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Molecular-dynamics study of the vacancy and vacancy-hydrogen interactions in silicon

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The neutral vacancy (V) and the four vacancy-hydrogen complexes ($\{V,\mathrm{H}_n\}$, $n = 1,\ldots,4$), in silicon are studied in $\mathrm{H}_n\mathrm{Si}_{63}$ periodic supercells with the *ab initio* pseudo-atomic-orbital molecular-dynamics method developed by Sankey and co-workers. Results are presented for (i) the equilibrium configurations of V and the $\{V,\mathrm{H}_n\}$ complexes, (ii) the diffusion properties of V and $\{V,\mathrm{H}_1\}$, (iii) the vibrational modes of the $\{V,\mathrm{H}_n\}$, and (iv) the interactions between isolated H and V.

I. INTRODUCTION AND BACKGROUND

The behavior of hydrogen in silicon has received a great deal of attention in the past 15 years.[1,2] It interacts with many impurities and defects, forming covalently bound pairs and larger aggregates, and altering the electrical and optical properties of the centers involved. H has been known for a long time to tie up dangling bonds at vacancies, vacancy aggregates, surfaces, and extended defects such as dislocations, grain boundaries, and interfaces.[3] These interactions profoundly affect the optical properties of the material. In particular, a number of infrared (IR) active Si-H stretching (and wagging) local vibrational modes have been reported in hydrogenated samples. The stretching modes are observed in the range 1600–2200 cm^{-1}, indicating a wide variety of configurations, which correspond to a range of Si-H bond strengths.[4,5] Only a few of the absorption lines have been identified with a high degree of confidence.

On the other hand, the vacancy (V) is one of the most important intrinsic defects in Si.[6] Vacancies may be present in a crystal for a number of reasons. Rapidly grown materials tend to have more V's quenched in than slowly grown ones. High concentrations of oxygen (or a few other impurities) are also believed to result in the creation of vacancies. Ion implantation generates vacancies as well. Furthermore, some surface treatments such as etching, exposure to a H plasma, or deposition of Al contacts, may also increase the bulk concentration of vacancies.[7,8] Finally, vacancies are more abundant in p- than n-type Si because self-interstitials easily trap at group III dopants, leaving an excess of vacancies.[6]

The vacancy readily interacts with various impurities and defects, including dopants, other vacancies and, of course, hydrogen.[6,9] The vacancy is one of the strongest traps for H in Si,[10,11] and it was even suggested that Frenkel pairs (vacancy-self-interstitial) can be created by hydrogen.[12] Thus, H and V interact with the same impurities and defects and with each other, which is bound to have profound implications in situations where H and V coexist. This is the main motivation for the present work, which presents the results of molecular-dynamics (MD) simulations involving V and H.

The vacancy in Si is a negative-U center,[13,14] and is stable only in the charge states for which a spin singlet configuration can be realized, that is V^{2-}, V^0, and V^{2+}. Each of these states is mobile, even at low temperatures. The activation energies are estimated to be 0.33, 0.45, and 0.18 eV, respectively.[6] The t_2 levels of a vacancy are about midgap. They are empty only in the case of V^{2+}, which is stable in T_d symmetry. The other charge states have a partially occupied t_2 level in T_d symmetry. They are orbital triplets, which undergo a Jahn-Teller distortion. V^0 and V^{2-} have tetragonal symmetry, with two pairs of equivalent Si nearest neighbors (NN's). The four dangling bonds reconstruct and form two long Si-Si bonds, which show a substantial amount of covalent overlap,[10] despite being rather weak bonds.

Many H-related stretching vibrational modes are observed in hydrogenated Si (see above). Some have been assigned[3-5,15-18] to $\{V,\mathrm{H}_n\}$ complexes, with $n = 1,\ldots,4$. However, few of the lines have been identified with a high degree of certainty. The current situation is as follows.

