Stability, geometry and electronic properties of BH$_n$ ($n = 0$ to 3) radicals on the Si\{001\}$_{3 \times 1}$:H surface from first-principles

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Abstract

A new generation of radiation detectors relies on the crystalline Si and amorphous B (c-Si/a-B) junctions that are prepared through chemical vapor deposition of diborane (B$_2$H$_6$) on Si at low temperature ($\sim$400 $^\circ$C). The Si wafer surface is dominated by the Si\{001\}$_{3 \times 1}$ domains that consist of two different Si species at low temperature. Here we investigate the geometry, stability and electronic properties of the hydrogen passivated Si\{001\}$_{3 \times 1}$ surfaces with deposited BH$_n$ ($n = 0$ to 3) radicals using parameter-free first-principles approaches. \textit{Ab initio} molecular dynamics simulations using the density functional theory (DFT) including van der Waals interaction reveal that in the initial stage the BH$_3$ molecules/radicals deposit on the Si(–H), forming (–Si)BH$_4$ radicals which then decompose into (–Si)BH$_2$ with release of H$_2$ molecules. Structural optimizations provide strong local relaxation and reconstructions at the deposited Si surface. Electronic structure calculations reveal the formation of various defect states in the forbidden gap. This indicates limitations of the presently used rigid electron-counting and band-filling models. The attained information enhances our understanding of the initial stage of the PureB process and the electric properties of the products.

Keywords: depositions and chemical reaction, BH$_n$ radicals, Si\{001\} surface, \textit{ab initio} molecular dynamics, electronic properties

Supplementary material for this article is available online

(Some figures may appear in colour only in the online journal)
2. Computational details

2.1. Reactions and formation energetics on the H passivated Si(001)3 × 1 surface

Experiments revealed that on Si surfaces at elevated temperature, one B3H6 molecule decomposes into two boron trihydride molecules [1–3, 15, 22]:

\[
\text{B}_3\text{H}_6 \leftrightarrow 2 \text{BH}_3.
\]

Then the depositions of dilute BHn radicals occur from the BH3 molecules on the Si surfaces in the following reactions:

For the reaction on Si1 which has one H on top (figure 1(b)),

\[
(-)\text{Si-H} + \text{BH}_3 \leftrightarrow (-)\text{Si-BH}_n + (4 - n)/2 \text{H}_2 + \Delta H_{1}.
\]

(2a)

There are two possibilities for the reaction on Si2 which has two H on top (figure 1(c))

\[
(-)\text{Si-H}_2 + \text{BH}_3 \leftrightarrow (-)\text{SiH-BH}_n + (4 - n)/2 \text{H}_2 + \Delta H_{2},
\]

(2b)

\[
(-)\text{Si-H}_2 + \text{BH}_3 \leftrightarrow (-)\text{Si-BH}_n + (5 - n)/2 \text{H}_2 + \Delta H_{3}.
\]

(2c)

The above reactions can be summarized as

\[
(-)\text{Si-H}_m + \text{BH}_3 \leftrightarrow (-)\text{SiH}_{m-1}(-)\text{BH}_n
\]

\[
+ (3 + m - n - p)/2 \text{H}_2 + \Delta H_{\text{map}}.
\]

(3)

where \(m = 1 \text{ or } 2; n = 0 \text{ to } 3; p = 0 \text{ or } 1.

For the replacement of one SiHm (\(m = 1, 2\)) by one BHn at the Si surface,

\[
(-)\text{Si-H}_m + \text{BH}_3 \leftrightarrow (-)\text{SiH}_{m-1} + (3 + m - n)/2 \text{H}_2 + \text{Si}_i + \Delta H_{\text{map}}.
\]

(4)

Here Siₖ represents a Si atom that belongs to the solid substrate.

