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Boron, hydrogen and silicon adatoms on the Si(111) surface: an *ab initio* Hartree–Fock/density functional cluster study

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Abstract. Silicon and boron adatoms on the Si(111) surface have been studied using atomic clusters and Hartree–Fock/density functional theory. The equilibrium geometries of the B-S_5, B-T_4 and Si-T_4 structures, and those formed by the chemisorption of a single hydrogen atom onto these structures, have been obtained. The binding energies of the B and Si adatoms, and the resultant SiH and BH complexes, have also been determined. The electronic structures of the clusters have been investigated via a Mulliken population analysis. The calculated results are shown to be in good agreement with both the available LEED and synchrotron x-ray diffraction data, and other simulations. It is found that the binding energy of the Si adatom of the B-S_5 structure is greater than that of the B adatom of the B-T_4 structure by 1.93 eV, and 1.15 eV larger than the binding energy of the Si adatom of the Si-T_4 structure. The chemisorption of atomic hydrogen stabilizes the Si-T_4 geometry through the formation of a silicon adatom–hydrogen (SiH) complex located at the threefold T_4 position. In contrast to this, the Si adatom in the B-S_5 structure, and the B adatom bonded with a chemisorbed hydrogen atom in the B-T_4 structure, are observed to move away from their T_4 positions to the adjacent bridge sites.

1. Introduction

Deposition of adsorbates which can alter the atomic and electronic structure of clean semiconductor surfaces is one of the most important activities in surface science. The observed changes are usually directly related to the behaviour of the adatoms which may reside in bulk-terminated positions, in highly coordinated adatom surface sites, or in interstitial or substitutional sites below the surface. In this paper we report a theoretical study of boron, hydrogen and silicon adatoms adsorbed onto the ideal, unreconstructed (111) silicon surface.

Hybridization of the surface dangling bonds on the clean Si(111) surface leads to either the well known 2×1 π-bonded chain model surface reconstruction [1], or the 7×7 dimer–adatom–stacking-fault (DAS) structure, with the latter being the most energetically favourable reconstruction of the clean Si(111) surface [2]. When silicon adatoms, however, are placed at either the 'hollow' (H_3), or 'top' (T_4), threefold adatom sites of the clean Si(111) surface, a $\sqrt{3} \times \sqrt{3}$R30° layer above the truncated bulk is formed. This is referred to as the Si(111)$\sqrt{3} \times \sqrt{3}$R30° surface. The local adatom bonding structure in this $\sqrt{3} \times \sqrt{3}$R30° surface is identical to the Si adatom environment in the Si(111) 7×7

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DAS structure [3]. The $\sqrt{3} \times \sqrt{3}$R30° surface is also higher in energy than both the 2×1 π-bonded chain and the 7×7 DAS surface [4–6]. The $\sqrt{3} \times \sqrt{3}$R30° and 7×7 reconstructions give similar numbers of reduced surface dangling bonds, 0.33 ML for the $\sqrt{3} \times \sqrt{3}$R30° structure and 0.39 ML for the 7×7 DAS structure. While the presence of the Si adatoms minimizes the number of surface dangling bonds in both cases, it also causes some of the surface bond angles and bond lengths to deviate significantly from the bulk values. It is these competing effects which determine the role of the silicon adatoms on these two surfaces [7], although Vanderbilt [8] has shown that the 7×7 periodicity is energetically favourable even without the Si adatoms.

The recent discovery of the unusual behaviour of boron atoms chemisorbed on the Si(111) surface has added a new dimension to this problem [9, 10]. Boron atoms, in contrast to the other trivalent metals (Al, Ga and In), chemisorb at an S_5 substitutional site in the second layer of the Si(111) surface to form the so-called B-S_5 Si(111)$\sqrt{3} \times \sqrt{3}$R30° surface (hereafter referred to simply as B-S_5). This geometry is around 1.0 eV per surface unit cell lower in energy than the B-T_4 configuration [10, 11] in which the boron atoms occupy the threefold T_4 adatom positions [11–24]. The B-S_5 structure has the same surface topology as the Si(111)$\sqrt{3} \times \sqrt{3}$R30°–Si(adatom) clean surface and is the most energetically favourable Si adatom structure of the Si(111) surface. The B-S_5 topology is also the optimum final geometry for the B/Si(111)7×7 chemisorption system [20].

The basic properties of the B-S_5 surface have already been discussed in the literature. The first core-level spectroscopy study of this surface showed that the Si(2p) core-level shift spectrum has only one component, indicating uniform bonding between each boron atom and its surrounding silicon atoms [16]. Recent studies have revealed, however, that the Si(2p) core-level shift is composed of at least four surface components, although their precise origin remains unclear [17, 18]. The fourfold coordination of the subsurface trivalent boron atom should cause charge transfer from the surrounding Si atoms and stabilize the structure. The chemical reactivity of the B/Si(111) surfaces resulting from such charge transfer is of considerable interest. The chemisorption of ammonia on the Si(111)$\sqrt{3} \times \sqrt{3}$R30°:B system, for example, appears to yield behaviour very different from that of the NH_3/Si(111)7×7 chemisorption system [23]. The low reactivity of the Si(111)$\sqrt{3} \times \sqrt{3}$R30°:B surface towards hydrogen has been demonstrated by studies of the etching of this surface by atomic hydrogen [20]. The interaction of the Si(111)$\sqrt{3} \times \sqrt{3}$R30°:B system with oxygen [21] and alkali metals [18, 24] has also been investigated.

