

***Ab initio* studies of H chemisorption on Si(100)**

Z. Jing and J. L. Whitten

Departments of Physics and Chemistry, North Carolina State University, Raleigh, North Carolina 27695-8202

(Received 24 April 1992)

Ab initio configuration-interaction theory is used to study the chemisorption of hydrogen on the Si(100) 2×1 reconstructed surface in the monohydride and dihydride phases. A three-layer cluster, that consists of 12 silicon atoms and 20 hydrogen saturators is used to simulate the major features of surface reconstruction. The chemisorption of H atoms changes the surface reconstruction slightly in the monohydride phase, shifting the dimer length from 2.401 Å in a 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 first H atom and 3.58 eV for the chemisorption of the second H atom, including the zero-point vibrational energy. The Si-H stretch frequency is computed to be 2099 cm^{-1} . In forming the dihydride phase, the chemisorption of H atoms destroys surface dimers and changes the reconstructed 2×1 surface to the unreconstructed 1×1 surface. The interactions between surface SiH₂ groups are found to be repulsive. The desorption of H₂ from the monohydride and dihydride phases is also discussed.

I. INTRODUCTION

There have been numerous experimental and theoretical studies on silicon surfaces¹⁻⁴² due to their great technological importance. A great deal has been learned about surface features: surface reconstruction, surface irregularities (steps, kinks), Si film growth, chemisorption on Si surfaces, etc.¹ However, due to the complexity of surface processes, our knowledge in many areas is still limited. For example, the H₂ desorption energetics and reaction pathways on Si surfaces are not fully understood.²⁻⁷ Experiments have found that the recombinative desorption reaction in the monohydride coverage regime is first order for H on Si(100) and second order for H on Si(111). The measured activation barriers for desorption for H on Si(100) range from 45 to 66 kcal/mol.³⁻⁵ On the other hand, theoretical calculations have not yet found a reaction pathway with an activation barrier within the range of experimental values.^{6,7} Our goal is to study the reactivity of silicon surfaces and the energetics of surface processes by *ab initio* quantum-mechanical techniques. The cluster method, describing the surface by a cluster of atoms, is suitable for studying local electronic properties. With a proper choice of silicon cluster, we can study the reaction pathway of H₂ desorption on Si surfaces.^{8,9}

Early low-energy electron-diffraction (LEED) studies¹⁰ revealed the presence of a 2×1 reconstruction of the Si(100) surface. It is now generally accepted that this reconstruction involves alternate rows of surface atoms moving toward each other to form rows of silicon dimers. As to the details, the various models differ. Some favor symmetric and others asymmetric dimers. However, all of the current models involve large surface-atom displacements with small distortions extending down to as deep as the sixth layer.¹⁰⁻³² In a previous paper, we have studied the reconstruction of the Si(100) surface by the cluster method.³² It is found that the calculated surface

dimer bond length is very sensitive to the level of theoretical treatment. A single-determinant self-consistent-field (SCF) treatment of a single surface dimer gives a closed-shell singlet state higher in energy than the triplet state and a dimer length for the singlet of 2.21 Å, 0.26 Å shorter than the triplet. The correct ground state is a singlet, but a multideterminant wave function is required for its description. At the configuration-interaction (CI) level, the surface dimer in the ground state is found to be symmetrical with a dimer bond length of 2.40 Å and the energy decrease for dimer formation with respect to the ideal Si(100) 1×1 surface is 1.98 eV per dimer. This dimer bond length is in good agreement with LEED measurements. We note that a similar conclusion has been reached earlier by Redondo and Goddard.³¹

The chemisorption of atomic hydrogen on Si(100)³³⁻³⁹ has been found to form two distinct phases: monohydride and dihydride phases, designated as Si(100) 2×1 :H and Si(100) 1×1 :2H, respectively. High-resolution electron-energy-loss-spectroscopy studies of H on Si(100) by Butz *et al.*³⁹ have found the Si-H stretch frequency at 2080 cm^{-1} . Koehler *et al.*⁴⁰ have studied hydrogen and deuterium desorption from Si(111) 7×7 using laser-induced thermal desorption and have obtained an upper-limit value of 82.6 kcal/mol (3.58 eV) for the Si-H bond energy under the assumption that the activation barrier to desorption is equal to the heat of adsorption. They have estimated the Si-H bond energy to be 80.5 kcal/mol (3.49 eV) using an activation barrier of 4.2 kcal/mol for H₂ adsorption on Si(111) obtained from a theoretical prediction.⁴¹ From the similarities of isothermal desorption kinetics, they suggested that the Si-H bond strengths and possibly the hydrogen surface mobilities are similar on the Si(111) 7×7 and Si(100) 2×1 surfaces.