The reaction of two BHn radicals on two Si surface atoms of the same type is:

\[
2(-)\text{Si-H}_m + 2\text{BH}_3 \leftrightarrow 2(-)\text{SiH}_{m-1}(-)\text{BH}_n
\]

\[
+ (4 - n)\text{H}_2 + 2\Delta H_{\text{map}}.
\]

(5a)

For the reaction of two BHn radicals simultaneously on one Si1 and on one Si2 surface atom,

\[
(-)\text{Si-H}_m + (-)\text{SiH}_{m2} + 2\text{BH}_3 \leftrightarrow (-)\text{SiH}_{m1-1}(-)\text{BH}_n
\]

\[
+ (4 - n)\text{H}_2 + \Delta H_{\text{map}}.
\]

(5b)

and the reaction of two BHn radicals on one Si2 of the surface is:

\[
(-)\text{Si-H}_2 + 2\text{BH}_3 \leftrightarrow (-)\text{Si-(BH}_n)_{2} + (4 - n)\text{H}_2 + \Delta H_{\text{map}}.
\]

(5c)

Here, \(\Delta H\) represents the formation enthalpy of reactions. At temperature \(T = 0\) K, and pressure \(P = 0\) Pa, the corresponding enthalpies, such as that of the silicon surfaces systems \(H(-\text{SiH}_m)\), here \(m = 1\) for Si1 for \(m = 2\) for Si2, of the...
isolated BH\textsubscript{3} molecule \(H(BH_3)\), as well as those of the products, e.g. \(H(H_2)\) for an isolated \(H_2\) molecule, \(H(Si-BH_3)\) for (--) Si–BH\textsubscript{3}, are equal to the corresponding total enthalpies which can be obtained from our first-principles calculations. The formation energy is equal to the formation enthalpy, \(\Delta E = \Delta H\), when contributions from zero-point vibrations are ignored. A negative value of \(\Delta H\) indicates that the left to right direction of the reaction is energetically favoured (exothermic).

2.2. \(Si(001)3 \times 1\) surface and its 2D cells

Si has a diamond structure with the (cubic) lattice parameter of 5.431 Å. The Si atoms are in a tetrahedral coordination [23]. A cleavage perpendicular to the [001] axis produces two Si\{001\} surfaces. The Si surface atoms have only two nearest neighbours from the subsurface layer. This pristine Si\{001\} surface is unstable at elevated temperature. At temperature around 400 °C, it reconstructs into the \(3 \times 1\) domain with two inequivalent Si surfaces: Si1 with three neighbours and Si2 with two Si neighbours [15]. This reconstructed surface can be stabilized by hydrogen passivation [15]. After H passivation each Si1 absorbs one H and each Si2 is terminated by two H. In this way the tetrahedral coordination is restored for the surface Si atoms (figure 1). The unit cells for the Si\{001\} \(3 \times 1:1\) domains are orthorhombic with the surface plane lattice parameters: \(a = \sqrt{2} a_0\), \(b = 3 \sqrt{2/2} a_0\) (\(a_0\) is the lattice parameter of bulk Si). We utilize a supercell to investigate the Si\{001\} \(3 \times 1:1\) reconstructed surface where the thickness of the slab is along the \(c\)-axis, and where every Si layer contains 6 Si atoms. The slab is 16 atomic layers (AL) thick to assure that bulk-like properties are attained in the middle of the slab. The thickness of the vacuum region is at least 12 Å to avoid inter-slab interactions. In this way we employed an orthorhombic supercell with \(a = 7.77\) Å, \(b = 11.65\) Å and \(c = 34.96\) Å which contains 96 Si atoms in the substrate with consideration of the localized nature of influence of the deposited BH\textsubscript{n} at the Si substrate (see section 3.4). We employed these supercells to balance the reliability and accuracy of calculations and the computational requirements.

For the deposition of an isolated BH\textsubscript{n} on the Si\{001\} \(3 \times 1:1\) surface, we put one BH\textsubscript{n} radical on either a Si1 or a Si2 atom. Furthermore, we also consider the cases with two BH\textsubscript{n} in one surface cell in order to understand the possibilities of BH\textsubscript{n} interaction with each other on the surface.