It is very likely that a strong line near 2210 cm^{-1}, which corresponds to a defect complex with T_d symmetry, should be assigned to $\{V,\mathrm{H}_4\}$. Recently, the IR modes associated with the H_2^* pair (or $\mathrm{H}_{\mathrm{BC}}\mathrm{H}_{\mathrm{AB}}$, where BC and AB stand for the bond centered and antibonding, respectively) have been unambiguously identified.[19] At 77 K, the stretch modes are at 2061.5 cm^{-1} (H_{BC}) and 1838.3 cm^{-1} (H_{AB}), with one wag mode at 817.2 cm^{-1} (H_{AB}). These modes had previously been observed, but assumed to belong to some of the $\{V,\mathrm{H}_n\}$ complexes. Further, Stein[15] has reported that a line near 1990-cm^{-1} anneals at around room temperature into two lines at 1835 and 2065 cm^{-1}. The latter are most likely the H_2^* pair, which suggests that the 1990-cm^{-1} line could well correspond to H_{BC}. This is close to the 1945 and 2210 cm^{-1} frequencies proposed by Van de Walle *et* *al.*[12] for H^0_{BC} and H^+_{BC}, respectively. Our MD simulations for H^0_{BC} (preliminary) are consistent with such an assignment.[20] However, other authors reported much lower frequencies for H_{BC}.[21,22] Thus, some uncertainty remains as to the 1990-cm^{-1} line. A line at 1946 cm^{-1} has been proposed[17] for $\{V,H_1\}$ and one at 1980 cm^{-1} for $\{V,H_2\}$.[18] However, the most recent work[23] suggests the assignment of the 2060-, 2120-, 2160-, and 2220-cm^{-1} lines to $\{V,H_n\}$ with $n = 1, 2, 3$, and 4, respectively.

Semiempirical Hartree-Fock (HF) calculations in five and eight host atom clusters propose the values 2252 cm^{-1} (Ref. 24) and 2332 cm^{-1} (Ref. 25) for $\{V,H_4\}$, while cyclic cluster calculations[26] predict the values 2057, 2080, 2106, and 2109 cm^{-1} for $\{V,H_n\}$, with $n = 1$, 2, 3, and 4, respectively. Again, the highest frequency corresponds to the fully saturated vacancy, and is close to the IR line near 2210 or 2220 cm^{-1}. These theoretical numbers are scaled in a way that the theory reproduces a known vibrational frequency such as that of silane.

In addition to calculations of vibrational frequencies, there have been many theoretical studies of V and of some or all of the four $\{V,H_n\}$ complexes in Si. Only a few of these studies have involved total energy calculations and systematic geometry optimizations. The methods and results have recently been reviewed in the introductory section of Ref. 10, and only a summary is needed here.

There is agreement among the various authors on the following (qualitative) features. (i) H-V interactions lead to the formation of strong Si-H bonds, with H pointing toward the center of the vacancy, approximately along a $\langle 111\rangle$ direction. This configuration was assumed by most authors, and confirmed by Deák *et al.*[26] and Roberson and Estreicher.[10] (ii) Only $\{V,H_4\}$ has no electrically active levels in the gap. (iii) The Si-H bond lengths decrease and the corresponding vibrational frequencies increase as more H atoms get into a vacancy. (iv) The Si-H bond strengths are of the order of 2.2–3.5 eV.[10,11] These fall in between the Si-H bond strength at *internal* surfaces[27] (2.5 eV) and in SiH_4 (~ 4 eV).

Roberson and Estreicher have performed extensive static potential energy surface calculations[10] for $\{V,H_n\}$, $n = 0, \ldots, 4$ near, at, and beyond the *ab initio* HF level. Only the neutral charge state of these complexes was examined, except for $\{V,H_1\}$, which was studied in the 0 and +1 charge states. The present work is a MD study, which goes beyond the static HF work. Therefore, it is useful to summarize here the main results of Ref. 10.