Using a local spin-density method, Selmani and Salahub⁴² determined interaction potentials from an 11-atom cluster, neglecting reconstruction of the surface, for use in molecular-dynamics simulations of hydrogen ad-

sorption on a silicon surface. Their binding energy for H adsorption on the unreconstructed (100) silicon surface is calculated to be 3.0 eV with a Si-H equilibrium distance of 1.5 Å. Recently, Nachtigall, Jordan, and Janda⁶ performed *ab initio* calculations on Si₉H₁₂, Si₉H₁₃, and Si₉H₁₄ cluster models of the Si(100)2×1 surface and its hydrides. They found that the bond energy of the first Si-H of a silicon dimer D₀(SiSi-H) is 76 kcal/mol (3.30 eV), while the second Si-H bond energy D₀(HSiSi-H) is 81 kcal/mol (3.51 eV). Using the generalized-valence-bond method and the same Si₉H_x clusters (and CI calculations on smaller clusters Si₂H₄, Si₂H₅, and Si₂H₆), Wu and Carter⁷ obtained a larger Si-H bond energy for the two cases, 86.1 kcal/mol (3.73 eV) for D₀(SiSi-H) and 87.9 kcal/mol (3.81 eV) for D₀(HSiSi-H).

In this paper, we use Si₁₂H₂₀ to model the Si(100)2×1 surface reconstruction and study the interaction of H atoms with the surface and the effect of H chemisorption on the surface reconstruction in the monohydride and dihydride phases. We also discuss H₂ desorption from the monohydride and dihydride phases. 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

Cluster total energies and adsorption energies are determined from *ab initio* self-consistent-field and configuration-interaction calculations. Silicon atoms of the dimer are treated at the all-electron level, while those in the second layer are described by a 1s-2p pseudopotential; all nonlocal exchanges and Coulomb interactions are explicitly included. The objective is to treat the surface region and adsorbed species with sufficient accuracy to describe reaction energetics.⁴³⁻⁴⁵ 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 42 possible localized virtual orbitals. All configurations arising from single and double excitations with an interaction energy greater than 1.5×10^{-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 about 5000 configurations.

Two silicon basis sets are employed in the cluster calculations: one is Dunning's near-hartree basis,⁴⁶ augmented by a set of *d* functions (with exponent 0.4); and the second is the set of double- ζ five-term 3*s* and four-term 3*p* bases used in Ref. 47. 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.⁴³ 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).⁴⁷ A four-term *s* basis is used for H_{sat} atoms.

III. RESULTS AND DISCUSSION

The three-layer cluster model depicted in Fig. 1 is designed to focus on a single Si-Si dimer on the Si(100)2×1 surface. All peripheral dangling bonds of the boundary atoms are saturated by H atoms (not shown in the figures) along the dangling (tetrahedral) bond directions. The Si-H bond length is 1.48 Å. Previous calculations³⁸ have shown that the electronic properties of the cluster are not very sensitive to the distance between the boundary silicon atoms and their hydrogen saturators. These H saturators are not fixed in space, but move during the surface reconstruction following the movement of the Si atoms to which they are bonded. All nearest-

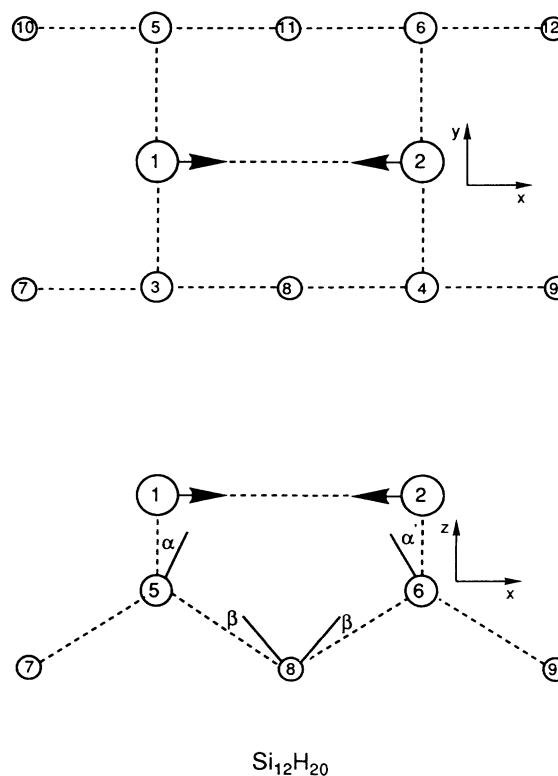


FIG. 1. Top and side views of the Si₁₂H₂₀ cluster model of Si(100). All peripheral dangling bonds of the boundary atoms are saturated by H atoms (not shown in the figure) along the dangling (tetrahedral) bond directions. The angles α , α' , and β are angles of rotation about the *y* axis from the unreconstructed, ideal Si(100)1×1 surface. All of the nearest-neighbor Si-Si distances are kept the same as in the bulk, 2.35 Å, and only the angles α , α' and β are allowed to vary in the surface reconstruction.

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.

