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# Energies of various configurations of hydrogen in silicon

Chris G. Van de Walle
*Xerox Palo Alto Research Center, 3333 Coyote Hill Road, Palo Alto, California 94304*
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Results are reported of a set of first-principles calculations for hydrogen interacting with bulk Si, the Si surface, and with other impurities and defects in the Si lattice. The total energy values corresponding to the various structures are all expressed with respect to a common reference (the free H atom). The resulting energy diagram provides immediate insight in the relative stability of different configurations. It also allows the derivation of formation energies, which allow calculation of concentrations. Among the topics discussed are hydrogen solubility and desorption from a Si surface.

## I. INTRODUCTION

The interactions of hydrogen with silicon have recently been studied in great detail with various theoretical and experimental methods. The ability of hydrogen to terminate dangling bonds on the Si surface, to passivate both deep and shallow defects, and to induce extended defects has fueled the interest.[1,2] Using pseudopotential-density-functional theory in a supercell geometry, we have previously explored the behavior of hydrogen as an isolated interstitial impurity, as well as its interaction with other H atoms, with defects, and with other impurities. Energy differences between some of these configurations were investigated in those studies, but so far no comprehensive overview has been given. In particular, it is relevant and useful to express the energies of the various configurations with respect to a common reference; here we choose this reference to be the energy of a neutral H atom in free space. In this paper, such values are listed for H in crystalline Si (*c*-Si). We are building, to a certain extent, upon our previously published results for structures and for certain total-energy differences; for the most part, however, new calculations have been carried out to ensure uniform levels of convergence. Some preliminary aspects of the present study were mentioned in a prior publication.[3] Chang and Chadi[4] have also published information about energies of hydrogen configurations in Si. The present work, however, is more comprehensive in that it includes a larger number of configurations. The calculations reported here were also carried out at a higher level of convergence (supercell size and plane-wave cutoff) than those reported in Ref. 4, which accounts for quantitative differences.

In addition to a discussion of the theoretical approach (Sec. II) and of the physical meaning of the calculated results (Sec. III), the paper contains several illustrations of how these values can be used to analyze or predict physical properties, providing a link with experimental observations (Sec. IV).

## II. THEORETICAL APPROACH

### A. Formalism for extracting energy values

Our calculations are performed in a supercell geometry, which implies that the impurity is surrounded by a finite volume of the host semiconductor, and this structure is periodically repeated. Convergence tests as a function of supercell size ensure that the values extracted are representative of an isolated impurity. The energy values that we will report are obtained as follows: Suppose we carry out a calculation for a supercell containing $n_{\mathrm{H}}$ H atoms and $n_{\mathrm{Si}}$ Si atoms. We then define an energy $E'$ for this configuration:

$$E' = [E_{\mathrm{tot}} - n_{\mathrm{H}}E_{\mathrm{H}} - n_{\mathrm{Si}}E_{\mathrm{Si}}]/n_{\mathrm{H}}, \tag{1}$$

where $E_{\mathrm{tot}}$ is the calculated supercell energy, $E_{\mathrm{H}}$ is the calculated energy of a free H atom, and $E_{\mathrm{Si}}$ is the calculated energy of a Si atom in the bulk. The factor $1/n_{\mathrm{H}}$ on the right-hand side is introduced in order to express the energy *per H atom.*

If we want to use our energies to evaluate stability of different configurations, they should include the contribution from zero-point energy; such contributions will be discussed in Sec.II C. For the configuration defined above we then obtain

$$E = E' + E_Z, \tag{2}$$

where $E_Z$ is the zero-point energy per H atom.

In Eq. (1) we chose our reference energy for H to be the free H atom, and for Si to be Si bulk. In practice, the reservoirs from which H and Si atoms are taken may be different; e.g., the reference for H may be $H_2$ molecules in the gas. In general, the formation energy of a configuration should therefore take the choice of reservoirs into account, which in a thermodynamic context corresponds to choice of chemical potentials. For the configuration considered above, with energy $E$ per H atom, the formation energy at $T = 0$ is given by

$$E_{\mathrm{form}} = n_{\mathrm{H}}E - n_{\mathrm{H}}\mu_{\mathrm{H}} - n_{\mathrm{Si}}\mu_{\mathrm{Si}}. \tag{3}$$

$\mu_{\mathrm{H}}$ is the chemical potential for H, i.e., the energy of the reservoir from which H atoms are taken; this chemical potential should be expressed with respect to the same reference as the other energies, in this case the free H atom. Similarly, the Si chemical potential $\mu_{\mathrm{Si}}$ should be referred to bulk Si.

