Vacancy and vacancy-hydrogen complexes in silicon

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The neutral vacancy (V) and the $\{V,H_n\}$ $(n = 1, \ldots, 4)$ complexes in silicon are studied in various molecular clusters at the approximate *ab initio* and *ab initio* Hartree-Fock levels, with post-Hartree-Fock corrections in electron correlation. The quantities calculated are the equilibrium configurations and electronic structures, dissociation energies, diffusion paths, and activation energies. The dissociation energies are compared to those of other traps for H calculated at the same level of theory, such as substitutional C, interstitial Ti, or the $\{B, H\}$ pair. The calculations predict that the $\{V,H_1\}$ pair in Si should be mobile above room temperature. A part of the barrier for diffusion of $\{V,H_1\}$ is lower than that of V, due to a mechanism analogous to the H-enhanced diffusion of interstitial O in Si. Another part of this barrier is higher than that for V. The consequences of this process include the possibility of enhanced diffusion of H in polycrystalline versus crystalline Si and leads us to propose a mechanism for the nucleation of platelets in the subsurface region of plasma-exposed Si.

I. INTRODUCTION

Vacancies (V) and self-interstitials (I) are the most important intrinsic defects in silicon.[1] Isolated Frenkel pairs $(V$-$I)$ are created by radiation damage at low temperatures, or during many processing steps, such as ion implantation, exposure to a H plasma, etching, or chemical treatments of the surface. Both V and I are highly mobile. They can of course annihilate each other, but each can also form pairs (or larger complexes) with dopants or other impurities. The efficiency of pair formation is sample dependent. For example, p-type Si contains more vacancies than n-type Si because self-interstitials tend to become trapped at group III dopants, leaving an excess of vacancies. In contrast, V-I recombination is more prevalent in n-type Si in which vacancy production is less efficient.

Electron paramagnetic resonance (EPR) studies[1,2] have shown that the spin doublets V^- and V^+ can be created by illuminating the sample, but are less stable than the charge states for which the electrons are paired. On the basis of Green's function calculations,[3] Baraff *et al.* have shown that the vacancy is an Anderson "negative-U" system, i.e., that the gain in correlation energy achieved by pairing two electrons (or holes) in a dangling bond exceeds the Coulomb repulsion of the two electrons (or holes). Thus, the stable charge states of the vacancy in Si are the spin singlets[4,5] V^{++}, V^0, and V^{--}. As discussed in Ref. 1, in all but the $++$ charge states, the vacancy is an orbital triplet in T_d symmetry. It is therefore Jahn-Teller unstable and spontaneously distorts to a lower symmetry configuration. The reconstructed neutral vacancy has tetragonal (D_{2d}) symmetry, and the two electron pairs are believed to reside in two long Si$-$Si bonds.

The isolated vacancy is highly mobile. The activation energies for V^{++}, V^0, and V^{--} are 0.33 ± 0.02 eV (Ref. 6), 0.45 ± 0.04 eV (Ref. 7), and 0.18 ± 0.02 eV (Refs. 7 and 8), respectively. Which charge state is stable in a given sample depends on the Fermi level and the temperature, but V^0 is the most stable center up to about room temperature.[1]

A number of authors have calculated the properties of the vacancy in diamond and silicon (for recent reviews, see Refs. 9 and 10). The problem is difficult to handle because of the variety of charge states involved, the orbital degeneracy of the undistorted center, the amount of lattice reconstruction, and the deep-level character of the gap states associated with the vacancy. Even though the electronic structure can be qualitatively described using just a few orbitals corresponding to the four dangling bonds,[11] accurate total energy calculations which include lattice relaxations and distortions are needed to get the correct ground state geometry of the defect. Further, electron correlation plays an important role,[12] mostly because of the presence of stretched covalent bonds. Recent local density-functional calculations[13] in large supercells have been used to explain the main features of electron nuclear double resonance data[14] on V^-.

As mentioned above, the vacancy is mobile in Si, even at low temperatures, and readily interacts with various impurities and defects, including other vacancies. The impurity of interest in the present work is hydrogen. Interstitial H in semiconductors has been the subject of intense studies, in particular in the past ten years.[15] Hydrogen interacts with many impurities and defects, forming covalently bound pairs and larger aggregates, and changing the electrical and optical properties of the centers involved. In particular, hydrogen ties up dangling bonds at surfaces, interfaces, grain boundaries, dislocations, as well as vacancies.[16]

Infrared (IR) absorption studies of hydrogenated samples show an abundance of sharp lines corresponding to

H stretching and wagging vibrational modes in a variety of configurations.[17,18] Not all the lines have been identified, but some of them are now known to correspond to specific defects. In particular, the Si$-$H stretching frequencies at 1832 cm^{-1}, 1980 cm^{-1}, 2066 cm^{-1}, and 2210 cm^{-1} have been assigned to the vacancy decorated with 1, 2, 3, and 4 H atoms, respectively.[19] The increase in frequency is caused by the interactions between Si$-$H dipole moments and by the "crowding" experienced as more H atoms squeeze inside the vacancy, resulting in shorter Si$-$H bond lengths. The $\{V,H_2\}$ complex has recently been identified also by optically detected magnetic resonance.[20]

It should be noted that a large number of possible geometrical configurations may lead to similar IR bands. For example, the Si$-$H vibrational frequencies for H in a vacancy, grain boundary, or dislocation, are within 100$-$200 cm^{-1} from each other and from other complexes, such as one or two H's in a divacancy or an internal surface.[21] Further, more than one charge state is a $priori$ possible for many complexes. For example, $\{V,H_1\}^0$ and $\{V,H_1\}^+$ could coexist and have slightly different IR frequencies and symmetries. There are a few situations where symmetry considerations suffice at identifying a center. In particular, $\{V,H_4\}$ should be the only vacancy-hydrogen complex with T_d symmetry, unless a lower-symmetry complex reorients fast enough to average out to T_d symmetry. Calculations of Si$-$H stretching frequencies are not accurate enough to pinpoint with confidence one particular mode out of the many lines near 2 000 cm^{-1}. Even accurate calculations have an $average$ error of about 5%. This "error bar" almost always includes several observed IR modes. As a result, relatively few complexes containing vacancies and hydrogen atoms are identified with a high degree of certainty. As more accurate theoretical studies become available, the geometrical configurations and electronic structures are becoming known, and the number of possible candidates for a given IR line or EPR spectrum is reduced.