This cluster has been used previously in the study of the Si(100) 2×1 surface and has yielded excellent results for the clean surface reconstruction. 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, in good agreement with LEED results for Si(100). The optimized geometry for the cluster model of Si(100) 2×1 (see Fig. 1) corresponds to

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

A. Monohydride phase

To determine the effect of H chemisorption on the surface reconstruction in the monohydride coverage regime, we bring two H atoms to the surface, successively, as shown in Fig. 2(a), and optimize the geometry in each case. The Si-H bond lengths are found to be 1.534 and 1.507 Å for the chemisorption of one and two H atoms, respectively. The Si-H bond orientation is 19.4° from the surface normal in both cases, which differs by 7.5° from the surface dangling (tetrahedral) orbital direction (26.9° from the surface normal). The chemisorption of the first H atom shifts the Si-Si dimer bond length from $r_0 = 2.401$ Å to $r_1 = 2.466$ Å. The increase in distance is due to the breaking of the weak second bond of Si-Si dimers on the Si(100) 2×1 surface. This bond is somewhat π -like, but is formed from sp^3 orbitals. Since the stronger σ bond, which is mainly responsible for the Si-Si bonding in the dimer, is not broken, the basic dimer structure remains unchanged, and the energy decrease accompanying the small increase in distance is only 0.02 eV. The chemisorption of the second H atom increases the dimer bond length slightly to $r_2 = 2.472$ Å. Unlike the chemisorption of the first H atom, the chemisorption of the second H does not break a bond, and thus the values of r_1 and r_2 are similar. Both values are very close to the distance calculated for the triplet coupling of dangling orbitals on the clean surface, 2.470 Å. The triplet state is a low-lying excited state of the system, 0.06 eV, above the singlet-coupled dimer. We conclude that although the H chemisorption in the monohydride phase increases the Si-Si dimer bond lengths somewhat, the basic dimer structure remains unchanged.

Figure 3 shows the SCF energy of the cluster (relative to the cluster energy at $R_{\text{SiH}} = 20$ a.u.) as a function of Si-H distance for the chemisorption of two H atoms on the cluster (simultaneous adsorption of both H atoms). The Si-H equilibrium distance is 1.507 Å. By fitting the energy versus SiH bond-distance curve to a third-order polynomial, as described in Ref. 48, the Si-H stretch frequency is computed to be 2314 cm^{-1} . It is known that SCF calculations generally overestimate the frequency, and the error may be as large as 15%. To overcome this systematic error, Ho *et al.*⁴⁹ developed a scaling formula that multiplies the calculated vibrational frequencies by a

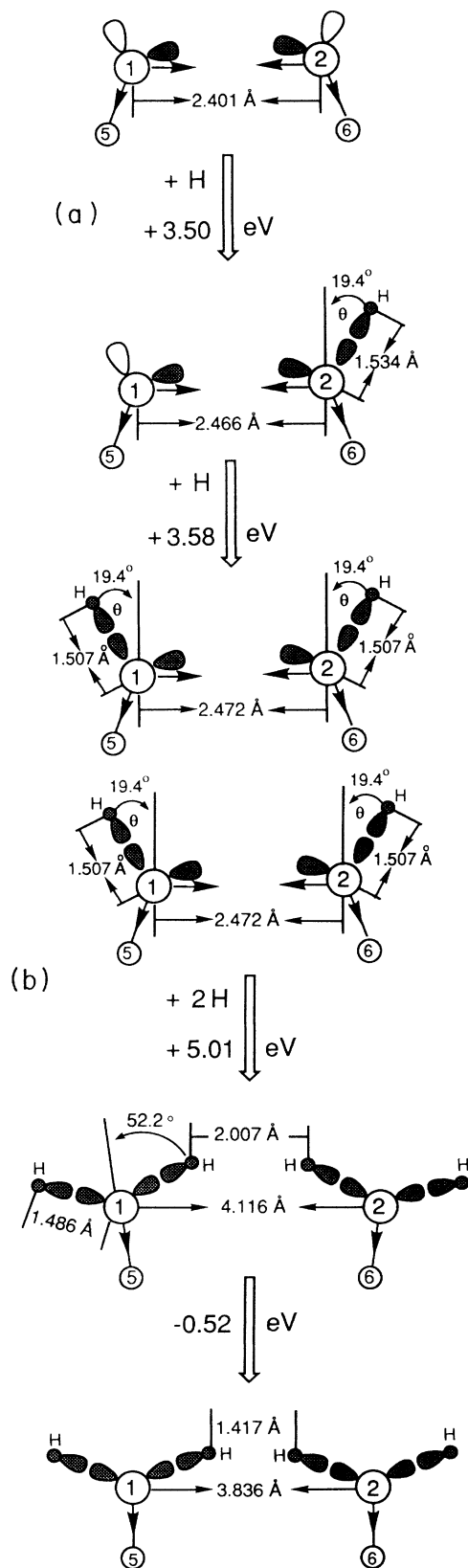


FIG. 2. The chemisorption of H atoms on the $\text{Si}_{12}\text{H}_{20}$ cluster (only the first two layers of the cluster are shown). The open orbitals represent surface dangling bonds and the shaded orbitals represent contributions to the dimer and Si-H bonds. A positive energy is exothermic.