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### B. Methods

The calculations were carried out using density-functional theory in the local-density approximation,[5] using *ab initio* pseudopotentials[6] (except for H, for which the Coulomb potential was used). A supercell geometry was employed, with typically 32 atoms in a cell with bcc symmetry. Relaxation of the host atoms around the impurity was always included. Convergence with respect to supercell size was checked in a number of preceding studies.[7,8] Additional details can be found in Ref. 7.

The plane-wave cutoff required to obtain converged results depends on the configuration studied. For some configurations (e.g., the $SiH_4$ molecule) we were able to explicitly converge the desired energy difference; in those cases, we could verify that the convergence as a function of plane-wave cutoff is usually well described by a fit to an exponential. In cases where convergence was more difficult to obtain we have therefore used fitting to an exponential function to obtain an extrapolated value. The difference between the extrapolated value and the explicitly calculated numbers at the highest cutoff never exceeded 0.1 eV. The highest plane-wave cutoffs applied to the various configurations were 42 Ry for free H, $H_2$, and $SiH_4$, and 18 Ry for the configurations involving bulk Si or Si surfaces.

The calculations for free atoms and molecules were carried out by placing the atom or molecule in a supercell which otherwise contains vacuum, and using the same plane-wave cutoff as in the calculation for the solid, to eliminate systematic errors. For the cases studied here we found that a simple cubic cell with $a$=5.0 Å was sufficient to obtain results for an isolated atom or molecule. Spin polarization has only a small effect on the energies for H inside the crystal (see Ref. 7), but is essential for H in free space.

The Ceperley-Alder formula for the exchange and correlation (XC) potential was used, as parametrized by Perdew and Zunger.[9] With this XC potential, a spin-polarized calculation for the free H atom yields an energy of −13.03 eV, i.e., 0.57 eV above the known experimental value. We have investigated whether this inaccuracy affects our calculated numbers, where we use the energy of the free H atom as a reference. For that purpose we have carried out calculations in which the von Barth–Hedin[10] form of the XC potential was used. The von Barth–Hedin potential yields an energy for the free H atom of −13.50 eV, i.e., within 0.1 eV of the experimental value and much closer than the Ceperley-Alder form. However, the calculated energy difference between H at a bond-center site inside the solid and the free H atom turned out to be insensitive (to within 0.01 eV) to the choice of XC potential. The error involved in the Ceperley-Alder potential is thus systematic, occurring both for the free atom and for the atom bound in the solid, and does not affect our results.

Given the wide variety of structures discussed in this paper, it is difficult to assign a uniform error bar. References 7 and 8 contain an analysis of the convergence with respect to plane-wave cutoff, Brillouin-zone integration, and supercell size; it was found that the results should be accurate to within a *numerical* uncertainty of ±0.1 eV. Beyond that, some intrinsic (and hard to estimate) uncertainty may be associated with the basic method (density-functional theory in the local-density approximation) used in our approach. A reassuring check in this respect is provided by the above-mentioned calculation using a different exchange and correlation potential (von Barth–Hedin instead of Ceperley-Alder).

### C. Zero-point energies

For molecules such as $H_2$ and $SiH_4$, we obtain the zero-point energy from summing $\frac{1}{2}\hbar\omega$ over the vibrational modes, whose frequencies are known from experiment.[11] For many configurations of H in the Si lattice, the vibrational modes have been studied, and frequencies for stretching and wagging modes have been calculated. Table I contains a list of references, and the resulting calculated zero-point energies. In cases where no calculated values were available, the frequencies were estimated based on similarity to other configurations.

