. Of course, vacancy aggregates can dissociate into other fragments. The MD calculations predict the following dissociation energetics. $V_2 \rightarrow V_1 + V_1$ costs 1.69 eV and $V_3 \rightarrow V_2 + V_1$ costs 2.08 eV. $V_4 \rightarrow V_3 + V_1$ and $V_4 \rightarrow V_2 + V_2$ cost 1.92 and

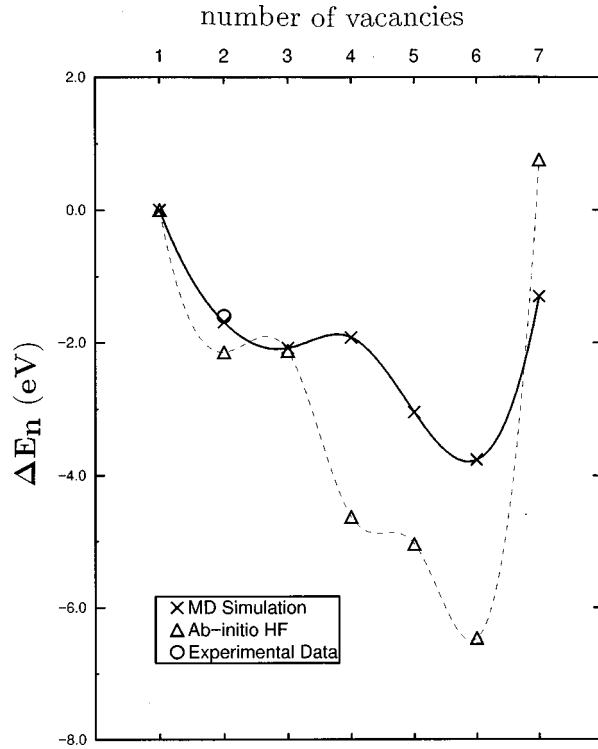


FIG. 2. Energy gained by adding a monovacancy to an aggregate of $(N-1)$ vacancies. The open circle is the experimental binding energy of the divacancy Ref. 13. The solid line is the MD result, which includes complete lattice relaxations. The dashed line is the *ab initio* HF result obtained in the PRDDO/M geometries with only NN relaxations. The qualitative features are the same except for V_7 . The HF result (exothermic) is suspect because the low-symmetry structure assumed for V_7 is not necessarily the lowest-energy heptavacancy, and because only a few NN's were allowed to relax. The MD result is completely quenched and is therefore much more reliable.

2.31 eV, respectively. $V_5 \rightarrow V_4 + V_1$ and $V_5 \rightarrow V_3 + V_2$ cost 3.05 and 3.28 eV, respectively. $V_6 \rightarrow V_5 + V_1$, $V_6 \rightarrow V_4 + V_2$, and $V_6 \rightarrow V_3 + V_3$ cost 3.76, 5.12, and 4.96 eV, respectively. Finally, $V_7 \rightarrow V_6 + V_1$ costs only about 1.3 eV. Thus, up to $n=6$, the lowest dissociation energy of V_n increases with n and occurs for the dissociation $V_n \rightarrow V_{n-1} + V_1$. However, the dissociation energy of V_7 is less than that of V_2 .

Figure 2 shows only the lowest-energy configuration of each aggregate of vacancies. The energies of the metastable configurations of the V_n 's calculated at the MD level are as follows.

V_4 has four inequivalent configurations. The three which do not have four Si atoms removed from a hexagonal ring are 0.08, 0.24, and 0.44 eV higher in energy, respectively. Clearly, at least two (and possibly three) metastable configurations of the tetravacancy may coexist.

V_5 has six inequivalent configurations. The five which do not have Si atoms removed from a hexagonal ring are 0.05, 0.24, 0.27, 0.30, and 0.55 eV higher in energy, respectively. Again, one would expect several metastable configurations to coexist. The one at 0.05 eV has the missing Si atoms in the $\{110\}$ plane in a "zig-zag" configuration.

