PHYSICAL REVIEW B **94**, 195210 (2016)

Vanadium interactions in crystalline silicon

D. J. Backlund, T. M. Gibbons, and S. K. Estreicher[*]
Physics Department, Texas Tech University, Lubbock, Texas 79409-1051, USA

(Received 1 August 2016; revised manuscript received 12 October 2016; published 28 November 2016)

The properties of interstitial vanadium (V_i) in Si and its interactions with the vacancy and the self-interstitial, as well as with hydrogen, are calculated using first-principles techniques. The stable configurations, gap levels, and binding energies agree well with the available experimental data. The nudged-elastic-band method is used to calculate the activation energies for diffusion of V_i in various charge states. They range from 1.46 (for V_i^{+}) to 2.04 eV (for V_i^{-}). The (trigonal) $\{\mathrm{V}_i,\mathrm{H}\}$ pair has a binding energy of 1.15 eV, a donor level at $E_c - 0.61$ eV, and possibly an acceptor level $E_c - 0.07$ eV. Substitutional vanadium (V_s) can also trap H interstitials and form electrically active $\{\mathrm{V}_s,\mathrm{H}\}$ and $\{\mathrm{V}_s,\mathrm{H},\mathrm{H}\}$ complexes.

DOI: 10.1103/PhysRevB.94.195210

I. INTRODUCTION

Vanadium is an unwanted impurity in Si-based devices, especially for solar-grade Si photovoltaic applications. It is often present in Si feedstock that has not been purified using the Siemens process. It has been known for a long time that very low concentrations of electrically active V suffice to substantially reduce the efficiency of solar cells [1–3]. Like other transition-metal impurities of the 3*d* series, isolated V prefers to be interstitial. However, the solubility of V in Si is of the order of $2 \times 10^{13}\mathrm{cm}^{-3}$ at 800° C, and much lower at room temperature. Only a fraction of the total V in the sample is electrically active [2,3].

Electron paramagnetic studies (EPR) [4] of 3*d* transition-metal (TM) impurities identified interstitial V^{++} in the 3/2 spin state (we denote this ${}^{3/2}\mathrm{V}_i^{++}$). Surface potential and capacitance measurements [5] in metal-oxide-semiconductor structures have revealed two electrically active gap levels associated with V_i at $E_v + 0.40$ eV (E_v is the top of the valence band) and $E_c - 0.49$ eV (E_c is the bottom of the conduction band), two years before the invention of the more accurate deep-level transient spectroscopy (DLTS) technique [6].

A number of authors have reported the results of DLTS measurements of V-related defects in Si [3,7–13]. There is agreement that V_i has a double-donor $(+/++)$ level at $E_v + \{0.31\ \mathrm{to}\ 0.49\}$ eV, a single donor level $(0/+)$ at $E_c - \{0.43\ \mathrm{to}\ 0.48\}$ eV, and an acceptor level at $E_c - \{0.18\ \mathrm{to}\ 0.21\}$ eV. In the most recent review [2], those levels are placed at $E_v + 0.34, E_c - 0.45$, and $E_c - 0.20$ eV, respectively.

Hydrogen is commonly used to increase minority-carrier lifetimes, especially in solar-grade *p*-type photovoltaic Si [14,15]. Hydrogen penetrates into the bulk of the material during the heat treatment that follows the plasma-enhanced chemical-vapor deposition of a H-rich SiN_x layer (antireflection coating) [16–18]. Even though it is not known precisely which defects are passivated, the lifetime of minority carrier often increases substantially.

New DLTS levels associated with $\{\mathrm{TM},\mathrm{H}_n\}$ complexes often appear following hydrogenation [19,20]. The gap levels of the TMs shift within the gap but the unwanted electrical activity is rarely fully removed by hydrogen. In the case of V, early studies [21] failed to detect any V-H interactions. This was confirmed [12,22] to be true in *p*-Si where the long-distance repulsion between V_i^{++} and interstitial bond-centered hydrogen $\mathrm{H}_{\mathrm{bc}}^{+}$ prevents the interaction from taking place. However, in *n*-Si, a new trap at $E_c - 0.49$ eV [12] or $E_c - 0.51$ eV [22] has been assigned to a $\{\mathrm{V}_i,\mathrm{H}\}$ complex. Another weak line at $E_c - 0.18$ eV [22] may also be related to a {V,H} complex. The H-related lines anneal out at 175° C and V_i fully recovers [22].

The diffusivity of V_i has been measured [11,23,24] from in-depth profiling and DLTS in the range 873–1423 K: $D(\mathrm{V}_i) = 9.0 \times 10^{-3}\exp\{-1.55\,\mathrm{eV}/k_{\mathrm{B}}T\}\mathrm{cm}^2/\mathrm{s}$. The 1.55 eV migration barrier of V_i is slightly smaller than that of Ti_i in Si, which has been measured [25] to be 1.79 eV and calculated at the same level of theory [26] to be 1.79, 1.66, 1.75, and 1.66 eV for $\mathrm{Ti}_i^{++}, \mathrm{Ti}_i^{+}, \mathrm{Ti}_i^{0}$, and Ti_i^{-}, respectively.