2.3. The computational details

Our approach is based on the first-principles density-functional theory (DFT) [24, 25]. The first-principles code VASP (Vienna \textit{ab initio} simulation program) [26, 27] was employed. This code uses periodic boundary conditions. We use the projector augmented-wave (PAW) method within [28, 29] the generalized gradient approximation (GGA) as formulated by Perdew, Burke and Ernzerhoff (PBE) [30]. The electronic configurations for the present calculations are \(H 1s^1 2p^2\), B [He] 2s\(^2\) 2p\(^1\) and Si [Ne] 3s\(^2\) 3p\(^1\).

For all the calculations, we employ \(E_{\text{cut}} = 550.0\) eV for the plane wave expansion of the valence electrons and \(E_{\text{aug}} = 700.0\) eV for the augmented waves. The present settings are significantly higher than the corresponding default cut-off energy values in the potentials (the default energies, \(E_{\text{NMAX}} = 400.0\) eV for H, 322.069 eV for Si and 318.64 eV for B, respectively). Test calculations confirmed good convergence of the stress tensor and the atomic force for the strongly covalent solids using the present settings. We used the same settings for all calculations. This provides a systematic cancellation of errors. Calculations included spin-polarization but converged to spin-degenerate states for most calculations. Although in principle all the valence electrons belong to the whole crystal rather than to the individual atoms/ions, the calculated plane waves/electron density can be projected onto atomic orbitals to obtain the atom decomposed local charges and partial and total density of states (DOS). The electronic wave functions were sampled on \(9 \times 6 \times 1\) grid (20k-points) in the Brillouin zone (BZ) of crystals using \(\Gamma\)-centred \(k\)-meshes for all supercells [31]. Tests of \(k\)-meshes and cut-off energies showed energy convergence within 1 meV/atom.

The \textit{ab initio} MD simulation utilizes the finite-temperature density functional theory of the one-electron states, the exact energy minimization and calculation of the exact Hellmann–Feynman forces after each MD step using the preconditioned conjugate techniques, and the Nosé dynamics for generating a canonical NVT ensemble [26]. For \(\Lambda/MD\) simulations, only the \(\Gamma\)-point (0,0,0) was used and smaller cut-off energies \((E_{\text{NMAX}} = 320\) eV\) were employed.

3. Results and discussions

We first study the reactants, the isolated \(H_2\) and BH\textsubscript{3} molecules, as well as Si bulk and the Si\{001\} \(3 \times 1:1\) slab. The calculated H–H bond length for \(H_2\) is 0.748 Å, in good agreement with the experimental value (0.7414 Å) [32]. An isolated BH\textsubscript{3} molecule has a planar structure with a calculated B–H bond-length of 0.965 Å (experimental value: 0.924 Å) [33]. Furthermore, our structural optimization for the slab of the passivated Si\{001\} \(3 \times 1:1\) surfaces, the square unit cell in plane has a length of 5.494 Å. This value is slightly larger than that of experimental values of the bulk silicon (5.431 Å) [23]. Such slight overestimations of the bond-lengths/lattice parameters are not unusual for the DFT-GGA approximation [34].

3.1 Clean and H passivated Si\{001\} \(3 \times 1\) surfaces

The bond lengths of hydrogen-passivated Si1 are 2.39 Å (\(2 \times\)) and 2.44 Å for Si–Si and 1.49 Å for Si–H. The bond lengths of the H passivated Si2 are 2.38 Å (\(2 \times\)) for Si–Si and 1.49 Å (\(2 \times\)) for Si–H (figure 1). The calculated Si–H bond-lengths agree well with the experimental values (1.49 Å) [10, 15]. The good agreement between the theoretical calculations and experimental values suggest that the present accuracy settings are adequate for making predictions concerning borane
molecules, silicon surfaces with/without hydrogen termination, as well as Pure B on and in the Si surfaces.

We analyzed the charges at atomic sites using Bader’s charge model [35–37]. The obtained atomic charges for the Si[001]3 × 1:H surface are found to be (−)(Si1) +0.57H−0.60 and (−)(Si2) +1.18H−0.62, respectively. Such charge transfers from Si to H are in line with the electronegativity difference between Si (1.9 in Pauling scale) and H (2.2).

