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Localized model for hydrogen chemisorption on the silicon (111) surface

K. Hermann* and P. S. Bagus
IBM Research Laboratory, San Jose, California 95193
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The interaction of a hydrogen atom with the silicon (111) surface is studied with cluster models. On the basis of *ab initio* Hartree-Fock–LCAO (linear combination of atomic orbitals) theory the electronic structure of silicon-hydrogen clusters with up to four silicon atoms is calculated where the embedding of the clusters into the substrate is simulated by surrounding hydrogen atoms. The distance of the adsorbing hydrogen perpendicular to the surface is optimized with respect to the total energy of each cluster. The adsorbate-substrate binding which is always highly covalent seems to be quite localized so that the cluster approach should be reasonable for this system. From the calculations, the adsorbate energy and the energy for adsorbate vibrations perpendicular to the surface can be determined. Our cluster results are in good agreement with those of band-structure-type studies and with experimental data.

I. INTRODUCTION

Extensive experimental and theoretical efforts are being made to understand the chemical and electronic properties of chemisorption on semiconductors. Probably the most studied system is the silicon (111) surface with chemisorbed hydrogen. It is well known from experiment[1] that atomic hydrogen is easily adsorbed on the Si (111) surface up to monolayer coverage whereas molecular hydrogen does not seem to react with the surface. During the adsorption the 2×1 reconstruction of the freshly cleaved (111) surface is removed as can be seen in low-energy electron diffraction (LEED) experiments.[1] This indicates that the silicon surface bonds are strongly affected by the presence of the chemisorbed hydrogen.

The usual interpretation of the silicon-hydrogen surface bond is based on the nature of the chemical environment at the Si (111) surface. Each surface atom has only three nearest neighbors compared to the tetrahedral four-atom environment in the bulk. This leaves one broken bond (dangling bond) per atom on the surface which causes the 2×1 reconstruction. The hydrogen stabilizing on top of the surface silicon can saturate this dangling bond and form a strong silicon-hydrogen bond so that an almost tetrahedral symmetry for the surface silicon is created. This would explain the removal of the 2×1 reconstruction during hydrogen adsorption. However, it is still unclear why the 7×7 reconstruction of the annealed surface is not completely removed after chemisorption.[2,3] Ultraviolet-photoelectron-spectroscopy (UPS) data of a freshly cleaved Si (111) surface exposed to hydrogen show an additional peak at ~11 eV below vacuum due to the presence of hydrogen.[1] Its energy is quite close to the ionization energy,[4] 12.67 eV, of the bonding T_2 orbital in gas-phase silane, SiH_4. This might be a further indication for the type of surface bond described above.

Thermal-desorption experiments give information about the strength of the silicon-hydrogen surface bond. It is found that the desorption of two hydrogen atoms on the surface combining into an H_2 molecule leads to a desorption energy of 1.7–2.0 eV per molecule.[5] Further, the vibration of adsorbed hydrogen atoms perpendicular to the surface can be measured with inelastic low-energy electron scattering. The experiment gives a vibrational energy $\hbar\omega = 257$ meV.[6]

Most of the theoretical studies of the H-Si(111) system are based on band-structure-type models[7–9] where a two-dimensionally periodic adsorbate layer corresponding to monolayer coverage is considered. Appelbaum and Hamann[10] have studied the modification of the silicon surface-state bands by the presence of the adsorbed hydrogen using a self-consistent pseudopotential method in a semi-infinite substrate. The resulting density of states can explain the adsorbate-induced peaks in the UPS spectrum of the adsorption system. The hydrogen equilibrium position and the force constant for vibrations perpendicular to the surface are determined via the Hellman-Feynman theorem and reasonable values are obtained. Pandey[8] arrives at almost the same results for the electronic situation on the basis of a semiempirical tight-binding method for a semi-infinite substrate. Ho *et al.*[9] apply a self-consistent pseudopotential method in a slab geometry where they study two different structural adsorption models, the monohydride phase (also used by Appelbaum and Hamann) and the trihydride phase.[11]

In these band-structure-type studies the binding energy of the adsorbed hydrogen has not been given. The reason is that the binding energy has to be determined by comparing the total energy of the substrate with and without the adsorbate. Unfortunately, the computation of total energies by band-structure methods is extremely difficult and yields rather inaccurate results. Thus, small differences of the total energy like a binding energy are almost impossible to calculate. This applies also to the multiple-scattering$-X_\alpha$ (MS-X_α) method which has been used in a cluster study of the adsorption system.[12]

In the present paper we treat the adsorption system on the basis of cluster models where the interaction of a single adatom with the substrate is considered. Here it is assumed that the adsorbate-substrate interaction is localized on a few substrate atoms near the surface. Then this interaction can be described with a fictive molecule (cluster) which contains only the adsorbate and a few substrate atoms. The coupling of this "surface molecule" to the rest of the substrate can be neglected if the cluster is large enough.