The early theoretical studies of 3*d* TM impurities in Si were empirical. Utzig [27] used a hard-sphere model to calculate the activation energy for diffusion of V_i along the assumed tetrahedral-hexagonal-tetrahedral path within an elastic energy approach and obtained 0.99 eV. DeLeo *et al.* used the scattering Xα method within the $\mathrm{Si}_{10}\mathrm{H}_{16}$ cluster (centered at the T site) to predict the spin states of interstitial 3*d* TMs [28], and found good agreement with the EPR data [4]. They also calculated [29] the position of the single donor level of V but found it to be in the conduction band (i.e., V_i should be in the positive charge state for all positions of the Fermi level).

Zunger *et al.* [30–32] studied the electronic structures of 3*d* TM impurities at unrelaxed interstitial and substitutional using a spin-polarized local-density functional Green's function method and found good agreement with the EPR dat. They also reproduced the observed trends in DLTS activation energies [4]. They predicted [33] the double-donor, donor, and acceptor levels of V_i to be at $E_c - 0.30, E_c - 0.23$, and $E_c - 0.19$ eV, respectively.

Beeler *et al.* [34] obtained total energies for interstitial and substitutional 3*d* TM impurities using density-functional theory plus the linear muffin-tin-orbital Green's function method. They predicted the lowest-energy spin states of interstitial and substitutional (V_s) vanadium to be ${}^{3/2}\mathrm{V}_i^{++}, {}^{1}\mathrm{V}_i^{+}, {}^{1/2}\mathrm{V}_i^{0}, {}^{0}\mathrm{V}_i^{-}$, and ${}^{0}\mathrm{V}_s^{+}, {}^{1/2}\mathrm{V}_s^{0}, {}^{1}\mathrm{V}_s^{-}$, respectively. The calculated double-donor, donor, and acceptor levels of V_i are $E_v + 0.45, E_c - 0.40$, and $E_c - 0.25$ eV,

---

[*] stefan.estreicher@ttu.edu

respectively, close to the measured values. The donor and acceptor levels of V_s were predicted to be near $E_v + 0.35$ and $E_c - 0.35$ eV, respectively.

Zhang *et al.* [35] used a first-principles approach in Si_{32} and Si_{64} periodic supercells to study the magnetic properties of the formation energies of isolated $3d$ TM impurities at interstitial and substitutional sites, but no gap level or activation energies for diffusion were reported.

A recent DFT and DFT+U study [36] discussed the details of the electronic structure of interstitial early third- and fourth-row interstitial TM impurities in Si. They used the marker method to calculate the gap levels. The double-donor, donor, and acceptor levels of V_i calculated with DFT (DFT+U) using the perfect crystal as a marker differ from each other but are in reasonable agreement with the measured values: $E_v + 0.34(0.30), E_v + 0.62(0.86) = E_c - 0.50(0.26)$, and $E_c - 0.34(0.01)$ eV, respectively. As mentioned above, the measured values [2] are at at $E_v + 0.34, E_c - 0.45$, and $E_c - 0.20$ eV, respectively. The migration barriers were taken to be the total energy difference between (optimized) tetrahedral (T) and hexagonal interstitial sites. For $^{1/2}V_i{}^0$, the barrier is 1.30 (DFT) or 1.52 eV (DFT + U). In the + charge state, it is 1.41 (DFT for $^1V_i{}^+$) and 1.19 eV (DFT + U for $^2V_i{}^+$).

In this work we present the results of first-principles calculations for V_i in Si and its interactions with the vacancy (V_{Si}), the self-interstitial (I_{Si}), and interstitial hydrogen. The binding energies of V_i to V_{Si} and I_{Si} are comparable to those obtained for other TM impurities at the same level of theory. The activation energy for diffusion of V_i in all the possible charge states are calculated using the nudged-elastic-band (NEB) method. V_s is found to be electrically active. The complexes between V_i and H as well as those of V_s and one of two H interstitials are calculated. The structures and binding energies of these complexes are calculated, and their electrical activities predicted. The predictions for V_i and $\{V_i,H\}$ are compared to the most recent experimental data. The level of theory is discussed in Sec. II. Section III contains the results and the key points are summarized in Sec. IV.

II. METHODOLOGY

Our spin-density-functional calculations are based on the SIESTA method [37,38] in the Si_{216} periodic supercells, except for the computationally demanding NEB calculations which are done in the Si_{64} supercell. This combination of tools has been used in earlier studies of Ti [26,39], Fe [40–42], Ni [43], and Cu [44–46]. The defect geometries are obtained with a conjugate gradient algorithm. A 3 × 3 × 3 Monkhorst-Pack [47] mesh is used to sample the Brillouin zone except for the NEB calculations which involve a 2 × 2 × 2 mesh.

The electronic core regions are removed from the calculations using the Troullier-Martins norm-conserving pseudopotentials [48] optimized for SIESTA [49]. To be compatible with the spin-orbit interaction, all the pseudopotentials have relativistic and core corrections.

The valence regions are treated with spin-density-functional theory within the revised generalized gradient approximation for the exchange-correlation potential [50]. This potential leads to the prediction of accurate activation energies for diffusion for impurities in Si [51]. The charge density is projected on a real-space grid with an equivalent cutoff of 350 Ry to calculate the exchange-correlation and Hartree potentials. The basis sets for the valence states are linear combinations of numerical atomic orbitals [52,53]: double-zeta for elements of the first two rows of the periodic table (H to Ne) to which a set of polarizations functions (five $3d's$) are added for Si. The basis functions of V include two sets of s and d orbitals, and one set of $p's$.