There are two possible sites that feature Si dangling bonds on the surface that get saturated by H: One by desorbing H on Si1 and another two on Si2. Our first-principles calculations showed that de-absorption of one H at the Si[001]3 × 1:H surface costs 1.57 eV for an H on Si1 and 1.72 eV for an H on Si2 site, respectively. Such moderate enthalpy difference (0.15 eV) indicates that at elevated temperature and in an H-poor atmosphere, H desorption may occur at both Si1 and Si2 though its occurrence at Si1 is slightly favored at elevated temperature.

3.2. AIMD simulations for BH3 deposition on Si[001]3 × 1:H

To get some insight into the deposition of BH3 molecules on the Si[001]3 × 1:H surface, we performed AIMD simulations. We added four BH3 molecules into the vacuum between the Si surfaces. The simulation temperature was selected as 673 K (400 °C). van der Waals interaction correction [38, 39] was included as it has been shown that the standard DFT method without van der Waals interaction correction describe improperly the interaction between molecules themselves and between molecules and substrate [39, 40]. The simulations lasted over 10 ps (7000 steps at 1.5 fs/step). The processes and the reactions are schematically shown in figure 2.

During the MD processes we observed the movements of the BH3 molecules on the H passivated Si[001]3 × 1 surfaces, the formation of a B2H6 molecule from two BH3 molecules in the space, and the formation of (−)SiBH4 molecules on the surface (figure 2). The deposition of BH3 molecules occurs on the Si1 site during our simulation. Here we address this surface reaction in more detail. After a few picoseconds (ps), one BH3 molecule approaches an H which is bonded to Si1. At this moment, the B in the BH3 was having two extra neighbors: one H and the related Si. Finally, the BH3 becomes deposited on the Si surface with four H bonded to it to form (−)SiBH4 configuration. This configuration persists in the following 10 ps (about 7000 steps) in the simulations. Further MD simulations reveal the decomposition of the (−)SiBH4 configurations. As shown in figure 2(c), two H atoms in the (−)SiBH4 radical approach to each other and bond to each other gradually, and finally the formed H2 molecule moves away from the radical. The final products are one H2 molecule and the remaining (−)SiBH2 radical.

3.3. Isolated BHn (n = 0 to 3) radicals on and at the Si(100) 3 × 1:H surface

Total energy calculations for the optimized structures showed that an isolated B on the Si[001]3 × 1:H surface has high formation enthalpy (about +4.3 eV) (see the supplementary materials, figure SM-1 (stacks.iop.org/JPhysCM/32/235201/ smmedia)). This value is close to that (+4.2 eV) for one B on Si in the Si[001]2 × 1:H surface [22]. This indicates little possibility to form dilute bare B on the Si surfaces in a H-rich environment according to the definition in the equations (2)–(5). Meanwhile, H passivation of the isolated B increases the stability. The formation of one BH deposition on the surface Si costs about 2.3 eV. Figure 3 shows that the formations enthalpies of an isolated BH2 or BH3 on the Si surface are positive ranging from −0.15 to −0.36 eV (figures 3(a)–(d)). This suggests that both dilute BH2 and BH3 can be formed on the Si[001]3 × 1:H surface. The stability of BH2 radicals on this surface was also reflected in the molecular dynamics simulations (figure 2(c)). This corresponds to the
The structural analysis also showed that deposition of isolated BH\textsubscript{n} radicals on Si\{001\} 3 \times 1:H surfaces cause local structural relaxations. The important chemical bonds and charges at the surface atoms/ions are shown in table SM-1.

Next we discuss the exchange of the B in the deposited BH\textsubscript{n} radicals and the adjacent Si, an important step for B depositing on Si. The results are shown in figures 3(e)–(h) for the configurations of high stability.