We examine the chemisorptive hydrogen-silicon interaction in three model clusters of different size. *Ab initio* Hartree-Fock–LCAO calculations are used to determine the electronic structure. The hydrogen equilibrium position, its binding energy, and the energy for hydrogen vibrations perpendicular to the surface are obtained for each of the three clusters. We find that the chemisorptive Si-H bond is always highly covalent as one would expect. In the larger clusters the data for the energetic and geometric quantities are quite similar, thus indicating that the chemisorptive interaction is highly localized. Therefore, the cluster approach seems to be appropriate. Our result for the adsorbate equilibrium position is in good agreement with the theoretical value obtained by Appelbaum and Hamann.[10] The computed hydrogen binding energy and the energy for vibrations perpendicular to the surface compare well with the respective experimental data.

In Sec. II we discuss the computational details of our calculations and in Sec. III we present the results. In Sec. III A we present our results for the separated systems, the free-adsorbate atom and the substrate clusters; in Sec. III B the results for the interacting adsorbate-substrate systems are given. Finally, in Sec. IV the conclusions for the hydrogen adsorption on the silicon (111) surface are summarized.

II. COMPUTATIONAL DETAILS

As mentioned before, it is generally accepted that the atomic hydrogen stabilizes on the silicon (111) surface directly above a silicon atom of the first layer. For this situation, we consider three hydrogen-silicon clusters of different size. The smallest cluster is the diatomic SiH. The binding situation in this molecule should give a rough idea of the hydrogen-silicon binding on the surface. However, the silicon surface atom sees three nearest neighbors of the second layer in a tetrahedral geometry. This environmental geometry should affect the electronic structure of the surface atom as it does in the bulk where sp^3 hybrid orbitals are formed (compared to the s and p orbitals of the free-silicon atom). To account for this geometry effect on the surface atom in a first approximation, we simulate the nearest-neighbor environment by three hydrogen atoms in a tetrahedral orientation. This defines the second cluster, $(SiH_3)H$, which is in its composition identical to the silane molecule SiH_4. The simulation of the Si-Si binding by Si-H bonds seems to be reasonable because the Si-H bond strength (3.1 eV)[13] is not too different from the Si-Si bond strength (3.3 eV).[13] This embedding procedure was first used for cluster calculations modeling bulk Si.[14]

In a third cluster we include, in addition to the surface silicon, its three nearest neighbors. Each of these atoms belonging to the second layer of the crystal possesses a complete bulk environment of four atoms: the central and two peripheral surface atoms (first layer) and one atom of the third layer. Here we simulate the peripheral surface atoms and the third layer atoms by hydrogens. Together with the adsorbing hydrogen, this gives a $(Si_4H_9)H$ cluster. Figure 1

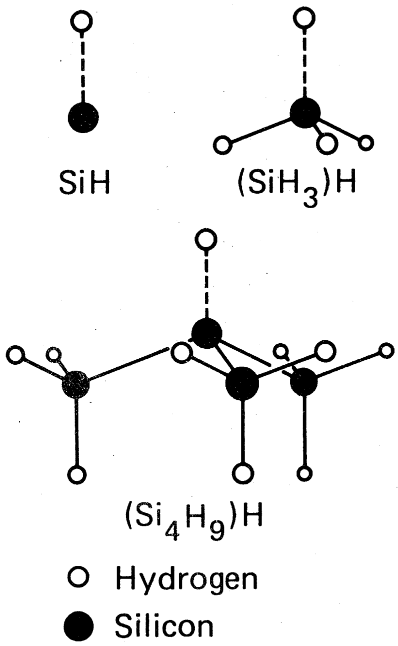

FIG. 1. Size and structure of the three adsorption clusters used in this study. The adsorbing hydrogen atom is always on top of the central silicon atom in the cluster.

shows the structure of the clusters used in this study. In order to obtain a reference state for infinite adsorbate-substrate separation, we also study atomic hydrogen, silicon and the "substrate" clusters SiH_3 and Si_4H_9.