The gap levels are evaluated using the marker method [54,55]. The perfect crystal is the universal marker for all the defects: the reference donor and acceptor levels are the top of the valence band and the bottom of the conduction band, respectively. This works well for a wide range of defects provided that the defect geometries and the lattice constant of the supercell are optimized in each charge state. Indeed, the lattice constant is slightly different for each basis set, exchange-correlation potential, and charge state. Since the marker method involves comparing total energies of the defect in different charge states, this small correction leads to more accurate gap-level predictions. A 3 × 3 × 3 k-point sampling gives converged energies for the supercell size used here. No Madelung correction is used.

The migration paths and activation energies are calculated using the NEB method [56] in the Si_{64} supercell and a 2 × 2 × 2 Monkhorst-Pack mesh. Our implementation uses the climbing image method [57] for finding the saddle points. Local tangents are estimated using the improved-tangent formalism [58]. The springs connecting the images have a 0.1 eV/Å spring constant. The converged diffusion path has maximum force components perpendicular to the path at each image smaller than 0.04 eV/Å.

III. RESULTS

A. V_i and its interactions with the vacancy or the self-interstitial

V_i in Si is at (or very near) the tetrahedral interstitial (T) site in the following spin/charge states: $^{3/2}V_i{}^{++}$($^{1/2}V_i{}^{++}$ is 0.15 eV higher in energy), $^1V_i{}^+$ ($^0V_i{}^+$ is 0.42 eV higher in energy), $^{1/2}V_i{}^0$ ($^{3/2}V_i{}^0$ is 0.10 eV higher in energy), and $^0V_i{}^-$ ($^1V_i{}^-$ is 0.16 eV higher in energy). These spin states agree with those found by other authors [33,34], with the exception of the DFT+U (but not the DFT) result for $V_i{}^+$ [34]. The spin state of $V_i{}^{++}$ is also consistent with the EPR data [4]. The calculated distances between V_i and its four Si nearest neighbors in the ++, +, 0, and − charge states are 2.499, 2.494, 2.445, and 2.445 Å, respectively, as compared to the ideal T-Si distance of 2.383 Å.

The calculated gap levels are (++/+) at $E_v +$ 0.40 eV, (+/0) at $E_v + 0.65 = E_c - 0.52$ eV, and (−/0) at $E_c - 0.24$ eV. These are in good agreement with the most recent experimental values [2] $E_v + 0.34$ eV, $E_c - 0.45$ eV, and $E_c - 0.20$ eV, respectively, and with some [33] but not all [36] of the earlier calculations.

In all the possible charge states, V_i migrates along T-hexagonal-T sites. The saddle point is at the hexagonal interstitial site. The activation energies for diffusion of $^{3/2}V_i{}^{2+}$, $^1V_i{}^+$, $^{1/2}V_i{}^0$, and $^0V_i{}^-$ are 1.57, 1.46, 1.57, and

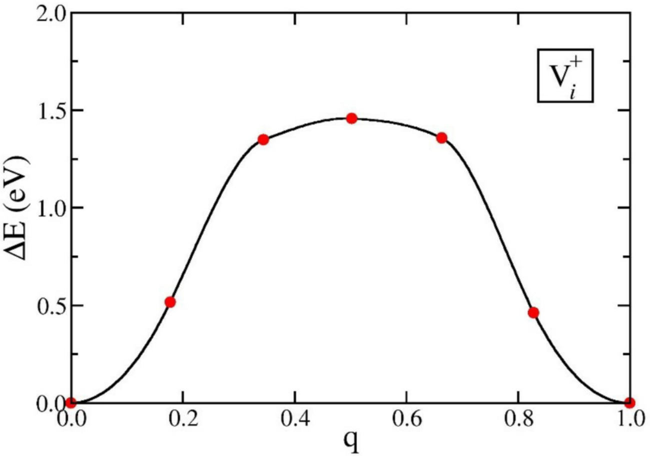

FIG. 1. Migration barrier along the T-H-T sites for ${}^1V_i{}^+$ obtained with seven images using the NEB method. q is a generalized coordinate. The curves in the other charge states are very similar.

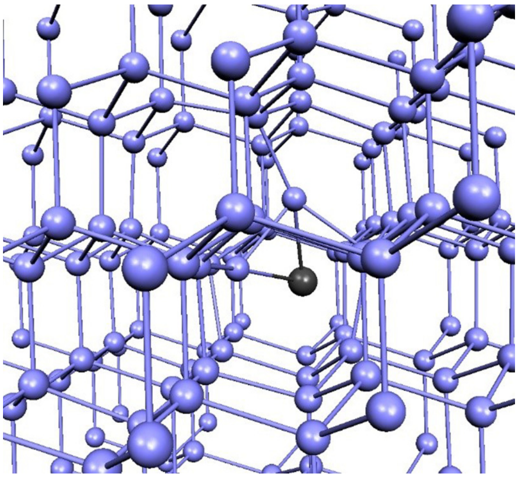

FIG. 2. The $\{I_{Si},V_i\}$ defect. The Si atoms are blue (light gray) and V is black.