The calculations showed that the (–B–Si and (B)–SiH depositions are not favored (figure SM-2), meanwhile, formations of (–B)–SiH\textsubscript{2} and (–B)–SiH\textsubscript{3} radicals at both Si1 and Si2 sites are favored with formation enthalpies ranging from −0.145 to −0.363 eV as shown in table SM-1. Figures 3(e)–(h) shows the schematic structures of the stable configurations with the exchange of B in the deposited BH\textsubscript{n} radical with the surface Si it attached to form B–SiH\textsubscript{n} (n = 2, 3). The unstable configurations with the exchange of B in the deposited BH\textsubscript{n} radical with the surface Si it attached to form B-SiH\textsubscript{n} (n = 0, 1) are schematically shown in figure SM-2. The corresponding bond-lengths and charges at the atomic sites for all structures are in table SM-1. As shown in figures 3(e)–(h), the frames of the optimized structures of the BH\textsubscript{n} (n = 2, 3) radicals on the Si atoms/ions remain while relaxation occurs.

In table SM-1, details of the local chemical bonds are given. From n = 1 to n = 3, the B–Si bond-length notably increases while the B–H bond-length increases only moderately. Charge analysis shows an interesting trend. The charges at H are almost constant: about −0.63\textit{e} for H on Si and about −0.59\textit{e} for the H at B (table SM-1). This corresponds to the slightly more electronegative nature of B than Si. Structural optimizations

**Figure 3.** Schematic structures and the related formation enthalpies of the exchange between Si on/at the surface and B in BH\textsubscript{n} (n = 2, 3) radicals at and on Si\{001\} 3 \times 1:H surfaces: (a) BH\textsubscript{2} on Si1, (b) BH\textsubscript{2} on Si2, (c) BH\textsubscript{3} on Si1 and (d) BH\textsubscript{3} on Si2; and (e) SiH\textsubscript{2} on B2-at-surface; (g) SiH\textsubscript{3} on B1-at-surface and (h)SiH\textsubscript{3} on B2 at surface. The blue, green and white spheres represent Si, B and H, respectively. The local bonding is summarized in table SM-1.
for the B/Si exchange systems (figures 3(e)–(h)) showed that all the B atoms are four fold coordinated. In fact there is no reconstruction for the B atoms/ions now at the surfaces. All the B atoms/ions in the Si1 site are in four-fold coordinated by Si and all the B at the Si2 sites are coordinated by 3 Si and one H. The local structure after the Si/B exchange changes little, displaying only minor local relaxation.

Formation of \((-\)BH\(_n\) \((n = 0\) to \(3\)) radicals at the Si\((100)3 \times 1\):H is also investigated. As shown in figure SM-2 and table SM-1, when a BH\(_3\) molecule replaces a Si–H on the Si\(\{001\}\)\(3 \times 1\):H surface, the formation enthalpies using equation (4) are moderately high (about +2.0 eV). Therefore, one expects low possibility of formation of such configurations. However, these configurations may form at special conditions such as under ion attack and at elevated temperature in an H-poor atmosphere, etc. Therefore, we also include their electronic properties in table SM-1. Overall from the calculations, one can conclude that the high stability of a BH\(_3\) on one of the two Si sites indicates a high probability of direct BH\(_3\) deposition at the initial stage and those BH\(_3\) originate from the decomposition of diborane molecules.

We performed electronic structure calculations for the isolated BH\(_n\) \((n = 0\) to \(3\)) radicals deposited on the Si\(\{001\}\)\(3 \times 1\):H surfaces. The obtained electronic densities of states (DOS) are shown in figure 4.

Figure 4 shows that the frames of all the curves are similar to that of pure Si\(\{001\}\)\(3 \times 1\):H surface. However there are defect states in the forbidden gap. Clearly these defect states are dispersion-less and very localized. Therefore, we analyzed the energy positions of the defect/impurity states in the band gaps of the surfaces and summarized the results in table SM-1. The notable defects are the most stable B–SiH\(_2\) at the Si1 and Si2 which have unoccupied defect states at about 0.5 eV above the valence band maxima (VBM). Naturally these defect states have strong influence on the electronic properties of the system even at such low coverage. These defect states could not be predicted by the simple rigid electron-counting and band-filling model [3–5].

