Binding Sites, Migration Paths, and Barriers for Hydrogen on Si(111)-(7 × 7)

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We present density functional calculations of the potential energy surface for the binding and diffusion of a hydrogen atom on a Si(111) adatom structure with two adatom and one rest-atom dangling bonds per unit cell, which we use to model the Si(111)-(7 × 7) surface. We find that hydrogen binding is stronger at rest-atom than at adatom sites by ~0.2 eV, in good agreement with desorption experiments. This result together with a detailed analysis of H diffusion paths and barriers indicates that $R \rightarrow A \rightarrow R$ jumps provide the mechanism of H diffusivity at low coverages. The computed barrier for these jumps agrees well with experiment.

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The interaction of hydrogen with the Si(111)-(7 × 7) surface gives rise to a variety of processes depending on temperature and exposure conditions [1]. In the low H-coverage regime, which is of interest in this paper, it is well established that hydrogen reacts with the available dangling bonds (DB's), without disrupting the 7 × 7 periodicity of the clean surface. According to the Takayanagi model [2] of this surface, there are 19 DB's per 7 × 7 cell: 12 belong to the adatoms, 6 to the restatoms (i.e., the surface atoms not saturated by the adatoms), and 1 to the Si atom at the bottom of each corner hole. These DB sites are believed to exhibit different affinities towards hydrogen [1,3]. In particular, H_2 recombinative desorption experiments [4,5] have been interpreted in terms of the presence of two (or more) adsorption sites, one of which is energetically preferred. This is consistent with the results of a recent scanning tunneling microscopy (STM) study of the reactivity of the Ge(111)-*c*(2 × 8) surface to hydrogen, which has shown that H binds more strongly to rest-atom (*R*) than to adatom (*A*) sites [6]. However, first principles calculations of the difference between H-adatom and H-rest-atom binding energies for Ge(111) [6] have obtained a value, 0.7 eV, much larger than that, ~0.1–0.2 eV, estimated for Si(111)-(7 × 7) on the basis of the H_2 desorption data [45]. Thus a detailed understanding of the energetics and the bonding structures of hydrogen on Si(111)-(7 × 7) is still missing.

Another question raised by the desorption experiments concerns the role of the surface diffusion of the chemisorbed H atoms. For Si(111)-(7 × 7) the H surface diffusivity has been determined via second harmonic generation (SHG) measurements [7]. These have shown that the H diffusion process is thermally activated with a barrier of 1.5 ± 0.2 eV and a preexponential factor of 10^{-3} $\mathrm{cm^2\,s^{-1}}$. These values appear to support the usual assumption (see, e.g., [5]) that H diffusion on this surface is a fast process when compared, e.g., to desorption. However, the microscopic mechanisms responsible for the measured barrier are still not well understood.

In this paper we try to obtain insight into the above issues by means of density functional calculations of hydrogen binding and diffusion on a Si(111) simple adatom structure, for which the ratio $\mathcal{R} = n_A/n_R$ between the number of available *A* and *R* sites can be varied between 1 and 2. Previous theoretical work on H diffusion on the Si(111)-(7 × 7) surface [8] used empirical interatomic potentials whose reliability is not well established. In agreement with [3–6], our results show that hydrogen prefers to adsorb at the rest-atom than at the adatom site. Moreover, we find that the binding energy difference $\Delta E \equiv E_A - E_R$ between these sites depends strongly on $\mathcal{R}$. When $\mathcal{R} = 1$, as on Ge(111)-*c*(2 × 8), we obtain $\Delta E \sim 0.75$ eV, very similar to the first principles results of Ref. [6]. Instead, when $\mathcal{R} = 2$, as on Si(111)-(7 × 7), $\Delta E \sim 0.2$ eV, in agreement with desorption experiments [4,5]. Finally, this result combined with the analysis of the potential energy surface (PES) for H at different surface sites suggests that at low coverage the relevant processes for H diffusion are $R \rightarrow A$ jumps. The calculated barrier for such jumps, ~1.3 eV, is quite close to the value found in the SHG experiment [7].

