

Chapter 2. Semiconductor Surface Studies

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2.1 Introduction

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Understanding the properties of the surfaces of solids and the interactions of atoms and molecules with surfaces has been of extreme importance both from technological and academic points of view. The advent of ultrahigh vacuum technology has made microscopic studies of well-characterized surface systems possible. The way atoms move to reduce the energy of their surfaces, the number of layers of atoms involved in this reduction, the electronic and vibrational states that result from this movement, and the final symmetry of the surface layer are all of utmost importance in arriving at a fundamental and microscopic understanding of the nature of clean surfaces, chemisorption processes, and the initial stages of interface formation.

The theoretical problems associated with these systems are quite complex. However, we are currently at the forefront of solving the properties of real surface systems. In particular, we are continuing our efforts in developing new techniques for calculating the total ground-state energy of a surface system from "first principles," so that we can provide accurate theoretical predictions of surface geometries and behavior. Our efforts in this program have been concentrated in the areas of surface defects, surface reconstruction geometries, structural phase transitions, and novel computational techniques.

2.2 H₂ Molecules on the Si(111)-(7×7) Surface

The interaction of molecules with solid surfaces is a subject of great practical and theoretical interest. It is the essence of surface catalysis. It represents one of the most challenging problems to theory, because of the complexity of the systems involved and the wide variety of possible outcomes. Typically, such phenomena are studied on metal surfaces that have spatially extended electronic states which can be shared easily with molecular states, thus affecting drastically the structure of the molecule when it is in the vicinity of the surface. Surfaces of covalent solids, are a different class of systems where the surface electronic states tend to be spatially localized and provide a different perspective into the physics of surface-molecule interactions. Experimental studies of such systems have proliferated recently, while in most cases a detailed understanding of the microscopic phenomena, such as adsorption and desorption mechanisms, is lacking except for some empirical model studies.

One of the most interesting equilibrium structural patterns of a covalent solid is the Si(111)-(7×7) dimer-atom-stacking fault (DAS) surface reconstruction (Figure 1). The complexity of this structure reflects the extensive atomic rearrangement that the system undergoes in order to minimize the number of broken covalent bonds on the surface without introducing excessive strain. Even after this elaborate reconstruction, there remains a number of dangling bonds of which seven are inequivalent types. The simplest chemical probe of this surface is atomic hydrogen, and the simplest molecule that reacts in nontrivial ways with this surface is the H₂ molecule.

Despite our relatively good understanding of H-H bonding and Si-H bonding, at present there exists no detailed microscopic picture of the adsorption and

desorption processes of H_2 on the $Si(111)-(7\times 7)$ surface. In fact, H_2 adsorption and desorption experiments have produced controversial results concerning the adsorption energy barrier. Adsorption experiments at room temperature give a very small H_2 sticking coefficient, indicating the presence of a significant adsorption energy barrier, and the reported activation energy of H_2 adsorption is 0.9 ± 0.1 eV. On the other hand, a low coverage desorption experiment has shown the H_2 desorption energy barrier to be 2.4 ± 0.1 eV, while measurement of the kinetic energy indicates that the desorbed H_2 experiences a very small energy barrier of 0.1 ± 0.1 eV. The desorption kinetics has also indicated the presence of two different surface sites from which the two H atoms, forming the H_2 molecule, are dissociated.

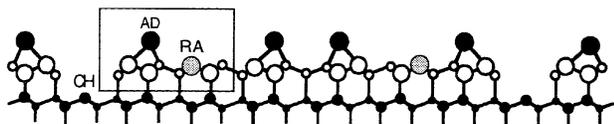


Figure 1. Ball-and-stick model of the $Si(111)-(7\times 7)$ reconstruction (a side view along the long diagonal of the unit cell). AD, RA, and CH indicate the adatom (large black dots), rest atom (large gray dots), and corner hole sites. The rectangular box indicates the region used to display valence charge densities in Figure 2.

In order to resolve this controversy, we have performed an extensive and accurate theoretical investigation on the dissociative interaction of the H_2 molecule with the $Si(111)-(7\times 7)$ surface.

H_2 Adsorption Energy

In Figure 1 we show ball-and-stick representation of the (7×7) reconstruction, with a side view of a (7×7) unit cell. As far as adsorption and desorption of H_2 molecules are concerned, an important consideration is the relative position of pairs of dangling bond sites, to which H atoms can bind upon adsorption of the H_2 molecule or from which H atoms can detach in order to form a desorbing molecule. There are three basic types of dangling bond sites on the surface: the adatom (denoted in short by AD); the rest atom (denoted by RA); and the corner-hole atom (denoted by CH). The adsorption energies of an H atom at these sites are calculated to be 2.9 eV at AD, 3.2 eV at RA, and 3.5 eV at CH. Different pairs of dangling bond sites are at various distances, with only the AD-RA pair at

a reasonably small distance (4.4 Å) to participate in the adsorption or desorption process (other pairs are at distances larger than 7.6 Å).