2.04 eV, respectively, as compared to 1.55 eV obtained experimentally [23]. The migration barrier for ${}^1V_i{}^+$ is shown in Fig. 1.

The Si vacancy (V_{Si}) is a negative-U defect stable in the $2+$, 0, and $2-$ charge states with spin 0 [59]. The second donor level is located at $E_v + 0.13$ eV, above the first donor level at $\sim E_v + 0.05$ eV [60] (the location of the second acceptor level is not known). In equilibrium, the strong long-range $V_i{}^{2+} - -V_{Si}{}^{2+}$ (in p-type Si) and $V_i^- - V_{Si}^{2-}$ (in n-type Si) repulsion prevents the formation of V_s. However, the interactions are possible for a range of Fermi-level values around midgap, as one or both species is stable in the 0 charge state. We therefore investigated the interactions between a *pre-existing* vacancy ${}^0V_{Si}{}^0$ and either ${}^1V_i{}^+$, ${}^{1/2}V_i{}^0$, or ${}^0V_i{}^-$. In each case, V_i becomes V_s. The reaction involves a spin change in the $+1$ and -1 charge states: ${}^0V_{Si}{}^0 + {}^1V_i{}^+ \to {}^1V_s{}^+ + 2.19\,\mathrm{eV}$ followed by ${}^1V_s{}^+ \to {}^0V_s{}^+ + 0.13\,\mathrm{eV}$, for a total gain of 2.32 eV;

$${}^0V_{Si}{}^0 + {}^{1/2}V_i{}^0 \to {}^{1/2}V_s{}^0 + 3.02\,\mathrm{eV};$$

${}^0V_{Si}{}^0 + {}^0V_i{}^- \to {}^0V_s{}^- + 2.94\,\mathrm{eV}$ followed by ${}^0V_s{}^- \to {}^1V_s{}^- + 0.78\,\mathrm{eV}$, for a total gain of 3.72 eV.

These total energy gains are the binding energies of V_i to the vacancy, and should be compared to the formation enthalpy of the vacancy. This number is difficult to pin down precisely. Positron annihilation experiments [61] gave 3.6 ± 0.2 eV, a value slightly lower than the one extracted from self-diffusion experiments: 3.6–4.0 eV [62] and about 4.2 eV [63], respectively. The value calculated at the present level of theory is 4.0 eV [64]. Thus, the calculated binding energies are smaller than the formation energy of the vacancy, albeit by only a small number in the case of V^-. Thus isolated V in Si prefers to remain interstitial, but the presence of substitutional V is likely when vacancies are provided by implantation, irradiation, surface treatments, high-T anneals, or other energetic processes. Then, V_i readily becomes V_s with a gain in energy comparable to that calculated for Ti [26] ($\sim$2.0 eV), Fe [41] ($\sim$3.0 eV), Ni [26] ($\sim$2.6 eV), and Cu [46] ($\sim$3.1 eV). This corresponds to bond strengths of about 0.5–0.9 eV for each of four TM-Si bonds. Note that adding electrons to V^+ allows for the formation of stronger V-Si bonds.

V_s has a calculated acceptor level at $E_c - 0.94$ eV. It is predicted to be in the 0 charge state in p-type Si and the $-$ charge state in intrinsic and $n-$type Si. Thus, if $V_i{}^+$ interacts with $V_{Si}{}^0$, the resulting $V_s{}^+$ immediately traps an electron and becomes $V_s{}^0$ since the donor level is in the valence band. The calculated TM-Si distances in the 0 and $-$ charge states are 2.441 and 2.438 Å, respectively, slightly longer than the ideal Si-Si distance of 2.383 Å.

V_i is unlikely to interact directly with an isolated self-interstitial (I_{Si}). Indeed, the I_{Si}'s quickly precipitate or expel substitutional impurities such as C. However, the strained environment at a self-interstitial is comparable to that found near dislocations or grain boundaries. The interactions between an interstitial TM impurity and a self-interstitial give us an estimate of the energetics of V_i at strained regions of the Si crystal. The reaction ${}^0I_{Si}{}^0 + {}^{1/2}V_i{}^0 \to {}^{1/2}\{I_{Si}V_i\}^0$ releases 0.73 eV, and the resulting complex is shown in Fig. 2. The $\{I_{Si},V_i\}$ complex has no level in the gap. However, we find the donor level to be about 0.1 eV above the conduction band minimum and this complex should always be in the $+$ charge state.

