

## Hydrogen chemisorption on Si(111)

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Valence-electron energy spectra of two different structural models for hydrogen adsorption on Si(111) surfaces are calculated employing self-consistent pseudopotentials. The two structural models correspond to attaching hydrogen atoms to one (monohydride) or three (trihydride) silicon dangling bonds per substrate surface atom. The spectral results for the monohydride phase are in excellent agreement with earlier calculations and with experimental data obtained on hydrogenated surfaces starting with clean annealed  $7 \times 7$  surfaces. It has recently been proposed by Pandey *et al.* that the drastic spectral changes occurring for hydrogen adsorbed on  $1 \times 1$  quenched surfaces may be accounted for by the trihydride model. While the present calculations basically confirm this result, some discrepancies remain between the experimental and theoretical spectra. Possible explanations for the discrepancies are given.

### I. INTRODUCTION

As part of our present effort to quantitatively understand the physics and chemistry of semiconductor surfaces, we report in this paper self-consistent quantum-mechanical calculations of different structural models for hydrogen-atom chemisorption on Si(111) surfaces.

Hydrogen chemisorption on Si(111) surfaces has recently become the subject of extensive studies. Because of its believed simplicity, the system was regarded as basic and fundamental for chemisorption processes. Following older experimental studies,<sup>1,2</sup> Ibach and Rowe<sup>3</sup> first applied ultraviolet photoemission spectroscopy (UPS) to the system. From additional low-energy-electron diffraction studies, it was found that hydrogen atoms readily form a monolayer with  $1 \times 1$  structure on freshly cleaved Si(111)  $2 \times 1$  surfaces. Further studies on annealed Si(111)  $7 \times 7$  surfaces,<sup>4,5</sup> in contrast, indicate the persistence of  $7 \times 1$  superstructures grouped into domains after chemisorption.

While the UPS measurements<sup>3</sup> on the freshly cleaved surface reveal the appearance of only one broad peak at about 6.5 eV below valence-band maximum after hydrogenation, for the annealed surface two main peaks are resolved around -4.8 and -7.0 eV. The latter results have been interpreted first by a self-consistent pseudopotential calculation by Appelbaum and Hamann.<sup>6</sup> These calculations were performed on the "obvious" structural model, with primitive  $1 \times 1$  translation symmetry, in which the single broken Si(111) bonds were each saturated by one hydrogen atom (monohydride). While these calculations seem to explain

the data obtained for the equilibrium  $7 \times 7$  surface, they disagree with the results obtained for the cleaved  $2 \times 1$  surface. No explanation for this puzzling result has been given so far.

The monohydride phase has recently been contrasted by the experimental observation and theoretical identification of a trihydride phase.<sup>7</sup> The monohydride and trihydride surfaces are produced by hydrogenation of different clean starting surfaces. The starting surface for the monohydride phase is the annealed and well-ordered Si(111)  $7 \times 7$  surface. The starting surface for the trihydride phase shows a  $1 \times 1$  low-energy-electron diffraction pattern with relatively strong background scattering. This surface is obtained from the clean  $7 \times 7$  surface by heating to about 800 °C for 10 min. followed by quenching to room temperature. The surface obtained this way is believed to represent a disordered  $7 \times 7$  surface. Pronounced differences in the UPS spectra of the two phases are found.<sup>7</sup> The two peaks at -4.8 and -7.0 eV of the monohydride phase are replaced by one broad peak at about -6.0 and a smaller peak at -10.0 eV in the trihydride phase. These spectral changes have been reproduced by empirical tight-binding calculations<sup>7</sup> using molecular bond strength parameters as input.

The studies thus reveal an unexpected complicated nature of the Si(111)-hydrogen chemisorption system. Part of the purpose of the present work is to present a unified theoretical treatment of the various identified Si(111)-hydrogen systems.

In Sec. II of this paper we shall present the details of our calculations followed in Sec. III by a discussion of the results in the light of various experimental data.

## II. CALCULATIONS

The calculations presented here are done on a periodic system with slab configuration. Twelve layers of silicon (10 layers in the trihydride phase) with one adsorbed layer of hydrogen on each side form the slabs. A separation of  $\Delta > 8$  a.u. between hydrogen atoms of adjacent slabs guarantees virtually noninteracting slabs. Several chemisorption bond geometries are considered: (i) For the monohydride phase, the Si(111) surface is terminated as usual by Si atoms with one dangling bond each, protruding into the vacuum. Hydrogen atoms are attached to this partially filled dangling-bond orbital and form a covalent bond. A Si-H bond length of 2.73 a.u. is chosen initially, in accordance with the results of Appelbaum and Hamann.<sup>6</sup> This bond length is comparable to molecular bond lengths (2.97–2.76 a.u.) for molecules containing Si-H pairs. An independent calculation is performed with an increased bond length of 3.03 a.u. to determine an equilibrium position and a force constant for H-adsorbate–Si-substrate vibrations. (ii) For the trihydride phase, the structural model proposed in Ref. 7 is chosen. In this model the Si(111) surface is terminated by Si atoms with *three* dangling bonds and only one backbond. This surface can be obtained by removing the outermost Si layer of the usual Si(111) surface. The three dangling bonds are in turn saturated by one hydrogen each, which increases the surface density of hydrogen by a factor of three with respect to the monohydride phase. A Si-H bond length of 2.73 a.u. is chosen in accordance with the monohydride model. As pointed out in Ref. 7, the SiH<sub>3</sub> radicals are relatively free to rotate around the Si-Si backbond with the substrate. Repulsive interactions between the hydrogen atoms, which would be only 2.79 a.u. apart, arise from overlap and electrostatic effects. An energetically most favorable arrangement of the SiH<sub>3</sub> radicals is obtained when each SiH<sub>3</sub> radical is rotated around the Si-Si axis by 30° with respect to the ideal starting configuration. This rotation maximizes the distances between hydrogen atoms of neighboring SiH<sub>3</sub> radicals for fixed bond lengths and bond angles. The distance between hydrogen atoms of neighboring SiH<sub>3</sub> radicals in this configuration is 4.07 a.u. compared to 4.46 a.u. for hydrogen atoms within the same SiH<sub>3</sub> radical and to 7.26 a.u. for the monohydride phase. Stronger interactions are thus expected between the hydrogen atoms in the “turned” trihydride phase than in the monohydride phase.