## III. RESULTS

Table II and Fig. 1 summarize the results for a neutral H atom and its interactions with crystalline Si. The

TABLE I. Frequencies of vibrational modes, and resulting zero-point (ZP) energies, for various configurations involving H and Si (db stands for dangling bond). For degenerate modes the degeneracy is indicated in parentheses.

| Configuration | Reference | Modes ($cm^{-1}$) | ZP energy per H atom (eV) |
|---|---|---|---|
| $H_2$ | 11 | 4400 | 0.13 |
| $SiH_4$ | 11 | 2187, 2183, 978, 910 | 0.21 |
| H at *BC* | 7 | 1945, 500[a] (2) | 0.18 |
| $H_2$ in Si | 21, 24 | 2300, 300[a] (5) | 0.12 |
| $H_2^*$ in Si | – | 2100[a], 1500[a], 600[a] (2), 700[a](2) | 0.19 |
| HB complex | 8 | 1830, 500[a] (2) | 0.18 |
| HP complex | 16 | 1460, 740 (2) | 0.18 |
| Si-H on Si(111) | 29 | 2080, 630 (2) | 0.21 |
| Si-H at db | 21 | 2000, 650[a] (2) | 0.21 |

[a] Estimated.

TABLE II. Calculated values of the quantities $E'$ [Eq. (1)] and $E$ [Eq. (2)], i.e. the energy (per H atom) of a configuration, expressed with respect to Si bulk atoms and free H atoms. $E$ is obtained by adding the zero-point energy (Table I) to $E'$. Values of $E$ are also shown in Fig. 1. db indicates dangling bond.

| Configuration | $E'$ (eV) | $E$ (eV) |
|---|---|---|
| $H_2$ | -2.44 | -2.31 |
| $SiH_4$ | -2.43 | -2.22 |
| H at *BC* | -1.23 | -1.05 |
| $H_2$ in Si | -2.04 | -1.92 |
| $H_2^*$ in Si | -1.84 | -1.65 |
| HB complex | -2.32 | -2.14 |
| HP complex | -2.22 | -2.04 |
| Si-H on Si(111) | -2.35 | -2.14 |
| Si-H at isolated db | -2.38 | -2.17 |
| Si-H at (preexisting) isolated db | -3.76 | -3.55 |
| Si-H on (preexisting) Si(111) | -3.81 | -3.60 |
| Si-H at (preexisting) db in hydrogenated vacancy | -3.36 | -3.15 |

energy of the H atom in free space is chosen as the zero of energy. All quantities are expressed in eV, and per H atom. The values appearing in the diagram will now be discussed one by one.

### A. $H_2$ molecules in free space

We calculate (using a 36-Ry cutoff) a bond length for the $H_2$ molecule of 0.79 Å, compared to the experimental value of 0.74 Å.[12] Our calculated energy for H in a $H_2$ molecule is $-2.31$ eV (per atom); this implies a binding energy for the $H_2$ molecule of 4.62 eV, which is quite close to the experimental value (4.52 eV, Ref. 12).

### B. $SiH_4$

Our calculations (at 36 Ry) for the $SiH_4$ molecule yield a Si-H bond length of 1.50 Å, quite close to the experimental value (1.48 Å, Ref. 12). Referred to bulk Si and free H atoms we find the energy of $SiH_4$ to be $-2.22$ eV (per H atom). Note that this value places $SiH_4$ at an energy 0.09 eV (per H atom) above the $H_2$ molecule; this translates into a heat of formation for $SiH_4$ (expressed with respect to Si bulk and $H_2$ molecules) of 0.36 eV, which is (fortuitously) exactly the same as the experimental value.[13]

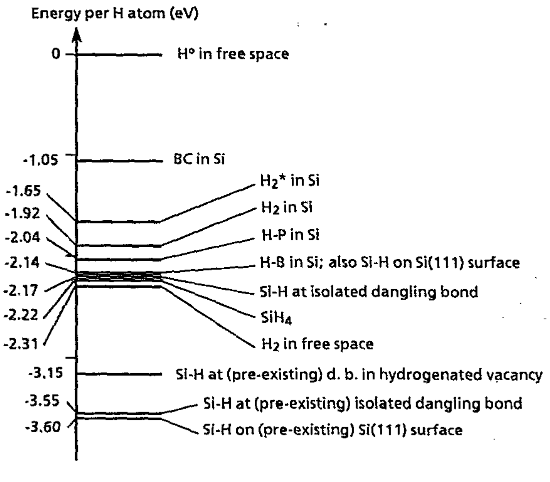

FIG. 1. First-principles energies for various configurations of H in Si. The zero of energy corresponds to a free H atom. The energy values are determined according to Eqs. (1) and (2), with values for $E_Z$, $E'$, and $E$ listed in Tables I and II.