Many authors have studied $\{V,H_n\}$ complexes in Si.[22] Singh et $al.$[23] used extended Hückel theory, a semiempirical (not self-consistent) molecular orbital approach, to study $\{V,H_n\}$ complexes, with $n = 1,\ldots,4$ in the Si$_{35}$ cluster, without surface saturators. All the host atoms were assumed to be at their perfect crystal sites, but the Si$-$H bond lengths were optimized and found to be near 0.65 times the Si$-$Si equilibrium bond length, i.e., about 1.53 Å. The key results of this study are that the successive H's saturate Si dangling bonds with H pointing toward the center of the vacancy, and that the calculated vibrational frequencies increase with the number of H's in the vacancy.

Pickett[24] used the semiempirical self-consistent pseudopotential method to study $\{V,H_4\}$ assuming T_d symmetry in 7 atoms/cell periodic supercells. The Si$-$Si and Si$-$H bond lengths were picked to be 2.35 and 1.52 Å, respectively. The $\{V,H_4\}$ complex was found to be electrically inactive. Grekhov et $al.$[25] used the semiempirical Hartree-Fock (HF) method of intermediate neglect of differential overlap in the Si$_4$H$_{12}$ cluster to study $\{V,H_n\}$, with $n = 1,\ldots,4$, with Si$-$Si and Si$-$H bond lengths

set at 2.352 and 1.48 Å, respectively. No gap levels were found in the case of $\{V,H_4\}$, in contrast to $\{V,H_n\}$ ($n = 1,2$, or 3) for which such levels were present. A similar conclusion regarding $\{V,H_4\}$ was reached by Di-Vincenzo et $al.$[26] on the basis on Green's functions calculations. No relaxations or distortions were allowed, and the Si$-$H bond length was picked to be 1.48 Å. The complete passivation of $\{V,H_4\}$ was also reported by DeLeo et $al.$[27] on the basis of scattering-wave (SW-$X\alpha$) calculations in the H$_4$Si$_4$H$_{12}$ cluster.

Frolov and Mukashev[28] also studied $\{V,H_4\}$ in T_d symmetry in the H$_4$Si$_4A_{12}$ cluster, where the A's are 3s orbitals centered at perfect lattice sites outside the cluster and are there to saturate the surface dangling bonds. The optimized Si$-$H bond lengths were found to be 1.40 Å, and the authors suggest that the IR frequency of this complex should be near 2223 cm^{-1}. Bai et $al.$[29] reached the same conclusion on the basis of valence force field as well as semiempirical HF modified neglect of differential overlap (MNDO) calculations of $\{V,H_4\}$ in hydrogen-saturated Si$_{11}$H$_4$ and Si$_{16}$H$_4$ clusters, with all Si atoms at their perfect lattice sites.

More systematic studies of $\{V,H_n\}$ complexes were conducted by Deák et $al.$[30] with the semiempirical HF method of modified intermediate neglect of differential overlap (MINDO/3) in periodic clusters with a 32 atom unit cell. The symmetry of the complexes and the optimized Si$-$H bond lengths were calculated to be C_{1h} (but close to C_{3v}) and 1.499 Å for $\{V,H_1\}$, C_{2v} and 1.489 Å for $\{V,H_2\}$, C_{3v} and 1.485 Å for $\{V,H_3\}$, T_d and 1.490 Å for $\{V,H_4\}$. After scaling, the associated stretching modes were predicted to be 2057, 2080, 2106, and 2109 cm^{-1}, respectively. Finally, the calculated dissociation energies of one H from $\{V,H_n\}$ were found to be 2.50, 2.47, 2.41, and 2.54 eV for $n = 1$, 2, 3, and 4, respectively. These energies are close to the 2.2 eV obtained from first principle calculations[31] for H attached to a dangling bond in Si.

Finally, the electronic structures and energy levels of $\{V,H_n\}$, $n = 1,\ldots,4$ were recently examined by Xu[32] using a semiempirical tight-binding approach in very large supercells. The calculations assumed that the Si atoms are all at ideal lattice sites and that the H atoms point toward the center of the vacancy with Si$-$H=1.45 Å. Only $\{V,H_4\}$ is found to be fully passivated, and the hyperfine structures of $\{V,H_1\}$ and $\{V,H_3\}$ are predicted.

Many of the above-mentioned studies used empirical or semiempirical methods and/or small clusters or cells. Only a few authors performed total energy calculations, optimized Si$-$H bond lengths, or allowed for relaxations and distortions of host atoms around the vacancy. Nevertheless, these studies provide critical insight into the problem of the interactions between hydrogen and dangling bonds in Si. Several results predicted by a number of authors seem to be independent of the level of theory or the way the host crystal is approximated. In particular, there is general agreement on the following points.

(i) Hydrogen-vacancy interactions lead to the formation of covalent Si$-$H bonds, with the H's pointing toward the center of the vacancy (approximately along trigonal axes).

(ii) Only the $\{V,\mathrm{H}_n\}$ complexes with $n < 4$ have electrically active levels in the gap.

(iii) The Si—H bond lengths get shorter as the number of H's in the vacancy increases, and the vibrational frequencies increase correspondingly.

(iv) The IR line near 2220 cm^{-1} should be assigned to $\{V,\mathrm{H}_4\}$ rather than interstitial SiH$_4$.

(v) The Si—H dissociation energy in crystalline Si is of the order of 2.2–2.6 eV, a value which agrees with the measured dissociation energy (2.5 ± 0.2 eV) of H from Si dangling bonds at *internal* surfaces.[21,33]

Note that point (i) above was assumed by most authors, and that less probable configurations such as an H$_2$ molecule in the vacancy vs the $\{V,\mathrm{H}_2\}$ complex or more exotic configurations for other $\{V,\mathrm{H}_n\}$ complexes, were not considered. Further, no method free of semiempirical parameters has yet been used to optimize geometries around the hydrogen-decorated vacancy. Finally, all methods allowing total energy calculations used small clusters or cells.