The neutral vacancy distorts from T_d to D_{2d} symmetry. Its four NN's move slightly away from the vacancy and toward each other in pairs. This leads to the formation of two long (3.76 Å) Si-Si bonds, which show a high degree of covalent overlap. The interpair Si-Si distance is 3.93 Å, with zero covalent overlap. The reorientation energy between equivalent configurations is about one-third of an eV. The activation energy for diffusion is very sensitive to the level of theory: 4.3 eV with approximate *ab initio* HF, 3.0 eV with *ab initio* HF (split-valence polarized basis set), and 1.1 eV when second-order Møller-Plesset corrections in electron correlation are added. The lowest of these numbers is still some 0.6 eV above the measured value.

The symmetry of the $\{V,H_n\}$ complexes and optimized Si-H bond lengths were calculated to be C_1 and 1.397 Å ($\{V,H_1\}^0$), C_{3v} and 1.381 Å ($\{V,H_1\}^+$), C_{2v} and 1.387 Å ($\{V,H_2\}$), C_{3v} and 1.382 Å ($\{V,H_3\}$), and T_d and 1.378 Å ($\{V,H_4\}$). These geometries are close to those obtained by Deák *et al.*[26] Recently,[28] Van de Walle and Street, reported the results of local density-functional (DF) calculations. They obtained a Si-H bond length in $\{V,H_4\}$ of 1.47 Å, about 0.1 Å longer than the HF result. It is not uncommon that DF calculations predict somewhat longer bond lengths than HF does.[2]

Finally, the possibility that the $\{V,H_n\}$ complexes are mobile was examined. The diffusion of such complexes was postulated by Corbett *et al.*[7] to explain the shape of deuterium concentration profiles, then by Sopori *et al.*[29] to explain the enhanced diffusion of hydrogen in vacancy-rich samples. Roberson and Estreicher[10] found that only $\{V,H_1\}$ is likely to be mobile. The calculated diffusion path has two steps. First, a Si NN moves toward the center of the vacancy. This occurs with a lower potential barrier than the same motion when no H is in the vacancy. Second, H breaks its bond and attaches to the Si atom moving toward V. This is accomplished at a cost in energy lower than the dissociation energy of the Si-H bond calculated at the same level of theory. It was assumed that H could somehow tunnel through that part of the barrier or jump over it with the help of a phonon, resulting in the migration of $\{V,H_1\}$.

In the present contribution, we present the results of MD simulations of V and $\{V,H_n\}$ complexes, $n = 1, \ldots, 4$, in Si. We obtain the equilibrium configurations (at 0 K) and the high-temperature behavior of isolated V, of isolated H, of V and H in the same cell, and of the $\{V,H_n\}$ complexes. We also calculate the vibrational frequencies of the four complexes. The details of our simulations are discussed in Sec. II. Section III contains the results, and a discussion follows in Sec. IV.

II. DETAILS OF THE MD SIMULATIONS

We use the first-principles, pseudo-atomic-orbital MD method developed by Sankey and co-workers.[30] The theoretical foundation of this method is the DF theory within the local-density and pseudopotential approximations, with a basis set of pseudoatomic orbitals. Its suitability for covalent systems such as Si and C is well documented.[30–34] The essential ingredients of the method are (i) a spin averaged (non-self-consistent) version of DF theory using the Harris functional and the local-density approximation; (ii) nonlocal, norm-conserving pseudopotentials of the type developed by Hamann *et al.* for the core states;[35] (iii) a minimal basis set with localized atomiclike wave functions for the valence orbitals (one s and 3 p functions per site) with an orbital confinement radius for Si and H of $5.0a_B$. The exchange-correlation potential term assumes the Ceperley-Adler[36] form as parameterized by Perdew and Zunger.[37]

In the present work, the host crystal is approximated by the periodic supercell H_nSi_{63} with $n = 0, \ldots, 4$, which contains a vacancy. First, we prepared a 64 Si atom supercell, and optimized its lattice constant using the total energy minimization method. This led to the bond length Si-Si=2.381 Å, a value close to the experimental one for crystalline Si (2.352 Å). We kept the bond length at 2.381 Å in all subsequent calculations. The calculated bulk modulus of this supercell is 1.001 Mbars (1.001×10^{11} N/m^2), which agrees well with the experimental value (0.99 Mbars).[38]

