

Pathway of H₂ desorption from dihydride Si(100)

Z. Jing

Department of Physics, Box 8202, North Carolina State University, Raleigh, North Carolina 27695

J. L. Whitten

Department of Chemistry, North Carolina State University, Raleigh, North Carolina 27695

(Received 3 June 1993; revised manuscript received 2 August 1993)

In the present paper, the pathway of H₂ desorption from a dihydride species —SiH₂ on the Si(100) surface, —SiH₂ → —Si + H₂ (—Si represents a surface Si atom site), is investigated. This pathway involves the recombination of two H atoms bonded to the same surface silicon atom. A three-layer cluster that consists of 12 silicon atoms and 20 hydrogen saturators is used to simulate the Si(100) surface and *ab initio* self-consistent-field and configuration-interaction theory is used to treat the cluster and desorption reactions. With the correction of zero-point vibrational energies, the H₂ desorption energy and activation barrier are computed to be 48 and 53 kcal/mol, respectively. The corresponding adsorption barrier is 5 kcal/mol. Considering the experimental uncertainty and the uncertainty of our calculations, we conclude that the barrier of H₂ desorption from the dihydride surface via —SiH₂ is consistent with the experimental result.

I. INTRODUCTION

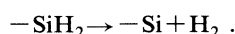
Despite recent intensive experimental and theoretical studies of hydrogen adsorption and desorption on silicon, the mechanism of H₂ desorption from the Si(100) surface remains controversial.^{1–11} Using transmission Fourier-transform infrared (FTIR) spectroscopy, Gupta, Colvin, and George¹ have found that desorption from both monohydride and dihydride surfaces is second order with activation energies of 65 and 43 kcal/mol, respectively. On the other hand, Schulze and Henzler² found the desorption from dihydride Si(100) to be first order with an activation barrier estimated to be 44 ± 7 kcal/mol. Several desorption models have been proposed; however, none provide quantitative details.

Most experimental and theoretical work on H₂ desorption from the monohydride Si(100) surface seems to point to first-order desorption kinetics. The laser-induced thermal desorption (LITD) and temperature-programmed desorption (TPD) experiments by Sinniah *et al.*³ found that H₂ desorption follows first-order kinetics with an activation energy of 45 kcal/mol in the coverage range of 0.006 to 1.0 monolayer. They proposed a desorption mechanism in which the rate-limiting step is the promotion of a hydrogen atom from a localized bonding site to a delocalized band state. The delocalized atom then reacts with a localized atom to produce molecular hydrogen which desorbs. Using the same experimental techniques, Wise *et al.*⁴ also concluded that H₂ desorption follows first-order kinetics. However, they obtained a higher activation energy of 58 kcal/mol by LITD experiments and 66 kcal/mol by TPD analysis. They proposed a different mechanism in which H₂ desorption occurs as the concerted desorption of two hydrogen atoms paired on different atoms of a single dimer. This mechanism is supported by experiments by Kolasinski, Shane, and Zare⁵ who found that H₂ desorbing from Si(100) is rotationally cool and vibrationally hot, suggest-

ing that desorption involves paired H atoms in a high-symmetry transition state. Chabal⁶ obtained evidence for preferential pairing of hydrogen on Si(100) dimers by infrared multiple internal reflection. Scanning tunneling microscopy⁷ has also provided direct evidence for preferential pairing of hydrogen on Si(100) dimers. On the theoretical side, calculations by D'Evelyn, Yang, and Sutco⁸ support the preferential pairing which is attributed to π bonding on clean Si(100) 2 × 1.

However, theoretical calculations of H₂ desorption from the monohydride Si(100) surface predicted much higher energy barriers.^{9,10} Wu and Carter⁹ calculated a desorption barrier of 94 kcal/mol and concluded that the pairwise desorption mechanism is not applicable. Nachtigall, Jordan, and Janda¹⁰ calculated the desorption energy to be nearly equal to the measured values of the activation energy. The barrier for this process would then have to be less than about 5 kcal/mol for a concerted desorption mechanism to be consistent with their calculations and experiment. They compared the π -bond strengths in the surface dimer and in Si₂H₄, and concluded that although the barrier to dissociative adsorption will be much smaller than that for H₂ addition to Si₂H₄, it is likely to be large enough such that the simple pairwise desorption mechanism would not be consistent with the observed desorption energy.