In the present contribution, we perform systematic calculations near, at, and beyond the *ab initio* HF level for the neutral $\{V,\mathrm{H}_n\}$ complexes $(n = 0, \ldots, 4)$ in various molecular clusters. The lowest-energy configurations are calculated including the relaxations and distortions of the crystal around the vacancy. We also calculate the diffusion paths and activation energies of the neutral vacancy and of the neutral and positively charged $\{V,\mathrm{H}_1\}$ pairs, and estimate the activation energies of other $\{V,\mathrm{H}_n\}$ complexes. No attempt is made to study the neutral vacancy in T_d symmetry, since it is an orbital triplet which needs to be described with a multideterminant wave function. The relaxed vacancy, however, is an orbital singlet and is well described at the theoretical level used here. We used a closed-shell (spin 0) restricted HF wave function (RHF) for V^0, $\{V,\mathrm{H}_1\}^+$, $\{V,\mathrm{H}_2\}$, and $\{V,\mathrm{H}_4\}$, and an open-shell (spin 1/2) unrestricted HF wave function (UHF) for $\{V,\mathrm{H}_1\}^0$ and $\{V,\mathrm{H}_3\}$. We repeated the RHF calculations using a UHF wave function to compare the energies, as will be discussed below. We did not compare total energies for, e.g., $\{V,\mathrm{H}_2\}$ in the singlet and triplet states. Because the vacancy and $\{V,\mathrm{H}_n\}$ complexes reconstruct in a way that *pairs* of dangling bonds have covalent overlap, it is unlikely that a spin triplet state (no covalent overlap) would be lower in energy than the spin singlet state. For this reason, we do not expected Hund's rule to hold in the present situation.[1]

The possibility that hydrogen-decorated vacancies could be mobile in Si was first raised by Corbett *et al.*[34] as a possible explanation for the shape of secondary-ion mass spectrometry (SIMS) profiles of hydrogen and deuterium in the subsurface region of Si. Vacancies, generated at the surface in concentrations unrelated to the concentration of impurities, could trap hydrogen just below the surface, then diffuse into the bulk. As noted in Ref. 34, "the vacancies are not in equilibrium, being pumped in from the surface." Thus, in this process, the energy needed to generate the vacancies is provided by the plasma on the surface of the sample, and there is no need to assume that H creates Frenkel pairs in the bulk.

The suggestion that $\{V,\mathrm{H}_n\}$ complexes may be mo-

bile has been all but forgotten until recent hydrogenation studies by Sopori *et al.*[35,36] In these experiments, hydrogenation was performed in float-zone (FZ), Czochralski (CZ), and polycrystalline (poly) Si. The studies involved the passivation by hydrogen of electrically active defect centers in photovoltaic devices using back-side hydrogenation with a Kaufman ion source for 15–30 min with ion energies of 1.5 keV at 250 °C. Under the conditions of these experiments, hydrogen was able to reach and passivate defects in the active regions of the devices (observed indirectly via *I-V* characteristics) *much faster* in material rich in vacancies (poly-Si) than in higher-quality but vacancy-poor material. The back side to active region distance is a few hundred microns. Extensive SIMS and transmission electron microscopy studies resulted in the conclusion that grain boundaries in poly-Si were not responsible for the enhanced diffusion of hydrogen. Instead, they were found to be traps for H, thus impeding rather than enhancing diffusion. This observation is consistent with another study of grain boundaries.[37] The explanation proposed in Refs. 35 and 36 involved rapidly diffusing vacancy-hydrogen pairs, using the vacancies already present in the bulk of poly-Si, rather than vacancies pumped from the surface during the hydrogenation or created by the implantation.

This paper is organized as follows. The theoretical level and cluster description of the host are described in the following section. Then, we present our results for the configurations of the isolated (neutral) vacancy and the $\{V,\mathrm{H}_n\}$ complexes, and for the diffusion paths and barriers. A summary and the implications of our findings regarding hydrogen diffusion and platelet formation are in the last section.

II. METHODOLOGY

The host crystal is approximated by the following hydrogen-saturated[22] molecular clusters: Si$_5$H$_{12}$, Si$_8$H$_{18}$, Si$_{35}$H$_{36}$, and Si$_{44}$H$_{42}$. The surface saturators are located at optimized Si—H bond lengths along trigonal axes and the lattice constant is optimized, as described in Ref. 38. In these clusters, a centrally located host atom was removed to create the vacancy, and zero to four H atoms were added in and around the vacancy. For each of these five defect centers, the nearest neighbor (NN) host atoms were allowed to relax and distort, and the 0–4 hydrogen atoms in or near the vacancy were also optimized.

In the case of V, we allowed for trigonal and tetragonal distortions in addition to the breathing mode. In the case of $\{V,\mathrm{H}_1\}$, we optimized a wide variety of configurations, including atomic H at the center of the vacancy, bridging one of the reconstructed Si—Si bonds (see next section), at an antibonding (AB), a nearby bond-centered (BC), or a tetrahedral interstitial (T) site, and saturating a Si dangling bond inside the vacancy. In the case of $\{V,\mathrm{H}_2\}$, we compared total energies for a number of optimized conformations, including the H$_2$ molecule in the vacancy, two H's saturating two Si dangling bonds, etc. We also tried various possibilities for $\{V,\mathrm{H}_3\}$ and $\{V,\mathrm{H}_4\}$.

The geometries were all optimized with the approximate *ab initio* HF method of partial retention of diatomic differential overlap (PRDDO).[22,39,40] This method contains no semiempirical parameters and allows geometry optimizations to be performed in C_1 symmetry in systems far beyond the reach of true *ab initio* techniques. PRDDO predicts approximate energies and wave functions, but is very good at reproducing the charge distributions and geometries obtained at the *ab initio* (minimal basis set) level. The newest version of the code produces average errors (relative to *ab initio* HF results) of $0.016e$ for atomic charges and 0.010 Å for bond lengths, except for transition metal-ligand bond lengths for which PRDDO is systematically superior (relative to experiment) to *ab initio* minimal basis set results.