In all three adsorption clusters the Si-H distance of the adsorbing hydrogen is optimized with respect to the cluster total energy whereas the Si-H distance of the hydrogens simulating the cluster environment [three atoms in $(SiH_3)H$ and nine in $(Si_4H_9)H$] is set equal to the experimental distance in silane $d_{\text{Si-H}} = 2.80$ a.u.[15] The Si-Si distance in $(Si_4H_9)H$ is chosen to be the experimental nearest-neighbor distance in bulk silicon $d_{\text{Si-Si}} = 4.44$ a.u.[16]

For the calculation of the electronic states in the clusters, we use the self-consistent-field (SCF) Hartree-Fock (HF) LCAO method described by Roothaan for both closed[17] and open shell[18] systems. It has proven to give reasonably accurate results for both geometric and energetic quantities in a large number of free molecules.[19] Thus, it seems reasonable to apply this method to surface clusters. The SCF-HF-LCAO method is implemented in the program system MOLALCH[20] which is used for all calculations of the present study.[21]

The contracted Gaussian basis set for silicon was taken from HF calculations on the free atom.[22] Here 10 s and 6 p functions were contracted to (6,4) in the usual way[23] and one d function[24] (exponent $\alpha = 0.3$) has been added. The basis set for hydrogen was taken from a cluster study on the hydrogen chemisorption on Be(0001).[25] For those hydrogens simulating the crystalline environment in the clusters, a $4s$ basis contracted to $2s$ was used. This basis was expanded by one p function (exponent $\alpha = 1.0$)[24] in the case of the adsorbing hydrogen to allow for more flexibility in forming the chemisorptive Si-H bond. On the whole, the basis sets used in the present calculations are of or better than "double-ζ" quality[19]; it is very unlikely that the results obtained will change significantly if larger basis sets are used.

The symmetry behavior of the three clusters is described by the point group $C_{\infty v}$ (SiH) and by C_{3v} [$(SiH_3)H$ and $(Si_4H_9)H$], respectively. Thus in all calculations, symmetry adapted basis functions are used. For computational reasons, we did not take advantage of the full symmetry in the clusters with C_{3v} symmetry. Here we used basis functions transforming according to the irreducible representations of the C_s point group. However, it turned out that the computed orbitals all reflected the C_{3v} symmetry quite accurately.

For the electronic structure of the larger clusters, we consider only low-spin wave functions as possible ground states, i.e., singlet states for $(SiH_3)H$ and $(Si_4H_9)H$ and doublet states for SiH_3 and Si_4H_9. Wave functions of higher multiplicity are not likely to be ground states, since we do not expect these clusters to show any magnetic behavior.

III. RESULTS AND DISCUSSION

A. Free adsorbate and substrate clusters

The computed total energy E_{tot} of the ground states for the free-hydrogen atom, the silicon atom, and the substrate clusters SiH_3 and Si_4H_9 are given in Table I. The value of E_{tot} for the hydrogen atom deviates from the exact result (0.5 Hartree) by less than 0.07 eV. Also, the result for the silicon atom is quite close to the original value obtained with the uncontracted basis set (−288.773 Hartree).[22]

Detailed information about the electronic structure of different atoms in the cluster can be obtained from Mulliken's population analysis.[26] Table II gives the gross atomic populations for the substrate clusters SiH_3 and Si_4H_9. The data for the total populations indicate that the atoms remain mostly neutral in the clusters, the bonds formed between these atoms being mainly covalent. The redistribution of $3s$- and $3p$-type electrons in the silicon of SiH_3 compared to the free atom is due to the formation of sp^3 hybrid orbitals that determine the Si-H binding in the cluster. The same effect also causes the redistribution of the $3s$- and $3p$-type silicon electrons in Si_4H_9. How-

TABLE I. Electronic ground states and total energies E_{tot} of the hydrogen and silicon atom and the substrate clusters SiH_3 and Si_4H_9.

Cluster	Point-Group Symmetry	Ground State	E_{tot} (Hartree)
H	O(3)	^2S	−0.4977
Si	O(3)	^3P	−288.7323
SiH_3	C_{3v}	$^2A_1$	−290.5043
Si_4H_9	C_{3v}	$^2A_1$	−1160.4621

TABLE II. Distribution of the valence electrons on the different atoms in the substrate clusters and its decomposition into *s*, *p*, and *d* contributions. The values are obtained from a gross population analysis. (Note that the *d* population includes contributions of *s* character from the $x^2+y^2+z^2$ combination.)

Cluster	Contribution	$N(\mathrm{Si}_{(1)})^{\mathrm{a}}$	$N(\mathrm{Si}_{(2)})^{\mathrm{b}}$	$N(\mathrm{H}_{(1)})$	$N(\mathrm{H}_{(2)})^{\mathrm{d}}$
SiH_3	*s*	1.29	...	1.02[b]	...
	p	2.46	...	...	...
	d	0.20	...	...	...
	total	3.95	...	1.02[b]	...
$\mathrm{Si}_4\mathrm{H}_9$	*s*	1.23	1.03	1.02[c]	1.02
	p	2.74	2.51	...	...
	d	0.20	0.35	...	...
	total	4.17	3.89	1.02[c]	1.02

[a] Central atom of the first layer.

[b] Neighboring atom of the second layer.

[c] Atom of the first layer.