The ionic pseudopotentials Si<sup>4+</sup> and H<sup>1+</sup>, which are fixed input quantities into the self-consistent treatment, are derived from atomic calculations fitted to term values. The Si<sup>4+</sup> potential has been

used with success in previous calculations on Si bulk band structures,<sup>8</sup> molecules,<sup>9</sup> surfaces,<sup>8</sup> interfaces,<sup>10</sup> and vacancy problems.<sup>11</sup> The hydrogen H<sup>1+</sup> “pseudopotential” is fitted to yield correct atomic 1s, 2s, and 2p energy levels and wave functions within an accuracy of less than 5%. The fit is done under the constraint that the potential has to be of short range in Fourier space with a cutoff  $\leq 4$  a.u., to allow reasonable convergence of the used plane-wave expansions. In the pseudopotential the slowly convergent  $1/q^2$  Coulomb tail of the “true” hydrogen potential is replaced by an exponentially decaying curve which corresponds to smearing out the proton charge. Both Si<sup>4+</sup> and H<sup>1+</sup> ionic potentials are fitted to analytical curves of the form

$$V(q) = (a_1/q^2)(\cos a_2 q + a_3)e^{a_4 q^4}, \quad (1)$$

where  $a_3 = -(2z/a_1)(4\pi/\Omega) - 1$  to yield the correct behavior for  $q \rightarrow 0$ . We allow  $a_3$  to deviate slightly from this exact value to achieve a better fit for larger  $q$  values. The parameters  $a_1$  to  $a_4$  (in a.u.) for Si<sup>4+</sup> and H<sup>1+</sup> are given in Table I for unit volume  $\Omega$ .

The standard self-consistent pseudopotential scheme as described in Ref. 8 is used in the calculations. Hartree screening potentials are calculated exactly at each interaction step and the local  $\sim \alpha\rho^{1/3}$  approximation is used to represent exchange and correlation effects. As in earlier calculations,<sup>8</sup> a value of  $\alpha=0.794$  is used. The use of the statistical exchange approximation might at first sight seem to pose problems for hydrogen. However, for hydrogen adsorbed on Si, strong covalent bonds are formed which lead to high charge accumulations comparable to those of the silicon substrate. Thus, as to the validity of the statistical exchange approximation, there should be no qualitative difference between the hydrogen-silicon chemisorption system and the clean silicon surface.

Plane waves up to  $G^2 = 3.0$  Ry included directly, combined with waves up to  $G^2 = 6.0$  Ry included by second-order perturbation theory, are used to expand the pseudo wave functions. The charge-density expansion is cut off at  $G^2 = 8$  Ry. The potential is iterated to self-consistency using valence charge

TABLE I. Potential parameters for Si<sup>4+</sup> and H<sup>1+</sup> entering Eq. (1). The values are given for unit volume and in atomic units.

	Si <sup>4+</sup>	H <sup>1+</sup>
$a_1$	-77.5451	23.3273
$a_2$	0.7907	0.2800
$a_3$	-0.3520	-1.5380
$a_4$	-0.0181	-0.0070

distributions calculated from several representative high-symmetry  $\vec{k}$  points in the two-dimensional Brillouin zone ( $\Gamma, K, M$ ). For general  $\vec{k}$  points, symmetry distinctions have to be made between the monohydride and trihydride phases. The point group for the monohydride phase is  $D_{3d}$  [as for the clean Si(111) surface] if one considers a twelve-layer Si slab. In the trihydride phase, the three vertical reflection planes are absent and the resulting point group is  $C_{3i}$ . Thus,  $\frac{1}{6}$  of the two-dimensional hexagonal Brillouin zone has to be sampled in evaluating  $\vec{k}$  space integrals for the trihydride phase, whereas the usual  $\frac{1}{12}$  has to be considered in the case of the monohydride phase. Typically, about 28  $\vec{k}$  points for  $\frac{1}{12}$  of the Brillouin zone are calculated in evaluating density of states integrals.