B. Vanadium-hydrogen interactions

In equilibrium, H is positively charged in p-type Si and diffuses as the bond-centered interstitial ${}^0H_{bc}{}^+$. It is negatively charged in n-type Si and diffuses from T-site to T-site as ${}^0H_T{}^-$. Interstitial H is a negative-U impurity [65] with a $(+/-)$ transition level very close to midgap, but the neutral charge state is metastable and can be long-lived [66]. ${}^{1/2}H_{bc}{}^0$ is at the bc site, but ${}^{1/2}H_T{}^0$ is only slightly higher in energy. All four species are highly mobile. Their migration barriers [66,67] have been calculated. The bc-to-bc barriers are 0.47 and 0.38 eV in the $+$ and 0 charge states, respectively, and the T-to-T barriers are 0.16 and 0.39 eV in the 0 and $-$ charge states, respectively. In p-type Si, $V_i - H$ interactions are unlikely because of the long-range Coulomb repulsion between $V_i{}^{++}$ (or $V_i{}^+$) and $H_{bc}{}^+$. For the same reason, pair

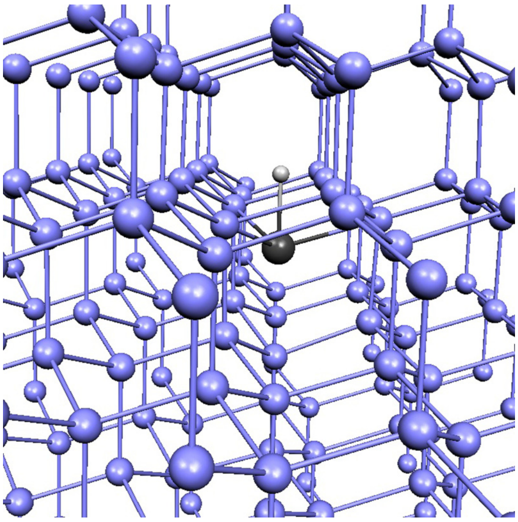

FIG. 3. The $\{V_i,H\}^+$ complex. The Si atoms are light gray (blue), V is dark gray, and H is white.

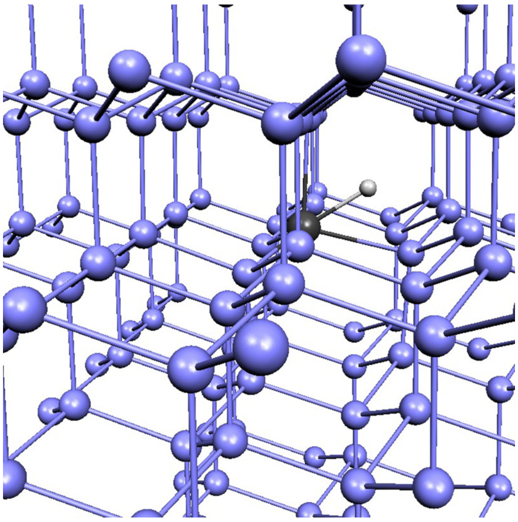

FIG. 4. The $\{V_s,H\}$ complex. The Si atoms are light gray (blue), V is dark gray, and H is white.

formation is unlikely in heavily doped *n*-type Si because it involves $V_i{}^-$ and $H_T{}^-$. However, in moderately doped or intrinsic Si, interactions involving at least one electrically neutral species (V or H) are possible.

The interactions between $^{1/2}V_i{}^0$ and $^0H_{bc}{}^+$ result a trigonal complex (Fig. 3) with H near the hexagonal site along the $\langle 111 \rangle$ axis: $^{1/2}V_i{}^0 + {}^0H_{bc}{}^+ \rightarrow {}^{1/2}\{V_i,H\}^+ + 1.15\,\text{eV}$. This binding energy is consistent with an annealing temperature of the order of 150 to 200° C [12,22]. The interactions between $^0H_T{}^-$ and $^1V_i{}^+$ produce a very similar pair with a 0.96 eV energy gain. The $\{V_i,H\}$ complex is electrically active with a donor level at $E_v + 0.56\,\text{eV}(= E_c - 0.61\,\text{eV})$ and an acceptor level just below the bottom of the conduction band at $E_c - 0.07$ eV. Two DLTS lines have been assigned [12,22] to the $\{V_i,H\}$ complex at about $E_c - 0.49$ eV [12] or $E_c - 0.51$ eV (E_3 line) [22], and a weak line at $E_c - 0.18$ eV (E_5 line) [22]. The latter has not been assigned to a specific defect. However, this line appears after hydrogenation, anneals at about the same temperature as E_3, and is quite close to our acceptor level for VH. On the other hand, the prediction of levels that are close to a band is always questionable.

H interacts with V_s in *p*-type and intrinsic Si. In *n*-type Si, the Coulomb repulsion between $^1V_s{}^-$ and $H_T{}^-$ prevents pair formation. The reactions $^1V_s{}^- + {}^0H_{bc}{}^+ \rightarrow {}^1\{V_s,H\}^0 + 1.10\,\text{eV}$ and $^{1/2}V_s{}^0 + {}^0H_{bc}{}^+ \rightarrow {}^{1/2}\{V_s,H\}^+ + 1.03\,\text{eV}$ produces the same configuration (Fig. 4). The V-H bonds length is 1.73 Å. The $\{V_s,H\}$ complex has an acceptor level at $E_c - 0.70\,\text{eV}$. $\{V_s,H\}$ can trap a second H (Fig. 5): $^1\{V_s,H\}^0 + {}^0H_{bc}{}^+ \rightarrow {}^1\{V_s,H,H\}^+ + 1.44\,\text{eV}$. The V-H bond lengths are 1.70 Å. This complex has an acceptor level at $E_c - 0.51$ eV.

