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A theoretical study of the initial stages of the hydrogenation of Si(111) 7 × 7

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We have used the periodic extended Hückel method to examine the initial stages of the hydrogenation of Si(111) 7 × 7. Energies, atomic charges and reduced overlap populations are considered, and we discuss the inequivalence of the adatoms. The adatom dangling bond (DB) level positions with respect to E_F are also discussed. On the basis of our results, we propose the following adsorption sequence: first, saturation of the five occupied adatom DBs, then hydrogenation of the remaining atoms by pairs, the hydrogenation of an adatom being coupled with that of a restatom or that of the corner atom. We also show that the atomic charges of the surface become more uniform when the 19 DBs are saturated, and that this modification occurs in discontinuous stages.

Keywords: Hückel method; hydrogenation of Si(111) 7 × 7; adsorption sites

1. Introduction

The chemisorption of hydrogen on the Si(111) 7 × 7 reconstructed surface has been extensively studied for several years with many different techniques such as photoelectron spectroscopy [1–4], LEED (low energy electron diffraction) [5], RHEED (reflection high energy electron diffraction) [6], electron-energy loss spectroscopy [7-11], infrared spectroscopy [12] and STM (scanning tunnel microscopy) [13]. It appears that the monohydride phase is formed within the 7 × 7 unit cell and that the reconstruction subsists [12]. Nevertheless, the distribution of H with the Si(111) 7 × 7 surface remains unclear. In the case of a slightly H-reacted surface, two main features are observed in the photoemission spectra. They are centered around 5.6 and 7.6 eV below the Fermi level (E_F) and are commonly attributed to Si–H bonds [3–4] and to an increase of a bulk transition, respectively [2,3]. At the same time, the surface states S_1 and S_2 observed on the clean Si(111) 7 × 7 surface disappear [2–4].

In a previous paper, we presented an electronic structure calculation of the H/Si(111) 7 × 7 system in the DAS (dimer adatom stacking fault) model [14] where the 19 dangling bonds (DBs) of the reconstructed surface are saturated by H atoms [15]. Here, we go a step further by performing a theoretical study of the initial stages of the hydrogenation of Si(111) 7 × 7. Indeed, as we shall see, the 19 DBs create a variety of chemically active surface sites, and in this paper we investigate the role of local structure on reactivity. In section 2, we present our model for the Si(111) 7 × 7 surface. Sections 3 and 4 deal with single and multiple hydrogen atom adsorption, while atomic charges and overlap populations (OP) are studied in sections 5 and 6. This is a study of the 0 K thermodynamically stable adsorption sites. We recognize that kinetics may limit the accessibility of the lowest configuration.

2. Model

In agreement with most of the experimental results for low exposure of the Si(111) 7 × 7 surface to atomic hydrogen (produced, for example, by H_2 dissociation with a hot tungsten filament [3]), we assume that the reconstruction of the clean Si(111) 7 × 7 surface subsists. The DAS model [14] for the Si(111) 7 × 7 unit cell is shown in fig. 1. Twelve threefold coordinated adatoms lie above the first layer. The dimerization leads to only 42 atoms in the first plane: 36 have their dangling bond saturated by the bonds with the 12 adatoms, and the remaining 6, the restatoms, are only threefold coordinated. The 48 second layer atoms dimerize along the boundaries of each triangular subunit. At the corner of each cell, a bonded ring of 12 atoms surrounds a large "hole": here is the corner C atom which also has a dangling bond. The atoms of the third and fourth layers (49 in each layer) are relaxed from their normal positions, but they are not reconstructed. We saturate the Si DBs at the bottom of the slab by one orbital atoms denoted BFA (backface atoms). The stacking sequence in the surface layers is faulted in one half of the unit cell called F. U represents the unfaulted half.