We then looked for diffusion paths for the vacancy as well as the $\{V,H_n\}$ complexes. In the case of V, we moved a Si atom NN to V along a trigonal axis toward the vacancy, leaving a new vacancy behind. In these calculations, the crystal was allowed to relax for many intermediate locations of the moving Si atom. In the case of $\{V,H_n\}$ with $n \geq 1$, we looked for plausible mechanisms which involve the motions of V and of one or more H atoms. These will be described below.

Once the optimized geometries are known, it is possible to perform single point calculations at higher levels of theory. We performed *ab initio* HF calculations with split-valence polarized (SV*) basis sets in the smaller cluster, using the PRDDO geometries. At selected points of the potential energy surface, we also performed post-HF calculations to include electron correlation into the calculations. These were second-order Møller-Plesset expansions in electron correlation (MP2).[41] We recently obtained activation energies at the SV*+MP2 level very close to experimental values in the case of interstitial O in Si.[42]

The potential energy surfaces obtained at the *ab initio* SV* level are more reliable than the PRDDO ones, and the MP2 values are again better than the *ab initio* ones. However, there is a price to pay. A single point PRDDO calculation in C_1 symmetry in a cluster containing 44 Si atoms takes about 60 min of CPU time on an RS6000/355 workstation. On the other hand, the requirements in CPU time and disk space for the higher level calculations are *much* greater. For example, a single MP2 calculation in C_1 symmetry in HSi_7H_{18} takes over 17 h of CPU time and nearly fills our 1.8 gigabytes of available disk space. As a result of having to use a small cluster, only the NN's to the vacancy can be relaxed, and their relaxations are hindered by the nearby presence of strong surface Si−H bonds. Thus, although the *ab initio* SV* and MP2 potential surfaces are much smoother than the PRDDO ones, we expect them to overestimate the real ones: In the real crystal, not only are further host atom shells able to relax, but the immediate NN atoms can move more freely than in our small clusters. If one assumes, e.g., a 0.05 eV correction for each NN and second NN that cannot relax in the small cluster, the total correction may be of the order of several tenths of an eV. Further, although the MP2 calculations include one- and two-electron excitations, the three-, four-, (and

higher) electron excitations are missing. These terms are exceedingly small, but there are many of them. The error resulting from these omissions is difficult to estimate. However, we know that it will be larger at saddle points of the energy than at local minima, because the stretched bonds at saddle points involve more electron correlation than those in the stable configurations.

Thus, we expect that even our best calculations overestimate potential energy barriers (activation energies). It is, however, possible to *scale* the results by comparing calculated and known barriers. In our case, the experimental activation energy for diffusion of the neutral vacancy is 0.45 ± 0.04 eV. As will be discussed below, our calculated value at the MP2 level is 1.1 eV, i.e., about 0.6 eV too high. The calculated potential energy barrier for V is compared to that for other complexes, calculated at the same level of theory.

III. RESULTS

A. Configuration of the neutral vacancy

The optimization of the local geometry around a neutral vacancy in Si was performed at the PRDDO level in the $Si_{34}H_{36}$ cluster with a minimal basis set on all the atoms except the four NN's to the vacancy which had an additional set of d orbitals. The result shows that the neutral vacancy distorts to D_{2d} symmetry. The four NN's to the vacancy move slightly away from the vacancy and toward each other by pair, as schematically illustrated in Fig. 1. The motion away from V shortens the three Si−Si bonds left: The sp^3 hybridization is no longer possible because Si is adjacent to a vacancy, and becomes a little closer to sp^2, which has shorter bond lengths. The motion of each Si atom off the trigonal axis is imposed by the Jahn-Teller theorem and maximizes the covalent overlap between two pairs of Si atoms. The net displacement of each Si atom is only 0.12 Å, which is sufficient to replace the four dangling bonds by two pairs of very long but covalent bonds.

In each pair, the two Si atoms are 3.759 Å apart, but the degree of bonding[43] is 0.73. This indicates that the character of the reconstructed bonds corresponds to 73%
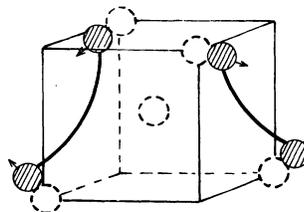
FIG. 1. Reconstructed neutral vacancy in Si. In the reconstructed bonds, the Si−Si internuclear distance is 3.759 Å, and the amount of covalent (bonding) overlap amounts to 73% of a two-electron bond. As for Si atoms in different pairs, Si−Si=3.929 Å, and there is no covalent overlap. The symmetry is D_{2d}. The dashed circles show the perfect lattice sites.

of a two-electron covalent bond. *Ab initio* calculations confirm that the overlap population is indeed large and positive (0.84), showing a bonding overlap. The distance between Si atoms in different pairs is 3.929 Å, but the degree of bonding is only 0.003, i.e., there is no covalent overlap at all between these two atoms.

We also calculated the activation energy for the re-orientation of the neutral vacancy between two tetragonal orientations. This energy is 0.33 eV with PRDDO in the $Si_{34}H_{36}$ cluster and 0.37 eV at the *ab initio* SV* level with MP2 corrections in the Si_7H_{18} cluster. In this case, electron correlation corrections are small and the better result is the one obtained in the largest cluster. Stress-induced alignment experiments provide the value 0.23 eV, a number reasonably close to our result. These experiments, described in Ref. 1, involve applying stress at high temperatures in the dark, then cooling down to about 20 K, relieving the stress, illuminating the sample, and monitoring the resulting V^- species.

Note that the good agreement between the experimental number and even the PRDDO one can be understood as follows. The transition point configuration for this re-orientation is very close to the equilibrium configuration (small atomic displacements). Therefore, the errors resulting from the use of a minimal basis set and the neglect of electron correlation are very similar at both points, and the energy difference cancels out most of the error. In contrast, the large difference between the transition point configuration for the diffusion of V and its equilibrium configuration is much greater. This suggests that the correlation corrections are quite different at these two points. As a result, the PRDDO activation energy for diffusion is much larger than the experimental number, and the effect of SV*+MP2 calculations is much more significant.