In the case of the monohydride phase, the force on the H atom is calculated in a similar manner as in Ref. 6, using the Hellmann-Feynman theorem. The resulting force on the  $H^{1+}$  nucleus can be divided into a repulsive nuclear force  $\vec{F}_n$ , resulting from all remaining silicon- and hydrogen-ion cores and into an attractive electronic force  $\vec{F}_{e1}$ , originating from the ensemble of valence electrons. This latter force can be written as

$$\vec{F}_{e1} = - \sum_i \frac{dE_i}{d\vec{r}_H} = - \sum_i \left\langle \varphi_i \left| \frac{\partial H}{\partial \vec{r}_H} \right| \varphi_i \right\rangle, \quad (2)$$

where the sum runs over all occupied states. If "exact" ground-state wave functions  $\varphi_i$  are used, the force is obtained from the partial derivative of the Hamiltonian, i.e., from deriving the explicit structure dependence of the *ionic* pseudopotential. Thus in Fourier space

$$\begin{aligned} \vec{F}_{e1} &= \sum_{\vec{G}} \rho_{\text{tot}}(\vec{G}) \left( - \frac{\partial V_{\text{ion}}^H(\vec{G})}{\partial \vec{r}_H} \right) \\ &= \sum_{\vec{G}} \rho_{\text{tot}}(\vec{G}) \frac{\sin(\vec{G} \cdot \vec{r}_H)}{N} \vec{G} V_{\text{ion}}^H(|\vec{G}|), \end{aligned} \quad (3)$$

where  $\rho_{\text{tot}}(\vec{G})$  and  $V_{\text{ion}}^H(|\vec{G}|)$  are the Fourier components of the total valence charge and the  $H^{1+}$  ion potential, respectively;  $N$  is the number of atoms per unit cell as defined in the structure factor and  $\vec{r}_H$  is the position of the hydrogen atom. In this formulation, using the Hellmann-Feynman theorem, the force is calculated assuming that all hydrogen atoms on the surface (monolayer) behave identically.

In Eq. (3)  $\rho_{\text{tot}}(\vec{G})$  should be the Fourier transform of the exact (*non*-pseudo) valence charge and  $V_{\text{ion}}^H(|\vec{G}|)$  should be  $8\pi/\Omega G^2$ , the exact Fourier transform of the Coulomb potential. In the approximation used in this work, however,  $\rho_{\text{tot}}(\vec{G})$  differs from the "exact" charge density in the regions close to the nuclei. Analogously, the Fourier

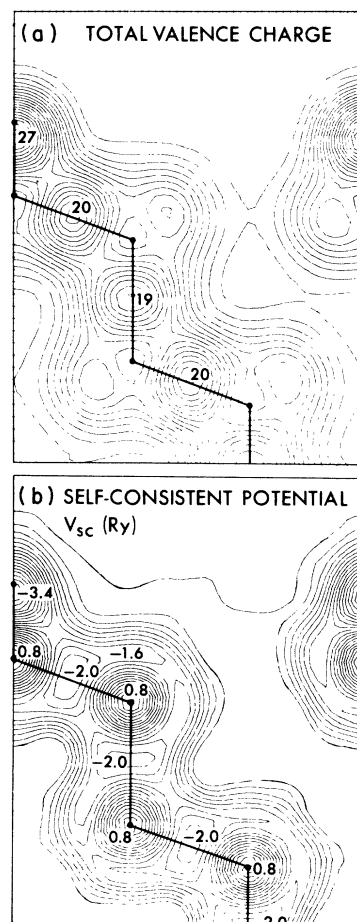


FIG. 1. Total valence charge (a) and self-consistent potential (b) for the Si(111)-H monohydride structural model. The contours are plotted in a (110) plane cutting the (111) surface at right angle. The topmost atoms are hydrogen, the remaining atoms represent the silicon substrate. The charge contours are given in units of electrons per Si bulk unit cell, the potential contours in Ry, normalized to zero in the vacuum.

transform of the "pseudo" hydrogen ion (i.e., with smeared-out proton charge) is used. Thus the terms in the sum of Eq. (3) decay exponentially for large  $\vec{G}$ 's and convergence is assured. By inspecting the contributions to the sum in Eq. (3) coming from various ranges of  $\vec{G}$  vectors, one finds that the pseudo approximations for large  $\vec{G}$ , mentioned above, do not introduce significant errors. The main contribution to the sum in Eq. (3) originates from  $\vec{G}$  vectors with lengths ranging between 1.2 and 2.5 a.u., corresponding to the main charge modulation of the Si-H bond. On the other hand, in this intermediate range of  $\vec{G}$ 's, the magnitudes of  $\rho_{\text{tot}}(\vec{G})$  are still strongly dependent on the high Fourier components in the wave functions  $\varphi(\vec{G})$ . We believe that the main potential source of error in calculating  $\vec{F}$  lies in the convergence quality of

the wave functions. To achieve sufficiently converged wave functions,  $\varphi(\vec{G})$  has to be expanded at least up to  $\vec{G}^2 = 6$  Ry. The remaining error introduced into  $\rho_{\text{tot}}(\vec{G})$  is estimated to be about 3% by comparing Si bond charges to highly converged bulk charge densities as calculated by Walter and Cohen.<sup>12</sup>

The repulsive nuclear force  $\vec{F}_n$  can either be summed in real or in Fourier space. It should be noted that in contrast to "half-space" calculations, in the periodic geometry neither  $\vec{F}_{e1}$  nor  $\vec{F}_n$  individually diverge and thus can safely be evaluated separately. On the other hand, the periodic arrangement may cause small errors in the resulting total force  $\vec{F} = \vec{F}_{e1} + \vec{F}_n$  due to contributions from neighboring slabs. To minimize the small errors ( $\vec{F}$  is of relative short range due to its higher multipole characters), the separation between the slabs is increased up to 32 times the original spacing by a Fourier convolution technique, assuming rigid electron charge profiles.