Recently, Shane, Kolasinski, and Zare¹¹ (SKZ) have compared the internal-state distribution of hydrogen desorbed from monohydride and dihydride phases on Si(100). From the similarity between the dynamics of desorption from the monohydride and dihydride phase, SKZ proposed that desorption from the monohydride phase occurs through a dihydride species —SiH₂, in which these two H atoms recombine to form an H₂ molecule:



Based on our calculated energy barriers, we proposed a

slightly different model for H₂ desorption from the monohydride phase, which also requires that H₂ desorb through a dihydride species via $-\text{SiH}_2 \rightarrow -\text{Si} + \text{H}_2$.¹²

In this paper, we use a cluster Si₁₂H₂₀ to model the Si(100) surface and study the proposed desorption pathway by *ab initio* self-consistent-field (SCF) and configuration-interaction (CI) total-energy calculations. The present paper is organized as follows: Section II gives a brief review of the general theory and Secs. III and IV report the results and summarize the conclusions.

II. THEORY AND COMPUTATIONAL METHODS

The three-layer cluster model is depicted in Fig. 1. All peripheral dangling bonds of the boundary atoms are saturated by H atoms (not shown in the figures) along the dangling (tetrahedral) bond directions. All nearest-neighbor Si-Si distances are kept the same as in the bulk, 2.35 Å, and only the bond angles α , α' , and β (see Fig. 1 for definition) are allowed to vary. Although the surface atoms are known to have large displacements in the reconstruction of Si(100), the change of the nearest-neighbor Si-Si distances has been found to be less than 2.1% of the bulk value. Thus, the constraint of constant Si-Si bond length is not likely to affect our modeling of the major features of surface reactions. Concerning the Si₁₂H₂₀ model, the close distances between the H atoms on opposite Si atoms of the third layer are not expected to affect the surface reaction, since all Si and H atoms below

the second layer are fixed in space. If they were allowed to move freely, the positions of these atoms would be distorted dramatically such that the cluster would no longer resemble the Si(100) surface.

This cluster has been used previously in the study of the Si(100) 2×1 surface and its hydrides and has yielded excellent results.^{12,13} For the clean surface, it is found that the correct ground state is a singlet, but a multideterminant wave function is required for its description. At the CI level, the surface dimer in the ground state is found to be symmetrical with a dimer bond length of 2.40 Å. The optimized geometry for the cluster model of Si(100) 2×1 (see Fig. 1) corresponds to

$$\alpha = \alpha' = 26.7^\circ, \quad \beta = 2.4^\circ, \quad r_0 = 2.401 \text{ \AA},$$

The dimer bond energy is calculated to be 2.0 eV. The chemisorption of H atoms in the monohydride phase changes the surface reconstruction slightly, shifting the dimer length from 2.401 Å in an H-free surface to 2.466 and 2.472 Å for a dimer bonded with one and two H atoms, respectively. The Si-H bond energy is calculated to be 3.50 eV for the chemisorption of the second H atom. Both values are close to the 3.52-eV (81.1-kcal/mol) value deduced from thermal-desorption experiments.⁴ The Si-H stretch frequency is computed to be 2099 cm⁻¹, in close agreement with the experimental value of 2080 cm⁻¹. Chemisorption of H atoms to form the dihydride phase changes the reconstructed Si(100) 2×1 to the unreconstructed Si(100) 1×1 surface. The general agreement of our calculations with experiment suggests that we can describe the surface and H₂ desorption processes accurately.