### C. Hydrogen at the bond-center site

The value for "*BC* in Si" in Fig. 1 refers to the lowest-energy configuration for an isolated neutral H interstitial in crystalline Si, which is at the bond-center site. A detailed discussion of the atomic and electronic structure of this configuration can be found in Ref. 7. Its energy is 1.05 eV below the value for H in free space.

### D. $H_2$ molecules in the Si crystal

Calculations for $H_2$ molecules in the Si crystal were reported in Ref. 7. We found that the molecule is most stable at a tetrahedral interstitial site, oriented along [100]. Calculations at 36 Ry produce a bond length of 0.82 Å (i.e., slightly larger than the bond length in free space). The energy of this configuration is $-1.92$ eV per H atom. This implies that, when two isolated interstitial H atoms (at *BC*) combine and form a $H_2$ molecule in Si, an energy of $(-1.05) - (-1.92) = 0.87$ eV per atom is gained (or 1.74 eV per molecule). In Ref. 14, an upper limit of 1.44 eV was placed on the binding energy of the $H_2$ molecule; however, the same work suggested the possibility that formation or dissociation of the molecule would involve charged monatomic species, which would lower the binding energy with respect to the theoretical value calculated here.

A metastable structure involving two H atoms has been proposed by Chang and Chadi.[4] The complex, which they labeled "$H_2^*$", has $C_{3v}$ symmetry and consists of one H in a *BC*-like position, and one H in an antibonding-type position.[15] The Si atom in between the two H atoms is substantially relaxed from its equilibrium site, breaking the original Si-Si bond; the resulting dangling bond is tied off by the *BC*-type H. In agreement with Ref. 4 we find the binding energy of this complex to be 0.4 eV less than the binding energy of the $H_2$ molecule. The energy per H atom is therefore 0.2 eV higher than in the $H_2$ molecule, which leads to the values listed in Table II and Fig. 1.

### E. Hydrogen-impurity complexes

The energy for the B-H complex represents the energy necessary to split up the complex into a neutral H atom and a neutral substitutional B atom. The structure and energy of this complex were discussed in Ref. 8. There the binding energy of the complex was calculated with respect to a substitutional B in the negative charge state, and an interstitial H in the positive charge state (which is the stable state in $p$-type material). We can relate the energies of the charged species to the energies of the neutral species using the experimental ionization energy of the B acceptor, and our calculated values for hydrogen charge states (see Ref. 7). We then find that the BH complex has an energy of −2.14 eV on our energy scale.

A similar procedure can be followed for the HP complex, the structure of which was discussed in Ref. 16. We obtain an energy, expressed with respect to a neutral P donor and the free H atom, of −2.04 eV.

### F. Hydrogen on the Si surface

We have studied the structure of the fully hydrogenated Si(111) 1 × 1 surface, and found the Si-H bond length to be the same as in the $SiH_4$ molecule. The Si atom to which the H atom is bound relaxes into the surface by 0.05 Å. These results are very similar to those of Kaxiras and Joannopoulos.[17] Following the definition given in Eqs. (1) and (2) (i.e., referred to the energy of Si bulk), we find the energy of this configuration to be −2.14 eV. This energy of H on the Si(111) surface (tying off a dangling bond) is quite close to its energy in a $SiH_4$ molecule. We note that a very similar value was found by Northrup[18] for H on a (100) surface (in the "1 × 1 canted dihydride" structure).

However, in this case there is another energy value which is relevant to characterize the configuration. Instead of comparing the energy with respect to Si bulk, we can ask how much energy is involved in removing the H atom from the surface, leaving a dangling bond on the bare surface behind. In order to address this question, one should carry out a calculation for the bare (111) surface. Detailed investigations of this surface have been previously performed with first-principles techniques; it was found that the energy of the relaxed 1 × 1 surface is 1.46 eV (per atom) higher than the bulk.[19] We therefore conclude that when we remove a H atom from the hydrogenated (111) surface, leaving a dangling bond behind (and neglecting any interaction between this dangling bond and neighboring H atoms), the energy cost would be 2.14 + 1.46 eV = 3.60 eV. This value is also included in the diagram of Fig. 1. We also note that the energy of the reconstructed (111) surface in the 7 × 7 reconstruction is about 0.3 lower than the 1 × 1 surface;[20] if all H atoms were removed and the surface were allowed to reconstruct, the value of 3.60 eV would be reduced by this amount.