In this paper we present a comprehensive all-electron *ab initio* Hartree–Fock/density functional theory (HF/DFT) cluster study of the Si(111)–B and Si(111)–Si adatom systems. While our calculations show that the predicted cluster geometries represent both stable and topologically identical atomic structures, there are some properties that differ significantly for these two systems. One of the main aims of this paper is to undertake a comparison of these two related surfaces, paying particular attention to the aspects that are different. The stability of the various atomic configurations is discussed within the context of binding energy calculations. The affinity of the different adatom configurations towards atomic hydrogen is also investigated by studying the chemisorption of a single hydrogen atom onto each of the clusters.

2. Models, method and procedure

The widely accepted Si adatom configuration of the Si(111)1×1 surface is the $\sqrt{3} \times \sqrt{3}$R30° reconstruction proposed by Northrup [3]. In this model, the ideal (111) surface is covered by Si adatoms which saturate the surface dangling bonds at the T_4 sites (the Si-T_4

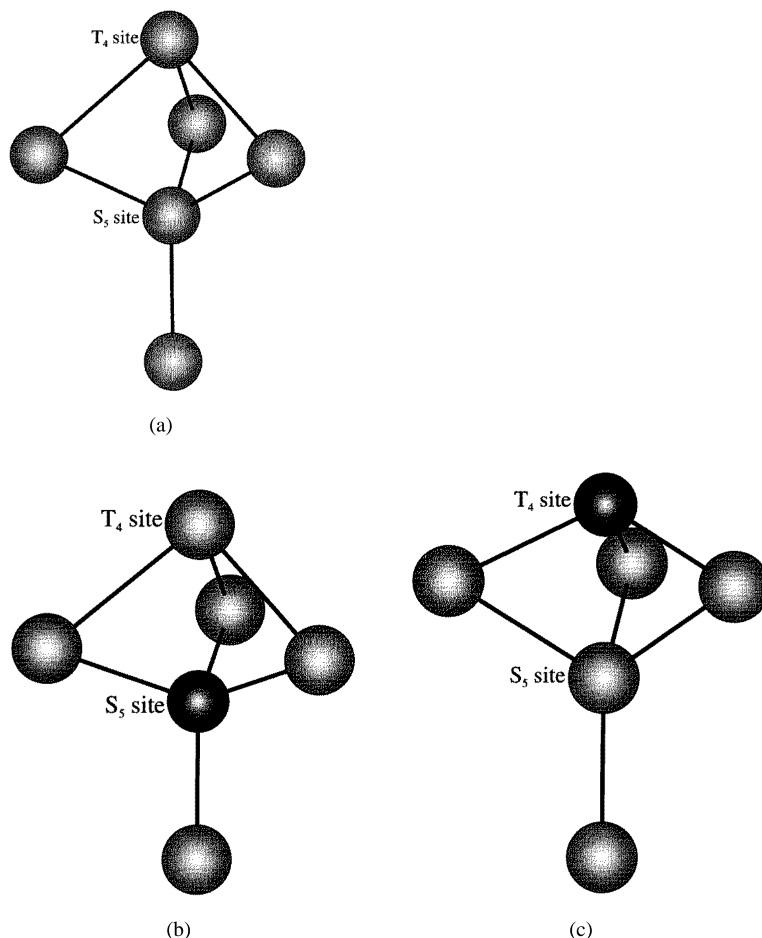

Figure 1. The cluster models used to simulate the Si(111)$\sqrt{3}\times\sqrt{3}$R30° adatom surface: (a) the Si_5H_9 + Si adatom (Si-T_4) cluster, (b) the Si_5H_9 + B adatom cluster with the B atom in the T_4 site (B-T_4), and (c) the Si_5H_9 + B adatom cluster with the B atom in the S_5 site (B-S_5). The hydrogen atoms employed to saturate the bulk dangling bonds are not shown in the figures. The dark spheres denote the boron atoms.

configuration). In addition to the T_4 site, there exists another high-symmetry site where an adatom can be incorporated into the surface, the surface threefold hollow site, H_3. Northrup [3] has shown, however, that this latter structure is around 0.64 eV/adatom higher in energy than the T_4 adatom reconstruction. As a consequence, in the present study, the Si(111)$\sqrt{3}\times\sqrt{3}$R30°–Si adatom surface is assumed to be represented by the T_4 adatom structure (hereafter referred to as the Si-T_4 structure). This topology has been simulated by the Si_5H_9 + Si cluster shown in figure 1(a). This cluster contains the centre Si adatom, its three nearest neighbours, and one second-layer silicon atom and one third-layer silicon atom positioned immediately below the adatom.