[d] Atom of the third layer.

ever, in $\mathrm{Si}_4\mathrm{H}_9$ the electronic structures of the central (first layer) silicon $\mathrm{Si}_{(1)}$ and the three neighboring (second layer) silicons $\mathrm{Si}_{(2)}$ are slightly different. This can be understood by the difference in the geometry of these atoms. The $\mathrm{Si}_{(1)}$ atom has a nearest-neighbor environment of three silicon atoms whereas each of the $\mathrm{Si}_{(2)}$ atoms is surrounded by one silicon and three hydrogen atoms which must necessarily lead to a somewhat different bonding situation. In particular, the $\mathrm{Si}_{(1)}$ becomes slightly negative (~ -0.2) and the $\mathrm{Si}_{(2)}$ slightly positive (~ 0.1). From electrostatic arguments, this indicates an attractive force between the two kinds of Si atoms with a tendency to pull the first layer atom towards the second layer. This inward relaxation of the first layer atoms on a pure Si(111) surface has first been proposed by Appelbaum and Hamann[27] in band-structure-type calculations. A tendency towards this effect seems to also exist in our cluster model. However, larger clusters as well as a variation of the position of the surface atoms in these clusters have to be considered to substantiate our findings.

TABLE III. Energy range of the silicon valence levels in the substrate clusters. The quantity ϵ_b (ϵ_t) gives the energy of the lowest (highest) occupied Si-type valence level and the energy range $\Delta\epsilon$ is defined by $\Delta\epsilon=\epsilon_t-\epsilon_b$.

Cluster	ϵ_b (Hartree)	ϵ_t (Hartree)	$\Delta\epsilon$ (eV)
Si	−0.5271	−0.2865	6.55
SiH_3	−0.7044	−0.3480	9.70
$\mathrm{Si}_4\mathrm{H}_9$	−0.7759	−0.3329	12.05

There are no strong electronic edge effects in our substrate clusters as have been found in cluster studies of metallic adsorption systems.[25,28,29] This is likely due to our use of H atoms to simulate the extended crystalline environment. The absence of edge effects suggests that the electronic structure in the silicon clusters might not change too drastically if the cluster size is increased beyond the maximum size used in this study. Interestingly, the energy difference $\Delta\epsilon$ between the highest and lowest occupied level of Si-type orbitals in the largest cluster $\mathrm{Si}_4\mathrm{H}_9$ ($\Delta\epsilon=12.0$ eV, see Table III) is quite close to the energy range of the silicon bulk valence band where from band-structure calculation a value of 12.6 eV is obtained[30] and x-ray photoelectron measurements (XPS) give 12.5 eV.[31] However, it is clear that our clusters are still too small to represent a bulk-like electronic situation.

B. Adsorption clusters

Our results for the cluster ground states are given in Table IV for SiH, $(\mathrm{SiH}_3)\mathrm{H}$, and $(\mathrm{Si}_4\mathrm{H}_9)\mathrm{H}$. Here, we report the equilibrium distance, $d_{\min}$, of adsorbing hydrogen and the total energy E_{tot} at $d_{\min}$. The data for the diatomic SiH agree fairly well with those of a different SCF study on this molecule by Wirsam[32] who used basis sets of comparable accuracy. He finds $d_{\min}=2.87$ a.u. and $E_{\mathrm{tot}}=-289.3150$ Hartree. The $(\mathrm{SiH}_3)\mathrm{H}$ cluster is, in its composition, identical to SiH_4, as has been mentioned before. In fact, the SiH_3 part of this cluster was required to have the same geometry as in SiH_4, and only the adsorbing hydrogen was varied in its distance with respect to the central silicon. It turns out that the $(\mathrm{SiH}_3)\mathrm{H}$ cluster with the adsorbing hydrogen in its equilibrium posi-

TABLE IV. Electronic ground state, total energy E_{tot}, and equilibrium position d_{min}, of the adsorbing hydrogen. The value of d_{min} (in bohrs) gives the distance between the central silicon and the adsorbing hydrogen.

Cluster	Point Group Symmetry	Ground State	E_{tot} (Hartree)	d_{min} (a.u.)
SiH	$C_{\infty v}$	$^2\Pi$	−289.3094	2.893
$(SiH_3)H$	C_{3v}	$^1A_1$	−291.1252	2.795
$(Si_4H_9)H$	C_{3v}	$^1A_1$	−1161.0732	2.808

tion is geometrically almost identical to SiH_4, as one would expect. The slight asymmetry in this cluster ($d_{\text{Si-H}} = 2.795$ a.u. for the adsorbing and 2.80 a.u. for the other three hydrogens) comes from the fact that a somewhat more flexible basis set is used for the adsorbing hydrogen compared to the others. However, this effect is very small, as can be seen from a comparison with SCF calculations on SiH_4 by Rothenberg *et al.*[33] They obtain with basis sets of greater flexibility a total energy $E_{\text{tot}} = -291.2355$ Hartree at $d_{\text{Si-H}} = 2.796$ a.u. compared to $E_{\text{tot}} = -291.1252$ Hartree of the present study.