This four layer Si slab, plus the adatom layer, plus the 49 BFA atoms lead to a unit cell of 249 Si atoms for the clean surface. We adopt, for all the atoms, the positions given in the LEED analysis of Tong et al. [16]. The adatoms can be separated into four inequivalent groups: the ones located next to a corner hole of the F or U half of the unit cell are called corner adatoms of type A or A′ respectively, while the center adatoms are noted type B or B′ for the F or U halves respectively. If we consider the vertical displacements d_A, $d_{A'}$, d_B, $d_{B'}$ of type A, A′, B and B′ adatoms relative to their backbond atoms, we remark that $d_A > d_{A'} > d_B > d_{B'}$ [16]. Type A adatoms thus are farthest away from the surface. On the other hand, the 6 restatoms are nearly equivalent [16]. The 19 Si dangling bonds (12 from the adatoms, 6 from the restatoms and 1 from the corner) create various chemically active surface sites.

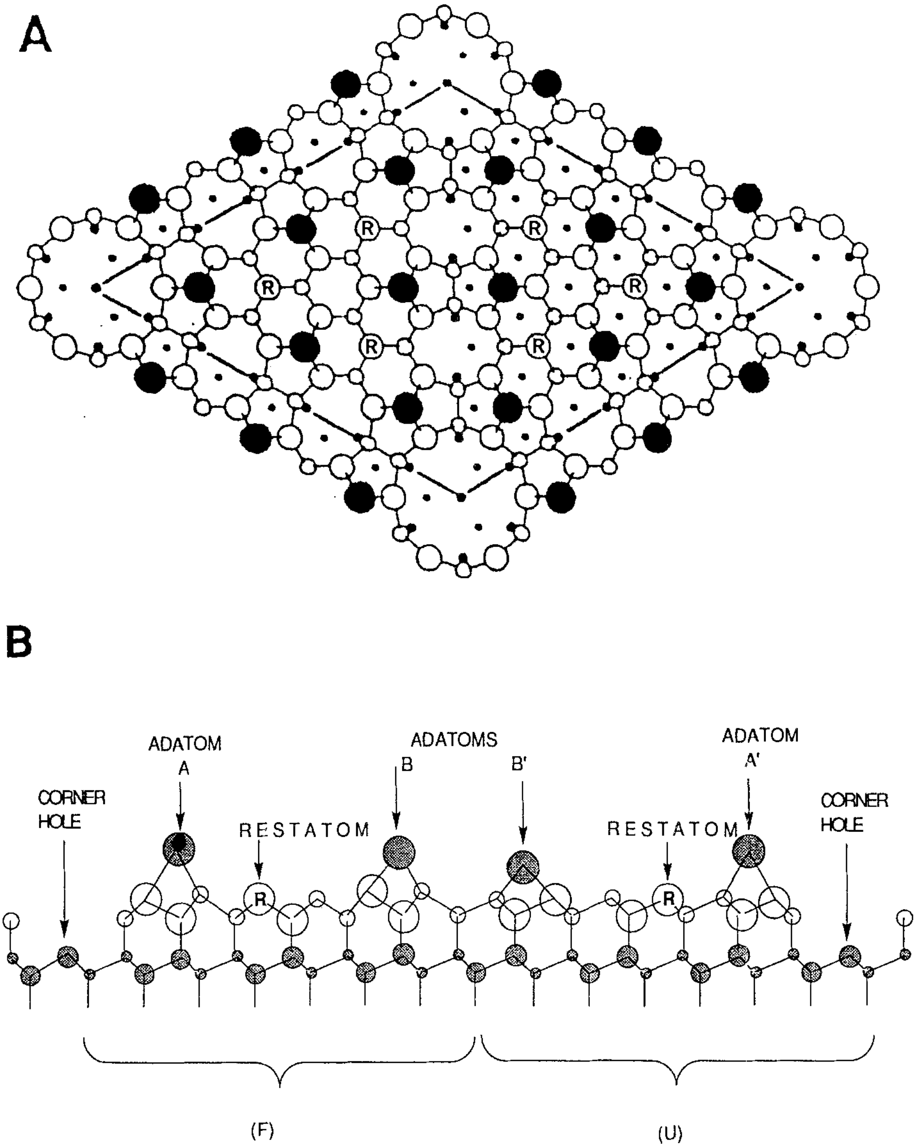

Fig. 1. (A) Top view of the Si(111) 7 × 7 unit cell (outlined) in the DAS model [14]. The large solid circles represent the adatoms, and the six restatoms are denoted by R. The deeper atoms are indicated as solid dots. The unfaulted half is the left one in this figure. (B) Side view. Atoms in the lattice plane normal to the surface along the long diagonal of the unit cell.