Boron atoms deposited on the Si(111) surface can occupy either the T_4 site, or the S_5 site in the second layer directly below the T_4 adatom. The T_4 geometry is represented by the Si_5H_9 + B(T_4) cluster of figure 1(b) (hereafter referred to as the B-T_4 structure). This cluster is identical to that of figure 1(a) except that the central T_4 adatom site is

now occupied by a boron adatom. The substitutional $Si_5H_9 + B(S_5)$ geometry (referred to subsequently as the B-S_5 structure) is shown in figure 1(c). This cluster is also the same as that of figure 1(a), except that the S_5 position directly below the central Si adatom is occupied by a boron atom.

Due to the small size of our adatom clusters, we have been able to employ *ab initio* all-electron Hartree–Fock and density functional theory components of the Gaussian 94 code [25] to obtain the equilibrium configurations of the above clusters. This has been done by minimizing the total energy with respect to the coordinates of all of the silicon atoms (and boron and chemisorbed hydrogen if present) employing a double-zeta 6-31G* basis set for all of the atoms within the clusters, using the straight HF method. In this optimization procedure, all of the terminating hydrogen atom positions are fixed. Several different starting geometries were employed in each case to adequately sample the configuration space. A final geometry was then obtained by reoptimizing the 6-31G* minimum-energy geometry, again using the 6-31G* basis set, but now incorporating correlation corrections via the BECKE3LYP option in Gaussian 94. This state-of-the-art hybrid method, which includes an exact Hartree–Fock exchange energy functional, and a semiempirical combination of a local spin-density (Vosko–Wilk–Nusair parametrization) and nonlocal spin-density (Lee–Yang–Parr parametrization) electron correlation functional [25, 26], is claimed to be accurate to around 0.1 eV [26]. In order to determine the binding energies, the final energy of the optimized original chemisorbed cluster and the energies of both the desorbed species and the residual cluster were calculated using 6-31 + G(3df, 2p) basis functions for all of the atoms. In this process, the geometries of both of the desorbed species, and the residual cluster remaining after the removal of the desorbed species, were first reoptimized with respect to the coordinates of the remaining silicon (and boron) atoms. The sum of the energies of the residual cluster and the desorbed species, minus the energy of the original chemisorbed cluster, gives the binding energy of the desorbed species and the substrate. This energy is the net amount of energy required to remove the desorbed species from the surface.

Table 1. The interatomic distances (in Å) and adatom binding energies (BE) for the B-S_5 structure using four clusters of different sizes. Si(A) and B denote the silicon adatom and boron atom. Si(1) and Si(3) denote first- and third-layer silicon atoms, respectively.

	$Si_5B_1H_9$	$Si_8B_1H_{15}$	$Si_{11}B_1H_{21}$	$Si_{14}B_1H_{27}$
$d_{Si(A)-Si(1)}$	2.435	2.434	2.400	2.401
$d_{Si(A)-B}$	2.202	2.210	2.196	2.195
$d_{Si(1)-B}$	2.116	2.122	2.118	2.107
$d_{Si(3)-B}$	1.973	1.993	1.995	2.020
$d_{Si(1)-Si(1)}$	3.414	3.417	3.378	3.379
BE (DFT)	7.47 eV	7.37 eV	7.52 eV	7.21 eV
BE (HF)	7.39 eV	7.26 eV	7.67 eV	7.43 eV

3. Results and discussion

3.1. Clean clusters

In order to validate the use of the small clusters discussed above, we have performed calculations for the B-S_5 structure using clusters of progressively increasing size. These comprise the Si_5H_9:B-S_5 cluster shown in figure 1(c), the Si_8H_{15}:B-S_5 cluster (formed by

replacing the hydrogen atoms that saturate the dangling bonds of the third-layer Si atom with silicons), the $Si_{11}H_{21}$:B-S_5 cluster (which is formed when the six hydrogen atoms saturating the first-layer Si atoms are replaced by silicons), and the $Si_{14}H_{27}$:B-S_5 cluster (where all of the original embedding hydrogens are replaced by silicons). The resulting optimized geometries and adatom binding energies are given in table 1. These values have been obtained following the procedure described in section 2, and employing a 6-31G* basis set for all of the clusters. We observe that the structure parameters and binding energies differ by only order 1% and 5%, respectively, across all four clusters. These results strongly suggest that saturating the extremities of the clusters with hydrogen atoms simulates the effects of the infinite Si covalent system extremely well. They also verify that reliable predictions can be obtained from the use of our chosen minimal-size Si_5H_9 clusters.

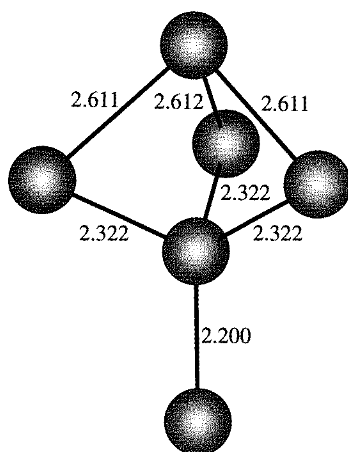

Figure 2. The minimum-energy Si-T_4 structure. All bond lengths in this and subsequent figures are given in ångströms.