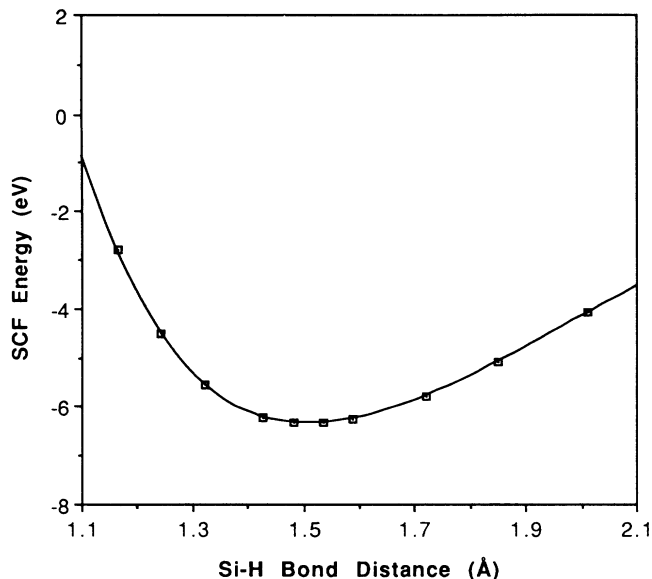


FIG. 3. The SCF energy of the cluster (relative to the cluster energy at $R_{\text{SiH}}=20$ a.u.) as a function of Si-H distance for the chemisorption of two H atoms on the cluster (simultaneous adsorption of both H atoms).

factor of 0.907. Using this scaling factor, our calculated value is corrected to 2099 cm^{-1} , in close agreement with the experimental value of 2080 cm^{-1} .

The SiH electronic-dissociation energy ($-E_{\text{ads}}$) is calculated as $E_f - E$, where E_f is the total energy of the system at $R_{\text{Si-H}}=20$ a.u. (infinite separation) and E is the total energy of the system at the optimized geometry. E_f is corrected for the H-basis superposition contribution which, in these calculations, is found to be very small, 0.02 eV. The SiH electronic-dissociation energy is found to be 3.63 eV for the chemisorption of the first H atom and 3.71 eV for the chemisorption of the second H atom. Including the zero-point vibrational energy, the dissociation energy for SiH becomes 3.50 eV for the first H and 3.58 eV for the second H. Both values are in excellent agreement with the value of 3.49 eV from experiment.⁴⁰ The smaller value of 3.0 eV, calculated by Selmani and Salahub⁴² may be due to the small unreconstructed cluster used in their calculations. Comparing with the recent theoretical studies of Nachtigall, Jordan, and Janda and Wu and Carter, our Si-H binding energies lie between the two results. Our calculated Si-H binding-energy difference between the first and the second H, 0.08 eV, is about the same as that obtained by Wu and Carter. Thus, our results support the conclusion that the first Si-H bond is nearly as strong as the second Si-H bond formed with a surface dimer.⁶

B. Dihydride phase

To determine the effect of H chemisorption on the surface reconstruction in the dihydride phase, we bring two H atoms to the monohydride surface, as shown in Fig. 2(b) and optimize the geometry of the cluster. The Si-H bond length is found to be 1.486 \AA , slightly smaller than

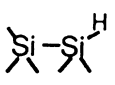
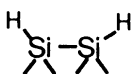
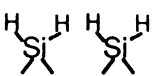
the value obtained for the monohydride phase. The angle $\langle \text{HSiH}$ is computed to be 104.4° 5.0° smaller than the corresponding tetrahedral angle. The surface Si atoms move away from each other to give the optimized geometry

$$\alpha = \alpha' = -8.11^\circ, \quad \beta = 1.1^\circ, \quad r_{\text{Si-Si}} = 4.116 \text{ \AA},$$

where $\alpha = \alpha' = -8.11^\circ$ means that both surface atoms rotate around the y axis by 8.11° away from each other. Since each surface Si atom in the dihydride phase is bonded to two H atoms, no dangling bonds remain, and there is no surface dimerization for this coverage. Furthermore, we note that the distance between two inner H atoms, each bonded to a surface Si atom, is only 1.417 \AA . Such a short distance produces repulsive interactions between surface SiH_2 groups. Indeed, our calculations show a 0.52-eV energy increase if the SiH_2 groups are rotated back to the geometry of the bulk-terminated dihydride surface, as shown in Fig. 2b. Because of the repulsive nature of the surface SiH_2 interactions, we expect the Si-Si distance between two nearest-neighbor surface Si atoms, each bonded to two H atoms, to be coverage dependent, i.e., at low coverage, when nearest-neighbor Si-Si dimers are still present, the lateral relaxation of SiH_2 groups is less constrained. Table I summarizes the optimized surface geometries for the clean Si(100) surface and surfaces at the monohydride and dihydride phases.

At low coverage, the adsorption energy of the two H

TABLE I. Si(100) 2×1 surface reconstruction with and without adsorbed hydrogen. Results of geometry optimization from total-energy (CI) calculations on a $\text{Si}_{12}\text{H}_{20}$ cluster model of the Si(100) surface. Angles α and β are defined in Fig. 1; $r_{\text{Si-Si}}$ is the Si-Si dimer bond length (\AA).