Next, a centrally located host Si atom was removed to create a vacancy, and from zero to four H atoms were added in and around the vacancy. In each case, the atomic coordinates were relaxed using the power-quenching technique.[39] The classical equations of motion for the nuclei were integrated using Gear's algorithm[40] with a time step $\Delta t = 0.3 \times 10^{-15}$ s = 0.3 fs when one or more H atoms were in the cluster, and 1.0 fs when no H was present. The canonical ensemble was used and the temperature controlled by velocity scaling with the Yang, Drabold, and Adams temperature controller.[32]

Note that because of periodic boundary conditions, defects in neighboring cells are correlated to each other. However, in our supercells, the minimum distance between the center of the defects is about 11 Å, while the orbital cutoff radius of the pseudoatomic valence orbitals is $5.0a_B$. Thus, there is no direct overlap between defects in neighboring cells. Of course there is indirect overlap caused by the host atoms displaced from their perfect crystal positions around the defect center.

Because of these approximations, the present calculations are much faster than true *ab initio* MD simulations of Car-Parrinello type.[41] This allows us to use the larger supercells required here and to perform longer simulations at lower temperatures than would be computationally tractable at the *ab initio* level. Comparisons of our $\{V,H_4\}$ geometries to first-principles local DF ones,[28] and the overall quality of our results when compared to other calculations or to experiment indicate that the loss of accuracy is not substantial.

III. RESULTS

A. Equilibrium configurations

We find that the four dangling bonds of isolated V^0 slightly reconstruct at 0 K. The optimized structure shows a slightly distorted configuration (D_{2d}, but very close to T_d symmetry). The distortion is much smaller than the one obtained with the HF cluster method.[10] However, it is significantly more pronounced for optimizations performed at $T > 0$. We believe that the ground state is correctly described in Ref. 10 and that the MD description is not quite as good at 0 K. However, we do not believe that this affects the dynamics very much. Our calculated equilibrium configurations for the four neutral complexes are as follows.

$\{V,H_1\}$ has C_{3v} symmetry, with three equivalent Si-Si bonds and a Si-H bond along a $\langle 111\rangle$ direction, with H pointing toward the center of the vacancy. The Si atom to which H is attached moves outward, while the other three Si NN's to V move toward the center of the vacancy. Note that HF calculations[10] predict that $\{V,H_1\}$ has C_1 symmetry when neutral and C_{3v} symmetry when positively charged. We assume that the spin-averaging prevents a dangling bond from being populated with a single electron, which results in our spin averaged $\{V,H_1\}^0$ looking like $\{V,H_1\}^+$.

$\{V,H_2\}$ has C_{2v} symmetry, with two equivalent Si-H bonds pointing toward the center of the vacancy and one reconstructed Si-Si bond. $\{V,H_3\}$ 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. Finally, $\{V,H_4\}$ has T_d symmetry, with four equivalent Si-H bonds. It is the only complex with no level in the gap. The geometries for $\{V,H_n\}$ with $n = 2$, 3, and 4 are close to the ones obtained in Ref. 10.

The optimized Si-H bond lengths are 1.508 Å ($\{V,H_1\}$), 1.504 Å ($\{V,H_2\}$), 1.498 Å ($\{V,H_3\}$), and 1.475 Å ($\{V,H_4\}$). The bonds are longer than those calculated at the HF level. However, the shortening of the Si-H bond lengths as the number of H atoms in the vacancy increases is consistent with the results of other authors. Further, the $\{V,H_4\}$ result is close to the 1.47 Å reported by Van de Walle and Street.[28] However, in the case of the fully saturated vacancy, we find that the four Si NN's relax outward by 0.38 Å, a larger relaxation than the one found in Ref. 28 (0.16 Å).