To determine the H_2 adsorption energy on the AD-RA pair of sites, we have performed total energy calculations for two H atoms adsorbed on the AD-RA sites. The accuracy of the calculations is 0.1 eV. The calculated H_2 adsorption energy is 1.6 eV, which is equal to the ideal adsorption energy (i.e., the energy obtained from two separate H atom adsorption energies at AD and RA sites: $[2.9 + 3.2 - 4.5]$ eV, where 4.5 eV is the H-H binding energy), indicating that nonlocal interaction between the AD and RA sites is negligible. This is to be contrasted with the AD-CH pair, for which the calculated H_2 adsorption energy is 2.1 eV, corresponding to a nonlocal interaction energy of 0.2 eV (the ideal adsorption energy in this case is $[2.9 + 3.5 - 4.5]$ eV = 1.9 eV).

H_2 Adsorption Energy Barrier

The most important physical quantity for adsorption is the energy barrier involved in the breaking of the H_2 molecule on the surface. To determine the adsorption pathway and the corresponding adsorption energy barrier in going from the initial to the final configurations, which are shown in the cross section in Figure 2b, we have performed extensive calculations for various positions of the H atoms in the vicinity of the AD-RA pair of sites.

We first study the nature of the surface-molecule interaction in which the molecule is moved as a unit and the surface is fully relaxed. As the center of the H_2 molecule is brought toward the surface (above the geometric center of the AD-RA sites, as shown in the top panel of Figure 2b) from a height of 7 Å to a height of 3 Å, the total energy change is negligibly small (less than 0.01 eV), indicating that in this range of distances from the surface the H_2 molecule is very inert, similar to a He atom. As the molecule is brought closer to the surface, a repulsive interaction gradually increases the energy by 0.3 eV at 1.5 Å above the AD-RA geometric center. The energy remains constant as the center of the molecule is further lowered by 1.5 Å down to the geometric center of the AD-RA pair. When the molecule is placed 1.5 Å above the individual AD or RA sites and the system is fully relaxed, the interaction is still repulsive, leading to an increase of the energy by 0.2 - 0.3 eV, relative to the energy of the molecule in the vac-

uum. This shows that there is a significant repulsive interaction between a H_2 molecule and the Si(111) surface.

We next consider the dissociative adsorption process of a H_2 molecule. A detailed description of the dissociation pathway is given in Figure 2. Figure 2a shows the total energy of the system relative to a reference configuration which corresponds to the H_2 molecule in the vacuum (top panel of Figure 2b). Initially, the H_2 molecule is placed 0.7 Å above the AD-RA geometric center, and the molecule is constrained to be in a plane perpendicular to the surface, which includes the AD and RA sites, indicated by the box in Figure 1. The axis of the molecule is parallel to the line connecting the AD and RA sites. The whole system is then fully relaxed under the single constraint so that the horizontal component of the center of mass of the H_2 molecule is fixed (the relaxation of this constraint would introduce a small energy change estimated to be smaller than 0.02 eV). The energy of the relaxed configuration corresponds to the point labeled A in Figure 2a. The points labeled B-F correspond to a successive increase of the H-to-H horizontal distance, while for each value of this distance the H atoms are relaxed vertically and the surface Si atoms are fully relaxed. The point labeled G corresponds to the final state of adsorption with the two H atoms attached to the AD and RA sites as shown in the bottom panel of Figure 2b.

This calculation gives an adsorption energy barrier of 0.8 eV. As the H-to-H distance increases by 0.4 Å (from configuration A to configuration B), the H-H bond starts to break, and this process increases the total energy by 0.8 eV. From B to D, the two H atoms are in the process of forming Si-H bonds while the H-H bond is being broken. The energy curve is very flat in going from configuration B to configuration D (corresponding to a 0.25 Å increase of the horizontal H-to-H distance). Apparently, the two processes compensate each other over the range of a 0.25 Å change in the H-to-H distance, leading to the flat energy curve. The cross-sectional plots of the total valence charge density in Figure 2c clearly indicate the simultaneous breaking of the H-H bond and formation of the two Si-H bonds. The total energy in going from configuration D to configuration G in Figure 2a is monotonically decreasing. For this part of the process, the H-H bond is already broken (see panel E in Figure 2c), and the total energy decreases as the Si-H bonds are being formed.

The charge density plots in Figure 2c also provide an important clue for understanding the detailed behavior of surface atoms and surface dangling bonds during the adsorption process. Panels C and E suggest that the adatom backbonds are significantly weakened, and the adatom is moved toward the dissociating H_2 molecule. Note that once one of the adatom backbonds is broken, the adatom is free to pivot at the remaining two backbonds, as schematically shown in Figure 3.