B. Configurations and relative stability of the $\{V,H_n\}$ complexes

For all $\{V,H_n\}$ complexes, we found that one configuration is always substantially lower in energy than any other. It corresponds to H saturating a Si dangling bond, pointing toward the center of the vacancy, along a trigonal axis. This result confirms the correctness of the geometries utilized by other authors. Schematic representations of the four complexes are shown in Fig. 2. Our geometries are close to those reported in Ref. 30

$\{V,H_1\}$ distorts to C_1 symmetry. It has one two-electron Si–H bond, one reconstructed Si–Si bond, and one dangling bond. The C_{3v} configuration is 0.25 eV higher, and is not a local minimum of the energy. The other configurations, with H at a variety of sites near V, are all more than 1 eV above the latter configuration. In particular, the two reconstructed Si–Si bonds are too long for H to form a bridged bond there: If placed midway between the two Si atoms in a pair, H moves off toward one of them and the $\{V,H_1\}$ complex reconstructs to C_1 symmetry as described above. The highest-energy configuration we found has H at the center of the vacancy.

This "on-center" defect has been assumed by several authors for $\{V,H_1\}$.[26,27] We find it to be a local maximum of the energy, far above the ground state.

$\{V,H_2\}$ distorts to C_{2v} symmetry, and has two two-electron Si–H bonds and one reconstructed Si–Si bond. The configurations where one H is at a bonding site and the other at an AB site, where both H's are at AB sites, or form an H_2 molecule in the vacancy are all several eV higher in energy.

$\{V,H_3\}$ has C_{3v} symmetry, with three equivalent Si–H bonds pointing toward the center of the vacancy, and a Si dangling bond along the trigonal axis. Again, other combinations involving AB or nearby BC sites, are at least 1.5 eV higher in energy.

Finally, $\{V,H_4\}$ has T_d symmetry, with four Si–H bonds. It is the only complex with no level in the gap.

The optimized Si–H bond lengths are 1.397 Å (for $\{V,H_1\}$), 1.387 Å (for $\{V,H_2\}$), 1.382 Å (for $\{V,H_3\}$), and 1.378 Å (for $\{V,H_4\}$). The shortening of the Si–H bond lengths as the number of H atoms in the vacancy increases is consistent with the increase in vibrational frequency recently reported.[19]

$\{V,H_1\}^0$ C_1
Si – –Si = 3.880 Å   (0.73)
Si – H = 1.397 Å   (0.91)

$\{V,H_1\}^+$ C_{3v}
Si – –Si = 4.160 Å   (0.28)
Si – H = 1.381 Å   (0.92)

$\{V,H_2\}$ C_{2v}
Si – –Si = 3.757 Å   (0.75)
Si – H = 1.387 Å   (0.97)

$\{V,H_3\}$ C_{3v}
Si – H = 1.382 Å   (0.98)

$\{V,H_4\}$ T_d
Si – H = 1.378 Å   (0.98)
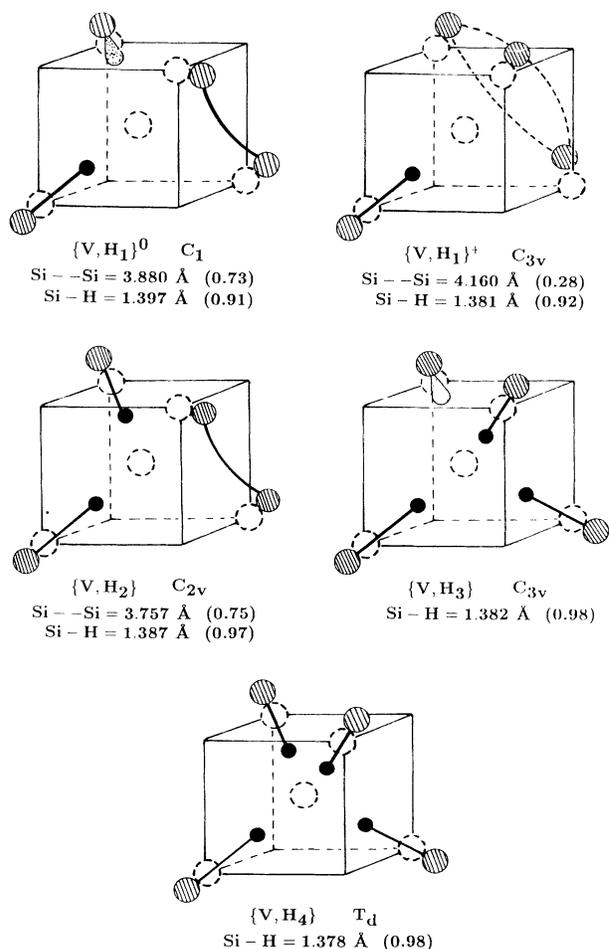
FIG. 2. Calculated configurations of the neutral $\{V,H_n\}$ complexes in Si, with $n = 1,\ldots,4$, and of $\{V,H_1\}^+$. The symmetry, internuclear distances (in Å) and degrees of bonding (between parentheses) are indicated.

Finally, we calculated the gain in energy accomplished by forming the most favorable configuration for $\{V,H_n\}$ starting with free hydrogen outside the cluster (H^{free}) and $\{V,H_{n-1}\}$ with $n = 1, \ldots, 4$. The *ab initio* SV* energy differences were all obtained with UHF wave functions (the closed-shell calculations were transformed into open-shell ones by the addition of a free H atom far outside the cluster). We obtained energy differences somewhat larger than the ones reported by other groups,[30,31] possibly due to the specific parametrization used by them, to the choice of a different zero of the energy, and/or to differences in the way electron correlation is accounted for. Our values are $V+H^{free} \to \{V,H_1\} + 3.6$ eV, $\{V,H_1\}+H^{free} \to \{V,H_2\} + 3.3$ eV, $\{V,H_2\}+H^{free} \to \{V,H_3\} + 3.2$ eV, and $\{V,H_3\}+H^{free} \to \{V,H_4\} + 3.0$ eV. We repeated the calculations in the case of $\{V,H_2\}$ and $\{V,H_4\}$ at the MP2 level and obtained 3.2 eV and 2.9 eV per H atom, respectively. In order to get these values, we used the MP2 energies for $\{V,H_{n-2}\}$ and $\{V,H_n\}$, and the SV* energy for H^{free}. Our numbers are between the Si–H bond strength in SiH_4 (3.9 eV) and that measured at internal surfaces in Si (Refs. 21 and 33) (2.5±0.2 eV). Note also that the energy gain becomes smaller as the number of H atoms increases in the vacancy.