The calculations are performed within the crystalline extension of the extended Hückel method [17]. Because of the large size of our unit cell, the dispersion of the surface bands is very weak: we limit our calculation to the Γ point, which is sufficient [18,19]. Because of the large number of orbitals to be considered, we neglect to add the Si d orbitals in the basis. Although this results in a slight overestimation of the energies, this limitation does not modify the relative ordering of energy levels. The Hückel parameters used for the different types of atoms are given in table 1. We assume the Si–H distance to be 1.57 Å; the Si–H bond is presumed to be normal to the surface plane.

3. Adsorption of only one hydrogen atom

The six atomic configurations with only one chemisorbed hydrogen atom are discussed first: one hydrogen successively fixed on type A, B, A′ and B′ adatoms, on a restatom R and on the corner site C. Although hydrogen is monovalent, we also study a few configurations with one hydrogen atom in bridge position: a hydrogen atom in a bridged position between the corner and one of its nearest Si atoms in the fourth layer, between an adatom (here type A′) and one of its Si backbond atoms.

In all cases, the total energy of the system and the adsorption energy per hydrogen atom are computed. The adsorption energy E (eV) is defined as

$$E = \frac{E_t - E_{surf}}{n} - 13.6 .$$

Here, E_t is the total energy of the considered system (surface plus adsorbed hydrogen), E_{surf} the total energy of the clean surface, and n is the number of adsorbed hydrogen atoms. Following the results presented in table 2, the most favorable sites for isolated hydrogen atom adsorption are the Si adatoms: first type A adatoms, followed by type B, A′ and finally B′ adatoms. This order is nearly the same as that found for the adatom contributions to the local densities of states in the case of the clean surface [20]: adatoms give peaks at $E_F - 0.05$ eV (type A), $E_F + 0.22$ eV (type B or A′) and $E_F + 0.32$ eV (type B′); the adatoms of type A contribute to the lowest peak and adatoms of type B′ to the highest peak.

The adsorption of an isolated hydrogen atom on an adatom involves the coupling of the electron from the hydrogen with an electron from a DB. If one considers that the levels related to the 19 DBs states in the naked surface are filled according to their stability, two electrons for the corner and twelve for the six restatoms, then only five electrons remain to fill the twelve adatom levels. The most

Table 1
Extended Hückel parameters: matrix elements H_{ii} (eV) and Slater exponents for Si, H and BFA (backface atoms).

	Orbital	H_{ii} (eV)	Slater exponent
Si	3s	−17.30	1.450
Si	3p	−9.20	1.450
BFA	3s	−11.22	1.450
H	1s	−13.60	1.300

Table 2
Adsorption energies when only one hydrogen is adsorbed (except two hydrogens in configuration (c)). The adsorption energy is defined by eq. (1). (a) and (b) denote configurations in which H is in a bridged position between the corner and one of its nearest neighbors in the fourth layer, and between an adatom (here type A′) and one of its backbond atoms. In configuration (c), two H are adsorbed; one H is fixed on a type A′ adatom, and another H in a bridged position between the same A′ adatom and one of its backbond atoms.

Type of configuration	Adsorption energy (eV)	Type of configuration	Adsorption energy (eV)
H on a type A adatom	−5.93	H on a restatom	−5.66
H on a type B adatom	−5.82	H on a corner	−5.04
H on a type A′ adatom	−5.79	H in bridged position (a)	−4.25
H on a type B′ adatom	−5.68	H in bridged position (b)	−1.35
		2 H atoms (c)	−3.69

favorable interactions correspond to the interaction with one of the five [#1] singly-occupied adatom DBs and are ordered according to their level positions with respect to the Fermi level.

As noted in section 2, type A adatoms are the farthest away from the surface [16]. The DB level is lowered when the adatom is raised [#2] [19]; thus the levels related to type A adatoms should be the lowest ones. The A adatoms correspond to the strongest interaction with the atomic hydrogen. One DB level of type A is singly-occupied. Thus the interaction can be considered as resulting from a two-orbital coupling with an optimal stabilization of two electrons.