3.1.1. Si-T_4 geometry. The optimized Si-T_4 geometry is presented in figure 2. The Si adatom located in the threefold T_4 position (hereafter referred to as Si(T_4)) saturates the first-layer silicon dangling bonds and forms three symmetric bonds, with a bond length of 2.61 Å. The second-layer Si atom in the S_5 position (Si(S_5)) is bonded to the three first-layer Si atoms, and the underlying third-layer silicon atom, at distances of 2.32 Å and 2.20 Å, respectively. While the distance of 2.65 Å between the Si(T_4) adatom and the second-layer Si(S_5) atom is comparable with the adatom back-bond lengths of 2.61 Å, there is no bond between these two atoms. A comparison between the atomic relaxations determined in this work, and those obtained from pseudopotential [3] and LDA [10] calculations, is presented in table 2(a), and indicates general agreement for both the HF-and HF-DFT-calculated geometries. The latter methods do, however, predict significantly larger values for the height of the adatom Si(A), and hence somewhat larger Si(A)–Si(1) and Si(A)–Si(2) distances, than the other two calculations.

The variation of the electronic density from atom to atom, and from layer to layer, has also been obtained for this optimized Si(T_4) geometry using a Mulliken population analysis, and is presented in table 3. The HF calculations show that charge is transferred to both the Si adatom ($-0.04e$) and the second-layer Si(S_5) atom ($-0.37e$), whilst both

Table 2. Adatom and substrate atom displacements (in Å) from their ideal positions, and the interatomic distances (in Å) for the three structures: (a) Si-T_4, (b) B-S_5 and (c) B-T_4. Si(A) and B denote the silicon adatom and the boron atom. Si(1), Si(2) and Si(3) denote the first-, second- and third-layer silicon atoms, respectively. The direction of the z-axis, the threefold symmetry axis in each of the clusters, is that of the surface normal which is perpendicular to the (111) plane. The r-coordinate is the perpendicular distance to the z-axis.

(a)

	Reference [3]	Reference [10]	Reference [5]	Present calculation (DFT)	Present calculation (HF)
$\Delta z_{Si(A)}$	0.53	0.48		0.66	0.61
$\Delta r_{Si(1)}$	−0.15	−0.18		−0.15	−0.16
$\Delta z_{Si(1)}$	−0.08	−0.18		−0.15	−0.18
$\Delta z_{Si(2)}$	−0.39	−0.52		−0.42	−0.48
$\Delta z_{Si(3)}$	−0.25	−0.40		−0.27	−0.30
$d_{Si(A)-Si(1)}$	2.492	2.498		2.611	2.592
$d_{Si(A)-Si(2)}$	2.487	2.568		2.649	2.657
$d_{Si(1)-Si(2)}$	2.348	2.327		2.322	2.322
$d_{Si(2)-Si(3)}$	2.212	2.232		2.200	2.178
$d_{Si(1)-Si(1)}$	3.583	3.528	3.519	3.583	3.561

(b)

	Reference [14]	Reference [10]	Reference [15]	Present calculation (DFT)	Present calculation (HF)
$\Delta z_{Si(A)}$	0.25 ± 0.1	0.28		0.24	0.19
$\Delta r_{Si(1)}$	-0.30 ± 0.2	−0.26	-0.26 ± 0.01	−0.24	−0.23
$\Delta z_{Si(1)}$	-0.30 ± 0.1	−0.30	-0.17 ± 0.2	−0.41	−0.40
Δz_{B}	-0.50 ± 0.1	−0.37		−0.39	−0.38
$\Delta z_{Si(3)}$	-0.34 ± 0.1	−0.06		−0.02	−0.04
$d_{Si(A)-Si(1)}$	2.336	2.457		2.435	2.412
$d_{Si(A)-B}$	2.320	2.216		2.202	2.179
$d_{Si(1)-B}$	2.154	2.216		2.116	2.137
$d_{Si(3)-B}$	2.190	2.042		1.973	1.972
$d_{Si(1)-Si(1)}$	3.326	3.390	3.390	3.414	3.431

(c)

	Reference [10]	Present calculation (DFT)	Present calculation (HF)
Δz_{B}	0.07	−0.06	−0.03
$\Delta r_{Si(1)}$	−0.24	−0.20	−0.21
$\Delta z_{Si(1)}$	−0.01	−0.15	−0.19
$\Delta z_{Si(2)}$	−0.52	−0.58	−0.60
$\Delta z_{Si(3)}$	−0.39	−0.40	−0.41
$d_{B-Si(1)}$	2.154	2.192	2.214
$d_{B-Si(2)}$	2.158	2.086	2.138
$d_{Si(1)-Si(2)}$	2.368	2.348	2.334
$d_{Si(2)-Si(3)}$	2.231	2.168	2.153
$d_{Si(1)-Si(1)}$	3.434	3.483	3.470

the third-layer (0.53e) and first-layer silicon atoms (0.26e) lose electronic charge. This is in contrast to the DFT results where charge is transferred to the second-layer Si(S_5) atom (−0.25e) from the first-layer (0.08e) and third-layer (0.27e) silicon atoms, and the adatom (0.07e). In general, one observes in the HF charge-density calculations, a tendency to form a dipolar layer charge distribution throughout the whole cluster, while in the DFT calculations,

Table 3. The net charge (in units of e) on the adatom, the chemisorbed hydrogen atom (if present), and the first-, second- and third-layer atoms of the substrate for the three structures Si-T_4, B-S_5 and B-T_4. The asterisks indicate the charge on the first-layer silicon atoms which are bonded to a chemisorbed hydrogen atom.