The hydrogen equilibrium distance d_{min} for the $(SiH_3)H$ and $(Si_4H_9)H$ clusters are almost identical, whereas the respective value for the diatomic SiH is somewhat larger (cf. Table IV). This indicates a difference in the Si-H binding to the adsorbing hydrogen in the diatomic SiH compared to the larger clusters which also becomes evident from the population analysis results. Table V gives the gross atomic populations for the adsorption clusters. The data show that the hybridization of $3s$ and $3p$ orbitals on the central $Si_{(1)}$ which partly characterizes the Si-H binding to the adsorbing hydrogen is different for the SiH and the two larger clusters. In SiH this hybridization leads to a population on the $Si_{(1)}$ which is almost atomiclike, whereas in the larger clusters, the $3s$ contribution becomes smaller and the $3p$ contribution becomes larger (more nearly sp^3) compared to the free atom. More quantitative information about the binding situation in these clusters requires a detailed knowledge of the electronic structure which goes beyond a rather qualitative population analysis.

A closer inspection of the occupied valence orbitals in the adsorption clusters fully reveals the binding situation of the adsorbing hydrogen. In SiH the almost purely covalent binding comes from two doubly occupied orbitals which are mainly characterized by

TABLE V. Distribution of the valence electrons on the different atoms in the adsorption clusters and its decomposition into s, p, and d contributions. The values are obtained from a gross population analysis. (Note that the d population includes contributions of s character from the $x^2+y^2+z^2$ combination.)

Cluster	Contribution	N(H)[a]	$N(Si_{(1)})$[b]	$N(Si_{(2)})$[c]	$N(H_{(1)})$	$N(H_{(2)})$[e]
SiH	s	1.05	1.95	. . .	. . .	. . .
	p	0.01	1.99	. . .	. . .	. . .
	d	. . .	0.00	. . .	. . .	. . .
	total	1.06	3.94	. . .	. . .	. . .
$(SiH_3)H$	s	1.08	1.10	. . .	1.03[c]	. . .
	p	0.01	2.41	. . .	. . .	. . .
	d	. . .	0.30	. . .	. . .	. . .
	total	1.09	3.81	. . .	1.03[c]	. . .
$(Si_4H_9)H$	s	1.03	1.00	1.03	1.02[d]	1.02
	p	0.01	2.78	2.53	. . .	. . .
	d	. . .	0.32	0.35	. . .	. . .
	total	1.04	4.10	3.91	1.02[d]	1.02

[a] Adsorbing hydrogen.
[b] Central atom of the first layer.
[c] Neighboring atom of the second layer.
[d] Atom of the first layer.
[e] Atom of the third layer.

Si(3s) +H(1s) and by Si(3p_z) −Si(3s) +H(1s). This situation is qualitatively described by a mixing of a silicon sp_z hybrid with the hydrogen 1s orbital. In contrast, the binding valence orbitals in both $(SiH_3)H$ and in $(Si_4H_9)H$ are mainly determined by a mixing of the H(1s) orbital with sp^3-type silicon orbitals with tetrahedral geometry. This comes very close to the usual interpretation of the Si-H binding on the silicon (111) surface as a saturation of the broken silicon bond per atom.

The different binding situation in SiH compared to the larger adsorption clusters explains the discrepancies in our results for the hydrogen equilibrium distance $d_{\min}$ (cf. Table IV). It also has consequences for the energetic quantities of the clusters, as will be shown in the following.

The binding curves for the three adsorption clusters are shown in Fig. 2. Here the cluster total energy for a given distance $d_{\text{Si-H}}$ of the adsorbing hydrogen to the central silicon is given with respect to the sum of the total energies of the separated H atom and the substrate cluster. The energy at the minimum of each curve defines the hydrogen binding energy D. The respective numerical values are given in Table VI. It is quite obvious from these data that the different Si-H binding situation in the clusters leads to large variations in the hydrogen binding energy. The value for the SiH cluster is much smaller compared to those of the larger clusters. On the other hand, the results for $(SiH_3)H$ and for $(Si_4H_9)H$ differ only by about 10% which might indicate that the adsorbate binding will not be modified substantially if the adsorption cluster is further increased by adding substrate atoms.