### G. Hydrogen at a dangling bond

We have studied the binding energy of hydrogen at a dangling bond in two configurations. The first configuration is that of a hydrogenated vacancy; i.e., one Si atom is removed, and the remaining dangling bonds are tied off by H atoms. Even after relaxation the H atoms are relatively close together (less than 1.7-Å separation) in this configuration, and hydrogen-hydrogen repulsion may play a role in the calculated energy. We have therefore investigated a second geometry, in which a H atom is attached to a dangling bond which is well separated from any other dangling bonds. This configuration is obtained by first creating one vacancy, focusing on one of its dangling bonds, and then removing the other three Si atoms surrounding the vacancy. This has the effect of generating nine new dangling bonds, which are much farther removed from the dangling bond we are focusing on. All of the dangling bonds are then hydrogenated. The "central" Si-H bond has a H atom which is 3 Å removed from any other H atoms in the structure, which virtually elimininates any undesired interactions. The details of the calculations on these structures, including relaxations, bond lengths, and a derivation of a H-H repulsion parameter, are reported elsewhere.[21]

Let us focus on the configuration in which a single, "isolated" dangling bond is far removed from other Si-H bonds. To determine the energy of this configuration, we can take the approach of Eqs. (1) and (2) and compare with the energy of Si bulk and free H atoms. This value is listed in Fig. 1, and is equal to −2.17 eV. As in the case of the (111) surface discussed above, however, it is relevant to ask the question: how much energy is needed to remove the H atom from a Si-H bond, leaving a dangling bond behind? To our knowledge, the energy of an isolated dangling bond has not been calculated before; calculations for vacancies (which contain four dangling bonds) are not helpful, since the dangling bonds in that case strongly interact. What we have to do, then, is explicitly carry out a calculation for the dangling bond, i.e., the configuration where the H atom has been removed from the Si-H bond, leaving a dangling bond behind. The final value, which we label the energy of a "Si-H at a (pre-existing) isolated dangling bond," is −3.55 eV, remarkably close to the energy of a Si-H bond on the (111) surface, when expressed compared to the bare surface.

As pointed out above, in the case of the hydrogenated vacancy the interactions between H atoms are significant. The repulsion between H atoms causes a reduction in the bond strength of the Si-H bond; we find that the energy to remove the H from the dangling bond and place it in free space is reduced by 0.4 eV,[21] leading to the value of −3.15 eV on our energy scale (Fig. 1).

## IV. DISCUSSION

### A. Hydrogen solubility

The value for "*BC* in Si" refers to the lowest-energy configuration for a neutral H interstitial in crystalline Si, which is at the bond-center site. Let us use this value to illustrate how our first-principles energies can be used in a thermodynamic formalism to obtain macroscopic quantities. In this example, we calculate the solubility of H in crystalline Si at high temperature (around 1400 K), which is the temperature range in which the permeability measurements of van Wieringen and Warmoltz[22] have been carried out.

We envisage a situation in which H inside the crystal is in thermal equilibrium with $H_2$ molecules outside. An overwhelming fraction of the H inside the crystal then occurs as isolated interstitials, since the binding energy of H to other impurities or defects is small enough to allow for complete dissociation at these high temperatures. The same applies to the binding energy of $H_2$ inside the crystal (see Fig. 1). Focusing on the interstitial, one should not assume that only the neutral charge state will occur; in fact, both theory and experiment indicate that hydrogen may occur in positive as well as negative charge states.[23] For the purposes of the present estimate, we assume that all hydrogen is in the neutral charge state, which is a reasonable approximation as long as the donor and acceptor levels are not too far removed from midgap (where the Fermi level is located at these high temperatures).

The equilibrium concentration of interstitial H is given by (see, e.g., Ref. 24),

$$[\mathrm{H}] = N_{\mathrm{sites}}\, g \exp\left(-\frac{G_{\mathrm{form}}}{kT}\right), \tag{4}$$

where $N_{\mathrm{sites}}$ is the appropriate site concentration, i.e., the number of bond-center sites per $\mathrm{cm}^{-3}$, $g$ is the degeneracy (2 for spin), and $G_{\mathrm{form}}$ is the Gibbs free energy of formation for the configuration of interest:

$$G_{\mathrm{form}} = E_{\mathrm{form}} - TS_{\mathrm{form}}. \tag{5}$$

$E_{\mathrm{form}}$ is the formation energy of a hydrogen interstitial; the formation energy at zero temperature was defined in Eq. 3. $E_{\mathrm{form}}$ can be expressed in terms of our calculated energy of interstitial H with respect to a free H atom ($E_0 = -1.05$ eV, from Fig. 1), and $\mu_{\mathrm{H}}$, which is the chemical potential of H. This chemical potential represents the energy of the reservoir that H atoms are taken from as they are placed inside the crystal. In the experimental situation described above, this reservoir corresponds to $H_2$ molecules outside the crystal. We know that the energy of H in a $H_2$ molecule is $-2.31$ eV on our energy scale (we consistently use our calculated values here); however, the chemical potential is a Gibbs free energy, which for a gas includes important entropy contributions. The enthalpy and entropy of $H_2$ have been tabulated as a function of temperature (see, e.g., Ref. 25). $S_{\mathrm{form}}$, finally, is the formation entropy of the interstitial (configurational entropy is effectively included in the factors $N_{\mathrm{sites}}$ and $g$); a determination of this quantity would involve a complicated analysis and calculation of vibrational modes.[24] We make the approximation of neglecting this contribution here, as well as any temperature-dependent contributions to the formation energy (except for the temperature dependence of the chemical potential of the gas).

Figure 2 shows the resulting calculated H concentration at high temperatures, along with the solubility data obtained in the van Wieringen and Warmoltz experiment. The agreement with experiment is quite satisfactory, given the error bar on our calculated formation energies (an uncertainty of ±0.1 eV at the temperatures of interest translates into an uncertainty in the concentration of more than a factor of 5). Van Wieringen and Warmoltz performed an Arrhenius analysis of their solubility data, yielding values for prefactor and activation energy. We make no attempt here to compare the theoretical and experimental activation energies. First of all, experimentally determined Arrhenius slopes are sensitive to temperature-dependent errors, and can be inaccurate if the temperature range is small.[24] More importantly, the measured Arrhenius slope does not directly yield the ground-state binding energy (which is the quantity we obtain theoretically); a more detailed thermodynamic analysis is required. Such an analysis will be the topic of future work.

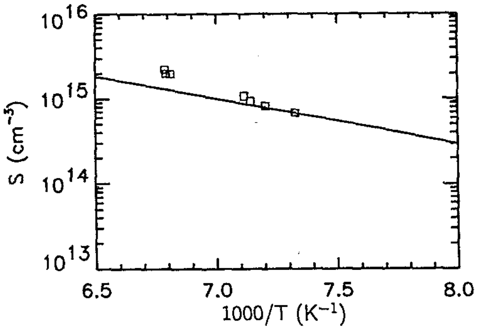

FIG. 2. Theoretical (solid line, see text) and experimental (Ref. 22, squares) solubility of H in Si (in $\mathrm{cm}^{-3}$) as a function of temperature.

The good agreement with experiment evident in Fig. 2 is actually somewhat surprising, in view of the fact that we have neglected entropy contributions in the formation energy; such contributions could be significant at high temperatures. It is conceivable, however, that these entropy contributions are compensated by other temperature-dependent terms in the formation energy; for instance, the increasing amplitude of the thermal motion of Si atoms is likely to make the bond-center site less favorable.

### B. Binding energy of hydrogen-impurity complexes

Comparing the theoretical binding energies for hydrogen-impurity complexes to experiment requires careful analysis. First of all, many experiments measure *dissociation* energies, which include a *barrier* for dissociating the complex, and will thus be higher than the binding energy, which is simply the difference in energy between initial and final state. Second, binding energies extracted from experiment refer to an initial state which is the neutral complex, and a final state in which the impurity and the H atom have been separated, but in which either or both of these species is charged. In contrast, the values included in Table II and Fig. 1 refer to *neutral* species.

For the example of the BH complex, if we assume that the initial state is the neutral complex, and the final state consists of a neutral B atom and a neutral H atom in an interstitial position far away, we can read off the binding energy from Fig. 1; it is equal to $-1.05 - (-2.14) = 1.09$

eV. The experimental situation is more likely to correspond to the case where the complex dissociates into a substitutional B in the negative charge state, and an interstitial H in the positive charge state (the stable charge state in *p*-type material). In that case we find a binding energy of 0.70 eV.[26] Trap-limited hydrogen diffusion experiments by Herrero *et al.*[27] have produced a value of 0.6 eV for this binding energy.