	Hydrogen		Adatom		First layer		Second layer		Third layer	
Geometry	HF	DFT	HF	DFT	HF	DFT	HF	DFT	HF	DFT
Si-T_4	—	—	−0.04	0.07	0.26	0.08	−0.37	−0.25	0.53	0.27
B-S_5	—	—	−0.08	0.03	0.26	0.22	−0.89	−0.50	0.20	0.27
B-T_4	—	—	−0.33	−0.19	0.31	0.13	−0.26	−0.14	0.53	0.26
H/Si-T_4	−0.09	−0.03	−0.03	−0.01	0.27	0.10	−0.24	−0.13	0.47	0.20
H/B-S_5	−0.14	−0.05	0.08	0.09	0.27	0.21	−0.95	−0.56	0.18	0.28
					0.16*	0.26*				
H/B-T_4	0.02	0.05	−0.18	−0.16	0.34	0.15	−0.42	−0.25	0.55	0.28
					0.32*	0.14*				

Table 4. The binding energy (in units of eV) of the adatoms, chemisorbed hydrogen atoms, and SiH and BH species, for the Si-T_4, B-S_5 and B-T_4 structures.

Geometry	Species	DFT (6-31 + G(3df, 2p))	DFT (6-31G*)	HF (6-31 + G(3df, 2p))	HF (6-31G*)
Si-T_4	Si	−6.34	−6.26	−6.12	−5.97
B-S_5	Si	−7.49	−7.47	−7.48	−7.39
B-T_4	B	−5.56	−5.56	−4.36	−4.42
H/Si-T_4	H	−3.22	−3.17	−2.75	−2.70
H/Si-T_4	SiH	−5.18	−5.09	−4.92	−4.81
H/B-S_5	Si	−4.84	−4.78	−3.99	−3.88
H/B-T_4	H	−3.13	−3.16	−3.38	−3.44
H/B-T_4	BH	−5.03	−5.10	−5.04	−5.19

a dipolar charge distribution is only observed in the electronic structure of the substrate (i.e., the first, second and third layers). Thus we find that the dipolar adatom–first-layer bonding ($-0.04e$, $0.26e$) predicted by HF for this Si(T_4) configuration is depolarized in DFT with homopolar ($0.07e/0.08e$) adatom back-bonds being formed instead. Interestingly, this sensitivity of the charge distribution to the level of calculations, and the different electrostatic interlayer interactions that result from it, does not seem to significantly affect the calculated equilibrium geometry of the cluster (see table 2(a)). The DFT-calculated adatom binding energy of 6.34 eV (see table 4) is, however, 3.6% higher than the binding energy obtained using the HF method for the same structure (6.12 eV). This difference can be accounted for by the electron correlation corrections which are included in the DFT method. The fact that this difference is relatively small can also be explained in terms of the so-called dispersive threefold bonding that characterizes a Si(T_4) adatom on the ideal Si(111) surface [27, 28].

3.1.2. B-S_5 geometry. The topology of the optimized B-S_5 structure is shown in figure 3. The boron atom at the subsurface S_5 position (B(S_5)) is bonded to four silicon atoms: three first-layer atoms at a distance of 2.12 Å, and one third-layer atom at a distance of 1.97 Å. While the distance between the Si(T_4) adatom and the B(S_5) atom is only 2.23 Å, there is no bond between these two atoms. The calculated atomic relaxations are presented in table 2(b). In contrast to the case for the Si-S_5 structure of figure 2, the position of the

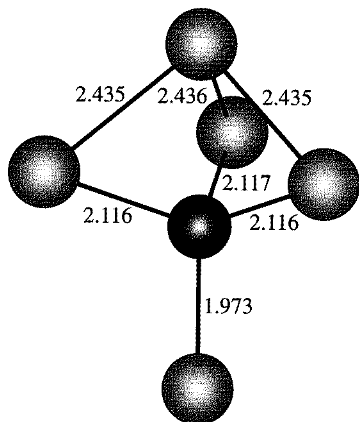

Figure 3. The minimum-energy B-S_5 configuration.

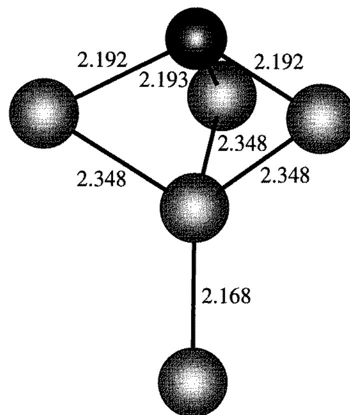

Figure 4. The minimum-energy B-T_4 atomic configuration.

third-layer silicon atom is seen to be almost unaffected by the presence of the chemisorbed boron B(S_5) atom. This is in agreement with other calculations [10] but disagrees with the LEED analysis of Huang *et al* [14] which predicts significant displacement of the third-layer silicon atom. It should be noted, however, that our small-cluster calculations cannot yield definitive results for the displacement of this atom, as its movement is restricted by the fixed hydrogen atoms modelling its interactions with the bulk.