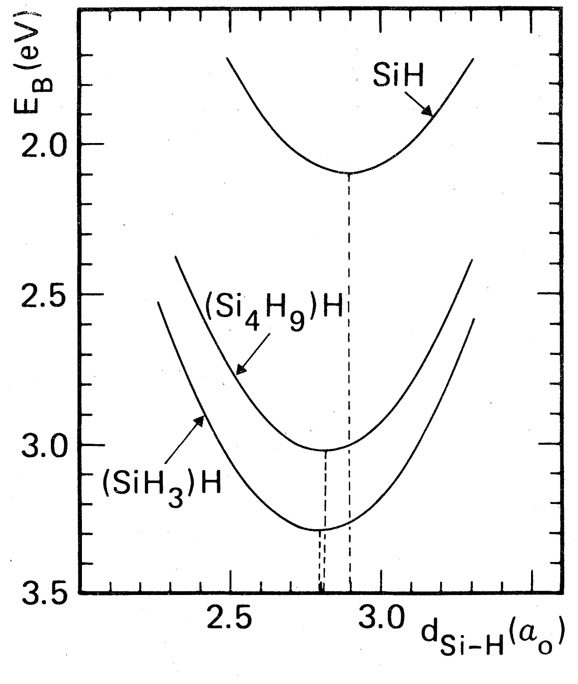

FIG. 2. Hydrogen binding energy as a function of the adsorbing hydrogen distance $d_{\text{Si-H}}$ to the central silicon in the cluster.

TABLE VI. Hydrogen binding energies D for the adsorption clusters. The quantity D gives the dissociation energy taken from the binding curves in Fig. 2. The experimental value is obtained from thermal desorption measurements as described in the text.

Cluster	D (eV)
SiH	2.10
$(SiH_3)H$	3.29
$(Si_4H_9)H$	3.02
Experiment	3.1−3.2

The binding energies D of Table VI cannot be directly compared with experimental results from thermal desorption measurements,[5] because in the experiment the desorbing hydrogen atoms immediately react to form molecular hydrogen H_2 which is observed. Thus the energetic data from the experiment refer to a process

$$2H_{\text{ads}} \rightarrow H_2 , \qquad (1)$$

where H_{ads} denotes the adsorbed atom on the surface. In contrast, our cluster calculations describe a transition

$$H_{\text{ads}} \rightarrow H_{\text{atom}} . \qquad (2)$$

In order to compare our calculated value of D with experiment, we must convert the experimentally derived value for desorption to H_2, denoted $D_{\text{ads}}(H_2)$, into desorption to H atoms, denoted $D_{\text{ads}}(H)$. The relation is

$$D_{\text{ads}}(H) = [D_{\text{ads}}(H_2) + D_e(H_2)]/2 ,$$

where $D_e(H_2)$ (=4.477 eV)[34] is the experimental dissociation energy of H_2. From the measured values[5] of $D_{\text{ads}}(H_2) = 1.7-2.0$ eV, we obtain $D_{\text{ads}}(H) = 3.1-3.2$ eV. Our results for the $(SiH_3)H$ and $(Si_4H_9)H$ clusters agree quite well with this value as shown in Table VI. This indicates that the cluster data for the hydrogen binding energy are consistent with the experimental findings. However, for a detailed study of the desorption process (1), extended calculations on larger clusters with more than one adsorbate atom are necessary.

From the binding curves shown in Fig. 2 the parameters for hydrogen vibrations perpendicular to the surface can be obtained. For a comparison of the three adsorption clusters, we suppose that the respective substrate part is rigidly connected to the rest of the substrate with infinite mass. Then the vibrational energy $\hbar\omega$ is given, in the harmonic approximation, by

$$\hbar\omega = \hbar(\kappa/m_{\mathrm{H}})^{1/2} ,$$

where κ is the curvature of the binding curve at equilibrium distance $d_{\min}$ and m_{H} is the mass of the hydrogen. The results are given in Table VII.

If we take into account the finite silicon mass in $^{28}\mathrm{Si}^{1}\mathrm{H}$, i.e., if we replace the hydrogen mass m_{H} by the reduced mass $m=(1/m_{\mathrm{H}}+1/m_{\mathrm{Si}})^{-1}$ we find a vibrational energy $\hbar\omega = 264.8$ meV which is in good agreement with the result of an *ab initio* study (272 meV).[32] The experimental value is $\hbar\omega = 253$ meV.[32]

It is evident from Table VII that the discrepancy in the electronic structure between SiH and the two larger clusters which affects the adsorbate equilibrium distance and its binding energy also influences the vibrational parameters. The curvature κ of the binding curve at minimum distance and thus the vibrational energy $\hbar\omega$ are smaller for SiH than they are for $(\mathrm{SiH_3})\mathrm{H}$ and $(\mathrm{Si_4H_9})\mathrm{H}$. On the other hand, the values of κ and $\hbar\omega$ are almost identical for the larger two clusters. This seems to be a further indication that the adsorbate-substrate binding is sufficiently localized so that it will not be strongly affected if the clusters are increased by adding substrate atoms.