The excitation from the A level to the Fermi level (provided that the Fermi level remains controlled by the adatom states) is not difficult, so that the hydrogenation of another adatom should not be very different from that of an adatom of type A. The highest adatom levels (B′) correspond to smallest interaction between the adatoms and the atomic hydrogen since the interaction with the hydrogen level decreases when the DB level is raised in energy. An alternative point of view would be that an electron has to be promoted from E_F to the B′ level ($E_F + 0.32$ eV) to populate the B′ DB orbital so that it can couple with the H atom by a two-electron interaction.

Let us now examine the case of an occupied DB below E_F: it concerns the restatoms (from $E_F - 0.58$ eV to $E_F - 0.91$ eV) and corner ($E_F - 1.14$ eV) DBs. The adsorption energies on these sites are −5.66 eV and −5.04 eV respectively. The interacting orbitals involve three electrons (two from the DB and one from the

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[#1] As the excitation from an adatom occupied level to an empty level is easy, we can consider that the state where the five lowest levels are singly occupied is close in energy to that with two doubly occupied and one singly occupied levels.

[#2] An extended Hückel calculation on a system consisting of a Si atom and its three nearest neighbors (backbond atoms) shows that when the Si atom is raised above the plane of its nearest neighbors, the dangling bond (DB) level is lowered, and that the percentage of s character of the DB, which is zero when the system is planar, increases. The bonding between the DBs and the backbond atoms also increases.

H atom); when a hydrogen atom approaches the surface, two electrons are stabilized, i.e. those occupying the $\sigma_{\mathrm{Si-H}}$ bonding orbital, while the third one is transferred to the Fermi level. This corresponds to an especially large *destabilization* at the corner position as the DB level is initially deeper. To a minor extent this is also the case for the restatoms.

The configurations with hydrogen in a bridged position lie much higher in energy than the singly-coordinated cases.

The results presented in table 1 agree with the UPS experimental data of Avouris et al. [21] for a Si(111) 7 × 7 surface exposed to atomic hydrogen according to which, at low temperature, hydrogen favors the adatom surface states.

4. Multiple adsorption

The excitation from a doubly-occupied A level to another adatom level is not difficult so that we can consider that five adatoms have singly-occupied DBs. Thus, hydrogenations similar to the first one can be performed five times (type A first, type B or A′ next). After the first five H atom additions, seven vacant adatom levels remain above the Fermi level and seven occupied levels below E_F (restatoms plus corner). Each individual H adsorption event should then correspond to a two-orbital interaction (H orbital plus DB) with either a one-electron count (for the vacant DBs) or a three-electron count (for the occupied DBs). Furthermore, the hydrogenations prefer to occur in pairs, hydrogenating at the same time one unoccupied and one occupied DB, the third electron of the three-electron system being transferred to the $\sigma_{\mathrm{Si-H}}$ orbital of the one-electron system. Thus the hydrogenations do not necessarily succeed one another by individual steps, but rather occur through a global process. The interdependence of the hydrogenation will also appear in the results for multiple adsorption.

Ten configurations with several H atoms adsorbed on the Si(111) 7 × 7 surface were investigated. In all cases, the total energy of the system and the adsorption energy per hydrogen atom have been calculated as discussed above: the results are reported in table 3. The average adsorption energy for the incremental addition of n hydrogen atoms to a surface that previously had j hydrogen atoms (per unit cell) is defined by the relation

$$E_{\mathrm{ads}}(\mathrm{eV}) = \frac{E(j+n) - E(j)}{n} - 13.6 .$$

Let us first consider the case of 5, 6 and 7 hydrogenated DBs. We find an average adsorption energy of −5.88 eV when 5 occupied adatom levels (3 type A and 2 type A′) are saturated. The adsorption energy for adding the sixth adatom (type B) is only −5.05 eV. We obtain adsorption energies of −5.04, −5.33 and −6.45 eV for the addition of the seventh hydrogen, depending on the site of addition: adatom of type B, corner atom or restatom respectively.