The DFT population analysis (table 3) shows that $-0.50e$ of charge is transferred to the boron atom from the Si adatom ($0.03e$), and from the first-layer ($0.22e$) and third-layer ($0.27e$) silicon atoms. The HF calculations, however, predict charge transfer from the first-layer ($0.26e$) and third-layer ($0.20e$) Si atoms to both the boron atom ($-0.89e$) and the Si adatom ($-0.08e$). The qualitative differences between the DFT and HF charge distributions for this B-S_5 atomic configuration are thus virtually identical to those reported above for the Si-S_5 structure (figure 2). The calculated DFT binding energy of the B(S_5) adatom of 7.49 eV is almost identical to the HF adatom binding energy of 7.48 eV, indicating that electron correlation effects play a negligible role in the B-S_5 bonding configuration (see table 4). It is interesting to note that the silicon adatom binding energy for the B-S_5 geometry is 1.15 eV greater than for the Si(T_4) configuration of figure 2.

Charge transfer from an adsorbate to a substrate is expected to produce a chemical shift in the substrate core-level position measured by x-ray photoelectron spectroscopy (XPS) which is directly proportional to the amount of charge transferred. According to Grehk *et al* [18], the Si(2p) core-level shifts for the B(S_5) structure should be composed of surface components corresponding to the first-layer atoms (including the contribution from the adatoms), the 2/3 ML of second-layer atoms and the 2/3 ML of third-layer atoms not bonding to the boron atoms, and the 1/3 ML of third-layer Si atoms bonding to the boron atoms. The contribution of the fourth layer and all subsequent layers is included in the bulk component. Our calculations, while admittedly being somewhat dependent on the size of the cluster, indicate significant variations in charge between the adatom and first-layer silicon atoms. Unlike Grehk *et al*, we would therefore expect a core-level-shift spectrum of the B(S_5) structure to comprise separately identifiable contributions from the adatoms and the first-layer silicon atoms. Including the fourth-layer atoms in our calculations (by employing larger Si_8H_{15} and $Si_{14}H_{27}$ clusters) did not significantly affect either the predicted

equilibrium geometries or the binding energies of the Si adatom. Moreover, the calculated charge transfer from the adatom and the first-layer silicon atoms to the B atom was not affected by inclusion of the fourth-layer Si atoms. This suggests that the contribution of the fourth-layer atoms to the core binding energy spectrum could be reliably included in the bulk component, as suggested by Grehk *et al* [18].

3.1.3. B-T_4 geometry. The topology of the optimized B-T_4 structure is shown in figure 4 and the calculated atomic relaxations are presented in table 2(c). The boron atom at the threefold T_4 adatom position (B(T_4)) is bonded to three silicon atoms from the first layer at a distance of 2.19 Å. The distance between the Si(S_5) atom and the first-layer Si atoms is 2.35 Å, while the length of the bond between the Si(S_5) atom and the third-layer silicon atom is only 2.17 Å. There is no bond between the B(T_4) adatom and the Si(S_5) atom even though the distance between these two atoms is only 2.09 Å. The DFT B(T_4) adatom binding energy has been calculated to be 5.56 eV. This is the lowest adatom binding energy of the structures discussed so far. It is also 28% larger than the HF B(T_4) adatom binding energy of 4.36 eV calculated for the same structure (see table 4).

Both the DFT and HF Mulliken population analyses (table 3) show that charge is transferred from the third-layer atom (DFT/0.26e, HF/0.53e) and the first-layer Si atoms (DFT/0.13e, HF/0.31e), to the second-layer Si(S_5) atom (DFT/−0.14e, HF/−0.26e) and the boron adatom (DFT/−0.19e, HF/−0.33e). These data also show that the correlation corrections introduced in the DFT calculations reduce the charge fluctuations of the ionic bonds by a factor of about 2. A dipolar structure for the whole cluster is, however, present in both methods. This is in contrast to the topologically identical Si-S_5 and B-S_5 clusters discussed above. Significant correlation effects can arise in the present case due mainly to the uniformly reduced polarization of the ionic bonds, and the short bond lengths between the boron B(T_4) adatom and the first-layer silicon atoms. While the effect of the former is reduced by the dispersive threefold bonding at the T_4 adatom adsorption site, the short B–Si bond lengths strengthen the electron correlation effects [27, 28].

The total energy of this B-T_4 clean surface cluster is 2.42 eV greater than that of the corresponding B-S_5 cluster discussed in section 3.1.2. This is consistent with the pseudopotential LDA calculations [10, 11] which indicated that the B-S_5 geometry is more stable than the B-T_4 configuration by around 1 eV per surface unit cell. Our DFT cluster value for the energy difference between these two structures is, however, considerably higher than the pseudopotential LDA value. We believe that this is only partly due to the cluster-size effect, as the larger Si_8H_{15}:B clusters yield a value of 2.15 eV which is still more than twice the LDA result.