The energy gained by forming Si–H bonds in a vacancy relative to H^{free} is substantial when compared to the energy gained by forming other H-containing complexes in Si, calculated in the same manner at the same (or comparable) level of theory. These energy differences are plotted in Fig. 3 for a variety of complexes.[44–46]
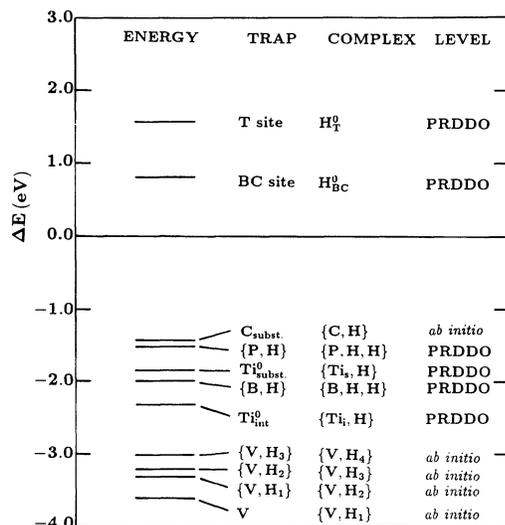
FIG. 3. Calculated energy differences between H in the lowest-energy configuration of a given pair or complex $\{X,H\}$ in Si and the optimized $\{X\}$ center plus free atomic hydrogen (the common zero of the energy): ΔE (eV) = $\{X\}+H^{free} - \{X,H\}$. The energies are negative when one *gains* energy by forming the hydrogen-containing complexes. Neutral interstitial hydrogen is labeled H_{BC} at the BC site and H_T at the T site. The C result is from Ref. 44, the B and P results from Ref. 45, and the Ti results from Ref. 46.

C. Diffusion properties of V and $\{V,H_n\}$

The diffusion of V consists in one Si atom NN to V moving toward the vacancy, leaving a new vacancy behind. The path is very much a straight line (except that the initial and final configurations are reconstructed), and the transition point has the Si atom and its six NN's midway between their initial and final configurations. More details about the equilibrium and transition point states are as follows. In the lowest-energy conformation, a Si atom NN to V forms three two-electron bonds with its three NN's and one reconstructed long Si–Si bond, which is 73% of a true two-electron covalent bond, as shown in Fig. 1. This stretched bond implies more electron correlation than a normal Si–Si bond, and the hybridization involves some d-orbital participation. At the transition point, the Si atom which is midway between two vacancies forms six equivalent stretched bonds with its six NN's. Each of these six bonds is stretched (23% longer than an ideal Si–Si bond) and its covalent character is 65% that of an ideal two-electron bond. There is substantial d orbital participation and electron correlation corrections are important in each of the six stretched bonds.

For these reasons, the calculated energy at the transition point varies with basis set size and with the amount of electron correlation included in the calculation. As discussed above, we calculated the diffusion path at the PRDDO level, and optimized the geometry at several intermediate points between the initial and final configurations. We then used the PRDDO geometries as inputs for single point calculations at higher levels of theory, but in small clusters. The calculated activation energies are 4.3 eV with PRDDO, 3.0 eV with *ab initio* HF, SV* basis set, and 1.1 eV with SV*+MP2. Thus, our best activation energy is still higher than the experimental value (0.45±0.04 eV). There are four reasons for this. (i) The MP2 energies were calculated in the small cluster Si_7H_{18} in which the stiff Si–H surface bonds prevent optimum relaxation of the crystal, (ii) only the first NN's can be relaxed in this cluster, (iii) the transition point geometry was not optimized at the MP2 level, and (iv) second-order corrections in electron correlation may not suffice. A similar calculation in a larger cluster, such as $Si_{43}H_{42}$, would be needed to correct the problems (i) and (ii). At present, such a calculation is far beyond the reach of today's computers. However, the barrier for diffusion of V can be used to estimate how much larger or smaller other barriers are, in particular the barriers involving very similar electronic configurations, such as those of $\{V,H_n\}$.

Our calculation show that $\{V,H_1\}$ is likely to be mobile in Si, but that $\{V,H_n\}$ with $n = 2$, 3, or 4 are not. The lowest activation energy we found for $\{V,H_2\}$ is of the order of 8 eV, implying that the crystal will melt before this complex becomes mobile. The numbers for $\{V,H_3\}$ or $\{V,H_4\}$ are even higher. We therefore focus now on $\{V,H_1\}$ which, in p-type material, is likely to exist in the 0 and +1 charge states. The equilibrium configurations are schematically shown in Fig. 2. The reason we suspect that both charge states are possible is that singly occupied dangling bonds in Si tend to exhibit

negative-U behavior, provided that a free electron or hole is available. Our calculations do not show that one of the charge states is more stable than the other, because we cannot directly compare total energies for systems having different numbers of electrons. As illustrated in Fig. 2, $\{V,H_1\}^0$ and $\{V,H_1\}^+$ have different equilibrium configurations. While $\{V,H_1\}^0$ has C_1 symmetry with a reconstructed Si–Si bond and a dangling bond, $\{V,H_1\}^+$ has C_{3v} symmetry with three equivalent, somewhat reconstructed "dangling bonds" opposite to the Si–H bond.