These results agree with the conclusion above: once the 5 occupied adatom

Table 3
Total energies and average adsorption energies when several DBs are saturated by hydrogen atoms. The adsorption energy is defined by eq. (1).

Type of configuration	Total energy (eV)	Adsorption energy (eV)
clean surface	−12215.52	
5 H on 3 type A and 2 type A′ adatoms	−12312.93	−5.88
6 H on 3 type A, 2 type A′, 1 type B adatoms	−12331.58	−5.74
7 H on 3 type A, 2 type A′ and 2 type B adatoms	−12350.22	−5.64
7 H on 3 type A, 2 type A′, 1 type B and 1 restatom	−12351.63	−5.84
7 H on 3 type A, 2 type A′, 1 type B adatoms and on the corner atom	−12351.01	−5.76
6 H on the restatoms	−12330.23	−5.52
12 H on the adatoms	−12442.99	−5.36
13 H on the 12 adatoms and the corner atom	−12462.45	−5.39
12 H on the adatoms and 6 H on the restatom	−12563.01	−5.71
19 H (all the DBs being saturated)	−12582.81	−5.73

levels are hydrogenated, the pairwise hydrogenation of one unoccupied adatom and one occupied restatom or corner DB in one unit cell is more favorable than the hydrogenation of them individually or than the hydrogenation of two similar DBs. The most stable hydrogenated systems are thus those with an odd number of hydrogen atoms ($5 + 2k$, with k ranging from 1 to 7).

The saturation of an even number of atoms DBs (for instance 6 restatoms, 12 adatoms, or 12 adatoms plus 6 restatoms leading respectively to adsorption energies of −5.52, −5.36 and −5.71 eV (as compared with −5.73 eV for 19 H)) seems to be unfavorable. We also note the progressive manifestation of saturation effects for the sequence of odd numbers of atoms: the adsorption energies decrease from −5.93 eV (saturation of one type A adatom), to −5.88 eV (for 5 adatom DBs saturated), to −5.84 eV (for 7 DBs saturated) and finally to −5.73 eV (all DBs saturated).

Let us now consider the case of H fixed on 6 restatoms. If these 6 restatoms are the only Si atoms saturated by hydrogen, the adsorption energy will be −5.52 eV per H. If one saturates 6 restatoms following the hydrogenation of the 12 adatoms, we obtain, using the results given in table 3, an adsorption energy of −6.40 eV per H on restatoms. Likewise, in the case of H fixed on 12 adatoms, we will find adsorption energies of −5.36 eV if these adatoms are the only Si atoms saturated by H, and −5.80 eV if the six restatoms are saturated before the 12 adatoms. In the case of H fixed on the corner, the adsorption energy will be −5.04 eV if the corner is the only Si atom saturated by hydrogen, −5.86 eV if the 12 adatoms are hydrogenated before the corner, and −6.20 eV if the 18 other DBs are occupied first. These important differences in the adsorption energies show that an already partly hydrogenated surface could become more reactive. However none of these correspond to a favorable electron count that fills the bonding orbitals by 2 electrons and avoids any expensive electron transfer from a DB at a low energy level to the Fermi level:

for instance the case of the hydrogenation of 6 restatoms DBs would be accompanied by the destabilization of 6 electrons transferred to the Fermi level.

Hydrogenation at the corner as a last step is particularly noteworthy since, from saturation effects, it would be expected to be the least energetic. The calculation instead shows it to be quite favorable (−6.20 eV). As mentioned above, this hydrogenation changes the system from an unfavorable even count (18) to a favorable odd count (19). The hydrogenation of the 19th DB (odd number) achieves the saturation of all the DBs, and leads to a gap between an occupied σ-bonding band and an unoccupied σ^*-antibonding band.

On the basis of our result, we propose the following mechanism for sequential hydrogenation of the Si(111) 7 × 7 surface: first, the saturation of five adatom DBs; then, that of the remaining DBs occurring by pairs, associating one adatom with one restatom (or corner atom) in every step.