3.2. Chemisorption of a single hydrogen atom

3.2.1. The H/Si-T_4 chemisorption system. Adsorption of a single hydrogen atom near the Si adatom of the Si(T_4) configuration results in the minimum-energy, dangling-bond-free structure shown in figure 5. The hydrogen atom attaches to the dangling bond which is directed normal to the surface and hence sits directly above the Si adatom threefold-coordinated position. The Si–H bond length is 1.50 Å and the Si–Si(T_4) adatom back-bonds are of length 2.54 Å, 0.07 Å shorter than before chemisorption (see figure 2). The lengths of the bonds between the second-layer Si(S_5) atom and the first-layer atoms of 2.33 Å remain close to the bulk nearest-neighbour distance of 2.35 Å. The distances between the second-layer Si(S_5) atom and the Si(T_4) adatom, and the Si(S_5) atom and the third-layer Si atom, are 2.67 Å and 2.17 Å, respectively. The Mulliken population analysis (presented in

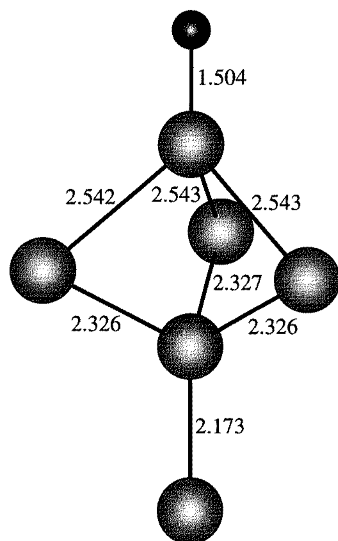

Figure 5. The minimum energy H/Si-T_4 geometry which results from the chemisorption of a single H atom onto the Si-T_4 cluster. The chemisorbed hydrogen atoms in this and subsequent figures are denoted by the smaller dark spheres.

table 3) shows that both the hydrogen atom (DFT/$-0.03e$, HF/$-0.09e$) and the Si adatom (DFT/$-0.01e$, HF/$-0.03e$) have a slight excess electronic charge. A dipolar distribution characterizes the substrate with a positive first layer (DFT/$0.10e$, HF/$0.27e$), negative second layer (DFT/$-0.13e$, HF/$-0.24e$) and positive third layer (DFT/$0.20e$, HF/$0.47e$). The observed uniform reduction of the charge fluctuations in the DFT data is also evident in the binding energy calculations, with the hydrogen atom DFT binding energy of 3.22 eV being 17% larger than the corresponding HF value of 2.75 eV (see table 4). This effect is typical for 'on-top' adsorption sites where the coulombic repulsive interactions within a single bond usually play a significant role. Our DFT value of 3.22 eV is 0.38 eV lower than the hydrogen atom desorption energy of 3.6 eV determined from LDA calculations for a single hydrogen atom chemisorbed onto the adatom site of the Si(111)7×7 surface [29]. The DFT energy required to remove the SiH complex from the cluster is calculated to be 5.18 eV, while the HF binding energy is 5% lower at 4.92 eV. This result is consistent with that presented for the bare Si-T_4 cluster where electron correlation was found to reduce the HF adatom binding energy by 3.6%. This is a consequence of the identical topology of the T_4 site for the Si adatom (figure 2) and the SiH complex (figure 5).

3.2.2. The H/B-S_5 chemisorption system. The addition of a single hydrogen atom near the adatom site of the B-S_5 cluster results in the minimum-energy structure shown in figure 6. In this topology, one of the Si(T_4) back-bonds is broken and the Si(T_4) adatom has moved from its original threefold position to a bridge site between two of its adjacent first-layer silicon atoms. The hydrogen atom saturates the dangling bond on the remaining first-layer silicon atom. The two Si(T_4)–Si back-bonds have a bond length of 2.40 Å, and the SiH bond length is 1.50 Å. The boron atom is located in the S_5 site (B(S_5)) at a distance of 2.12 Å from the first-layer Si atoms which are bonded to the Si(T_4) adatom, and 2.17 Å from the first-layer Si atom saturated by the hydrogen atom. The distance between the

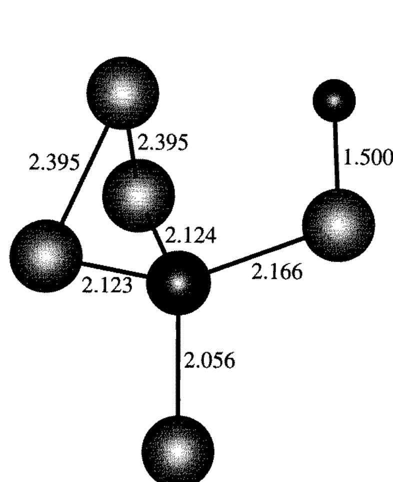

Figure 6. The minimum-energy H/B-S_5 chemisorption structure.

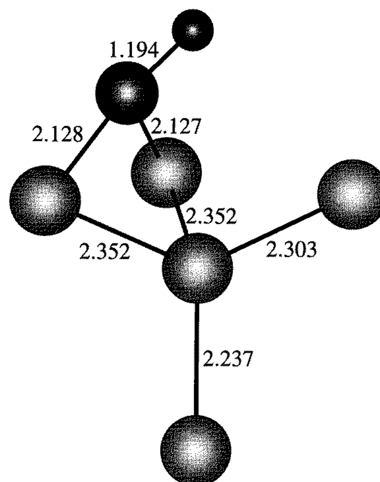

Figure 7. The minimum-energy H/B-T_4 chemisorption geometry.

