First-Principles Studies of Hydrogenated Si(111)–7×7

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The relaxed geometries and electronic properties of the hydrogenated phases of the Si(111)-7×7 surface are studied using first-principles molecular dynamics. A monohydride phase, with one H per dangling bond adsorbed on the bare surface is found to be energetically favorable. Another phase where 43 hydrogens saturate the dangling bonds created by the removal of the adatoms from the clean surface is found to be nearly equivalent energetically. Experimental STM and differential reflectance characteristics of the hydrogenated surfaces agree well with the calculated features.

The identification of the fascinating 7×7 reconstruction on the (111) surface of silicon has motivated continued interest in its structural and electronic properties over the years. The Si(111)-7×7 surface is perhaps the system that best exemplifies the important interplay between structure and electronic properties in surface physics. The work of Binnig et al. using scanning tunneling microscopy (STM) led Takayanagi et al. to propose their dimer-adatom-stacking fault (DAS) model whose structure is consistent with many experiments. The geometric and electronic properties of the 7×7 surface are well known through a combination of experiments and realistic calculations — especially the first-principles investigations of Stich et al. and Brommer et al. using large supercells in state-of-the-art approaches.

The structure of the hydrogenated phases of this important surface are not as well understood. Studies of this surface reaction and associated reconstruction are of technological relevance in the chemisorption processes of H, NH2, and hydrocarbons. In addition, the hydrogenated surface can be used as reference in clarifying the optical response of the bare 7×7 substrate, and is then important to have a better understanding of its structural and dynamical properties. From a computational standpoint, Si(111)-7×7:H surfaces are challenging due to the large size unit cells.

Experimental evidence suggests that adsorption of hydrogen on Si(111)-7×7 occurs in a two-step process. The first step likely occurs when only the 19 dangling bonds (DBs) per unit cell are saturated, corresponding to those of the 12 adatoms (ADs), 6 rest atoms (RAs) and corner hole atom (CH) of the DAS model, to form Si(111)-7×7:19H. The second step occurs when the adatom layer is missing and hydrogen saturates the corresponding 43 DBs to form Si(111)-7×7:43H. These findings have resulted in several unresolved issues, such as whether the DAS structure remains unchanged when the surface is terminated by H atoms, which of the two hydrogenated phases is more stable, and what are the main electronic properties of the Si(111)-7×7 surface after passivation with hydrogen. To date, the efforts to address these issues theoretically have been limited to different reconstructions of this surface, and-first-principles studies of the surface upon H and NH2 adsorption (using a cluster model for the substrate). An alternative and more reliable approach is to perform molecular dynamics supercell calculations that realistically model the surface using the full unit cell of the hydrogenated phase, combined with the accuracy of an ab initio treatment of the interatomic interactions.

Here, we present the first ab initio studies to characterize the Si(111)-7×7:19H and :43H systems using large supercell geometries approaching 400 atoms. Application of this method to elucidate the structural and electronic properties of the clean 7×7 surfaces yields results in good agreement with previous work. We find that H adsorption on the clean surfaces leads preferentially to a monohydride structure (Si(111)-7×7:19H), and is accompanied by considerable surface relaxation, in agreement with experiments. The other hydrogenated phase identified, the Si(111)-7×7:43H surface, is found to approach energetically the :19H phase, explaining the possible coexistence reported in experiments. Moreover, we find that the electronic density of states of these H-passivated surfaces exhibit no surface states in the gap, while still showing strong contributions from back-bonding states at low H-coverage, in agreement with STM and differential reflectance measurements.

Our computational scheme is molecular dynamics simulations based on density functional theory in the local density approximation, using the Harris functional, Hamann-Schlüter-Chiang pseudopotentials, and a minimal s-p basis representation. [A comprehensive discussion of this scheme, approximations used, and a description of various tests can be found in Ref. 14.] In silicon, the π-bonded (2×1) reconstruction of the (111) surface, the 2×1, p(2×2) and c(4×2) phases of the (100) surfaces, as well as the 5×5 DAS structure of Si(111) have all been studied by this technique.
As a test, we started applying this approach to investigate the structural properties of clean Si(111)-7×7. The substrate is represented by a supercell with ten Si-layers plus the adatoms on the slab surface (the initial coordinates of adatoms and the three uppermost Si layers were those of Ref. 6). The model system contains all the features of the DAS configuration (see Fig. 1a). Periodic boundary conditions are imposed parallel to the surface, and the bottom Si layer is terminated by H atoms to passivate dangling bonds. The equilibrium structure of the 543 atom slab is then obtained with a dynamical quenching minimization technique. All the atoms, except for the bottom Si layer, were allowed to relax until the forces on them converged to ∼0.1 eV/Å. Only the Γ point of the small Brillouin zone of the supercell is used to sample the electronic states. The calculated bondlengths of ADs with the first layer atoms are found to be stretched from 3 to 6% with respect to a typical Si-Si bond length (2.35 Å). The average distance between the AD and the second layer atoms directly beneath them is about 2.44 Å, except for two adatoms on the faulted region of the unit cell (shown as 1 and 2 in Fig. 1a), which have a distance 8% larger than the typical value. The bondlengths between RAs and second layer atoms are stretched by 4%, as they are 0.5 Å away from the first layer. The relative heights of AD 3 to 6 are 0.069, 0.055, 0.0 and 0.025 Å, respectively. These values are in qualitative agreement with those from LEED, 0.12, 0.08, 0.0 and 0.04 Å [18]. The second and third layer atoms directly below ADs move ∼0.5 Å towards the bulk, and their bondlengths are ∼2% shorter than the bulk Si-Si bondlength. Comparison of our relaxed atomic positions with those from Car-Parrinello work [17] show nearly identical geometry [17]. We adopted these equilibrated positions for the geometry of the clean surface, as it is in general agreement with values reported in previous work [16,18], and then proceed to saturate dangling bonds.