IV. KEY POINTS

We have calculated the properties of V_i in Si, its interactions with the vacancy, the self-interstitial, and the interactions between V_i or V_s and H. The equilibrium sites and spin states agree with the available experimental data and most recent theoretical studies. The activation energies for diffusion of V_i in the $++$,$+$, and 0 charge states (1.57, 1.46, and 1.57, respectively) are also close to the measured value (1.55 eV [23]). In the negative charge state, the migration barrier is higher (2.04 eV).

The binding energies to a *pre-existing* vacancy are comparable to those of other 3*d* TM impurities (2.3 to 3.0 eV), except for $V_i{}^-$ which becomes substitutional with a gain in energy of 3.7 eV, close to formation energy of the vacancy. Thus, V should become substitutional more easily in *n*-type than in *p*-type Si. The binding energy of V_i to a self-interstitial is low, 0.73 eV, and the resulting complex does not have a level in the gap. V_i (in *n*-Si) and V_s are traps for interstitial H. The V_i-H and V_s-H binding energies are 1.15 and 1.03 eV, respectively, but $\{V_s,H\}$ traps a second H with a larger gain in energy, 1.44 eV. The possibility that V_s traps additional H

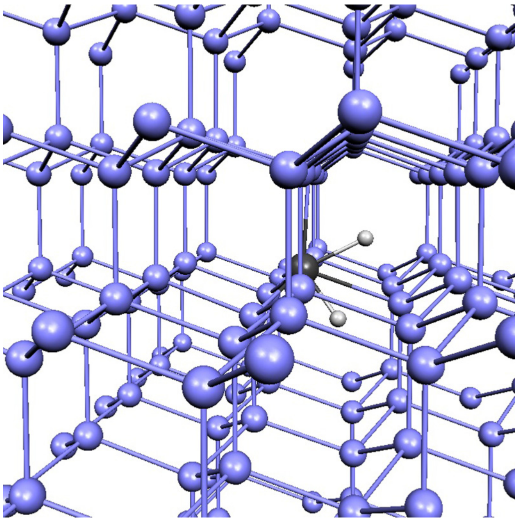

FIG. 5. The $\{V_s,H,H\}$ complex. The Si atoms are light gray (blue), V is dark gray, and H is white.

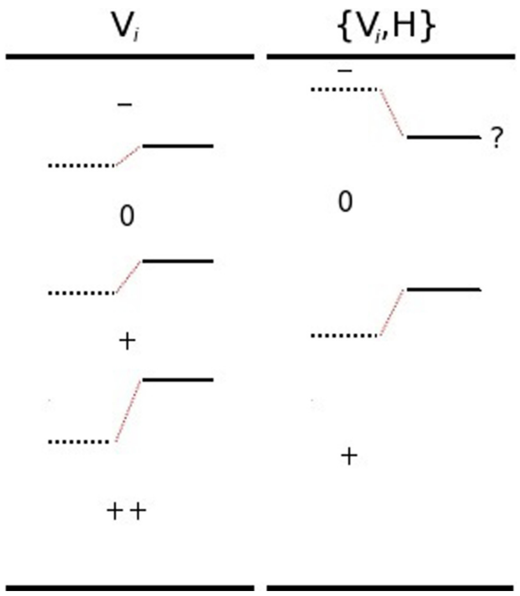

FIG. 6. Comparison of the calculated (dashed lines) and measured (solid lines [22]) gap levels associated with V_i and $\{V_i,H\}$. The calculated acceptor level of $\{V_i,H\}$ is close to the conduction band, well within the accepted error bar for the marker method. The E_5 DLTS line reported in Ref. [22] (question mark) may be associated with some other VH complex.

interstitials has not yet been investigated. When substitutional impurities trap more than two H's, the resulting complexes compete with the formation of H_2 molecules or result in the expulsion of the substitutional impurity leaving a (partially) H-saturated vacancy [39,68].

The calculated gap levels of V_i and $\{V_i,H\}$ are close to the measured values [22] (Fig. 6). Note that the calculated acceptor level at $E_c - 0.07$ eV of $\{V_i,H\}$ is too close to the conduction band to be reliable. It may or may not be related to the weak E_5 line [22]. V_s and the $\{V_s,H\}$ and $\{V_s,H,H\}$ complexes are predicted to be electrically active but have yet to be detected experimentally. Interstitial and substitutional TM impurities in Si are stable in numerous coordination numbers. In the case of V_s, for example, vanadium is fourfold coordinated, but it is five- and sixfold coordinated in $\{V_s,H\}$ and $\{V_s,H,H\}$, respectively. Hydrogen does not replace or strengthen existing bonds but creates additional bonds instead.

ACKNOWLEDGMENTS

This work is supported in part by a grant from the Bay Area Photovoltaic Consortium. The Texas Advanced Computer Center and Texas Tech's High Performance Computer Center at Texas Tech provided generous amounts of computer time.

---

[1] J. R. Davis, Jr., A. Rohatgi, R. H. Hopkins, P. D. Blais, P. Rai-Choudhury, J. R. McCormick, and H. C. Mollenkopf, IEEE Trans. Electron. Dev. **ED-27**, 677 (1980); A. Rohatgi, J. R. Davis, R. H. Hopkins, P. Rai-Choudhury, P. G. Mcmullin, and J. R. McCormick, J. Solid State Electron. **23**, 415 (1980); A. Rohatgi and P. Rai-Choudhury, Solar Cells **17**, 119 (1986).