B. Vibrational frequencies

The vibrational spectra of the $\{V,H_n\}$ complexes have been obtained as follows. The motion of the H atoms in the supercells was constrained so that the center of mass remains stationary and the supercell has no net linear or angular momentum. The positions and velocities of the H atoms were computed as a function of time. A simulation of 1000 time steps was done to collect a sample for statistics in each case. All the simulations were done at room temperature. The Fourier cosine transform of the autocorrelation function[30] gives the spectral density

$$g(\omega) = \frac{1}{\tau} \int_0^{\tau} g(t)\, W(t) \cos(\omega t)\, dt\,,$$

where τ is the total time of the simulation, $W(t)$ is the Blackman window function[42] used to reduce finite-time sampling oscillations, and $g(t)$ is the velocity autocorrelation function.

Figure 1 shows the results of these calculations. The peaks of the spectra at 2168, 2268, 2301, and 2334 cm^{-1} are our best estimates of the room-temperature vibrational frequencies for H in $\{V,H_n\}$, with $n = 1$, 2, 3, and 4, respectively. These values are slightly larger than the (scaled) frequencies proposed by Deák *et al.*[26] (2057, 2080, 2106, and 2109 cm^{-1}, respectively) and the most recent experimental values[23] (2060, 2120, 2160, and 2220 cm^{-1}, respectively). Note that our simulations were done at 300 K and that a shift of frequencies is to be expected at lower temperatures.

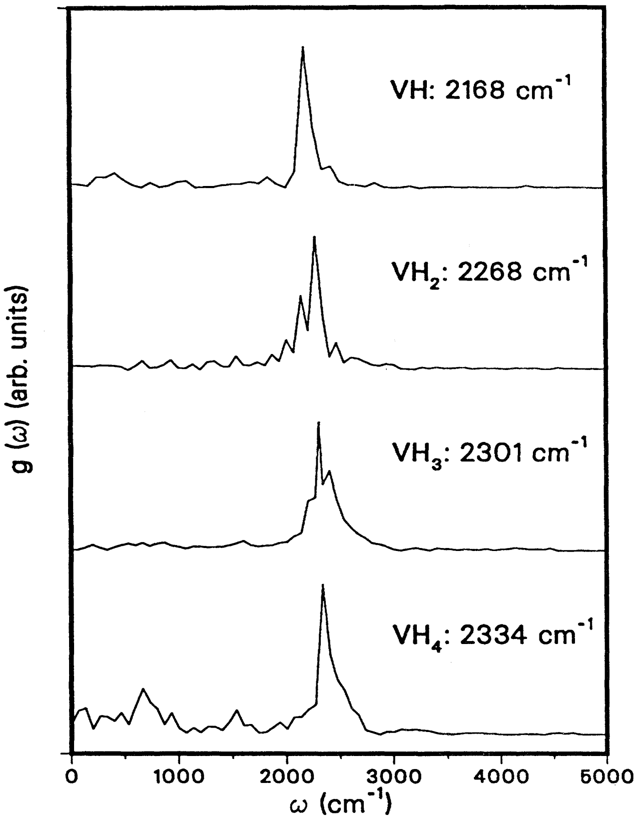

FIG. 1. Vibrational spectral densities of $\{V,\mathrm{H}_n\}$ complexes at 300 K. The peaks at 2168, 2268, 2301, and 2334 cm^{-1} are the stretching frequencies of H in $\{V,\mathrm{H}_n\}$ with $n = 1$, 2, 3, and 4, respectively.

C. Diffusion properties

In order to obtain the diffusivities[43,44] of V^0, we monitor the mean square displacement of all the atoms in the supercell and evaluate

$$D(T) = \frac{1}{6}\lim_{t\to\infty}\sum_{i=1}^{N}\frac{|R_i(t) - R_i(0)|^2}{t},$$

where $R_i(t)$ is the position of the ith Si atom at time t. This expression was approximated by considering 2000 time steps, i.e., a simulation time of 2 ps. Simulations were done in the temperature range of 300 to 1600 K. The temperature was held constant by use of the velocity scaling technique.[39] At 300 K, the diffusivity of V was $1.1\times10^{-4}\,\mathrm{cm}^2/\mathrm{s}$, a value consistent with that reported in Ref. 43. During the diffusion of V^0, we observed several Si atoms jump into the vacancy in succession, resulting in reasonable statistics even after the rather short simulation time. Each diffusion step consists of one of the Si NN's to V moving toward the vacancy, leaving a new vacancy behind. The path is very much a straight line and the transition point has the Si atom and its six NN's midway between their initial and final configurations, as predicted in Ref. 10 on the basis of static potential surface calculations.