3.4. Two BH\(_n\) \((n = 0\) to \(3\)) radicals on the Si\((100)3 \times 1\):H surface

The two different surface Si species (figure 1) indicates more possibilities to deposit two BH\(_n\) on the Si\(\{001\}\)\(3 \times 1\):H surface. Analysis showed that there are five ways to deposit two BH\(_n\) radicals on the Si\(\{001\}\)\(3 \times 1\):H surface: (1) on a bridging Si1 pair; (2) two separated Si1; (3) one Si1 and one Si2; (4) on one Si2 and (5) on two Si2. In next sections, we focus the optimized structure and formation enthalpies of the above mentioned systems in two parts. The formation enthalpies were calculated from the cohesive energies of the configurations and the related Si surfaces and boranes according to equations (5a)–(5c).

First we address the two B atoms or BH radical on the surface with the optimized structures and related formation enthalpies in figure SM-3. For two B deposited on two separated Si1, the formation enthalpy is about +4.24 eV/B, which is close to that of the dilute case (+4.20 eV, table SM-1). In fact the calculated B–Si bond lengths and the charge transfers in the two cases are also similar (tables SM-1 and SM-2). The present results indicate that the influence of the BH\(_n\) deposition at the Si surfaces is highly localized.

Meanwhile, when two B were put on a bridging Si–Si pair, structural reconstruction occurs. The two B atoms also form a B–B pair. As a consequence, the formation enthalpy is strongly reduced to about +2.5 eV/B (figure SM-3(d)) from about +4.24 eV/B (figure SM-3(a)). When two B atoms were put at a Si1 and at a Si2, interesting reconstruction occurs. The B on Si1 behaves normally as the dilute case while for the B on Si2, the H originally on the Si2 moves to the top of B, forming a Si–B–H chain. The calculated formation enthalpy is also reduced to about +3.5 eV mainly due to the
reconstruction of the B on Si2. Another notable case is the two B on one Si2 atom (figure SM-3(d)). The structural relaxation also causes a B–B bond. This structure has also quite low formation enthalpy (about $+2.8 \text{ eV/B}$). Figure SM-3 showed a structural reconstruction of two B at two Si2. The B atoms move inwards to form a one-dimensional (1D) B–Si–B–Si chain. Furthermore, the H atoms on Si2 also move on the B tops.

Comparison of figures SM-3(a) and SM-3(b) showed that the formation of B–B bond strongly reduces the formation enthalpy of the system. Figure SM-3 shows the optimized structures for 2BH radicals on the Si(001)3 × 1:H surface. When the two BH radicals were put at two separated Si1, the local structure relaxes similar to that of the dilute case, though the formation enthalpy is reduced to about $+1.4 \text{ eV/BH}$. Similar to the case of two B on a Si1–Si1 pair, when two BH radicals were put on a Si1–Si1 pair, there is also a B–B bond formed. The formation enthalpy is rather lower ($+0.94 \text{ eV/BH}$) as shown in figure SM-3 and table SM-2. When two BH radicals were put on one Si1 and on one Si2 at the same time, structural reconstruction occurs. The B on Si1 moves towards Si1. One H on Si2 also moves to the top of the B on Si2. As a result, both B atoms are three-fold coordinated: B1 has two Si neighbors and one H on top while B2 has one Si2 neighbor and two H on top. The formation enthalpy is also very low ($+0.65 \text{ eV/B}$). The cases of two BH on two Si2 are rather simple: one B–B bond for two BH on one Si2, meanwhile, only relaxation occurs for the case two BH on two separated Si2 with the formation enthalpies of $+1.3$ to $+1.7 \text{ eV/BH}$.

In summary, for the cases of BH radicals on Si, the calculations showed that B–B formation (figure SM-3) or one B connecting to two Si reduces the formation enthalpies notably. Such low positive formation enthalpies indicate possibilities of the formation of these configurations at elevated temperature and H-poor conditions.