Our calculations have been performed within the Car-Parrinello scheme [9]. All geometry optimizations have been carried out using the local density approximation (LDA); however, also a few point calculations using the generalized gradient approximation (GGA) in the form proposed by Becke-Perdew (BP) [10] have been performed. The Si(111) surface was modeled as a repeated slab, each slab consisting of six layers of 8 Si atoms each, corresponding to two primitive (2 × 2) cells, plus 2 Si adatoms and 1 or 2 H atom(s) added to the top surface (see below). The Si adatoms are located at the so-called T_4 sites, i.e., the threefold sites above second layer Si atoms, which are known to be the stable binding sites for group-IV adatoms on Si(111) and Ge(111) [11]. The other surface is saturated by 8 H atoms. The four topmost Si layers as well as the Si adatoms and the chemisorbed hydrogen(s) were allowed to relax. Norm conserving

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pseudopotentials and a local pseudopotential have been used for Si and H, respectively. LDA and GGA pseudopotentials were taken from Refs. [12] and [13], respectively. The wave functions were expanded in plane waves with energy up to 12 Ry, and only the Γ point was used. With these approximations, the resulting structure of the clean Si(111)-(2 × 2) surface (see Fig. 1) is very similar to that discussed in Ref. [11].

We start by considering the potential energy surface, $E(x,y)$, for H diffusion on a Si(111)-(2 × 2) simple adatom structure. This structure is a well-defined subunit of the 7 × 7 surface, and has proven to be very useful for elucidating its basic structural, dynamical, and electronic properties [11]. In our case, the analysis of $E(x,y)$ for H/Si(111)-(2 × 2) should reveal most of the important topological features of the PES for the full 7 × 7 surface. Differences between inequivalent A and R sites of the 7 × 7 cell are rather small [3,14] and will not be taken into account. We have mapped $E(x,y)$ for H/Si(111)-(2 × 2) along the lines A-A, A-R, and R-R joining the different DB sites, following the procedure outlined in Ref. [15]. Inspection of Fig. 1 indicates that the study of $E(x,y)$ along these lines together with symmetry and local stability analysis is sufficient to identify the main features of the PES throughout the 2 × 2 cell. Our results are summarized in Fig. 2, where the LDA potential energy curves corresponding to the A-A, A-R, and R-R paths are plotted (full lines). The large energy difference (LDA: 0.74 eV; GGA: 0.80 eV) between the A and R sites is evident. This value of ΔE is similar to that obtained for H on Ge(111) in Ref. [6]. As discussed in [6], the stronger hydrogen binding at R is related to the higher electron density at this site with respect to the A site, as well as to the surface relaxations accompanying the H-adsorption process. On the clean surface, an electronic charge transfer takes place from the adatoms to the rest atoms, such that the corresponding DB's are almost completely empty and filled, respectively [11]. At the same time, the rest atom (adatom) undergoes a strong outward (inward) relaxation with respect to its ideal position, such that its DB becomes more s- (p_z-) like. When H is adsorbed, a counter-relaxation takes place, indicating a reverse rest-atom → adatom charge transfer, which on Ge(111)-c(2 × 8) has been indeed observed by STM [6]. For H at the A (R) site, this counter-relaxation is such to increase (reduce) the strain in the adatom (rest-atom) backbonds, as well as to break (weaken) the bond between the adatom (neighboring adatoms) and the second layer atom(s) just below. Details of the different H bonding structures are shown in Fig. 3.

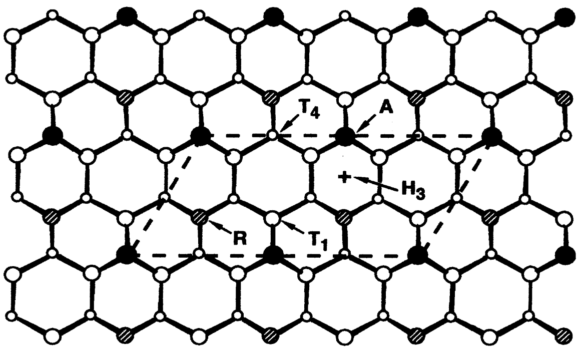

FIG. 1. Schematic top view of the clean Si(111)-(2 × 2) adatom structure. The dashed line indicates the surface supercell used in the present calculation. Relevant surface sites are indicated.