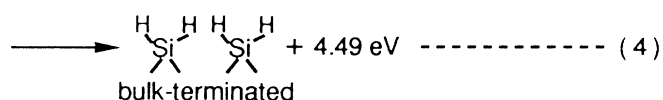
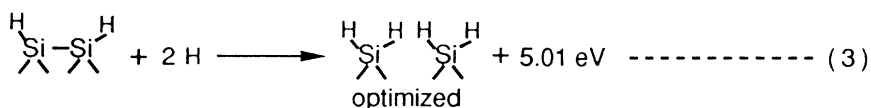
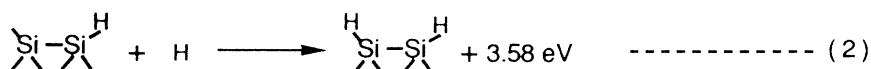
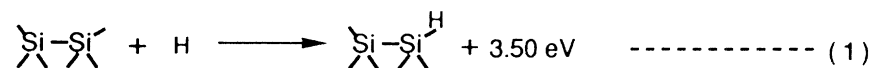
	α	β	$r_{\text{Si-Si}}$
Clean surface dimer			
Ground state (singlet)	26.67	2.4	2.401 ^a
Excited state (triplet) ^b	25.01	2.4	2.470
Dimer with one H ads.	25.11	2.4	2.466
			
Dimer with two H's ads.	24.96	2.4	2.472
			
Dihydride phase (optimized)	-8.11	1.1	4.116
			
Dihydride phase (bulk terminated)	0.00	0.0	3.836

^aExperimental values 2.45–2.54 \AA ; see Refs. 6–9.

^bThe triplet coupling of the dangling orbitals in a single-surface dimer is 0.06 eV higher in energy than the singlet coupling of the dimer orbitals.

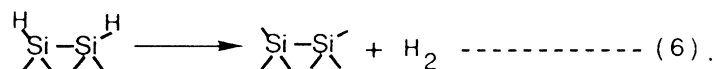
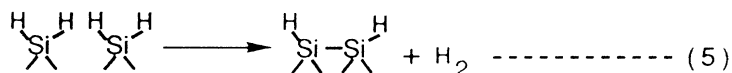
atoms is calculated as the energy difference between the two systems, $\text{Si}_{12}\text{H}_{20}\text{H}_2 + 2\text{H}$ and $\text{Si}_{12}\text{H}_{20}\text{H}_4$, each at its optimized geometry. Treating these two systems uniformly at the CI level gives an energy difference of 5.27 eV. Including the zero-point vibrational energy, the adsorption energy becomes 5.01 eV. At high coverage, the

energy of the $\text{Si}_{12}\text{H}_{20}\text{H}_4$ cluster at the bulk-terminated geometry is used to compute the adsorption energy. Because of the repulsive SiH_2 interactions, the adsorption energy is 0.52 eV smaller than that at lower coverage. Our results can be summarized as follows (including zero-point vibrational energies):



C. H_2 desorption pathway

This section considers the possible pathways of H_2 desorption from both the monohydride and dihydride phases. The overall desorption processes can be represented as



First, we consider the energetics. Using the adsorption energies in Eq. (1)–(4) and the H_2 dissociation energy of 4.48 eV, including the zero-point vibrational energy, we predict the heat of desorption for process (5) to be 0.53 eV (endothermic) at low coverage, where the SiH_2 groups relax outward, and nearly zero at high coverage when the surface Si atoms occupy the bulk-terminated positions. The heat of desorption for process (6) is calculated to be 2.6 eV (endothermic).

We now consider the pathway for H_2 desorption for each process. That for process (5) seems straightforward: the two inner H atoms form an H-H bond as they move away from the surface, and at the same time the two surface Si atoms form a dimer bond. Figure 4 shows a schematic drawing of this pathway. We expect a small desorption barrier, as indicated by the low-temperature $\beta_2\text{H}_2$ temperature-programmed desorption state.⁵

The pathway for process (6) would appear at first to be equally straightforward: the two H atoms move toward each other to form an H-H bond and then H_2 desorbs from the surface. However, the activation barrier for this pathway is very large. Wu and Carter have reported a value of about 120 kcal/mol. Our calculations indicate a barrier of 85 kcal/mol. Hence, this one-step pathway is ruled out. There exists, however, a multistep pathway

that has a much lower activation energy. This pathway, as depicted in Figs. 5(a)–5(e), involves the following steps.

(1) $a \rightarrow b$: In this step, since the dimer bond is broken, the activation energy is about the same as the dimer bond

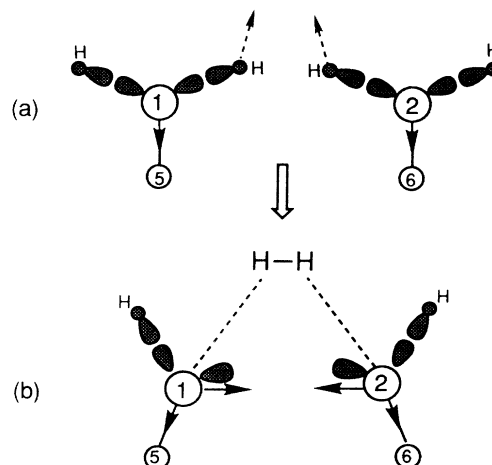


FIG. 4. Schematic drawing of the H_2 desorption pathway from the dihydride phase.