[2] A. R. Peaker, V. P. Markevich, B. Hamilton, G. Parada, A. Dudas, A. Pap, E. Don, B. Lim, J. Schmidt, L. Yu, Y. Yoon, and G. Rozgonyi, Phys. Status Solidi A **209**, 1884 (2012).

[3] E. R. Weber, Appl. Phys. A **30**, 1 (1983).

[4] G. W. Ludwig and H. H. Woodbury, Phys. Rev. Lett. **5**, 98 (1960); Sol. St. Phys. **13**, 223 (1962).

[5] W. Fahrner and A. Goetzberger, Appl. Phys. Lett. **21**, 329 (1972).

[6] D. V. Lang, J. Appl. Phys. **45**, 3023 (1974).

[7] E. Ohta and M. Sakata, Solid-State Electron. **23**, 759 (1980).

[8] H. Lemke, Phys. Status Solidi (a) **64**, 549 (1981).

[9] K. Graff and H. Pieper in *Semiconductor Silicon*, edited by H. R. Huff, R. J. Kriegler, and Y. Takeishi (The Electrochemical Society, Pennington, NJ, 1981), p. 331.

[10] L. Tilly, H. G. Grimmeiss, H. Pettersson, K. Schmalz, K. Tittelbach, and H. Kerkow, Phys. Rev. B **44**, 12809 (1991).

[11] H. Nakashima and K. Hashimoto, Mater. Sci. Forum **83-87**, 227 (1992).

[12] T. Sadoh, H. Nakashima, and T. Tsurushima, J. Appl. Phys. **72**, 520 (1992).

[13] R. Pässler, H. Pettersson, H. G. Grimmeiss, and K. Schmalz, Phys. Rev. B **55**, 4312 (1997).

[14] J. I. Hanoka, C. H. Seager, D. J. Sharp, and J. K. G. Panitz, Appl. Phys. Lett. **42**, 618 (1983).

[15] F. Duerinckx and J. Szlufcik, Sol. Energy Mater. Sol. Cells **72**, 231 (2002).

[16] F. Jiang, M. Stavola, A. Rohatgi, D. Kim, J. Holt, H. Atwater, and J. Kalejs, Appl. Phys. Lett. **83**, 931 (2003).

[17] S. Kleekajai, F. Jiang, M. Stavola, V. Yelundur, K. Nakayashiki, A. Rohatgi, G. Hahn, S. Seren, and J. Kalejs, J. Appl. Phys. **100**, 093517 (2006).

[18] G. Hahn, M. Käs, and B. Herzog, Solid State Phenom. **156-158**, 343 (2010).

[19] J. Weber, in *Hydrogen in Semiconductors and Metals*, edited by N. H. Nickel, W. B. Jackson, R. C. Bowman, and R. Leisure, (Material Research Society, Warrendale, PA, 1998), p. 345.

[20] J.-U. Sachse, E. Ő. Sveinbjőrnsson, N. Yarykin, and J. Weber, Mater. Sci. Eng. B **58**, 134 (1999).

[21] R. Singh, S. J. Fonash, and A. Rohatgi, Appl. Phys. Lett. **49**, 800 (1986).

[22] J. Mullins, V. P. Markevich, M. P. Halsall, and A. R. Peaker, Phys. Status Solidi (a) **213**, 2838 (2016).

[23] T. Sadoh and H. Nakashima, Appl. Phys. Lett. **58**, 1653 (1991).

[24] H. Nakashima, T. Sadoh, H. Kitagawa, and K. Hashimoto, Mater. Sci. Forum **143-147**, 761 (1994).

[25] S. Hocine and D. Mathiot, Appl. Phys. Lett. **53**, 1269 (1988).

[26] D. J. Backlund and S. K. Estreicher, Phys. Rev. B **81**, 235213 (2010).

[27] J. Utzig, J. Appl. Phys. **65**, 3868 (1989).

[28] G. G. DeLeo, G. D. Watkins, and W. B. Fowler, Phys. Rev. B **25**, 4962 (1982).

[29] G. G. DeLeo, G. D. Watkins, and W. B. Fowler, Phys. Rev. B **25**, 4972 (1982).

[30] A. Zunger and U. Lindefelt, Phys. Rev. B **26**, 5989(R) (1982).