For the hydrogen-phosporus complex, a similar analysis yields a binding energy of 0.99 eV in case the complex dissociates into neutral species, and a value of 0.54 eV for dissociation into $P^+$ and $H^-$. To our knowledge no direct measurements of the binding energy (as opposed to the dissociation energy) of donor-hydrogen complexes have been performed. However, the slightly lower value of the binding energy of the HP complex, compared to HB, is consistent with the experimental observation that efficient donor passivation can only be achieved at lower hydrogenation temperatures than those used for acceptor passivation.

### C. Desorption of hydrogen from a Si surface

In Sec. III F we found that the energy gained when a H atom ties off a dangling bond on a Si(111) surface is 3.60 eV. Note that the bond strength of the Si-H bond at the surface is comparable to the bond strength in a $SiH_4$ molecule: it takes 3.92 eV to remove the first H atom from a $SiH_4$ molecule (i.e., $SiH_3$-H);[28] subsequent H removals take somewhat less energy (2.78 eV for $SiH_2$-H, 3.65 eV for SiH-H, and 3.03 eV for Si-H). The vibrational frequency for the stretch mode is (see review of experimental values in Ref. 29) 2080 $cm^{-1}$ at the surface, and 2186 $cm^{-1}$ in $SiH_4$. Detailed calculations of bond lengths and relaxations for the hydrogenated Si(111) surface were performed by Kaxiras and Joannopoulos.[17] The resulting calculated vibrational frequencies for hydrogen stretching and wagging modes were in good agreement with experiment.

It is illuminating to interpret our calculated value for the Si-H bond strength on the surface in terms of the activation energy for desorption of hydrogen from Si surfaces, for which a value of 2.4±0.1 eV has been measured.[30] Some controversy exists regarding the interpretation of this desorption activation energy. One possibility is that the desorption of $H_2$ involves breaking two Si-H bonds, accompanied by immediate H-H recombination to produce $H_2$ (yielding the $H_2$ binding energy of 4.52 eV). This mechanism predicts $E_{\mathrm{desorption}} = 2E_{\mathrm{binding}}(\mathrm{Si-H}) - E_{\mathrm{binding}}(H_2)$; to be consistent with this mechanism, the Si-H binding energy should be about 3.5±0.1 eV. The other possibility is that the activation energy for desorption simply reflects the breaking of one Si-H bond, which would require a Si-H bond energy equal to the desorption energy of 2.4±0.1 eV. Our calculated first-principles value of 3.60 eV for the Si-H bond energy on the (111) surface clearly supports the first mechanism, which involves concurrent $H_2$ recombination.

### D. Ability of hydrogen to create defects in Si

Figure 1 shows that the formation energy of a Si-H bond on the (111) surface is −2.14 eV. As discussed above, this energy value *includes* the energy necessary to *create* the surface; i.e., starting from bulk Si and H atoms, one would gain 2.14 eV per H atom if the bulk crystal would separate, creating two surfaces, and H would tie off all the resulting dangling bonds. Kinetic barriers to this process may of course exist, but it is suggestive that this energy of −2.14 eV is lower than that of the $H_2$ molecule in Si (−1.92 eV), and much lower than that of the isolated interstitial (−1.05 eV). This low value is a consequence of the high strength of the Si-H bond, and indicates that, rather than simply sit in solution, H will attempt to disrupt the bulk crystal structure and form Si-H bonds. This mechanism is the likely driving force behind the formation of H-induced platelets;[31] although the microscopic structure of these extended defects is still being debated, it is well established that they contain H bonded in Si-H bonds. Rather than the actual formation of an internal surface, one may also envision the formation of individual point defects, as suggested in Ref. 7. The energy difference between Si-H at a dangling bond (−2.17 eV) and the isolated interstitial H (−1.05 eV) is large enough to allow spontaneous creation of a vacancy if the four dangling bonds were simultaneously hydrogenated, even if one allows for a certain amount of H-H repulsion in the hydrogenated vacancy.

## V. SUMMARY

We have presented an overview of various configurations that H can assume in its interactions with silicon, and the corresponding energies. The results are summarized in Table II and Fig. 1. These energy values provide immediate insight into the relative stability of different configurations; they can also be used to calculate concentrations, dissociation energies, etc. We have provided a number of illustrations of how the theoretical numbers can be used to produce results which directly relate to experimental observations, and we hope they will be usefully applied in many other situations.

## ACKNOWLEDGMENTS

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