Cluster total energies and adsorption energies are determined from *ab initio* SCF and CI calculations. Silicon atoms on the surface are treated at the all-electron level while those in the second layer are described by a pseudopotential for the 1s, 2s, and 2p electrons; all nonlocal exchange and Coulomb interaction are explicitly included. The objective is to treat the surface region and adsorbed species with sufficient accuracy to describe reaction energetics.¹⁴⁻¹⁶ Calculations are performed by first obtaining SCF solutions for the cluster. The occupied and virtual orbitals of the SCF solution are then transformed separately to obtain orbitals spatially localized about the surface atoms. This unitary transformation of orbitals is based on exchange maximization with the valence orbitals of atoms belonging to the surface region and is designed to enhance convergence of the CI expansion. The CI calculations primarily describe the surface dimer and the bonds to hydrogen. Calculations involve excitation within a 16-electron subspace to 34 possible localized virtual orbitals. All configurations arising from single and double excitations with an interaction energy greater than 5×10^{-6} hartree with the parent SCF configuration are explicitly retained in the expansion; contributions of excluded configurations are estimated using second-order perturbation theory. All configurations with relatively large coefficients (>0.06) are taken as parent configurations, and the CI procedure described above is repeated. Final wave functions typically contain

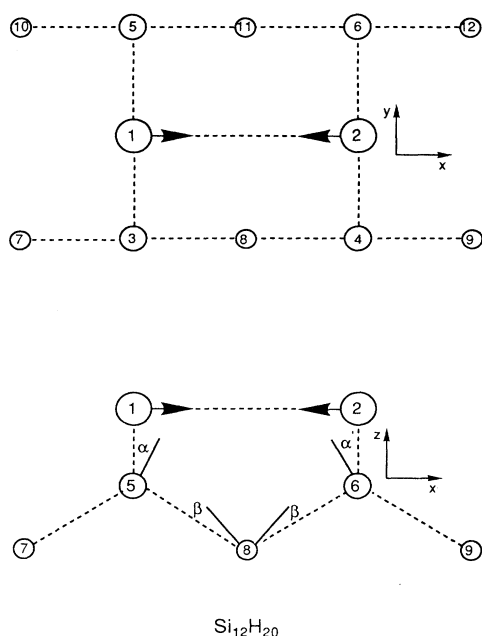


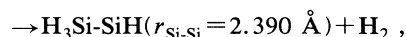
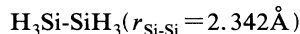
FIG. 1. Top view and side view of cluster Si₁₂H₂₀. All the peripheral dangling bonds of the boundary atoms are saturated by H atoms (not shown in the figures) along the dangling (tetrahedral) bond direction with a Si-H bond length of 1.48 Å. α is defined as the angle of rotation of atom 1 about atom 5 and β is defined as the angle of rotation of atoms 1 and 5 about 8 around the y axis.

about 5000 configurations.

Two silicon basis sets are employed in the cluster calculations: one is Dunning's near-Hartree basis,¹⁷ augmented by a set of d functions (with exponent 0.4), and the second is the set of double- ζ five-term $3s$ and four-term $3p$ basis used in Ref. 18. The first basis is used for the all-electron description of surface atoms and the other basis is used in valence calculations for atoms beneath the first layer.¹⁴ There are two types of hydrogen atoms in the cluster: H_{ads} , the adsorbate hydrogen atoms interacting with the surface atoms, and H_{sat} , the hydrogen atoms saturating the peripheral silicon atoms of the cluster. The H_{ads} atoms are described by double- ζ s , s' , and p basis functions (exponent of 0.6).¹⁸ A four-term s basis is used for H_{sat} atoms.

III. RESULTS AND DISCUSSION

The pathway of H_2 desorption from $-\text{SiH}_2$ involves the recombination of two H atoms bonded to the same Si atom, as shown in Fig. 2. In an ideal dihydride surface at unit coverage, the surface is unreconstructed and each surface Si atom has an $-\text{SiH}_2$ structure. After the desorption of H_a and H_b , the $\text{Si}_{(1)}$ atom cannot form a dimer with its adjacent atoms until an H atom transfer occurs and the surface is therefore not expected to undergo a major reconstruction. From the small change of the Si-Si bond length (0.048 Å) in the 1,1-H elimination from Si_2H_6 ,²⁰



the change in the positions of surface Si atoms is expected to be small with the desorption of H_2 from $-\text{SiH}_2$. Thus, in our calculations, the surface Si atoms are fixed at their bulk terminated positions before and after the desorption of H_2 .