V_6 has eighteen inequivalent configurations. However, those which do not correspond to a missing hexagonal ring are all much higher in energy. The lowest one is 0.87 eV

above the ring, and others are as much as 3.5 eV higher. We performed a constant-temperature (~ 1200 K) MD simulation starting with one of the metastable configurations of V_6 for about 3000 time steps (6 ps real time). During that time, a substantial rearrangement of the defect occurred. The host atoms around large vacancy aggregates hop in and out of the vacancies available. Although we were unable to pursue the simulation long enough for the defect to find its lowest-energy configuration (this may occur on the nano- or micro-second time scale), the behavior we observed shows that the metastable states of V_6 should quickly collapse into the ring configuration. Therefore, we believe that hexavacancies with configurations other than the ring are not realized in any appreciable concentration. We will call the ring configuration *the* hexavacancy, V_6 . After reconstruction, it has trigonal symmetry and is nearly planar. It is a disk-shaped void in the crystal, with a diameter of 7.8 Å (internuclear distance across the defect) and height of 4.4 Å (distance between the planes containing the NN's to V_6 perpendicular to the trigonal axis).

The plot of ΔE_n shows that V_6 is by far the most stable of the small vacancy aggregates. This result confirms an observation first made by Chadi and Chang³⁵ (see also Ref. 36). They obtained empirically an approximate formation energy for vacancy aggregates by counting the number of dangling bonds involved and multiplying it by the energy of a typical Si-Si bond. The energy of ring-structures such as V_6 (the next one is V_{10}) is lower because closed rings have fewer dangling bonds per missing atom than open vacancy structures. Our calculations confirm that the argument is correct.

The stability of V_6 suggests that the crystal is able to reconstruct much more efficiently around a ringlike structure than other configurations. This would not come as a surprise to chemists who are familiar with the stability of rings, with examples in many organic compounds. What is remarkable here is that the same stability exists when atoms are *missing* in a ringlike configuration.

B. Electronic structures

V_6 is very stable because the crystal reconstructs almost perfectly around it. Most of the reconstruction involves 14 host atoms around V_6 . Then, all the Si atoms adjacent to the hexavacancy are almost perfectly fourfold coordinated: the sum of the degree of bonding³³ associated with each of these atoms averages 3.83. In the bulk, all the valence electrons participate in covalent bonds and the sum is 4.00. In the perfect cluster, some polarization results from the presence of hydrogen surface saturators and this number drops to 3.94. In the V_n 's with $n \neq 6$, the degrees of bonding add up to much less (e.g., 3.38 for V_2) or are much smaller on individual atoms, indicating less efficient reconstruction.

The range of stabilities of the V_n 's means that the "dangling-bond-like" character which is often assumed for vacancy aggregates varies with n . This is clearly visible when plotting the energy eigenvalues of the various aggregates. We are well aware of the dangers associated with predicting the position or even number of energy levels in the gap on the basis of either HF or DF calculations. However, comparisons and trends are certainly more meaningful, especially when the same (qualitative) features are predicted by

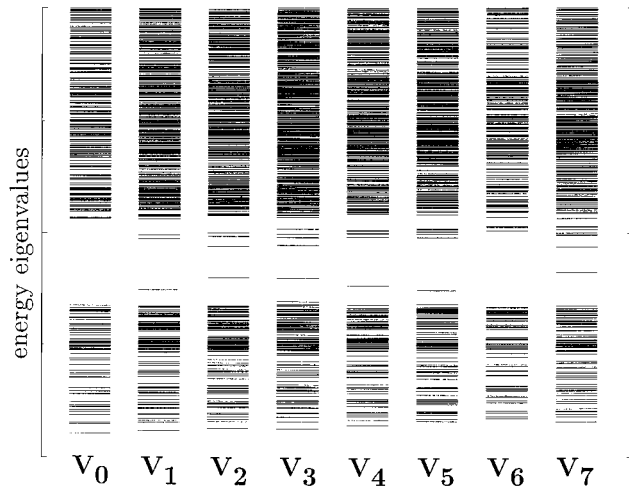


FIG. 3. Energy eigenvalues near the gap calculated at the *ab initio* HF level for the perfect cluster and the most stable vacancy aggregates V_n ($n = 1, \dots, 7$). While most aggregates have deep levels in the gap, V_6 is not “dangling-bond like.” The eigenvalues in the perfect cluster and the cluster containing V_6 differ only by some band tailing from the conduction band into the gap (unoccupied levels). A qualitatively identical result is obtained with MD simulations or a PRDDO/M calculation.

very different methodologies. This is clearly the case here, as the key features of the energy eigenvalues are identical in our PRDDO/M, *ab-initio* HF, and MD calculations.