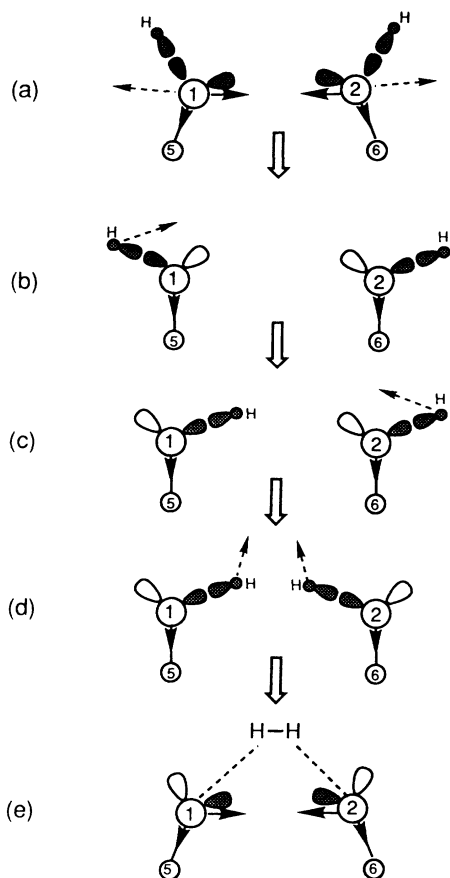


FIG. 5. Schematic drawing of the H_2 desorption pathway from the monohydride phase.

energy (~ 2.0 eV).

(2) $b \rightarrow c, d$: With the dimer bond broken, the H atoms migrate from outer dangling bonds to inner dangling bonds at a very small activation energy (~ 0.2 eV).

(3) $d \rightarrow e$: In this final step, the two inner H atoms move toward each other to form an H-H bond followed by H_2 desorption from the surface; the two surface Si atoms simultaneously form a dimer bond. Similar to process (5), this step is expected to have a small activation energy.

These steps proceed in a continuous fashion in a real

desorption process. Since the barrier for each step is small, the overall activation energy is expected to be close to the calculated heat of desorption of 2.6 eV (60 kcal/mol), which is within the range of experimentally measured values of 45–66 kcal/mol. It is possible that other pathways exist that have similar activation energies, and accurate calculations are needed to study the various possibilities. An investigation of these processes is in progress.

IV. CONCLUSIONS

The conclusions of the present study can be summarized as follows.

(1) The chemisorption of H atoms in the monohydride phase is found to change the surface reconstruction slightly, increasing the dimer length from 2.401 Å in an H-free surface to 2.466 and 2.472 Å in a dimer bonded with one and two H atoms, respectively.

(2) The Si-H bond length is calculated to be 1.534 Å for the 1-H case and 1.507 Å for the 2-H case. The Si-H bond angle is found to be 19.4° from the surface normal for both cases, within 7.5° of the dangling orbital on the clean surface. The Si-H stretch frequency is computed to be 2099 cm^{-1} , after scaling, in close agreement with the experimental value of 2080 cm^{-1} .

(3) The Si-H bond energy, subtracting the zero-point vibrational contribution, is calculated to be 3.50 eV for the chemisorption of the first H atom and 3.58 eV for the chemisorption of the second H atom. Both values are in excellent agreement with the experimental value of 3.49 eV.

(4) The chemisorption of H atoms in the dihydride phase destroys surface dimers and changes the reconstructed $Si(100)2 \times 1$ surface to the unreconstructed $Si(100)1 \times 1$ surface. The interactions between surface SiH_2 groups are found to be repulsive.

(5) Two possible H_2 desorption pathways from the monohydride and dihydride phases are proposed. The activation barriers for these pathways are expected to be within the range of experimental values.

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.

¹G. A. Somorjai, *Chemistry in Two Dimensions: Surface* (Cornell University, Ithaca, 1981).

²S. M. Gates, C. M. Greenlief, D. B. Beach, and P. A. Holbert, *J. Chem. Phys.* **92**, 3144 (1990).

³K. Sinniah, M. G. Sherman, L. B. Lewis, W. H. Weinberg, J. T. Yates, Jr., and K. C. Janda, *Phys. Rev. Lett.* **62**, 567 (1989).

⁴K. Sinniah, M. G. Sherman, L. B. Lewis, W. H. Weinberg, J. T. Yates Jr., and K. C. Janda, *J. Chem. Phys.* **92**, 5700 (1990).

⁵M. L. Wise, B. G. Koehler, P. Gupta, P. A. Coon, and S. M. George, *Surf. Sci.* **258**, 166 (1991).

⁶P. Nachtigall, K. D. Jordan, and K. C. Janda, *J. Chem. Phys.* **95**, 8652 (1991).

⁷C. J. Wu and E. A. Carter, *Chem. Phys. Lett.* **185**, 172 (1991).

⁸Z. Jing and J. L. Whitten, *Phys. Rev. B* **44**, 1741 (1991).

⁹Z. Jing and J. L. Whitten (unpublished).

¹⁰J. P. Levine, *Surf. Sci.* **34**, 90 (1973).

¹¹B. W. Holland, C. B. Duke, and A. Paton, *Surf. Sci.* **140**, L269 (1984).