### III. RESULTS

In this discussion the results for the monohydride phase Si(111)-H shall be presented first, followed by those for the trihydride phase Si(111)-SiH<sub>3</sub> and a concluding comparison.

In Fig. 1 the total valence charge (a) and the self-consistent potential (b) are presented for Si(111)-H. The results are shown for the lower stage of convergence, i.e., for wave functions truncated at 3.0 Ry. The contours are plotted in a (110) plane cutting the (111) surface at right angles. All atoms are indicated by full dots. The two topmost atoms are hydrogen; the remaining atoms represent the silicon substrate. Both charge and potential closely resemble the clean surface<sup>8</sup> beyond the second atomic layer. The adsorbed hydrogen therefore presents a relatively localized surface disturbance affecting mainly the surface dangling bonds, and only weakly the silicon backbonds. The potential is repulsive at the Si sites (see also Ref. 8) because of the core orthogonalization potential, but attractive at the hydrogen site. In fact, along atom-connecting lines the Si-H bond potential is about 50% stronger than the Si-Si bond potential. The overall strength of the two bond potentials, however, is more comparable due to compensating volume ratios. The potential shown in Fig. 16 compares reasonably well to the results of Appelbaum and Hamann.<sup>6</sup> The potential values given in Ref. 6 are at the hydrogen site, the silicon site, and the bulk bond site, -3.0, +0.6, and -1.8 Ry, respectively, which compares to our values of -3.4, +0.8, and -2.0 Ry. Overall, we find about 10% more potential modulation in the present results. Part of this

discrepancy originates from the use of different ionic core potentials, part from the relative lower convergence of electronic charge in the present calculation. In fact, for the high convergence stage (i.e., wave functions truncated at 6.0 Ry) which is used to calculate the Hellmann-Feynman forces, the difference between the two potentials decreases to a few percent. Similarly, the electronic charge distribution shows increased modulation for the higher convergence stage. While the bulk-bond charge maximum increases from 20 to 24 (in units of electrons/bulk unit cell) close to the value obtained by Walter and Cohen,<sup>12</sup> the Si-H bond charge maximum increases significantly from 27 to 38. While the increase in the total amount of bonding charge is less pronounced, these changes clearly show the need for highly converged wave functions for, e.g., force calculations. On the other hand, features in the electronic spectrum are found to change only weakly by increasing the convergence. A change in the surface dipole of ~0.15 eV is found to be produced by hydrogen adsorption. This value, however, is below the noise level of our calculations.

With the self-consistent potential, local density-of-states spectra are calculated. They are shown in Fig. 2 for regions labeled 1 to 6 starting in the bulk region (slab middle) and extending into the vacuum. At the right-hand side of Fig. 2 the total charge density, integrated parallel to the (111) surface is shown for reference; the atomic positions are indicated. Hydrogen chemisorption, forming the monohydride phase introduces two main structures in the spectrum, as indicated by arrows in Fig. 2. In addition, some enhancement is found in the lowest and highest peaks around -10 and -3 eV, respectively. The two main structures at -4.5 and -7.2 eV correspond to fractions of a (partially resonant) surface band in the two-dimensional Brillouin zone. The states are clearly associated with the hydrogen-substrate bond and are mainly localized around the zone center ( $\Gamma$ ) for the -7.2-eV peak and close to the zone boundary ( $K, M$ ) for the -4.5-eV peak. The results agree well with the findings of Ref. 6. In a recent paper<sup>13</sup> Appelbaum *et al.* emphasize the two-dimensional band picture leading to the two peaks in the spectrum by virtue of the hydrogen-hydrogen interaction within the monolayer. Based on the present results, we would like to emphasize the importance of the Si substrate band structure. The substrate band structure strongly influences the Si-H bond, i.e., the three backbonds of the outermost Si atoms to a large degree determine the amount of *s-p* mixing of wave functions on the Si sites. This restricts the fractions of Si *s* and *p* states available for hydrogen bonding. Consequently, the two peaks