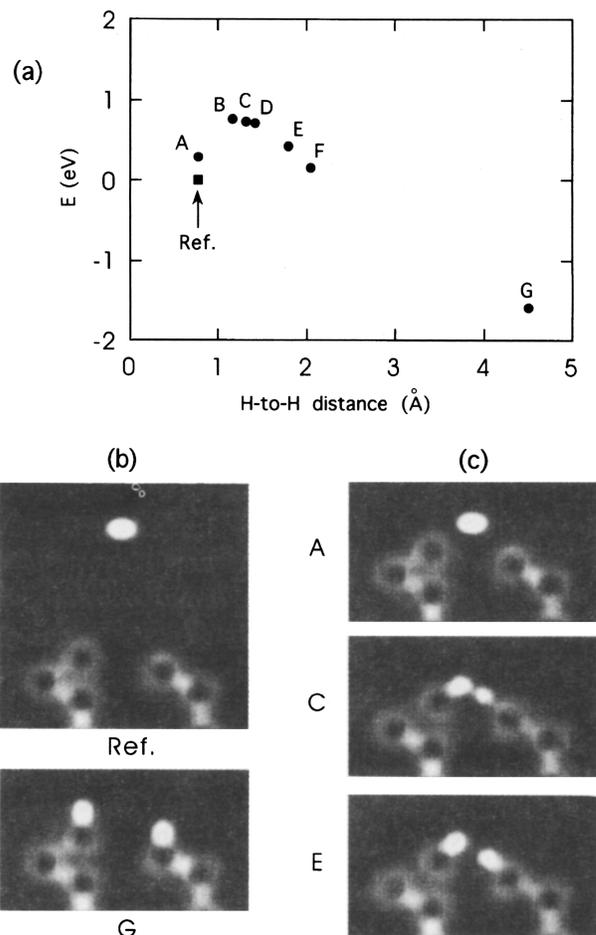


Figure 2. (a) Total energy relative to the reference state (with the center of the H_2 molecule situated at 7 Å above the surface) along the reaction coordinate of H_2 dissociation (represented by the H-to-H distance). Configurations labeled "Ref." and G correspond to the top (reference) and bottom panels of (b), and A through F correspond to panels of same label in (c). (b) Cross-sectional plots of the total valence charge density in the vertical plane corresponding to the box in Figure 1. Top panel shows the adatom site on the lower left side and the rest atom site on the lower right side. The H-H covalent bonding charge is shown as a white ellipse in the upper part of the panel. The bottom panel shows two H-Si covalent bonds at the AD and RA sites. (c) Cross-sectional plots of the total valence charge density in the same plane as in (b). Panels A, C, and E correspond to the H_2 breaking states along the reaction coordinate [same labels as in (a)].

This backbond breaking is also involved in the adatom surface diffusion process, and the corresponding energy barrier is 0.8 eV. The following picture of the microscopic mechanism of the adsorption process emerges: As thermal fluctuations provide enough kinetic energy to the adatom to overcome the 0.8 eV activation energy of breaking the backbond, the adatom can move closer to the RA site so that the incoming H_2 molecule can begin to form two Si-H bonds without significantly increasing the H-to-H distance. At this configuration, the Si(AD)-H, H-H, and Si(RA)-H bonds are all reasonably close to their equilibrium bond lengths, and the H_2 molecule dissociation is induced without a very high energy cost. After the adsorption process is completed, the adatom backbonds are restored to their original state, as shown in the lower panel of Figure 2b.

H_2 Desorption

The desorption process of H_2 on the Si(111) surface is not necessarily the reverse of the adsorption process since the initial state of the desorption depends on the surface conditions. It is possible that the H atom surface coverage and surface diffusion kinetics do not allow two H atoms to reach a configuration equivalent to the final state of the adsorption process. At low H coverage (Θ) of the Si(111)-(7 \times 7) surface, the adsorbed H atoms will first occupy CH sites until they are saturated at 0.02 monolayer (ML) coverage (1 ML is defined to be one H atom per (1 \times 1) surface unit area). For the coverage range $0.02 < \Theta < 0.14$ ML, the H atoms will gradually saturate the RA sites, and for $0.14 < \Theta < 0.39$ ML the AD sites will be saturated. For $\Theta = 0.39$ ML, all the dangling bonds on the (7 \times 7) surface are saturated so, for $\Theta > 0.39$ ML, the H atoms will begin to destroy the (7 \times 7) reconstruction and thereby create additional sites for saturation.