¹²W. S. Yang, F. Jona, and P. M. Marcus, *Phys. Rev. B* **28**, 2049 (1983).

¹³Y. S. Shu, W. S. Yang, F. Jona and P. M. Marcus, in *The Structure of Surfaces*, edited by M. A. Van Hove and S. Y. Tong (Springer, Berlin, 1985), p. 293.

¹⁴S. Y. Tong and A. L. Maldonado, *Surf. Sci.* **34**, 90 (1973).

- ¹⁵F. J. Himpsel and D. E. Eastman, *J. Vac. Sci. Technol.* **16**, 1297 (1979).
- ¹⁶H. A. van Hoof, G. V. Hansson, J. M. Nicholls, and S. A. Flodstrom, *Phys. Rev. B* **24**, 4684 (1981).
- ¹⁷R. M. Tromp, R. G. Smeeke, and F. W. Saris, *Phys. Rev. Lett.* **46**, 939 (1980).
- ¹⁸R. M. Tromp, R. G. Smeeke, F. W. Saris, and D. J. Chadi, *Surf. Sci.* **133**, 137 (1983).
- ¹⁹R. J. Hamers, R. M. Tromp, and J. E. Demuth, *Phys. Rev. B* **34**, 5343 (1986).
- ²⁰P. Avouris, *J. Phys. Chem.* **94**, 2246 (1990).
- ²¹N. Roberts and R. J. Needs, *Surf. Sci.* **236**, 112 (1990).
- ²²Zizhong Zhu, Nobuyuki Shuma, and Masaru Tsukada, *Phys. Rev. B* **40**, 11 868 (1989).
- ²³M. T. Yin and M. L. Cohen, *Phys. Rev. B* **28**, 2049 (1983).
- ²⁴B. I. Craig and P. V. Smith, *Surf. Sci.* **218**, 569 (1989).
- ²⁵J. A. Appelbaum and D. R. Hamann, *Surf. Sci.* **74**, 21 (1978).
- ²⁶F. F. Abraham and I. P. Batra, *Surf. Sci.* **163**, L752 (1985).
- ²⁷T. Hoshino, Oikawa, Tsuda, and Ohdomari, *Phys. Rev. B* **44**, 11 248 (1991).
- ²⁸W. S. Verwoerd, *Surf. Sci.* **129**, 419 (1983).
- ²⁹W. A. Goddard III and T. C. McGill, *J. Vac. Sci. Technol.* **16**, 1308 (1979).
- ³⁰I. P. Batra, *Phys. Rev. B* **41**, 5048 (1990).
- ³¹A. Redondo and W. A. Goddard, *J. Vac. Sci. Technol.* **21**, 344 (1982).
- ³²Z. Jing and L. L. Whitten, *Surf. Sci.* **274**, 106 (1992).
- ³³H. Ibach and J. E. Rowe, *Surf. Sci.* **43**, 481 (1974).
- ³⁴T. Sakurai and H. D. Hagstrum, *Phys. Rev. B* **12**, 5349 (1975).
- ³⁵T. Sakurai and H. D. Hagstrum, *Phys. Rev. B* **14**, 1593 (1976).
- ³⁶T. Sakurai and H. D. Hagstrum, *J. Vac. Sci. Technol.* **13**, 807 (1976).
- ³⁷H. Wagner, R. Butz, U. Backes, and D. Bruchmann, *Solid State Commun.* **38**, 1155 (1981).
- ³⁸F. Stucki, J. A. Schaefer, J. R. Anderson, G. J. Plapeyre, and W. Gopel, *Solid State Commun.* **47**, 795 (1983).
- ³⁹R. Butz, E. M. Oellig, H. Ibach, and H. Wagner, *Surf. Sci.* **147**, 343 (1984).
- ⁴⁰B. G. Koehler, C. H. Mak, D. A. Arthur, P. A. Coon, and S. M. George, *J. Chem. Phys.* **89**, 1709 (1988).
- ⁴¹L. M. Raff, I. Noorbachta, and D. L. Thompson, *J. Chem. Phys.* **85**, 3081 (1986).
- ⁴²A. Selmani and D. R. Salahub, *Surf. Sci.* **202**, 269 (1988).
- ⁴³J. L. Whitten and T. A. Pakkanen, *Phys. Rev. B* **21**, 4357 (1980).
- ⁴⁴J. L. Whitten, *Phys. Rev. B* **24**, 1810 (1981).
- ⁴⁵P. Cremaschi and J. L. Whitten, *Surf. Sci.* **149**, 273 (1985).
- ⁴⁶T. H. Dunning, Jr. and P. J. Hay, *Methods of Electronic Structure Theory* (Plenum, New York, 1977), Vol. 3, p. 1.
- ⁴⁷A. Chattopadhyay, P. V. Madhavan, J. L. Whitten, C. R. Fischer, and I. P. Batra, *J. Mol. Struct.* **163**, 63 (1988).
- ⁴⁸Z. Jing, J. L. Whitten, and G. Lucovsky, *Phys. Rev. B* **45**, 13 978 (1992).
- ⁴⁹P. Ho, M. E. Coltrin, J. S. Brinkley, and C. F. Melius, *J. Phys. Chem.* **89**, 4647 (1985).