Since the least motion of H_2 desorption, shown in Fig. 2(a), is symmetry forbidden, H_a and H_b likely desorb asymmetrically, as in Fig. 2(b). Instead of a two-dimension problem, the energy surface becomes four di-

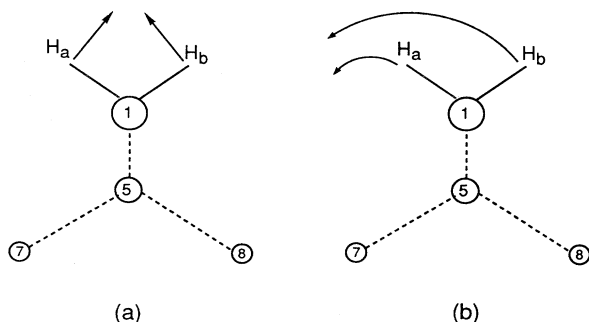


FIG. 2. Schematic drawing of H_2 desorption from H atoms bonded to the same surface Si atom. The least motion of H_2 desorption, shown in (a), is symmetry forbidden; H_a and H_b desorb asymmetrically, as shown in (b).

mensional. It is impractical to optimize fully the structure of the transition state for such a large system with our present program, but from past experience, we know that the Si-Si bond is fairly localized and the effect of distant Si atoms in the bulk is relatively small on the interaction of H with surface Si atoms. Thus, we expect that the transition state for H_2 desorption on the surface will be similar to that of molecular elimination of H_2 in silane or that of the 1,1 elimination of H_2 in disilane. The transition state for H_2 elimination in both silane and disilane has been well studied.^{19,20} As a first approximation, for H_2 desorption on the Si surface, we follow the pathway of H_2 elimination in silane and then optimize the geometry of the transition state.

The geometrical parameters determined for the silane system are used for the cluster depicted in Fig. 3 and Table I lists the energy of the system at several key points along the pathway. The parameters r_a , r_b , θ_a , and θ_b are the Si-H bond distances and angles defined in Fig. 3. Table I shows that the saddle point of H_2 desorption from the cluster differs slightly from that in silane. Without zero-point vibrational energy correction, the activation energy at the saddle point is calculated to be 53.6 kcal/mol for H_2 desorption and 4.6 kcal/mol for H_2 adsorption. The structure of the transition state for H_2 desorption from the cluster model is shown in Fig. 4(a). We note that H_a lies slightly below the surface layer, which is not likely for H_2 desorption from a real dihydride surface. Therefore, we need to explore other transition states that place both H_a and H_b above the surface layer. There are many ways to achieve this. The following simple rotations, as shown in Fig. 4(a), are the two most obvious: (1) rotation of the $\text{Si}_{(1)}\text{H}_a\text{H}_b$ unit around the Si atom in the second layer (labeled atom 5) about the Y axis and (2) rotation of H_aH_b around the surface Si atom (labeled 1) about the Y axis. The rotations associated with (1) and (2) are defined as φ_1 and φ_2 , respectively. Calculations show that the energy changes ΔE with respect to φ_1 and φ_2 are rather small: $\Delta E = 0.06$ and 1.7 kcal/mol for $\varphi_1 = 5^\circ$ and 10° ; $\Delta E = 0.4$ and 2.1 kcal/mol for $\varphi_2 = 10^\circ$ and 20° . The combination of $\varphi_1 = 5^\circ$ and $\varphi_2 = 10^\circ$ places both H_a and H_b well above the surface layer and the energy increase of the transition state is only 0.45 kcal/mol. Since the energy surface at the tran-

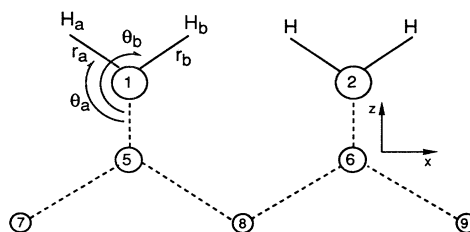


FIG. 3. The parameters involved in the characterization of the transition state. Since the positions of H_a and H_b vary dramatically from adsorbed state to transition state to desorbed state, θ_a (θ_b) is defined as the angle between SiH_a (SiH_b) and $\text{Si}_{(1)}\text{Si}_{(5)}$.