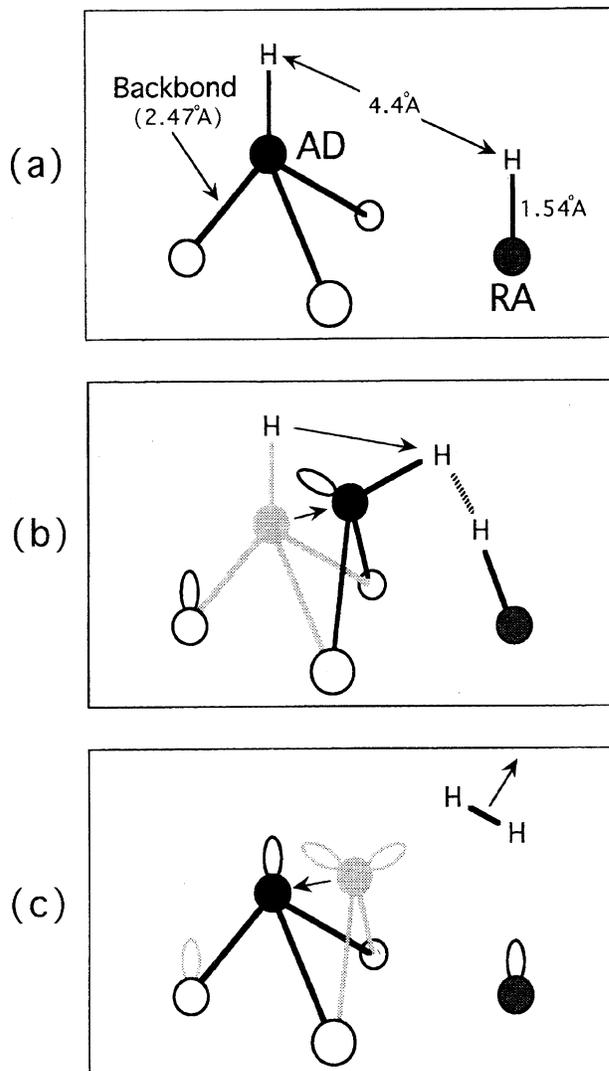


Figure 3. Schematic illustration of the H_2 desorption process: (a) The adatom backbond length, Si-H bond length, and H-to-H distance. (b) The breaking of one adatom backbond and the motion of the adatom which brings two H atoms close to the H-H bonding distance. (c) The desorption of the H_2 molecule and the subsequent reformation of the broken adatom backbond.

It is evident that the initial state for H_2 desorption depends on the H atom surface coverage. For the range $0.14 < \Theta < 0.39$ ML, the desorption process will be the reverse of the adsorption process since two H atoms can always be found at neighboring AD and RA sites. For the range $0.02 < \Theta < 0.14$ ML, the H atoms on the RA sites need to diffuse close to an AD site before the desorption can follow the reverse path of the adsorption process. The H atom diffusion barrier on the Si(111) surface is experimentally measured to be 1.5 eV; a recent total energy calculation using a (4×2) surface unit cell has shown that the energy barrier for H atom diffusion from a RA site to an AD site is about 1.3 eV. Since this diffusion barrier is much smaller than the experimental desorption energy barrier of 2.4 eV, H atom diffusion to AD sites will occur readily before desorption, so that the desorption process will be again the reverse process of the adsorption process. Finally, for $\Theta < 0.02$ ML, H atoms need to diffuse out of the corner hole sites before two H atoms can meet for desorption. This diffusion process is likely to have an energy barrier larger than 2.4 eV since it involves the breaking of Si-H bonds at CH sites, which have a binding energy of 3.5 eV. In this case, the diffusion of H atoms from the CH sites would be the rate limiting process.

Thus, for H coverage in the range $0.02 < \Theta < 0.39$ ML, the H_2 desorption process will follow the reverse path of the H_2 adsorption process, as illustrated schematically in Figure 3. From (a) to (b), the adatom backbond, indicated by an arrow in Figure 3a, is broken, which requires an activation energy of 0.8 eV. In (b), two H atoms are close to the equilibrium H-H bond distance so that only 1.6 eV extra energy is required to break two Si-H bonds and to form the H-H bond. The desorption energy barrier is then simply the sum of the adsorption energy and the adsorption energy barrier, i.e., $[1.6 + 0.8 = 2.4]$ eV. This value is in good agreement with the experimental measurement of desorption for low H coverage (2.4 eV at $\Theta = 0.15$ and 0.08 ML). After desorption, the surface adatom is left in a high energy state with a broken backbond, and the H_2 molecule leaves the surface without much kinetic energy as shown in Figure 3c. This process explains both the small kinetic energy of the desorbed H_2 molecule and the mechanism of the surface dynamics leading to a 0.9 eV activation energy for the adsorption and therefore resolves the controversy on the adsorption energy barrier.

2.2.1 Journal Articles

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