The mechanism of diffusion for both charge states of $\{V,H_1\}$ is illustrated in Fig. 4. This figure shows in fact two mechanisms, corresponding to going from (a) to (f) or the reverse. They involve moving a Si atom along an arc (away from H) toward the vacancy, then H attaching to this Si atom, and the pair rotating toward the final configuration. In the reverse situation, H first rotates toward a nearby BC site, then the Si atom it was attached to moves into the vacancy. At each intermediate step, the amount of covalent overlap between pairs of atoms is qualitatively shown via the use of lines connecting pairs of atoms. The thicker lines correspond to stronger bonds, and the dashed lines indicate a very weak (but still bonding) overlap. The barriers for diffusion (calculated at the SV*+MP2 level) of V, $\{V,H_1\}^0$, and $\{V,H_1\}^+$ are shown in Fig. 5. The (a)-(f) sequence

shown in Fig. 4 corresponds to going from left to right in Fig. 5. The horizontal coordinate scales with the vertical displacement of the Si atom that does most of the motion.

While the barrier for diffusion of V is smooth and symmetric as expected, the barriers for $\{V,H_1\}^0$ and $\{V,H_1\}^+$ are not. At first, the energy needed to displace Si some three-quarters of the way is *lower* when one H atom is in the vacancy than when it is not. A similar reduction in activation energy was reported in the case of the H-enhanced diffusion of interstitial O in Si.[47] In both cases, H ties up a dangling bond, allowing the moving species to form a more stable configuration at the transition point. Here, instead of having to form six stretched Si–Si bonds with its six NN's at the transition point (as in the case of V), only five Si–Si bonds need to be formed, and these are less stretched because the Si atom can move along an arc, away from the Si–H bond [Figs. 4(a)-4(b)]. The second part of the potential surface is a peak which corresponds to H moving from one Si atom to the other [Figs. 4(b)-4(c)]. This peak is less pronounced in the case of $\{V,H_1\}^0$ than $\{V,H_1\}^+$ because the missing electron makes it difficult for H to form a bond with the positively charged Si atom. In order to form a two-electron Si–H bond, an electron has to be removed from elsewhere, which alters the electronic configuration of the complex and costs some energy. Thus, the mobility of $\{V,H_1\}^+$ is smaller than that of $\{V,H_1\}^0$, unless the complex captures an electron first. On the other hand, given the fact that our barriers are upper limits, it is likely that $\{V,H_1\}^0$ is mobile. The peak in the barrier is probably of the order of 1 eV or less and quite narrow, which could allow for tunneling.

The process competing with the diffusion of $\{V,H_1\}^0$ is the breakup of the pair, followed by the diffusion of V and H independently with, possibly, subsequent recapture. Annealing studies[19] of the 1832 cm^{-1} IR line (which is associated with $\{V,H_1\}$) shows that this line disappears around 200 °C. This could mean that $\{V,H_1\}$ breaks up into V and H at this temperature, or that $\{V,H_1\}$ becomes sufficiently mobile to form some other complex with a different IR signature. A larger complex may involve for example a dopant, a second vacancy or hydrogen, or another $\{V,H_1\}$ pair. Note that the diffusion of $\{V,H_1\}$ involves H in a *bound state* and is therefore not trap limited in the usual sense. Of course, the $\{V,H_1\}^0$ pair itself may become trapped. However, in-

FIG. 4. Schematic representation of the diffusion mechanism for the $\{V,H_1\}$ pair in Si. The starting point can be either (a) or (f). The thick (thin, dashed) lines indicate qualitatively the strong (weaker, weakest) covalent bonds formed at various stages of the diffusion. To clarify the figure, only one Si and the H atoms are shown to move, although we optimized the coordinates of all the NN atoms in our calculations.

FIG. 5. Barriers for diffusion calculated at the SV*+MP2 level in a small cluster. As discussed in the text, the calculated barriers are upper limits. The figure compares the neutral vacancy (solid line) to the $\{V,H_1\}^0$ and $\{V,H_1\}^+$ pairs (dashed and dotted lines, respectively). The horizontal axis roughly scales with the vertical coordinate of the Si atom that moves toward the vacancy in Fig. 4.

terstitial H alone traps not only at virtually all defects and impurities in Si, but self-traps in the perfect crystal at the BC site as well. This is not the case for $\{V,H_1\}^0$. As a result, a mechanism for diffusion of H in a bound state, such as the one we propose here, may well play an important role below 200 °C, especially in vacancy-rich material (such as poly-Si) or in situations where vacancies are injected into the substrate as the result of a surface treatment.

IV. DISCUSSION

We have studied theoretically the neutral vacancy and $\{V,H_n\}$ complexes ($n = 1, \ldots, 4$) in Si. First, we used the approximate *ab initio* HF method of PRDDO to obtain optimized geometries and diffusion paths in small and large clusters ($H_nSi_7H_{18}$ to $H_nSi_{43}H_{42}$). Then we performed split-valence polarized basis set *ab initio* HF calculations followed by second-order Møller-Plesset corrections in electron correlation to obtain more accurate energetics and electronic structures. A variety of *a priori* possible configurations for the various $\{V,H_n\}$ complexes were considered, and the lowest-energy ones are shown in Fig. 2. The key results can be summarized as follows.

A. Summary of key results

(i) The neutral vacancy in Si distorts from T_d to D_{2d} symmetry, as observed experimentally.[1] In the distorted configuration, two pairs of long Si—Si bonds are formed, as shown in Fig. 1. These two bonds have a surprisingly large covalent character (about 73% of a two-electron covalent bond), while there is no covalent overlap between Si atoms in different pairs.

(ii) The diffusion path of the neutral vacancy involves a Si atom NN to V moving directly along the $\langle 111 \rangle$ axis (except for the initial and final distortion). At the transition point, this Si atom forms six stretched bonds with its six NN's.

(iii) The calculated activation energy is sensitive to the basis set size and the amount of correlation included. Our best result (SV*+MP2) overestimates the experimental number by about 0.6 eV: We get 1.1 eV vs the 0.45±0.04 eV in Ref. 1. The most obvious reason for our high value is that the MP2 calculation had to be performed in a small cluster in which first NN's are incompletely relaxed and second NN's are not relaxed. PRDDO calculations of the corrections for optimal relaxations are of the order of a few hundredths of an eV per atom, which would add up to several tenths of an eV in the present case, bringing our value much closer to the experimental results. Other reasons why our calculations overestimate activation energies are that the geometries had to be optimized at the PRDDO (rather than the MP2) level, and that second-order correlation corrections may not fully account for the actual amount of electron correlation. Nevertheless, we expect the same corrections in the case of the barrier for diffusion of $\{V,H\}$ to occur, and the *relative* barrier

heights should provide a much more quantitative prediction than the individual absolute numbers.