5. Atomic charges

The atomic charges on type A, A′, B, B′ adatoms, restatoms, corner and adsorbed hydrogen have been computed for various atomic configurations and are presented in table 4. Let us first consider, for instance, the atomic charge on a type A adatom. This atomic charge, which is −0.42 *e* in the case of the clean surface, becomes +0.42 *e* when this adatom is hydrogenated, and keeps the same value if other DBs are saturated afterwards (0.42 *e* when 12 adatoms or 19 DBs are saturated). On the other hand, the atomic charge on the type A adatom does not significantly vary when restatoms, corner or other adatoms are saturated first (table 4). The same remarks count for type B, B′ or A′ adatoms, restatoms or corner: on a given unsaturated site, the atomic charge varies significantly under atomic H

Table 4
Atomic charges in units of e ($e = 1.602 \times 10^{-19}$ C) on type A, A′, B and B′ adatoms, restatoms, corner and hydrogen atoms, with H in different configurations. Configurations with one hydrogen fixed successively on a type A adatom, a type A′ adatom, a type B adatom, a type B′ adatom, a restatom, the corner, each of the six restatoms, each of the twelve adatoms and each of the nineteen DBs are investigated. Atomic charges concerning the clean surface are given in the last column.

Atomic charge on atom	One H fixed on:									Clean surface
	A	A′	B	B′	R	corner	6 rest-atoms	12 adatoms	19 DBs	
A	0.42	−0.23	−0.30	−0.30	−0.56	−0.56	−0.63	0.42	0.42	−0.42
A′	0.02	0.43	0.04	0.04	0.01	0.0	−0.37	0.43	0.43	0.02
B	0.22	0.22	0.47	0.04	0.22	0.22	0.17	0.47	0.47	+0.22
B′	0.22	0.23	0.23	0.45	0.23	0.22	−0.07	0.45	0.45	0.22
R	−0.98	−0.98	−0.98	−0.98	0.27	−0.98	0.27	−0.01	0.26	−0.98
C	−0.85	−0.85	−0.85	−0.85	−0.85	0.27	−0.86	−0.86	0.27	−0.85
H	−0.27	−0.28	−0.29	−0.29	−0.29	−0.27	−0.29	−0.29 to −0.27	−0.29 to −0.27	–

adsorption, and does not change further, when the other DBs are hydrogenated. There is a levelling of the Si atomic charges when the 19 DBs are saturated but this modification occurs by discontinuous stages. This levelling of the charges can be understood if we consider that all the adatom levels are filled when the 19 DBs are saturated. The charges result from the polarization of $\sigma_{\mathrm{Si-H}}$ bonds.

Note that the absolute values have to be considered cautiously: the extended Hückel method, in absence of iteration processes, overestimates the polarization of the system, although the qualitative trends are meaningful.

6. Overlap populations

The overlap populations (OP) computed both for the clear surface and when the 19 DBs are saturated, are reported in table 5. Considering the results for the bonds between the adatoms and their backbond atoms, we notice that the OPs which were rather asymmetric in the case of the clean surface (OP from 0.62 to 0.75) become equivalent when the 19 DBs are hydrogenated (OPs from 0.70 to 0.72). In the same way, the OPs between the adatoms and the H atom fixed on them differ very little from one another (OPs from 0.62 to 0.63). In the case of the clear surface, the OPs between the adatoms and the second layer atoms located just

Table 5
Overlap populations (OPs) when the 19 DBs are saturated. The OPs for the clean surface are given in parentheses. A, B, B′, A′ denote type A, B, B′ and A′ adatoms, R: restatoms, $\mathrm{B_A, B_B, B_{B'}, B_{A'}}$: backbond atoms of type A, B, B′ and A′ adatoms, $\mathrm{J_R}$: backbond atoms of the restatoms, T: nearest neighbor of the corner in the fourth layer, H: hydrogen atoms, $\mathrm{G_A, G_B, G_{B'}, G_{A'}}$: atoms of the second layer located directly under type A, B, B′ and A′ adatoms.