The transition state along the A-R path (see Fig. 2) is halfway between the two DB sites, at the so-called H_3 site, which is the hollow site above a fourth layer Si atom. Because of the large energy difference between the A and R sites, the energy barrier E_b for the jump $R \rightarrow A$ (LDA: 1.45 eV; GGA: 1.57 eV) is much higher than that for the

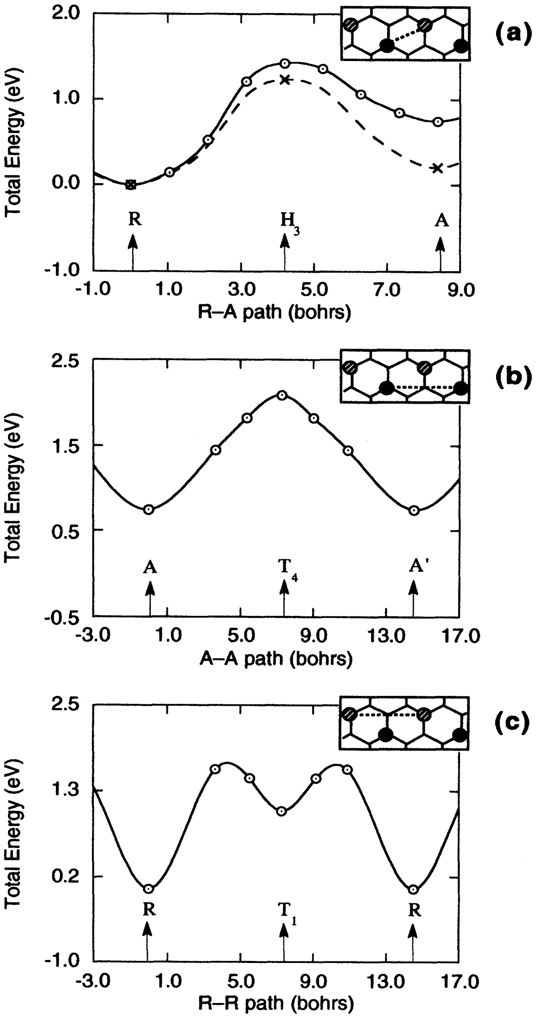

FIG. 2. Potential energy along the A-R (a), A-A (b), and R-R (c) H diffusion paths, calculated within the LDA. The paths are shown schematically in the insets. Circles and crosses represent calculated points for $\mathcal{R}$ = 1 and 2, respectively. Lines, both full and dashed, are only a guide for the eye.

reverse $A \rightarrow R$ process (LDA: 0.71 eV; GGA: 0.77 eV). Unlike H_3, the maximum along the A-A path, 1.35 eV higher in energy than the adatom, and halfway between the two DB's at a T_4 site, is a true maximum rather than a saddle point. A similar result was obtained also in a LDA study of H on the ideal Si(111)-(1 × 1) surface [16]. This indicates that A-A jumps will actually occur through an R intermediate, i.e., along an A-R-A pathway. An analogous conclusion holds also for R-R jumps. The midpoint along the R-R path is a local minimum, 1.07 eV higher in energy than the rest atom, and corresponds to a top (T_1) site, above a first layer Si atom which on the clean surface is bonded to an adatom. The maxima along the R-R path are at approximately 1/4 and 3/4 of the path, and have an energy of 1.65 eV (measured from the R site). These however are *not* saddle points, suggesting that R-R diffusion through an intermediate A site, i.e., R-A-R, is more likely than a direct R-R jump. From the above analysis we can conclude that the only relevant barrier for H diffusion on Si(111)-(2 × 2) is that corresponding to $R \rightleftharpoons A$ processes (saddle point at H_3).