The vibration of the adsorbed hydrogen perpendicular to the Si(111) surface can be measured with inelastic low-energy-electron scattering electron loss spectroscopy (ELS). The experiment gives a vibrational energy $\hbar\omega = 257$ meV,[6] which differs from our larger cluster values (~ 280 meV) by 10%. For molecules, the vibrational energies computed with the HF method are characteristically about 5–10% too large. (This is seen from the results given above for SiH.) Thus the fact that our $(\mathrm{SiH_3})\mathrm{H}$ and $(\mathrm{Si_4H_9})\mathrm{H}$ cluster values for $\hbar\omega$ are 10% larger than the experimental ELS value for H-Si(111) is probably a consequence of errors in the HF method rather than due to the limited cluster size. Roughly the same accuracy is obtained in the band-structure-type study by Appelbaum and Hamann.[10]

TABLE VII. Parameters for hydrogen vibrations perpendicular to the surface. Here, κ is the curvature of the adsorption cluster binding curve $E_B(d)$ at equilibrium distance $d_{\min}$ (see Fig. 2). The vibrational energies $\hbar\omega$ are determined in harmonic approximation for a rigid substrate cluster assumed to have infinite mass.

Cluster	κ (Hartree/a_0^2)	$\hbar\omega$ (cm^{-1}; meV)	
SiH	0.16796	2099	260
$(\mathrm{SiH_3})\mathrm{H}$	0.19969	2288	284
$(\mathrm{Si_4H_9})\mathrm{H}$	0.19720	2274	282

IV. CONCLUSIONS

The present Hartree-Fock SCF calculations on the adsorption clusters SiH, $(\mathrm{SiH_3})\mathrm{H}$, and $(\mathrm{Si_4H_9})\mathrm{H}$ as well as the respective substrate clusters give insight into the nature of chemisorption of hydrogen on the silicon (111) surface. Clearly, the substrate clusters used here are too small to reproduce all details of the electronic situation on the surface. However, it is interesting to note that in the largest substrate cluster $\mathrm{Si_4H_9}$ the purely covalent bonds between the silicons are described by orbitals similar to sp^3-type orbitals that are present in the bulk material. Also, the width of the valence energy region in $\mathrm{Si_4H_9}$ is comparable to the valence bandwidth in bulk silicon.

The interaction of hydrogen with the substrate clusters should converge more rapidly than the bulk parameters as the cluster size is increased if we assume the hydrogen-silicon surface interaction to be sufficiently localized. In the cluster model the adsorption properties are determined by differences in the properties of the two systems (Sub)H and Sub + $\mathrm{H_{atom}}$ where Sub stands for the substrate cluster. In this case, we expect the difference between the substrate cluster and the surface to cancel in first approximation.

The binding of the adsorbing hydrogen to the substrate which is always highly covalent differs for the smallest model cluster SiH compared to the larger models where the substrate environment of the surface silicon atom is included to some extent. The difference which can be seen in population analyses is also reflected in the results for the adsorbate equilibrium positon, its binding energy, and its vibrational parameters with respect to the surface. This suggests that the nearest-neighbor environment of the silicon surface atom is quite important for the adsorbate-substrate interaction. On the other hand, the adsorption data for the $(\mathrm{SiH_3})\mathrm{H}$ and the $(\mathrm{Si_4H_9})\mathrm{H}$ models are very close to each other which may indicate that the hydrogen-silicon surface bond is rather independent of substrate atoms further away from the adsorption site. Thus, model clusters as small as $(\mathrm{Si_4H_9})\mathrm{H}$ already give a good first approximation to the adsorption interaction. In this work the embedding of the surface cluster into the rest of the substrate is simulated by the surrounding hydrogen atoms. This approach appears to be adequate for the present system, and further treatment of the embedding is likely to be of minor importance. This could also be rationalized from the fact that there are no strong charge redistributions on the edge atoms of our clusters (edge effects) which have been found in cluster studies on other adsorption systems.[25,28,29]

The $(Si_4H_9)H$ cluster results for the hydrogen equilibrium position agree very well with those of an extended band-structure study of the adsorption system.[10] Further, the value for the adsorbate binding energy seems to be consistent with flash desorption data,[5] and the vibrational parameters are in good agreement with results from ELS experiments.[6] Altogether, the present cluster study seems to indicate that the adsorption of hydrogen on the silicon (111) surface is a good example for an adsorption process governed by a strongly localized adsorbate-substrate interaction and therefore can be described reasonably well by small cluster models. However, a more detailed study of the adsorption or desorption reaction path itself would require larger clusters including several adsorbate atoms to account for the direct and indirect adsorbate-adsorbate interaction. Calculations of this kind are expensive on the basis of *ab initio* methods but they might become possible with semiempirical schemes.