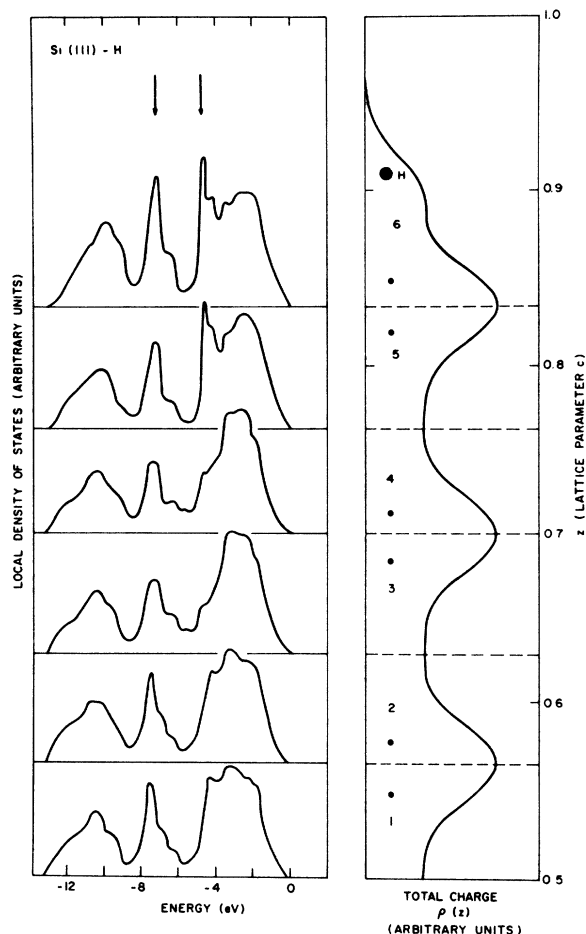


FIG. 2. Local density of states diagrams of Si(111)-H for six different regions as shown in the total charge profile. Prominent hydrogen-induced surface structures are indicated by arrows.

in the spectrum correspond to hydrogen orbitals (mostly  $s$ -like) which couple to Si  $s$ -like orbitals ( $-7.2$  eV) and to Si  $p$ -like orbitals ( $-4.5$  eV). This is confirmed by charge-density calculations for states under the two main peaks (Fig. 3). The silicon  $s$  and  $p$  character present in the wave functions can be seen from the nodal structure of the charge distribution. States at  $-4.5$  eV (around  $K, M$ ) are more strongly localized in the surface, whereas states at  $-7.2$  eV (around  $\Gamma$ ) couple considerably to Si band states. The position of the hydrogen-induced peaks is in very good agreement with the photoemission data, obtained in Refs. 4 and 5 for hydrogen chemisorption on Si(111)  $7 \times 7$  surfaces, confirming the monohydride model for this surface. A quantitative comparison of the peak positions between experiment<sup>4</sup> and theory is shown in Fig. 4 and summarized in Table II. Only the raw theoretical data are shown in Fig. 4, no matrix element or broadening effects are included. While the

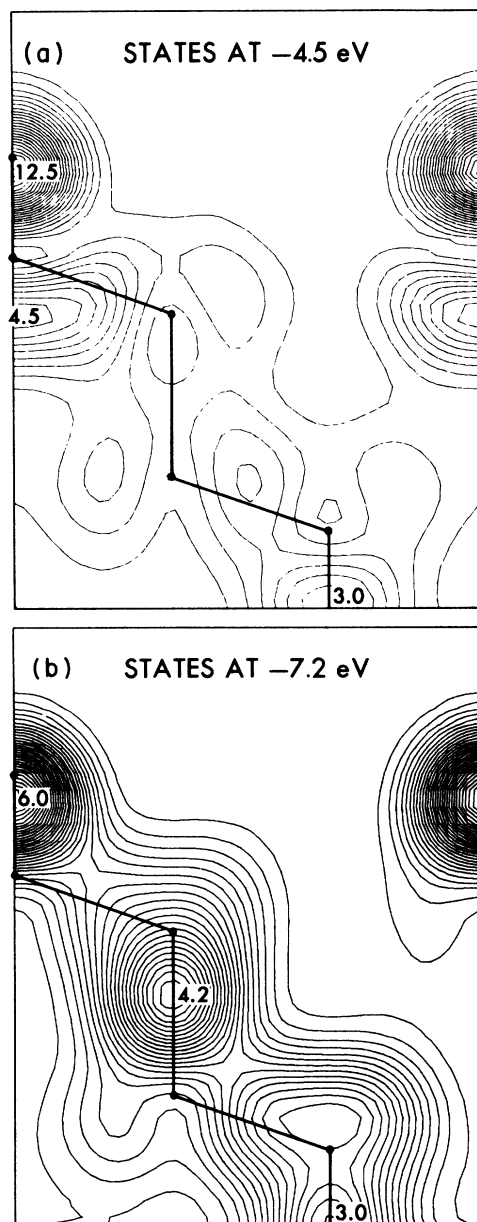


FIG. 3. Charge-density plots for two hydrogen associated states in the Si(111)-H monohydride phase. The states are located at 4.5 eV (a) and at 7.2 eV (b) below the valence-band edge.

agreement for structures  $A$ ,  $B$ , and  $\beta$  is very good, no enhancement could be resolved in the experimental curve below  $-10$  eV (peak  $\alpha$ ) which is mainly due to the strong increase of secondary electron scattering in this region.

The force on the hydrogen atoms is calculated using the Hellmann-Feynman theorem as discussed in Sec. II. With a Si-H bond length of  $d_1 = 2.73$  a.u. a small outward force is found. If the bond length