As already found for Si(100) [15], there are important surface relaxations accompanying the H diffusion process. This appears clearly from Fig. 4, where the (fully relaxed) atomic geometries for the transition state along the A-R path (H_3 site), and the local minimum along the R-R path (T_1 site) are shown. In particular, the displacements of the Si adatom closer to the H atom can be so large to substantially weaken (or even break) one of its bonds to first layer atoms. This is the case when H is at the H_3 saddle point. Even more striking is the case where H is at the T_1 site. In this case a bond is formed between the first layer Si atom and the H atom just above, while the original bond between that first layer atom and the Si adatom is broken. From these results, it is clear that the Si adatom backbonds are very reactive to hydrogen, and can be broken very easily. This fact is consistent with experimental observations [1,17], and in particular accounts for the surface reactivity following saturation of the DB's.

The value $\Delta E \sim 0.8$ eV for the Si(111)-(2 × 2) adatom structure shows a large discrepancy with the experimental estimate of ~0.1–0.2 eV based on H_2 desorption from Si(111)-(7 × 7) [4,5]. However, an important difference between the 7 × 7 and 2 × 2 surfaces is that the number of A sites is twice that of R sites for the former, whereas the number of adatoms and rest atoms is the same on the 2 × 2. Correspondingly, the difference between the electronic charges at the R and A sites is smaller for the 7 × 7 surface, as here the adatom DB's are partially occupied [3,14]. In turn this suggests that also the H-induced effects that we have described for the 2 × 2 case, in particular the energy difference ΔE, should be reduced. In order to understand more quantitatively the dependence of ΔE on $\mathcal{R}$, we have saturated one of the two rest atoms of our supercell with one H atom, leading to a 4 × 2 structure with two adatom and one rest-atom DB's per unit cell, i.e., with $\mathcal{R} = 2$ as on the clean 7 × 7 surface. Because of the

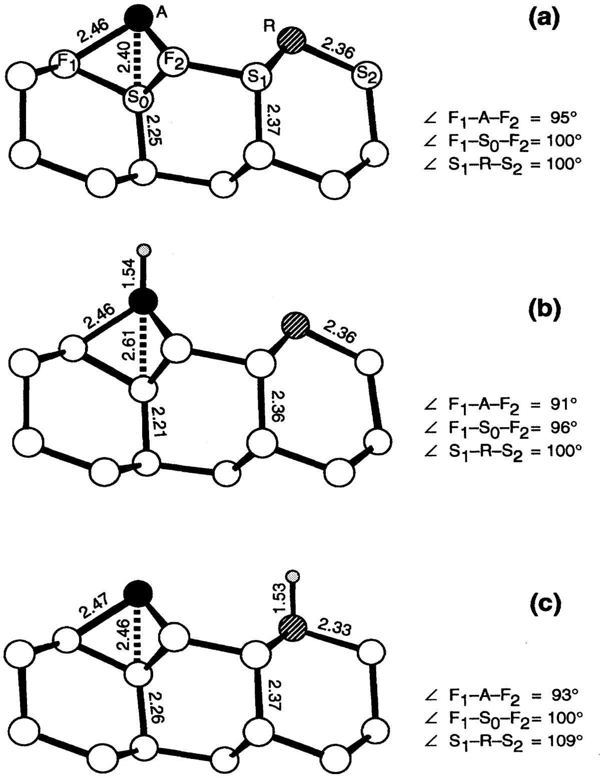

FIG. 3. Calculated equilibrium atomic configuration (side view) of adatoms and rest atoms for (a) clean surface, (b) H adsorbed at the A site, and (c) H adsorbed at the R site. Bond lengths in Å. H is represented by the small gray circle.

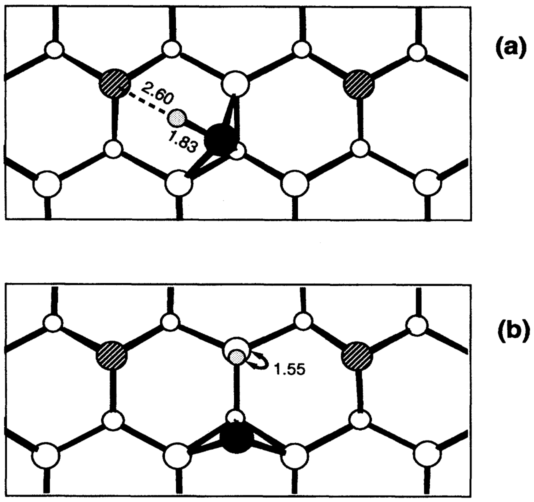

FIG. 4. Fully relaxed atomic geometries (top view) for (a) the transition state along the A-R path (H_3 site) and (b) the local minimum along the direct R-R path (T_1 site). Bond lengths in Å. H is represented by the small gray circle; other symbols are as in Fig. 1.