(iv) The reorientation energy of the vacancy between equivalent tetragonal configurations is 0.33 eV, rather close to the measured value.[1]

(v) The lowest-energy configuration of all the $\{V,H_n\}$ complexes has the H atoms forming a two-electron bond with one Si atom and pointing toward the center of the vacancy, as shown in Fig. 2. The Si—H bond lengths get shorter as n increases. The dissociation energies (energy of $\{V,H_n\}$ relative to $\{V,H_{n-1}\}$ plus free atomic hydrogen, H^{free}) vary from 3.6 eV (for $\{V,H_1\}$) to 3.0 eV (for $\{V,H_4\}$). These values are somewhat larger than those published by other groups[30,31] but fit between the experimental values for SiH_4 and Si—H bonds at internal surfaces in Si.[21,33] However, as shown in Fig. 3, it costs several tenths of an eV to insert H^{free} into a T site in Si. Thus, the dissociation energy of $\{V,H_n\}$ complexes with H remaining in the crystal is smaller.

(vi) The neutral $\{V,H_1\}$ pair is mobile, and its diffusion path is illustrated in Fig. 4. In the first step, the barrier for diffusion of $\{V,H_1\}$ is lower than that of V alone, a process that can be compared to the H-enhanced diffusion of interstitial O. However, the actual change of site of H itself involves the breakup of a Si-H bond, which costs more energy. In the case of $\{V,H_1\}^0$, this results in a small peak in the potential surface through which H might be able to tunnel or above which it could jump with the help of a phonon. In the case of $\{V,H_1\}^+$, this peak is somewhat higher. The mobility of $\{V,H_1\}$ provides a new mechanism for diffusion of H, which involves the motion of H in a *bound* state. Note that there is no *direct* experimental evidence that hydrogen-decorated vacancies are mobile.

(vii) The $\{V,H_n\}$ complexes with $n = 2$, 3, or 4 are not mobile below temperatures at which they break up.

B. Implications of the mobility of $\{V,H_1\}$

The diffusion of $\{V,H_1\}$ pairs should only play an important role in situations where vacancies are present in large concentrations. This is the case in bulk poly-Si[35,36] as well as in the subsurface region of Si samples exposed to a H plasma[34] or treated with some chemical or mechanical process (such as wet etching or chemomechanical polishing). Although our theoretical results are insufficient to demonstrate the occurrence of yet unobserved processes, they suggest that the following ones could occur and should be a part of the interpretation of experimental data.

1. Mobility of H in poly vs crystalline Si

Poly-Si is a material which contains an higher concentration of potential traps for interstitial H than the more expensive CZ or FZ Si. However, a higher mobility of

H in poly vs crystalline Si has been reported[35,36] below 250 °C in samples implanted with H. The explanation proposed involves mobile $\{V,H\}$ species. In this form, H could migrate without self-trapping, and actually diffuse further than interstitial H would by itself. Our calculations show that such a mechanism is *a priori* a possible one. A further step in our studies will involve the interactions of $\{V,H\}$ pairs with defects and impurities.

2. A mechanism for the nucleation of platelets?

Corbett *et al.* suggested[34] that a mobile $\{V,H\}$ complex is needed to explain the bumpy shape of SIMS profiles in the subsurface region of plasma-exposed Si samples. We would like to go one step further and propose that mobile $\{V,H\}$ pairs are a very tempting candidate to explain the formation of platelets. The explanations proposed so far include a variety of configurations involving hydrogen dimers[48,49] or assuming the presence of vacancies.[50] While the self-trapping of H interstitials in various configurations provides at best a few tenths of an eV stabilization energy per H, trapping at a dangling bond provides well over 2 eV per H atom. However, when assuming that vacancies are the culprit, one must explain how H creates enough Frenkel pairs and prevents the recombination of the vacancy and the self-interstitial.

In the present situation, vacancies are pumped from the surface by the plasma and exist in above-equilibrium concentration in the subsurface region.[34] In this region, the concentration of atomic H is very large as well. Thus, the probability of $\{V,H\}$ pair formation is high. This creates the needed conditions to have a large concentration of mobile $\{V,H\}$ pairs as well as mobile interstitial hydrogen. A $\{V,H\}$ pair can diffuse further into the bulk, or be trapped. Trapping may occur via the capture of one (or more) H interstitials, at a dopant or other impurities. It is tempting to speculate that these pairs could trap each other or other vacancies, just like isolated vacancies tend to form divacancies or larger aggregates. The result is

a larger complex which has six or seven dangling bonds. Each of those is a strong trap for H. The defect may grow further by trapping additional vacancies or $\{V,H\}$ pairs, thus adding more and more free dangling bonds, ready to trap more hydrogen atoms.

Thus, $\{V,H\}$ pairs could well initiate a process, the result of which is platelet formation. Since such a pair will be immobilized by the trapping of a second H interstitial, nothing will happen except $\{V,H_4\}$ formation if it moves too slowly: It must be sufficiently mobile for the probability of $\{V,H\} - \{V,H\}$ interaction to be significant. This suggests a *minimum temperature* below which platelets cannot be nucleated. On the other hand, if it moves too fast (as could be the case for isolated vacancies), the defect may move out of the region of interest before nucleating a platelet. Further, if the $\{V,H\}$ pair breaks up, no more nucleation is possible. This suggests a *maximum temperature* above which platelets cannot be nucleated either.

It has been reported[19] that the IR signature of $\{V,H_1\}$ pairs disappears around 175 °C. It has also been reported[51] that platelet nucleation readily occurs around 150 °C, but is suppressed at 250 °C. The disappearance of the IR signal could result from the break up of the $\{V,H\}$ pair or its disappearance into a sink. Whatever the reason, the coincidence between these two sets of data could easily be explained if mobile $\{V,H\}$ pairs are indeed required in order to nucleate platelets. Further theoretical and experimental studies along these lines will be needed to understand this issue more precisely.

ACKNOWLEDGMENTS

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