We calculated the activation energy E_a for the diffusion of V^0 in two different ways. First, we simply monitored the total energy as all the atoms involved were moved from the initial to their final coordinates in a single jump. This calculation, which overestimates the activation energy (the configuration at the transition point is assumed rather than optimized), yielded $E_a = 0.56$ eV at $T = 0$ K. Then, we pushed one Si atom adjacent to the V^0 into the vacancy and allowed all the other atoms in the cell to relax as they pleased, while quenching every few steps to keep the temperature near $T = 0$ K. This method, which allows optimal relaxation, gave $E_a = 0.44$ eV. Both calculations predict activation energies in excellent agreement with the experimental value 0.45 ± 0.04 eV.[6]

We performed additional simulations to see if the $\{V,\mathrm{H}_1\}$ pair is mobile. In 3000 time steps (1 ps) at 1000 and 1600 K, the pair does not move. One of the Si NN's to the vacancy makes several attempts at jumping into the vacancy. Its motion involves a smaller activation energy (about 0.3 eV) than a similar motion without H in the vacancy (about 0.5 eV). However, H failed to break its bond and attach to it: The Si-H unit instead moved back, away from the vacancy. This confirms that the rate-limiting step in $\{V,\mathrm{H}_1\}$ diffusion is indeed the motion of the H atom. It may be that the attempt frequency for that process is too low and/or the activation energy for H motion (the rate-limiting step) is too high to observe the motion of $\{V,\mathrm{H}_1\}$ in MD simulations lasting only a short time. Further, we cannot exclude the possibility that an electronic excited state is involved in the diffusion process (e.g., in the breakup of the Si-H bond). Finally, the diffusion may be enhanced by the capture of an electron or hole. Thus, our result does not prove that the pair is not mobile, but suggests that it is less mobile than isolated V or H, which we saw perform several jumps even at room temperature.

D. Interactions between isolated H and V

Finally, we have considered the situation where a H interstitial and a vacancy are both in the same cell, in order to see how quickly they would interact and form a pair. Simulations involving two possible initial configurations were performed: A vacancy plus H at a tetrahedral interstitial (T) site 4.8 Å away (V^0+H_T^0), and a vacancy plus H at a BC site 8.3 Å away (V^0+$\mathrm{H}_{\mathrm{BC}}^0$).

In the V^0+H_T^0 case, the missing Si atom belongs to the fourth NN shell to H_T^0. First, the system was allowed to relax for 500 time steps (~ 0.15 ps), then was quenched using the power-quenching technique to find the equilibrium configuration of the initial state. Lattice relaxations around the T site were found to be negligible. The system was allowed to evolve freely within the canonical ensemble at various temperatures between 1000 and 1600 K. During each simulation, the temperature was held constant. The H and V trajectories at 1200 K for about 1 ps are shown in Fig. 2.

V^0 and H_T^0 clearly attract each other and quickly form the $\{V,\mathrm{H}_1\}$ pair. The motion of the vacancy is jumplike.