reverse charge transfer effect discussed previously, the charge distribution at the adatom and rest-atom DB's of this 4×2 structure approaches the average adatom and rest-atom charges on Si(111)-(7×7) much more closely than the charge distribution of the 2×2 adatom structure with $\mathcal{R} = 1$. We then considered the difference in binding of an additional hydrogen at either the R or A sites of this 4×2 structure. While the structure of the H-reacted sites shows only a small variation with $\mathcal{R}$, ΔE decreases strongly with increasing $\mathcal{R}$: we find $\Delta E \sim 0.2$ eV for $\mathcal{R} = 2$, in good agreement with the H_2 desorption experiments. The dependence of ΔE on $\mathcal{R}$ suggests also a dependence of ΔE on H coverage. In particular preferential occupation of R sites, leading to an increase of $\mathcal{R}$, should be accompanied by a reduction of ΔE. This effect could be relevant for, e.g., the analysis of the desorption data [4,5].

As shown in Fig. 2, a weaker dependence on $\mathcal{R}$ is instead found for the $R \longrightarrow A$ diffusion barrier: $E_b(R \longrightarrow A) \sim 1.2$ eV for $\mathcal{R} = 2$, increasing to approximately 1.3 eV within the GGA. Turning now to a comparison of our results with the diffusivity data of Ref. [7], we remark that this experiment was performed in a low coverage ($\sim$0.15) regime at temperatures of about 700 K. Nonactivated tunneling contributions to the diffusivity were found to be negligible at these temperatures. We can estimate the mean lifetime $\tau_{R(A)}$ for a H atom to remain on a R (A) site using the Arrhenius equation $\tau = \nu^{-1} \exp(E_b/k_B T)$, where ν is the attempt frequency. With $E_b(R \longrightarrow A) = 1.4$ eV [$E_b(A \longrightarrow R) = 1.1$ eV] and $\nu \sim 10^{13}\,\mathrm{s}^{-1}$, we obtain $\tau_R \sim 2.5 \times 10^{-3}$ s ($\tau_A \sim 10^{-5}$ s) at $T \sim 700$ K for R (A) sites. The large ratio, $\tau_R/\tau_A \sim 25$, between the two mean lifetimes suggests that in the conditions of the diffusion experiment H atoms should be mostly at R sites, occasionally jumping to neighboring R sites through an A intermediate. Thus the rate determining process is the $R \longrightarrow A$ jump, for which the calculated activation energy of $\sim$1.3 eV compares reasonably well with the experimental value of 1.5 ± 0.2 eV.

At variance with our conclusions, Raff and co-workers [8] have recently proposed that the process responsible for the measured diffusivity is the jump between two neighboring A sites lying on the faulted and faulted regions of the 7×7 cell, respectively. Their suggestion was based on the assumption that $R \rightleftharpoons A$ processes within each region of the 7×7 are very fast, an assumption which is not supported by our calculations. It has also been suggested [18] that the H diffusivity on Si(111)-(7×7) might be due to Si adatom "walking" on the surface. However, it is known (see, e.g., [19]) that an adatom can easily jump back and forth from its T_4 binding site to a neighboring hollow site, whereas "real" diffusion of an adatom from a T_4 site to the next T_4 is very unlikely below the critical temperature for adatom disordering, which is about 1130 K for Si(111), i.e., much greater than the temperature of H diffusion experiments.

In summary, our first principles study shows that hydrogen binds more strongly at R than at A sites by an amount which is an increasing function of the difference between the electronic charges at these sites. On the basis of Ref. [3], a similar behavior can be expected also for other electrophilic reactants, such as halogen atoms, OH and NH_2 radicals, etc. Our results also indicate that $R \longrightarrow A$ jumps are the rate determining processes for the H diffusivity on Si(111)-(7×7) at low coverages. The calculated barrier for these jumps is close to the activation energy measured experimentally.

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