B(S_5) atom and the third-layer Si atom is 2.06 Å.

The Mulliken population analysis again shows a dipolar charge distribution for the substrate—first layer (DFT/$0.21e, 0.26e$, HF/$0.27e, 0.16e$), second layer (DFT/$-0.56e$, HF/$-0.95e$), and third layer (DFT/$0.28e$, HF/$0.18e$)—and positive homopolar bonding between the Si(T_4) adatom and its neighbouring first-layer silicon atoms. Some electronic charge has also been transferred to the chemisorbed hydrogen (DFT/$-0.05e$, HF/$-0.14e$). The DFT Si(T_4) adatom binding energy for this hydrogen-chemisorbed B-S_5 structure is 4.84 eV, 21% higher than the corresponding HF value of 3.99 eV. The electron correlation corrections to the Si(T_4) adatom binding energy are thus much larger than for the Si(T_4) adatom of the bare B-S_5 cluster (see table 4). This difference may be accounted for by the different topologies of the two clusters and the corresponding variations in the charge-density fluctuations.

3.2.3. The H/B-T_4 chemisorption system. Chemisorption of a single hydrogen atom onto the adatom site of the B-T_4 topology results in the breaking of one of the B(T_4)–Si back-bonds and the formation of a BH complex at the bridge site between two of the neighbouring first-layer silicon atoms (see figure 7). The B–H bond length is 1.19 Å and the B–Si back-bond lengths are 2.13 Å. The minimum total energy of this cluster is 1.34 eV higher than the total energy of the optimized H/B-S_5 structure shown in figure 6. The dipolar nature for the whole cluster (see table 3) is reflected in both the DFT and HF charge-density distributions (positive charge on the hydrogen atom (DFT/$0.05e$, HF/$0.02e$), first-layer atoms (DFT/$0.15e, 0.14e$, HF/$0.34e, 0.32e$) and third-layer atoms (DFT/$0.28e$, HF/$0.55e$), and negative charge on the boron atom (DFT/$-0.16e$, HF/$-0.18e$) and second-layer atoms (DFT/$-0.25e$, HF/$-0.42e$)). The DFT energy needed to remove the BH complex from the cluster is found to be 5.03 eV, almost identical to the HF value of 5.04 eV. The energy required to remove the hydrogen atom from the cluster determined using the DFT method is 3.13 eV. The corresponding HF value is 8.0% higher at 3.38 eV.

4. Conclusions

All of the clean-cluster geometries discussed above represent stable and topologically identical atomic structures. The energetically favourable B-S_5 geometry is characterized by the highest adatom (Si(T_4)) binding energy of 7.49 eV, and represents a minimally correlated electronic system. In contrast to this, the more unstable B-T_4 adatom configuration is characterized by high electron correlation and the lowest adatom (B(T_4)) binding energy of 5.56 eV. Intermediate between these two structures is the Si-T_4 topology which has a Si(T_4) adatom binding energy of 6.34 eV and is moderately affected by electron correlation effects. From these clean-cluster calculations, it would thus appear that there is a strong relationship between the stability of the various geometries, the adatom binding energies, and the degree of electron correlation. Correlation effects may also be important when considering the population dynamics and nonequilibrium excited states of these structures. Another interesting aspect of the above work is the role played by the second-layer atom in the S_5 position in stabilizing these structures. From our calculated charge-density distributions it is clear that the more stable the structure, the greater the amount of charge which is transferred to the S_5 site. This effect is independent of the level of the calculations (see table 3).

The chemisorption of a single hydrogen atom onto these three topologically identical Si-T_4, B-S_5 and B-T_4 clusters produces different chemisorbed final geometries in each case. This fact reflects the different chemical properties of the adatom-modified Si(111) surfaces. In the chemisorbed H/Si-T_4 topology, the only active bond on the Si adatom is saturated by the hydrogen atom without changing the geometry of the cluster. The two remaining structures, B-T_4 and B-S_5, are chemically passivated by the presence of the boron atom. In both of these cases, one of the adatom back-bonds must be broken in order to accommodate a hydrogen atom into the system. For the B-S_5 structure, this mechanism is consistent with the photoemission data which have been reported for the B/Si(111)$\sqrt{3} \times \sqrt{3}$R30° surface [30, 31]. These data show that when boron is incorporated into the Si(111) surface, the empty Si adatom dangling bond lies well above the Fermi level and the only active occupied surface states are those of the Si adatom back-bonds. This is in contrast to the electronic structure of the Si/Si(111)$\sqrt{3} \times \sqrt{3}$R30° adatom topology where the half-filled adatom dangling bond lies at the Fermi level and remains chemically active. The only way of incorporating hydrogen into the dangling-bond-free B-T_4 structure is by breaking one of the adatom back-bonds. Our cluster total energy calculations show that of the two structures, H/B-T_4 and H/B-S_5, the latter is the lower in energy.

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