The Si(111)-7×7:19H is modeled by terminating all the silicon DBs of the bare surface with H atoms (see Fig. 1b), and all atoms — except for the bottom Si layer — of the 366-atom supercell are allowed to relax (for computational speed, we take only six Si layers here, plus adatoms and chemisorbed hydrogens) [19]. The positions of the surface Si atoms change when the 19 DBs are terminated by H atoms, and the heights of ADs become nearly similar. Relative to the clean surface, adatoms and first layer atoms move away from the bulk layer, while RAs, CH and ADs 1 and 2 move towards the slab, leaving a nearly flat top layer [17]. The ADs BB lengths with first layer atoms are slightly shorter (∼1%) than in the clean substrate, while those of the RA with second layer atoms are comparable to the bare surface. The calculated Si-H bond distances are 1.54 Å, nearly 8% larger than the sum of the covalent radii of Si and H (1.43 Å), and comparable to the value obtained from other calculations (1.502–1.520) [2]. The dimer atoms and second and third layer atoms directly below ADs remain in their clean-surface positions. Our calculation predicts an energy of −0.27 eV/atom cell area for the hydrogen-covered surface, relative to clean substrate plus gas-phase H₂ molecules. This indicates that the formation of the monohydride phase on Si(111)-7×7 is stable, in agreement with experiments [1,2,3].

The Si(111)-7×7:43H surface has been suggested to coexist with :19H, based on STM observations [10]. The first two layers of the surface atoms in :43H (including surface H), both on the faulted and unfaaulted half of the unit cell, are found to resemble the hydrogenated bulk terminated Si(111)-1×1 surface. As in the :19H monohydride phase, dimers on the second layer and a corner hole atom are also present (see Fig. 1b). Although AD removal is found to have a considerable activation barrier, it is easily compensated by the formation of Si-H bonds [10]. This surface is modeled by removing the ADs from the clean slab model and passivating the resulting 43 DBs with H, allowing this 378-atom supercell to relax. The equilibrated structure shows Si-H bonds directed normal to the surface and bondlengths comparable to the :19H phase. The uppermost Si atoms are three-fold coordinated to the atoms directly below, with bondlengths stretched by 1 to 2% relative to the normal Si-Si bond, comparing well with LDA results of the hydrogenated 1×1 surface [14]. The RAs and CH move towards the bulk by about 0.5 Å, respect to the clean surface, while the second and third layer atoms, originally directly below ADs, move away from the slab and reach their typical bulk positions. The Si(111)-7×7:43H phase is found to be merely 0.12 eV/(Si-H bond) less stable than the :19H monohydride phase, indicating that these two structures are almost energetically equivalent. This result suggests the energetic may indeed allow these two phases to coexist, as reported in Ref. 10.

The calculated electronic density of states (EDOS) also contains important information on these systems. The clean Si(111)-7×7 surface contains midgap states which we can clearly identify with surface dangling bonds (see Fig. 3). These EDOS features, lying above 0.19 eV and from 0 to −0.29 eV, arise from the empty and filled AD DBs, respectively. [Energies are referred to the Fermi level, which is 0.64 eV above the valence band edge Eᵥ, in close agreement with the experimental value of 0.6 eV in Ref. 3.] The dangling bond states are localized at various sites with a predominant pₓ character. Between −0.88 and −0.98 eV, we find states resonant with the valence band which involve rest atom DBs, while AD backbonds lie between −1.38 and −1.44 eV. Corner hole states appear at −1.08 and −1.24 eV. Our results are in good agreement with several experiments that have reported occupied AD and RA dangling bonds at −0.25, and −0.85; AD backbonds and corner hole states at −1.8 eV; and AD back-antibonds at 0.55 eV [21].

Figures 3a–c exhibit simulated STM images according to the scheme of Tersoff and Hamann [22], with
the electronic states obtained in our calculation. The panels display constant charge density plots ($\rho \sim 0.01$ eV$/\text{Å}^3$) showing surface states at various energies below the Fermi level. Over a wide range of low bias values, for energies close to the Fermi level, we see a clear asymmetry between the faulted and unfaulted portions of the unit cell (not shown here), in agreement with low-bias STM measurements [21]. Figure 3a exhibits states between $−0.88$ and $−1.08$ eV, corresponding to DBs of RA and CH, while Fig. 3b exhibits BB states lying between $−1.38$ and $−1.40$ eV, arising from $p_x$ and $p_y$ orbitals of the AD bonded to $p_z$ orbitals of the first layer atoms. The general features of our calculated STM images for various RA/CH and AD are in excellent agreement with those obtained by Hammers et al. [2].