The *ab initio* HF eigenvalues are typical and are shown in Fig. 3. All the V_n 's have deep levels in the gap except V_6 , which has no deep levels at all. The top of the valence band in the perfect cluster or supercell is within a few hundredths of an eV within that of V_6 . The bottom of the conduction band shows band tailing into the gap (unoccupied states). The band tailing depends on the basis set, and is more pronounced in the MD calculations than in the HF ones. In any case, all our results show that V_6 is not vacancylike, and should be electrically inactive. In contrast to the other V_n 's, we do not expect V_6 to be an electron-hole recombination center, be visible by DLTS, or produce sharp PL features.

We also calculated the net dipole moment of the V_n 's at the HF level. In atomic units, they are 0.00 when no vacancy is present, 0.09 for V_1 , 0.22 for V_2 , 3.03 for V_3 , 0.19 for V_4 , 0.26 for V_5 , 0.01 for V_6 , and 1.67 for V_7 . The dipole moment associated with V_6 is exceedingly small. The intensity of the signal in FTIR depends on how much the dipole moment varies³⁷ rather than on its absolute magnitude. However, small oscillations of V_6 do not alter much the reconstruction and the dipole moment remains small. Therefore, this defect should be mostly invisible to FTIR spectroscopy.

Note that the dipole moments of V_3 and V_7 are surprisingly larger than those of the other V_n 's. Both defects have dangling bonds on host atoms that are too far apart from each other to reconstruct efficiently. One of the dangling bonds is doubly occupied and the other one empty. As a result, two distant atoms carry large and opposite charges, resulting in a large dipole moment. While this is consistent with the negative- U behavior of dangling bonds, this may also be caused by the use of a closed-shell HF wave function, which forces the orbital occupation to be 0 or 2. We suspect that the use of a multiple-determinant wave functions, allowing for

fractional occupancy, would reduce the magnitude of these dipole moments. Such calculations are computationally prohibitive at this time for the defects under study.

Raman-active modes could be visible if they are not degenerate with host atom vibrations and if high-enough concentrations of V_6 can be generated. We did not investigate the vibrational modes of V_6 . We estimate that much larger supercells will have to be used in order to obtain reliable vibrational properties. Such studies are being planned.

IV. DISCUSSION

A. Summary of the key results

We have calculated the configurations, stability, dissociation energies, and electronic structures of neutral vacancy aggregates in crystalline Si. We used very different theoretical techniques. DF-based MD simulations in large periodic supercells, approximate *ab initio* HF, and *ab initio* HF in molecular clusters. The results of these calculations agree on the following features.

(1) The lowest-energy configuration of vacancy aggregates V_n with $n = 1, \dots, 6$ occurs when the host atoms are successively removed from a hexagonal ring in the diamond lattice.

(2) One gains energy by forming an aggregate of n vacancies out of an isolated vacancy plus an aggregate of $(n - 1)$ vacancies. The gain in energy has a pronounced maximum for the ring-hexavacancy, V_6 .

(3) V_4 and V_5 have metastable configurations quite close to the lowest-energy one. We suspect that several configurations of these aggregates coexist.

(4) The lowest-energy metastable configuration of V_6 is nearly 0.9 eV above the ring structure. At high temperatures, the metastable configurations of V_6 begin to rearrange themselves at the picosecond time scale. It is highly unlikely that configurations of V_6 other than the ring are found in appreciable concentrations.

(5) V_6 has trigonal symmetry and is nearly planar. It is a large disk-shaped void in the crystal, with diameter of 7.8 Å (internuclear distance perpendicular to the trigonal axis) and height of 4.4 Å (interplanar distance along the trigonal axis). Because it is a large void, V_6 is likely to be a gettering center for a range of impurities.

(6) Up to $n = 6$, the lowest dissociation energy occurs for the process $V_n \rightarrow V_{n-1} + V_1$. This energy increases with n . The dissociation energy of V_7 is smaller than that of V_2 , which itself is much smaller than that of V_6 .

(7) All the vacancy aggregates have deep levels in the gap except V_6 , which shows only some band tailing from the conduction band into the gap (unoccupied levels). V_6 should not be visible by DLTS or give rise to sharp PL bands (the small dipole moment suggests a small electron capture cross section).

(8) All the neutral vacancy aggregates have a net dipole moment except V_6 , which should not be IR active. We cannot comment on Raman-active modes at this time. The dipole moments of V_3 and V_7 are much larger than those of the other vacancy aggregates. We suspect that the magnitude of

these dipole moments is exaggerated because of the use of a closed-shell wavefunction. We do not know how much the variations in the dipole moments of the V_n 's will affect positron capture cross sections in PAS experiments.