Bonds	OP	Bonds	OP
$\mathrm{A'{-}B_{A'}}$	0.722 (0.724)	$\mathrm{B{-}B_B}$	0.716 (0.720)
$\mathrm{A'{-}B_{A'}}$	0.722 (0.721)	$\mathrm{B{-}B_B}$	0.724 (0.744)
$\mathrm{A'{-}B_{A'}}$	0.708 (0.708)	$\mathrm{B{-}B_B}$	– –
$\mathrm{A'{-}G_{A'}}$	0.015 (0.180)	$\mathrm{B{-}G_B}$	0.000 (0.183)
A′–H (on A′)	0.627 –	B–H (on B)	0.624 –
$\mathrm{B'{-}B_{B'}}$	0.721 (0.730)	$\mathrm{R{-}J_R}$	0.798 (0.797)
$\mathrm{B'{-}B_{B'}}$	0.729 (0.751)	$\mathrm{R{-}J_R}$	0.793 (0.795)
$\mathrm{B'{-}B_{B'}}$	– –	$\mathrm{R{-}J_R}$	0.793 (0.795)
$\mathrm{B'{-}G_{B'}}$	0.017 (0.200)	R–H (on R)	0.670 –
B′–H (on B′)	0.620		
$\mathrm{A{-}B_A}$	0.701 (0.678)	C–T	0.804 (0.847)
$\mathrm{A{-}B_A}$	0.717 (0.694)	C–T	0.804 (0.847)
$\mathrm{A{-}B_A}$	0.717 (0.692)	C–T	0.804 (0.847)
$\mathrm{A{-}G_A}$	−0.001 (0.122)	C–H (on C)	0.015 –
A–H (on A)	0.630 –		

below (G_A, $G_{A'}$, G_B, $G_{B'}$) suggest the formation of a weak bond between an adatom and the subsurface Si atom directly below. This result is in agreement with the conclusions of Avouris et al. [22] and with an experimental study of the vibrational spectra of the Si(111) 7 × 7 surface [23]. The strength of these weak bonds in the naked surface increase (see table 5) in the same order as the adsorption energies found for the H atoms in table 2: first the type A adatom–G_A bond with an OP of 0.12, followed by type B adatom–G_B or type A′ adatom–$G_{A'}$ bonds (0.18) and type B′ adatom–$G_{B'}$ bond (0.20). The adatom p_z orbital interacts with the Si beneath it so that the corresponding level may be destabilized. This effect is seen in the change of the OPs. In presence of hydrogen, these weak bonds vanish and the OPs collapse; they range from 0.000 to 0.017.

Turning to the OPs between the restatoms and their backbond atoms, we note very few changes when the 19 DB are saturated. The OPs between the restatoms and the hydrogen atoms fixed on them, as well as the OPs between the restatoms and their backbond atoms are nearly equivalent. The most important OPs are found for the bond between the corner and its nearest neighbors in the fourth layer (0.847) on the clean surface. They slightly decrease when the 19 DBs are saturated.

7. Conclusion

We have studied the initial hydrogenation stages of the Si(111) 7 × 7 surface with the crystalline extension of the extended Hückel method. The most favorable adsorption sites seem to be the adatom sites (first type A adatom, followed by type B, A′ and B′ adatoms), in agreement with the observations of Avouris et al. [21]. Several interpretations of this inequivalence of the adatoms have been proposed:

(i) The 19 DBs levels are occupied in an order determined by their relative electronic stability (two electrons for the corner, twelve for the six restatoms and only five for the twelve adatoms); a distinction between the adatoms is thus introduced. The occupied adatom levels correspond essentially to adatoms of type A.

(ii) Since the type A adatoms are farthest away from the surface, the levels related to these adatoms should be lowest amongst the adatom levels, and consequently the first ones to be occupied.

(iii) The OPs between the adatom and the Si atom underneath it increases from 0.12 (type A adatoms–Si beneath) to 0.20 (type B′ adatoms–Si beneath) indicating a weaker bond in the case of type A adatoms. These OPs vanish when the 19 DBs are saturated.

In the case of multiple hydrogen atom adsorption, we propose the following adsorption mechanism: first, saturation of the 5 occupied adatom DBs; then associated hydrogenation of the remaining adatoms with the restatoms or the corner.

We have also shown that there is a levelling of the atomic charges when the 19 DBs are saturated, but that this modification occurs in discontinuous stages. On a given unsaturated site, the atomic charge varies significantly following atomic H adsorption; when the other DBs are hydrogenated, it retains its value.

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