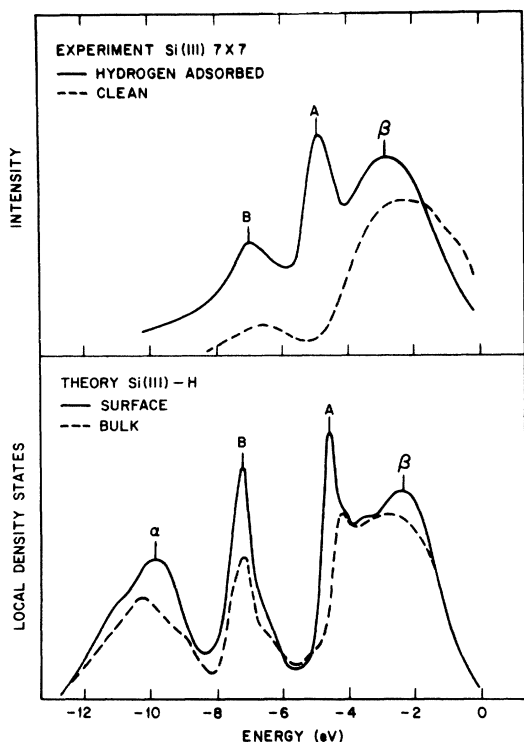


FIG. 4. Comparison of the calculated local density of states for the outermost layer in the Si(111)-H monohydride phase with an experimental UPS spectrum of Ref. 4. The experimental spectrum was obtained from hydrogenation of an annealed  $7 \times 7$  starting surface. The emission spectrum of the clean surface is indicated.

is increased to  $d_2 = 3.03$  a.u. and the calculation repeated, the force changes sign. Linear interpolation leads to an equilibrium distance of  $d_0 = 2.93$  a.u. which is about 5% larger than the Si-H bond length in  $\text{SiH}_4$  molecules. The equilibrium distance for the Si-H system calculated in Ref. 6 is 2.73 a.u. It should be noted that further improvement of the wave-function convergence should increase the absolute value of the electronic force  $\vec{F}_{e1}$  and thus somewhat reduce the equilibrium bond length. From the two configurations with different bond lengths a force constant of  $c \approx 0.25$  a.u. can be derived, which is about 40% larger than the value of 0.175 a.u. calculated in Ref. 6. The experimental value for  $\text{SiH}_4$  is 0.173 a.u.,<sup>6</sup> and recent electron-energy-loss spectroscopy results on the vibrational mode of hydrogen adsorbed on *cleaved* Si(111) yield a value of 0.158 a.u. by treating the Si-H complex simply as a binary molecule.<sup>14</sup> It emerges from our calculations that the calculated force constant almost exclusively results from changes in the nuclear force  $\vec{F}_n$ . The electronic force  $\vec{F}_{e1}$  is found not to change noticeably with slight displacements of the hydrogen atoms, i.e., the important parts of the electronic charge profile more

TABLE II. Structure in the experimentally observed and calculated spectra for different Si(111)-hydrogen systems. For the reported experimental values an average ionization potential of 5.0 eV is assumed to compare to the calculated values. The labeling corresponds to Figs. 4 and 9.

Reference	Monohydride		Technique
	A	B	
Sakurai, Hafstrum, <sup>4</sup> Rowe <sup>5</sup> $7 \times 7$	-4.8	-7.0	UPS
Ibach, Rowe <sup>3</sup> $2 \times 1$		$\sim -6.5$	UPS
Appelbaum, Hamann <sup>6</sup>	$\sim -4.0$	$\sim -7.0$	self-consistent pseudopotential
Pandey <i>et al.</i> <sup>7</sup>	-4.8	-7.0	tight-binding
This work	-4.5	-7.2	self-consistent pseudopotential
	Trihydride		
	A	B	
Pandey <i>et al.</i> <sup>7</sup> $1 \times 1$	-6.0 (broad peak)	-10.0	UPS
Pandey <i>et al.</i> <sup>7</sup>	-6.0	-10.5	tight-binding
This work	-3.5 ( $\beta$ ) -5.0 ( $\alpha$ ) -6.0 ( $A$ )	-9.8	self-consistent pseudopotential

or less rigidly follow such small displacements. Similarly to what was said above about the magnitude of the electronic force, further improved wave-function convergence may yield small changes in the electronic forces and thus a lower force constant. It follows from this study, that for simple systems like, e.g., hydrogen adsorption, forces and force constants may directly be derived with reasonable accuracy, provided well converged ground-state wave functions are used.

We now turn to the results of the trihydride phase Si(111)- $\text{SiH}_3$ . The calculations are done on a structural model proposed in Ref. 7 and outlined in Sec. II. In Fig. 5 contour plots of the total valence charge density (a) and the self-consistent potential (b) are shown. The contours are displayed in the same (110) plane as used in Fig. 1. With respect to Fig. 1 the adsorbed H layer and the outermost Si layer are removed and replaced by one H layer. Thus three H atoms are bound to each of the top Si atoms. The three H atoms are rotated by  $30^\circ$  around the [111] direction as described in Sec. I. Thus, *no* hydrogen atoms are cut by the (110) plane shown in Fig. 5. The Si-H bonds projected on the (110) plane are shown as dashed lines in Fig. 5.