Here we discuss two BH$_n$ ($n = 2, 3$) radicals the Si atoms/ions in a unit cell of the Si(001)3 × 1:H surface. The optimized structures are shown in figure 5 and in Table SM-2.

Due to the fact that the coordination number of B for the BH$_2$ radicals deposited on the Si is three, one expects no significant structural relaxation to occur. That is true as shown in figures SM-3(a) to (e). Each B is coordinated to one Si with B–Si bond lengths of about 2.0 Å and to two H (B–H: 1.19 Å). The formation enthalpies are also quite close in the range of $−0.15$ to $−0.36 \text{ eV}$ which also close to that of isolated BH$_2$ deposition (table SM-2). Structural reconstruction occurs for almost all the cases of two BH$_3$ molecules. The only exception is the case that two BH$_3$ were deposited on a Si1–Si1 pair whereby only structural relaxation occurs and each B is connected to one Si and three H as shown in table SM-2. When the two BH$_3$ were put on two separated Si1, one B (B1) still has a coordination similar to that of a dilute case with one Si and three H neighbors, the other B (B2) moves to a middle position and connected to two Si and therefore, it has five neighbors. Such structural reconstruction reduces its formation enthalpy to $−0.52 \text{ eV}$ (figure 5). Structural optimizations for two BH$_3$ on one Si1 and Si2 showed that the BH$_3$ molecule on Si1 tends to move away from the surface.

We repeated this configuration with various starting conditions but in each case the same qualitative behavior was observed.

When two BH$_3$ molecules were set on one Si2, structural reconstruction produced five-coordinated B atoms/ions with one B–B bond. That is, each B has one Si, one B and three H neighbors. This type of bonding is quite unusual, but such reconstruction produced a very stable surface structure.
as shown in table SM-2. Putting two BH$_3$ on two separated Si2 resulted in structural reconstruction as well. One of the B is connected to two Si, meanwhile, the other one is in four coordination.

The calculations also showed possibilities of BH$_n$ clustering on the surface. Overall, the formation enthalpies of two BH$_n$ radicals on the surface are equal to or lower than that of corresponding dilute cases. The calculations showed that formation of B–B bonds or B connected to two Si atoms on the surface strongly reduces formation enthalpies. That indicates a high probability of B clustering.

As shown in figure 6, the frames of the electronic structures of all the configurations are similar to that of the pure Si(001) $3 \times 1$:H. That is understandable since our simulated systems contain only dilute BH$_n$ radicals in accordance with the fact that at the initial stage the deposition of BH$_n$ radicals occurs locally. The structural optimizations showed a) for dilute cases with BH$_n$ on Si, only local relaxation occurs and the coordination number of B increases with increasing n of the BH$_n$ radical (table SM-1 and figure 3). For n = 0 and 2, there are no defect states at the forbidden gaps. Meanwhile, there are defect states exits for systems containing a BH radical on it. This is more or less corresponding to the rigid electron accounting and band-filling model. However, for n = 3 there are no defect states in the forbidden gaps, as shown in figure 4 and table SM-1. This violates the rigid electron accounting model. Another interesting issue is the high stability of the systems with B/Si exchanges to form B–SiH$_n$ configurations. All B in these configurations are four-fold coordinated. Meanwhile their electronic properties are rather complex: half of them have defect states in the energy gaps meanwhile the other half have no defect states (table SM-1).

For simple mBH$_n$ radicals, $m = 2$ in our cases, on the Si(001) $3 \times 1$:H surfaces, the structural optimizations showed strong relaxation and structural reconstructions. As a consequence, most of the configurations contain defect states at the forbidden gaps as shown in figure 6 and in table SM-2. These defect states are position deeper in energy in the forbidden gap than those of the isolated BH$_n$ on the surface. This trend implies that further deposition of boron/boranes on the silicon surface will induce more defects and finally form a Si/B interface.