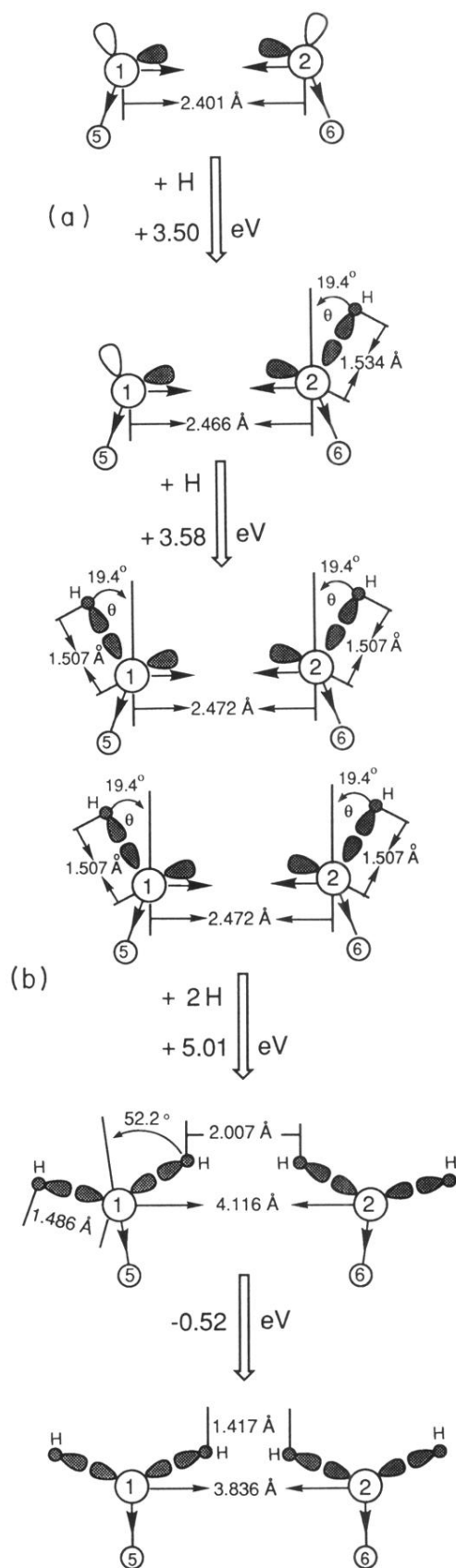


FIG. 2. The chemisorption of H atoms on the $\text{Si}_{12}\text{H}_{20}$ cluster (only the first two layers of the cluster are shown). The open orbitals represent surface dangling bonds and the shaded orbitals represent contributions to the dimer and Si-H bonds. A positive energy is exothermic.

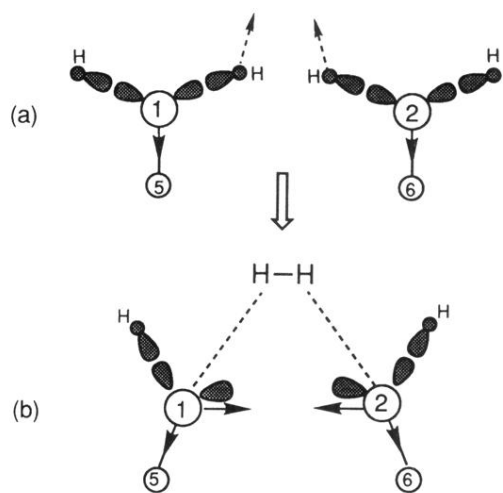


FIG. 4. Schematic drawing of the H₂ desorption pathway from the dihydride phase.

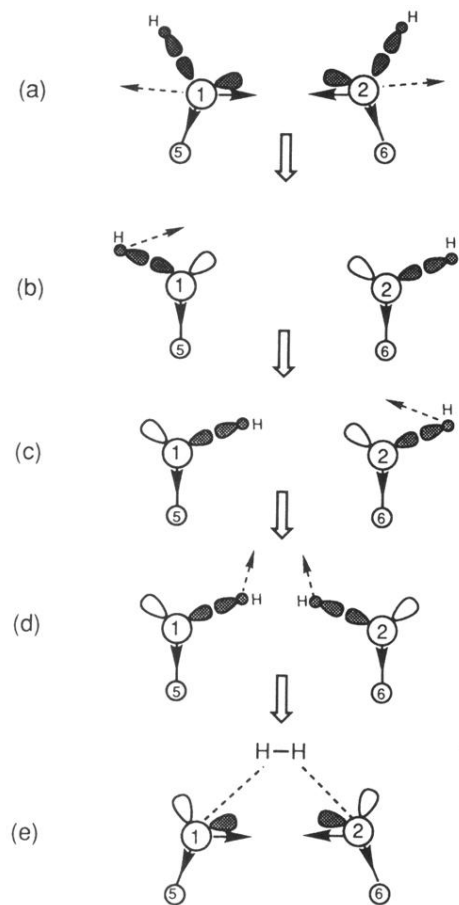


FIG. 5. Schematic drawing of the H₂ desorption pathway from the monohydride phase.