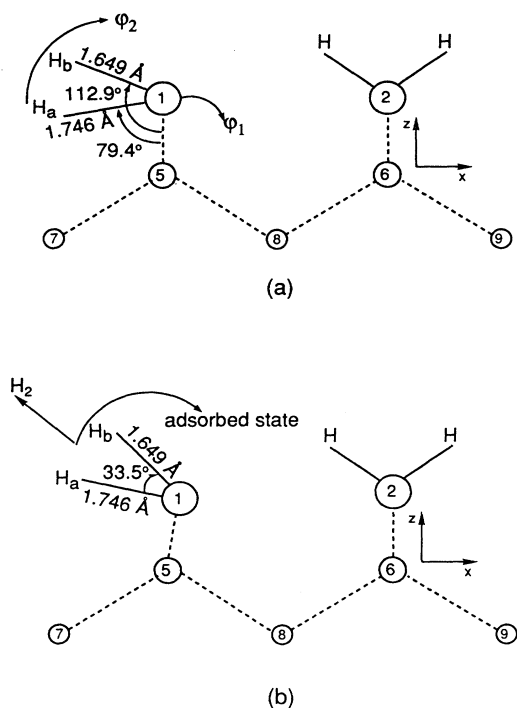


FIG. 4. Transition states for H₂ desorption from the cluster model (a) and the Si surface (b). (b) is obtained by the combination of a rotation of $\varphi_1 = 5^\circ$ of the Si₍₁₎H_aH_b unit around Si atom 5 and a rotation of $\varphi_2 = 10^\circ$ of H_aH_b around Si atom 1 about the Y axis. H_a is beneath the surface layer in (a) and above the surface layer in (b).

sition state is fairly flat, further optimization is not likely to yield a substantial change in activation energy. Thus, we consider the geometry shown in Fig. 4(b) to be the transition-state structure for the desorption of H₂ from a dihydride surface.

From the transition state shown in Fig. 4b, H atoms

TABLE I. The relative energy of the Si(100)1×1-2H dihydride system cluster at several key points along the pathway of H₂ elimination (the reference state is the desorbed state). $r_{\text{H-H}}$ is the H-H distance in Å. r_a, r_b are the Si-H_a, Si-H_b bond distances in Å and θ_a and θ_b are the bond angles in degrees, as defined in Fig. 3.

r_a	r_b	θ_a	θ_b	$r_{\text{H-H}}$	E (kcal/mol)
1.481	1.481	125.3	234.7	2.419	-49.0 ^a
1.636	1.515	85.1	127.0	1.135	2.4 ^b
1.746	1.649	79.4	112.9	0.982	4.6 ^c
1.858	1.786	73.5	98.5	0.792	4.0
6.0	6.0	176.4	183.6	0.745	0.0 ^d

^aThe adsorbed state with an energy 49.0 kcal/mol lower than the desorbed state.

^bThe transition state for molecular elimination of H₂ from silane.

^cThe transition state for the cluster model, which differs slightly from the corresponding transition state for molecular elimination of H₂ from silane.

^dThe desorbed state which is taken as the reference state.