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[*] Permanent address: Inst. f. Theor. Phys. B, TU Clausthal, 3392 Clausthal-Zellerfeld, West Germany.

[1] H. Ibach and J. E. Rowe, Surf. Sci. 43, 481 (1974).

[2] T. Sakurai and H. D. Hagstrum, Phys. Rev. B 12, 5349 (1975).

[3] J. E. Rowe, Surf. Sci. 53, 461 (1975).

[4] R. G. Cavell, S. P. Kowalczyk, L. Ley, R. A. Pollak, B. Mills, D. A. Shirley, and W. Perry, Phys. Rev. B 7, 5313 (1973).

[5] M. Henzler and G. Schulze (unpublished).

[6] H. Froitzheim, H. Ibach, and S. Lehwald, Phys. Lett. A 55, 247 (1975).

[7] J. A. Appelbaum and D. R. Hamann, Rev. Mod. Phys. 48, 479 (1976).

[8] K. C. Pandey, Phys. Rev. B 14, 1557 (1976).

[9] K. M. Ho, M. L. Cohen, and M. Schlüter, Phys. Rev. B 15, 3888 (1977).

[10] J. A. Appelbaum and D. R. Hamann, Phys. Rev. Lett. 34, 806 (1975).

[11] K. C. Pandey, T. Sakurai, and H. D. Hagstrum, Phys. Rev. Lett. 35, 1728 (1975).

[12] I. P. Batra and S. Ciraci, Phys. Rev. Lett. 34, 1337 (1975).

[13] *Handbook of Chemistry and Physics,* 56th ed., edited by R. C. Weast (Chemical Rubber, Cleveland, 1975), p. F215.

[14] B. Cartling, B. Roos, and U. I. Wahlgren, Chem. Phys. Lett. 58, 1066 (1973).

[15] D. R. J. Boyd, J. Chem. Phys. 23, 922 (1955).

[16] R. W. G. Wyckoff, *Crystal Structures,* 2nd ed. (Interscience, New York, 1964), Vol. II.

[17] C. C. J. Roothaan, Rev. Mod. Phys. 23, 69 (1951).

[18] C. C. J. Roothaan, Rev. Mod. Phys. 32, 179 (1960); C. C. J. Roothaan, and P. S. Bagus, Methods Comp. Phys. 2, 47 (1963).

[19] H. F. Schaefer III, *The Electronic Structure of Atoms and Molecules* (Addison-Wesley, Reading, Mass., 1972).

[20] The MOLALCH program package incorporates the MOLECULE integral program and the ALCHEMY SCF program. MOLECULE was written by J. Almlöf (University of Uppsala), ALCHEMY SCF by P. S. Bagus and B. Liu (IBM Research Laboratories, San Jose). The interfacing of the programs was performed by U. Wahlgren (University of Uppsala) and by P. S. Bagus. The wave-function contour plot part was written by K. Hermann (University of Clausthal).

[21] All calculations are performed for spin-restricted (see Refs. 16 and 17) HF wave functions.

[22] B. Roos and P. Siegbahn, Theor. Chim. Acta 17, 209 (1970).

[23] T. H. Dunning, J. Chem. Phys. 53, 2823 (1970).

[24] Following B. Roos and P. Siegbahn, Theor. Chim. Acta 17, 199 (1970).

[25] C. W. Bauschlicher, P. S. Bagus, and H. F. Schaefer III, IBM Research Report RJ 2131 (1977); IBM J. Res. Develop. 22, 213 (1978).

[26] R. S. Mulliken, J. Chem. Phys. 23, 1833, 1841, 2338, 2343 (1955).

[27] J. A. Appelbaum and D. R. Hamann, Phys. Rev. Lett. 31, 106 (1973).

[28] K. Hermann and P. S. Bagus, IBM Research Report RJ 2077 (1977), Phys. Rev. B 17, 4082 (1978).

[29] K. Hermann, Proceedings of the 3rd International Conference on Solid Surfaces, Vienna 1977, p. 943 (unpublished).

[30] M. L. Cohen and T. K. Bergstresser, Phys. Rev. 141, 789 (1966).

[31] J. Chelikowsky, D. J. Chadi, and M. L. Cohen, Phys. Rev. B 8, 2786 (1973).

[32] B. Wirsam, Chem. Phys. Lett. 10, 180 (1971).

[33] S. Rothenberg, R. H. Young, and H. F. Schaefer III, J. Am. Chem. Soc. 92, 3243 (1970).

[34] A. G. Gaydon, *Dissociation Energies and Spectra of Diatomic Molecules* (Chapman and Hall, London, 1968).