[31] A. Zunger and U. Lindefelt, Phys. Rev. B **27**, 1191 (1983).
[32] A. Zunger, Phys. Rev. B **28**, 3628 (1983).
[33] H. Katayama-Yoshida and A. Zunger, Phys. Rev. B **31**, 8317 (1985).
[34] F. Beeler, O. K. Andersen, and M. Scheffler, Phys. Rev. Lett. **55**, 1498 (1985).
[35] Z. Z. Zhang, B. Partoens, K. Chang, and F. M. Peeters, Rev. B **77**, 155201 (2008).
[36] A. G. Marinopoulos, P. Santos, and J. Coutinho, Phys. Rev. B **92**, 075124 (2015).
[37] D. Sánchez-Portal, P. Ordejón, E. Artacho, and J. M. Soler, Int. J. Quantum Chem. **65**, 453 (1997).
[38] E. Artacho, D. Sánchez-Portal, P. Ordejón, A. García, and J. M. Soler, Phys. Status Solidi (b) **215**, 809 (1999).
[39] D. J. Backlund and S. K. Estreicher, Phys. Rev. B **82**, 155208 (2010)
[40] M. Sanati, N. G. Szwacki, and S. K. Estreicher, Phys. Rev. B **76**, 125204 (2007).
[41] S. K. Estreicher, M. Sanati, and N. Gonzalez Szwacki, Phys. Rev. B **77**, 125214 (2008).
[42] N. G. Szwacki, M. Sanati, and S. K. Estreicher, Phys. Rev. B **78**, 113202 (2008).
[43] J. Lindroos, D. P. Fenning, D. Backlund, E. Verlage, A. Gorgulla, S. K. Estreicher, H. Savin, and T. Buonassisi, J. Appl. Phys. **113**, 204906 (2013).
[44] D. West, S. K. Estreicher, S. Knack, and J. Weber, Phys. Rev. B **68**, 035210 (2003).
[45] S. K. Estreicher, in *Copper Interaction with Silicon Based Materials: A Survey*, edited by A. Mesli and O. Aboelfotoh (Elsevier, New York, 2004), p. 101.
[46] A. Carvalho, D. J. Backlund, and S. K. Estreicher, Phys. Rev. B **84**, 155322 (2011).
[47] H. J. Monkhorst and J. D. Pack, Phys. Rev. B **13**, 5188 (1976).
[48] N. Troullier and J. L. Martins, Phys. Rev. B **43**, 1993 (1991).
[49] P. Rivero, V. M. García-Suárez, D. Pereñiguez, K. Utt, Y. Yang, L. Bellaiche, K. Park, J. Ferrer, and S. Barraza-Lopez, Comp. Mater. Sci. **98**, 372 (2015).
[50] B. Hammer, L. B. Hansen, and J. K. Nørskov, Phys. Rev. B **59**, 7413 (1999).
[51] S. K. Estreicher, D. J. Backlund, C. Carbogno, and M. Scheffler, Angew. Chem. **50**, 10221 (2011).
[52] O. F. Sankey and D. J. Niklewski, Phys. Rev. B **40**, 3979 (1989).
[53] O. F. Sankey, D. J. Niklewski, D. A. Drabold, and J. D. Dow, Phys. Rev. B **41**, 12750 (1990).
[54] A. Resende, R. Jones, S. Őberg, and P. R. Briddon, Phys. Rev. Lett. **82**, 2111 (1999).
[55] J. P. Goss, M. J. Shaw, and P. R. Briddon in *Theory of Defects in Semiconductors*, edited by D. A. Drabold and S. K. Estreicher (Springer, Berlin, 2007), p. 69.
[56] G. Mills and H. Jonsson, Phys. Rev. Lett. **72**, 1124 (1994); H. Jonsson, G. Mills, and K. W. Jacobsen, in *Classical and Quantum Dynamics in Condensed Phase Simulations*, edited by B. J. Berne, G. Ciccotti, and D. F. Coker (World Scientific, Singapore, 1998), p. 385.
[57] G. Henkelman, B. P. Uberuaga, and H. Jonsson, J. Chem. Phys. **113**, 9901 (2000).
[58] G. Henkelman and H. Jonsson, J. Chem. Phys. **113**, 9978 (2000).
[59] G. D. Watkins, in *Deep Centers in Semiconductors*, edited by S. T. Pantelides (Gordon and Breach, New York, 1986) p. 147.
[60] G. D. Watkins and J. R. Troxell, Phys. Rev. Lett. **44**, 593 (1980).
[61] S. Dannefaer, P. Mascher, and D. Kerr, Phys. Rev. Lett. **56**, 2195 (1986).
[62] R. Kube, H. Bracht, E. Hüger, H. Schmidt, J. L. Hansen, A. N. Larsen, J. W. Ager, III, E. E. Haller, T. Geue, and J. Stahn, Phys. Rev. B **88**, 085206 (2013).
[63] T. Sudkamp and H. Bracht, Phys. Rev. B **94**, 125208 (2016).
[64] S. K. Estreicher, Phys. Status Solidi (b) **217**, 513 (2000).
[65] C. G. Van de Walle, Y. Bar-Yam, and S. T. Pantelides, Phys. Rev. Lett. **60**, 2761 (1988).
[66] S. K. Estreicher, M. Stavola, and J. Weber, in *Silicon, Germanium, and Their Alloys: Growth, Defects, Impurities, and Nanocrystals*, edited by G. Kissinger and S. Pizzini (CRC, Boca Raton, FL, 2015), pp. 217–254.
[67] S. K. Estreicher, A. Docaj, M. B. Bebek, D. J. Backlund, and M. Stavola, Phys. Status Solidi (a) **209**, 1872 (2012).
[68] D. J. Backlund and S. K. Estreicher, in *Defects in Inorganic Photovoltaic Materials*, edited by D. Friedman, M. Stavola, W. Walukiewicz, and S. Zheng, Materials Research Society Symposium Proceedings (Materials Research Society, Warrendale, PA, 2010), Vol. 1268, pp. 19–24.