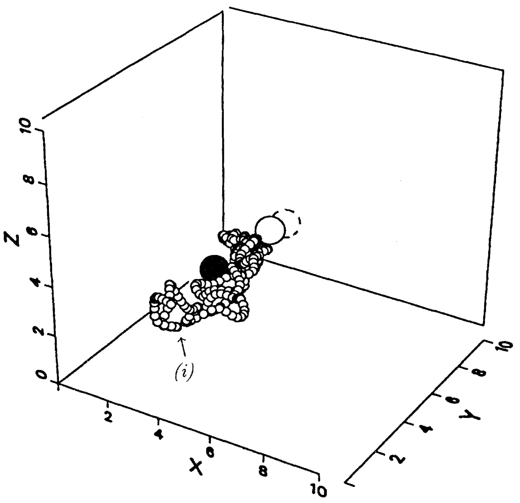

FIG. 2. Hydrogen and vacancy trajectories at 1200 K for about 1 ps, starting with V^0 and H^0_T located 4.8 Å apart. The full circle represents the Si NN to H after the latter was trapped at the vacancy. The dotted open circle represents the initial vacancy site. It jumped into the open circle site after 0.25 ps. The small open circles show the positions of H every 3×10^{-15} s, and (i) indicates the initial location of H.

One of the NN Si atom jumps into V in a way that results in the vacancy getting closer to H. The diffusivity of V at 1200 K is about 6×10^{-4} cm^2/s. The H interstitial moves very rapidly toward V with a diffusivity of the order of 10^{-3} cm^2/s. The vacancy traps H in less than 0.25 ps after which the $\{V,H_1\}$ pair remain stable until the end of the simulation ($\sim$ 1 ps). H^0_T moves toward V^0 while remaining in the low-density region of the crystal, without self-trapping at a BC site.

In the V^0+H^0_{BC} case, the missing Si atom is on the eighth-neighboring shell. First, the system was allowed to relax for 500 time steps ($\sim$ 0.15 ps), then was quenched. H^0_{BC} forms the usual three-center, two-electron, Si-H-Si bond.[45] In our calculations, the Si-Si bond expands by 34.5%, resulting in an Si-H bond length of 1.60 Å, in good agreement with other calculations.[2] Then, the system was allowed to evolve freely within the canonical ensemble. The hydrogen and vacancy trajectories were calculated at 1500 K for about 1.2 ps. Again, V and H attract each other and form the $\{V,H_1\}$ pair in $\sim$ 1 ps, after which the pair remains stable and immobile. Note that the formation time is about four times slower than in the H^0_T case, mostly because H oscillates around the BC site for a while before jumping to the next BC site.

In our simulations, H^0_{BC} diffuses by jumping from a BC site to an adjacent BC site via a saddle point near the C site, a diffusion path, which does not involve the low-density region of the crystal. This was predicted to occur at 0 K by potential surface calculations.[12] However, H^0_T diffuses through the low-density region of the crystal (via the hexagonal interstitial site) without self-trapping at a BC site. Note that (i) these are high-temperature simulations, near the experimental melting point of Si, and (ii) in both cases, a vacancy was not too far away from H. Further studies of H diffusion, with and without a V nearby and at lower temperatures, are planned.[20]

IV. SUMMARY AND CONCLUSIONS

We have performed first-principles pseudo-atomic-orbital MD simulations of a variety of situations involving a vacancy and one to four H interstitials in Si. We find the ground state configurations of H^0_{BC}, V^0, $\{V,H_2\}$, $\{V,H_3\}$, and $\{V,H_4\}$ to be in close agreement with those found by other groups, while $\{V,H_1\}$ converges toward a configuration similar to that obtained for $\{V,H_1\}^+$ at the HF level, possibly because of the use of spin averaging.

The vibrational frequencies of $\{V,H_n\}$, calculated at room temperature, are 2168, 2268, 2301, and 2334 cm^{-1}. The numbers are on the high side, but rather close to the expected values.[23]

The calculated diffusivity of V^0 is of the correct order of magnitude, $\sim 10^{-4}$ cm^2/s, and we can monitor the trapping of H at a vacancy while starting with either H^0_T or H^0_{BC}. Hydrogen makes several jumps toward V while V makes one (at most two) jump(s) toward H in the same amount of time.

Our simulation times are of the order of 1 ps (3000 time steps), which are too short to determine if the $\{V,H_1\}^0$ pair is mobile or not. Much longer simulation times may be required to resolve this issue. We can already conclude that the diffusivity of this pair, if nonzero, must be smaller than that of either V or H alone.

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