As noted in Refs. 35,36, the stability of V_6 is primarily caused by the fact that it is a closed ring. The fundamental argument that rings tend to be more stable than open configurations must remain true for a wide range of covalent materials. However, the formation probability of such vacancy aggregates depends on the diffusivity of neutral monovacancies and the thermal stability of the smaller aggregates, in particular, the divacancy. V_6 can only form at temperatures which are simultaneously high enough for monovacancies to be mobile and low enough for divacancies to be stable.

B. Relation to unexplained experimental data

There is no direct experimental evidence for the existence of V_6 , and indeed theory predicts that although V_6 must exist, it should be difficult to detect. However, there is experimental evidence that some invisible defect remains even after high-temperature anneals, suggesting that it is very stable. We are aware of the following cases.

(1) Neutron-transmutation doping is achieved by exposing Si to a flux of energetic neutrons. This exposure results in considerable radiation damage which is visible by electrical and optical means. The damage disappears following 850–1000 °C anneals. However, if the annealed material is exposed to atomic H, shallow donors appear.^{17,18} Hydrogen strongly traps at some invisible defect and activates it. A defect such as V_6 is sufficiently stable to survive the anneal, is electrically and optically inactive, and is likely to be a trap for (multiple) hydrogen interstitial(s). The properties of $\{V_6, H_n\}$ complexes are under investigation.

(2) Other defects that become visible after gettering are (or are related to) the D defects. These are large octahedral voids³⁹ which are believed to form near the solid/liquid interface during the growth of the crystal. Shallow donors are seen through the precipitation of interstitial Li ions.¹⁹ Lithium forms very long bonds³⁸ with Si and is not stable in a vacancy.⁴⁰ However, it should fit in the much larger hexavacancy.

(3) Theory predicts that large, stable, and essentially invisible V_6 defects should form during a variety of damage-inducing treatments and survive high-temperature anneals. This suggests that the history of the sample should affect its properties.

(4) The low-energy implantation of noble-gas (NG) ions into Si, followed by a brief anneal around 250 °C, gives rise to characteristic PL bands.¹⁶ These defects have recently

been assigned¹⁵ to $\{NG, V_2\}$ complexes. Further anneals at 450 °C lead to the disappearance of the sharp spectra, which are replaced by a broad PL, independent of the NG. Since the binding energies of the $\{NG, V_2\}$ complexes are very large and the complex itself not mobile, it is nearly impossible that the anneal dissociates the defect or drives it to a surface. However, since the stability of NG impurities increases with the volume around them, a likely explanation is that the complex binds more vacancies leading to the formation, for example, of $\{NG, V_6\}$ complexes. The free volume in V_6 is sufficiently larger than the atomic radius of the impurity that a NG-independent PL could result.

(5) The exposure of crystalline Si to a remote H (or D) plasma may result in the formation of huge, disk-shaped defect structures known as platelets.^{24–26} They appear in the sub-surface region and are visible by TEM.²⁶ Platelets are trigonal and planar. They appear to have a nucleation and a growth stage.²⁵ If a sample is hydrogenated at high temperatures, no platelets are generated. However, if the sample is exposed to a plasma first at low then at high temperatures, the concentration of platelets is maximized. One possible scenario could be as follows. Hexavacancies cannot form if the treatment is entirely done at temperatures at which divacancies are unstable. Thus, a low-temperature pretreatment may be needed for stable V_6 's to form. These defects could be the nucleus around which platelets grow. Then, high-temperature exposure would result in large concentrations of H diffusing into the material, maximizing the growth of the defect.

(6) The V_6 defect resembles small prismatic dislocations such as those nucleated by vacancy condensation.²⁷ It is also the smallest possible dislocation loop. Although it is not clear how one goes from an isolated V_6 to an extended structure, the MD calculations show that V_6 should trap more vacancies.

Note that we do not imply or even suggest that V_6 is related to all these observations. It is probably neither the only explanation, nor is V_6 the only stable vacancy aggregate. For example, V_{10} is another ring which has been predicted³⁵ to be very stable. What we do suggest is that V_6 is one simple defect that combines most of the properties needed to explain the experimental data. V_6 may well be a long-overlooked, fundamental, intrinsic defect in Si.

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