3.5. Summary of the energetics of BH$_n$ on Si(001) $3 \times 1$:H surface

Here we summarize the formation enthalpies, chemical bonding, and charge/charge transfer from the first-principles calculations. Figure 7 shows the dependences of formation enthalpies on the number of H in BH$_n$ radicals.
Clearly, the formation enthalpies decrease with increasing n in BH₄ radicals. For dilute cases, the formation enthalpies are positive when a B or BH deposited on Si1 and Si2, respectively. The formation enthalpies become negative when a BH₂ or a BH₃ deposits on the surface Si. That means that energetically, deposition of BH₃ on the surface Si or the reaction is favored.

Based on the electronic structure calculations, we summarize the electronic properties of the investigated configurations of high stability in figure 8.

Deposition of borane on the Si₀₀₀₁ × 1:H surface results a rich variety of electronic properties depending on the deposition molecules and the sites. Deposition of a BH₂ on either the Si1 or the Si2 site produces a shallow hole below the conduction band (Case I). When two BH₂ radicals were deposited on two Si1 sites which are not close to each other, the obtained system has the defect states similar to that of case II. Meanwhile, when two BH₂ radicals were deposited on one Si1–Si1 chain, structural relaxation occurs, which causes the disappearing of the defect states from the forbidden gap (Case II). As shown in cases III, IV and V, depositing two BH₂ at different sites induces defect states in the gap. Notably exchange a B in the BH₂ and the nearby Si causes a defect state at the middle of the energy gap (Case VI).

When an isolated BH₃ molecule is deposited on a Si site of the Si surface, the system becomes spin-polarized. This is due to the unpaired electron from the BH₃ radical (Case VII). The defect state for the spin-down electrons is about 01 eV above the Fermi level. The band for the spin-up electrons remain a semiconducting, whereas the band for the spin-down electrons becomes metallic. The exchange of B in the BH₃ molecule and the nearby Si keeps the defect state at the same energy but the spin-polarization disappears (Case X). Deposition of two BH₃ molecules at different sites induces defect states in the band gap (Case VIII and IX).

Overall the band structure calculations demonstrated a rich variety of defect states in the forbidden gap of Si. This also means that a rigid electron counting model can not be used to predict the electronic properties of the products prepared at the early stage of PureB process.

4. Conclusions

First, A/MD simulations for BH₃ molecules on Si₀₀₀₁ × 1:H surfaces at about 673 K have revealed the atomistic details of deposition of BH₃ and the correspondingly formation of –SiBH₄ radicals on the surfaces. The MD simulations showed the decomposition of –SiBH₄ via the surface reaction –SiBH₄ → –SiBH₂ + H₂(g). The present study also revealed the importance of the van der Waals correction to the standard DFT functional in description of molecular/surface interactions. Secondly, total energy calculations showed high stability of the formed –SiBH₂ and –SiBH₃ radicals at the initial stage which is similar to the case of BH₄ radicals depositing on the high temperature Si₀₀₀₁ × 1:H surface. However, the Si₀₀₀₁ × 1:H surfaces provides more deposition sites, which results a richer variety of local structures and electronic properties. The high stability of B/Si exchanged systems with –SiHₙ (n = 1 to 3) configurations indicates possibilities of B existing at and diffusing into the Si surface. Thirdly, calculations showed that mBH₄ clustering (the simple cases m = 2) can cause structural reconstructions. The reconstructed structures, especially the formation of B–B bond significantly stabilize the deposited systems. These results indicate further reactions for thicker BH₄ depositions, which deserves further investigation. Finally, the electronic structure calculations showed that surface structural relaxation and reconstructions have significant impacts on the electronic properties. There are different defect states in the energy gaps, depending on the deposited radicals and local bonding. The currently used electron counting model is violated in many cases. These defect states largely determine the electronic and optical properties of the deposited surfaces. The defect states obtained here provide an explanation for the experimental observations of dramatic changes of the electrical conductivity and optical properties with very thin atomic layer deposition.
of BH₄ radicals. These insights can aid development of new PureB processes for new heterojunctions for detection of UV photons.

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Supplementary materials

The supplementary materials associated with this article can be found in the online version.

Conflicts of interest

There are no conflicts to declare.

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