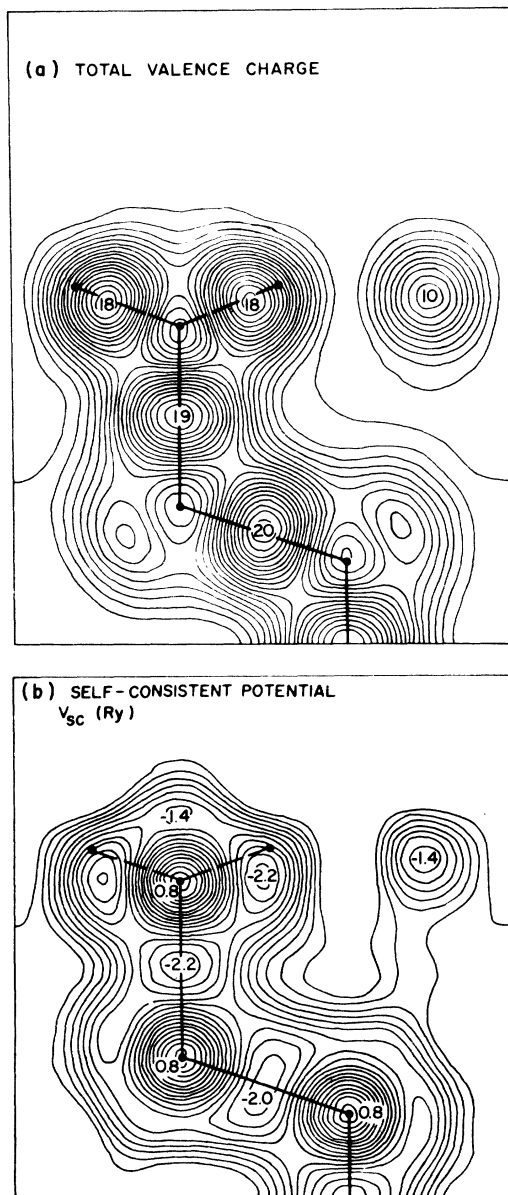


FIG. 5. Total valence charge (a) and self-consistent potential (b) for the Si(111)-SiH<sub>3</sub> trihydride structural model. Plane of display and units are chosen as for Fig. 1.

Similar to the results of the monohydride phase, the adsorbed hydrogen does not perturb the Si substrate electronic structure further than one or two atomic layers deep. The adsorbate monolayer itself now shows a three-times higher packing density than in the monohydride phase.

Using the self-consistent potential in Fig. 5(b), local density-of-states spectra are calculated. They are displayed in Fig. 6 for the regions 1 to 6 defined earlier. The charge-density profile in-

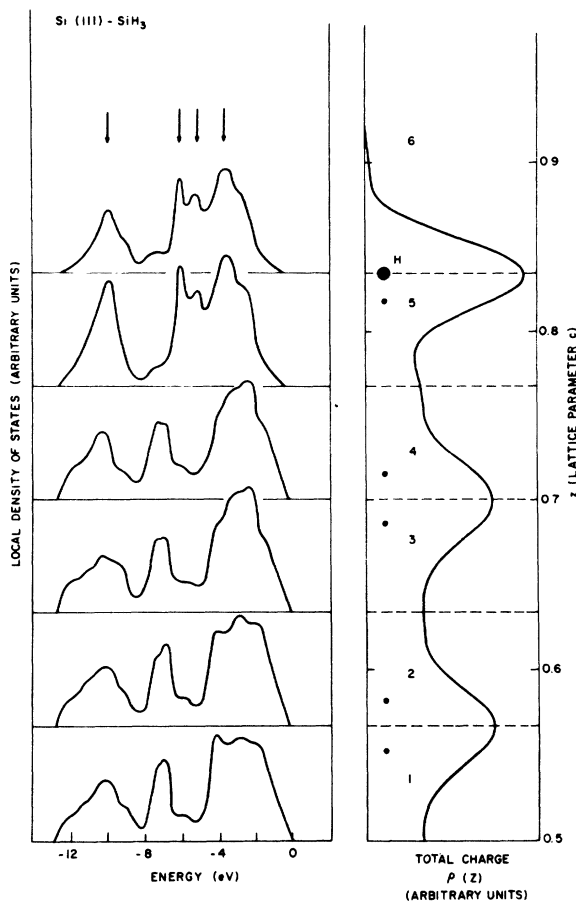


FIG. 6. Local density-of-states diagrams of Si(111)-SiH<sub>3</sub> for six different regions as shown in the total charge profile. Prominent hydrogen-induced surface structures are indicated by arrows.

tegrated parallel to the surface shows the strong charge accumulation in regions 5 and 6 due to the high atomic (Si and H) density. The surface density-of-states spectra show very pronounced differences compared to the monohydride phase. A strong enhancement of the silicon *s*-like low-energy peak around -9.8 eV is found. The *s-p* peak found around -7.2 eV in the monohydride phase is suppressed and structure above -6.0 eV appears. This structure fills the "second gap" in the silicon valence-band spectrum and produces a strong edge at -6.0 eV. Three main peaks at -6.0, -5.0, and -3.5 eV can be distinguished as indicated by arrows. The nature of the new surface states or resonances is displayed in the charge contour plots in Figs. 7 and 8. In these figures we show in addition to the usual (110) plane, a (111) plane running through the outermost Si layer. The orientation of the three hydrogen atoms bound to the top silicon atoms can thus be seen.