In marked contrast to the clean surface, the EDOS of Si(111)-7×7:19H has no midgap states, as shown in Fig. 2. This is intuitively expected, as the DBs responsible for these states in the bare surface are passivated by H atoms. This finding corroborates EDOS measurements in Ref. 10 and 20 where features due to DBs on the bare surface disappear as the substrate is dosed with hydrogen. [Also, theoretical STM images of states near $E_F$ yield featureless isodensity plots.] Moreover, we find that states lying between $−0.74$ eV and $E_F$ are extended and show no contribution from the surface H and AD states. Notice, however, that backbond states associated with the surface adatoms are still present, and lie between 1.07 and 1.21 eV below the Fermi level, and yield the STM image shown in Fig. 3c. This finding supports interpretation of recent differential reflectance experiments [1], as discussed below [3].

The EDOS of the Si(111)-7×7:43H also contains no midgap states (see Fig. 2). A clear reduction of the density of states in the region below $E_v$ and in the conduction band is produced by the disappearance of ADs states. [Notice in particular the absence of a sharp feature at $\sim 1.6$ eV.] Our results agree quite well with the local tunneling spectroscopy experiment of Mortensen et al. [11], who find no high density of states near the Fermi level for the :43H-coverage. Only extended states due to surface and bulk Si were found between $−0.8$ eV and the valence band edge $E_v$, as all the dangling bonds are fully saturated.

Our findings also provide strong support for the interpretation of differential reflectance (DR) measurements by Roy and Borensztein [4], who employ this powerful technique to explore the evolution of the surface electronic states under various chemisorption processes. In particular, at zero and low H-coverage, a strong DR feature at 1.6 eV is identified as coming from transitions involving the backbond states of adatoms, as supported by tight-binding calculations of model structures [5]. As the H-coverage increases, however, this feature saturates and higher energy transitions dominate the DR spectra. This behavior is consistent with the disappearance of the backbond states as the higher coverage is reached and the :43H phase forms. Notice that the saturation of the 1.6 eV feature is accompanied in experiments by a strong reconstruction of the surface, as probed by LEED, and as expected from the relaxation pattern shown in Fig. 1 [11]. Finally, we should also notice that an empirical-parameter calculation of the optical response of this surface using our fully relaxed atomic positions yields excellent agreement with the DR experiments, as will be discussed elsewhere [23].

In summary, we obtained significant geometrical relaxation arising from H-adsorption on the clean 7×7 surface, accompanied by strong shifts of the character and energies of the electronic states. These changes are found to be in excellent agreement with STM, differential reflectance, and LEED experiments, and provide the basis for detailed comparisons with new experimental measurements.

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1 and 2 on the faulted region of the supercell. These adatoms are displaced towards the vacuum by \( \sim 0.18 \) Å, relative to other adatoms. Calculations for slabs with different thickness and for the 5×5 reconstruction geometry show that as the slab becomes larger, the displacements of these two adatoms decreases. We have also explored the type of slab used in Ref.[5] and [6] consisting of two reconstructed surfaces. In this case only one of the adatoms in question is \( \sim 0.2 \) Å higher than other adatoms. Moreover, we find an energetically equivalent configuration where the relative heights of adatoms on the faulted region of the unit cell are nearly equal and the features in the EDOS near the Fermi level shift only slightly. This difference in the clean surfaces is however of no significance for the hydrogenated surfaces we study, as the relaxation occurring after chemisorption reduces the differences between adatoms (in the :19H surface), as discussed in the text.

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FIG. 1. Top view of (a) the DAS model for the Si(111)-7×7 bare surface (big gray, black and small gray circles represent adatoms (AD), rest atoms (RA) and corner hole atom (CH), and first layer atoms, respectively); (b) the :19H coverage (small white circles denotes H atoms); and (c) the :43H coverage surface. The faulted portion of the outlined unit cell is on the left. Unit cell shown by dashed lines.

FIG. 2. Electronic density of states for the clean Si(111)-7×7 surface, as well as for the two hydrogenated surfaces studied with 19 and 43 H-atoms per cell. All energies referred to the Fermi level; level broadening used 0.1 eV; curves displaced vertically for clarity.

FIG. 3. Simulated STM images in the Si(111)-7×7 system. (a) RA/CH levels (at \( \sim -1 \) eV in Fig. 2), and (b) AD back-bond states (\( \sim -1.4 \) eV) for the clean surface, (c) AD back-bond states in the monohydride :19H phase (\( \sim -1.2 \) eV in Fig. 2). The faulted portion of the outlined unit cell is on the right.
Electronic Density of States

(a)

(b)

(c)