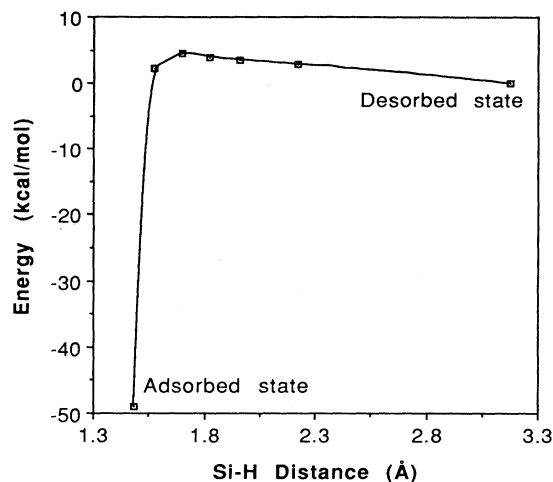


FIG. 5. The energy change of the cluster as a function of the Si-H distance which is the average of the Si-H_a and Si-H_b distances. The large Si-H distance corresponds to the desorbed state and the small Si-H distance corresponds to the adsorbed state.

can proceed either to desorb or return to the adsorbed state. Figure 5 shows the energy change with respect to the average distance of Si-H_a and Si-H_b. The following picture of H₂ desorption emerges: First, hydrogen atoms approach each other by the rotation of H_a and H_b around the surface Si₍₁₎ atom. At this stage, the Si-H bond length shows only a slight increase. Only when H_a and H_b come to a distance close to the H₂ bond length do Si-H bonds begin to stretch. The energy change with the stretching of Si-H bonds after H-H pairing is rather small, as shown by the rather flat curve in Fig. 5 for large Si-H bond lengths. At large Si-H distance, H_a and H_b form the H₂ molecule and desorb from the surface.

Zero-point vibrational energies are estimated from the Si-H and H-H frequencies in the study of SiH₄ → SiH₂ + H₂ (Ref. 19) for the adsorbed state, the transition state, and the desorbed state. Because of the small number of Si-H and H-H vibrational modes involved in the desorption process, the correction of zero-point vibrational energies is rather small. It changes the H₂ desorption energy and activation barrier to 47.9 and 53.1 kcal/mol, respectively. The corresponding adsorption barrier is 5.2 kcal/mol. If we use the experimental upper limit of 74 kcal/mol for the Si-H bond energy,¹ the upper limit of the desorption energy is 44 kcal/mol. Thus, our calculated desorption energy is at least 4 kcal/mol higher than the upper limit of the experimental result. Considering the experimental uncertainty of 7 kcal/mol (Ref. 2) and the uncertainty of our calculations, we conclude that the barrier of H₂ desorption from the dihydride surface via -SiH₂ is consistent with the experimental result. Recently, we became aware of *ab initio* calculations carried out by Wu and Carter⁹ on this system using a smaller cluster Si₉H₁₂. They calculated a desorption barrier of 53 kcal/mol, which is essentially the same as our value of 53.1 kcal/mol.

IV. CONCLUSIONS

The conclusions of our H₂ desorption study can be summarized as follows.

(1) A 19-silicon-atom cluster with 21 hydrogen atoms as cluster terminators is used to simulate the Si(100) surface and to study the H₂ desorption processes.

(2) The H₂ desorption mechanism $-\text{SiH}_2 \rightarrow -\text{Si} + \text{H}_2$, is calculated to be 49 kcal/mol endothermic without zero-point vibrational energy correction. With zero-point vibrational energy correction, the desorption pathway has been calculated to have an activation energy of 53 kcal/mol. The corresponding adsorption energy barrier is 5 kcal/mol.

(3) The desorption of H atoms via $-\text{SiH}_2 \rightarrow -\text{Si} + \text{H}_2$ can be viewed as a two-step process: hydrogen atoms on the same Si approach each other asymmetrically to a dis-

tance comparable to that in H₂; the H atoms then leave the surface as H₂. The asymmetric structure of the transition state is a consequence of the symmetric desorption pathway being symmetry forbidden.

(4) Considering the experimental uncertainty and the uncertainty of our calculations, we conclude that the barrier of H₂ desorption from the dihydride surface via $-\text{SiH}_2$ is consistent with the experimental result.

ACKNOWLEDGMENTS

This research was supported by a grant from the U.S. Department of Energy and a grant of computer time from the North Carolina Supercomputer Center. One of the authors (Z.J.) would like to thank Dr. G. Lucovsky for his support.

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