The states giving rise to the peak at -9.8 eV cor-

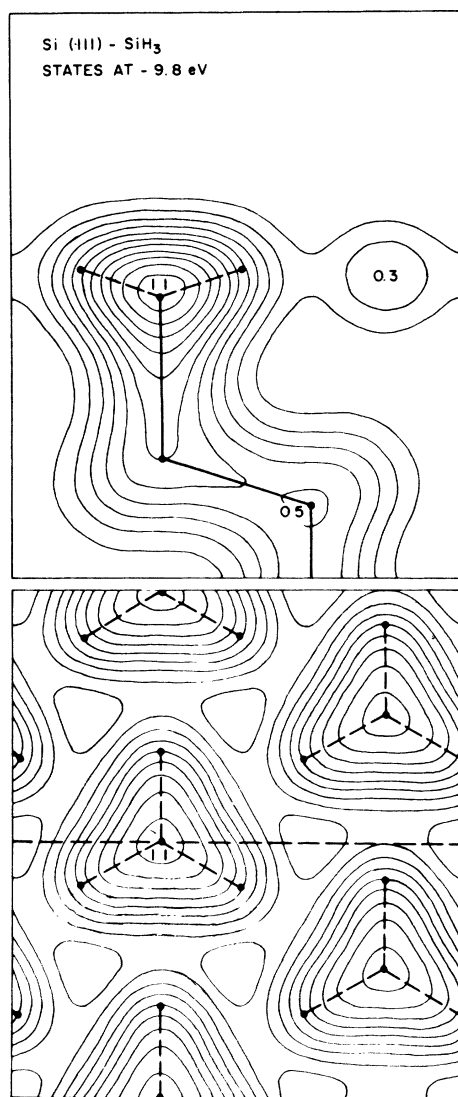


FIG. 7. Charge-density plot for the hydrogen-associated state at  $-9.8$  eV in the Si(111)-SiH<sub>3</sub> trihydride phase. In addition to the (110) plane, the charge is displayed in a (111) cut running through the outermost Si atoms.

respond mainly to a combination of hydrogen and silicon  $s$  orbitals with the center of the charge concentrated at the silicon atom (see Fig. 7). The contributing states are located around point  $K$  in the two-dimensional Brillouin zone. These surface states originate from a slightly more attractive potential above the silicon atoms [see also Fig. 5(b)] due to the clustering of three hydrogen atoms.

The three structures at  $-6.0$ ,  $-5.0$ , and  $-3.5$  eV correspond to states of very similar character. Figure 8 shows charge-density contours of states giving rise to the peak at  $-6.0$  eV. The states are

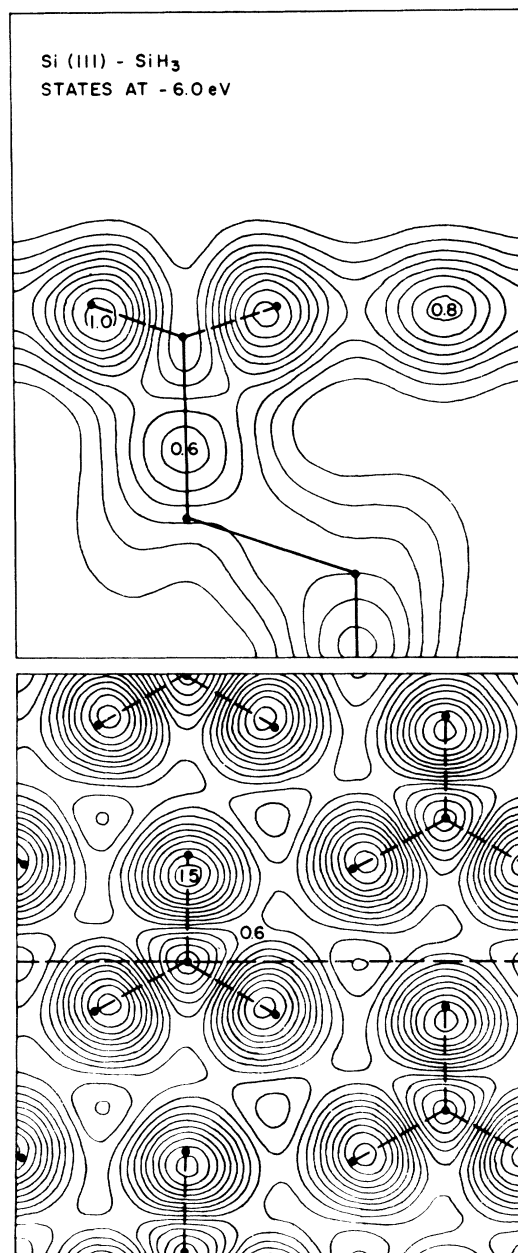


FIG. 8. Charge-density plot for the hydrogen-associated state at  $-6.0$  eV in the Si(111)-SiH<sub>3</sub> trihydride phase. (110) and (111) planes intersecting along the outermost Si atoms are shown.

of predominantly Si  $p_{xy}$  character combined with hydrogen  $s$ -type orbitals. The splitting into several peaks is due to hydrogen-hydrogen interaction which creates a surface-state band structure of about 3 eV width. States at  $-6.0$  eV are located around  $K$  and  $M$ , the enhancement around  $-5.0$  eV is a typical "volume effect," and states around



-3.5 eV are located around  $M$  exclusively. This surface-state band structure deviates somewhat from the tight-binding results of Ref. 7. In particular, a surface-state dispersion about three times as large is obtained from the present calculations. Since in the present calculation the hydrogen-hydrogen and hydrogen-silicon interactions are determined self-consistently rather than empirically, some doubt may be cast on the chosen interaction parameters of Ref. 7. On the other hand, the parameters in Ref. 7 are chosen to fit the experimental spectrum (after adding several broadening and background functions and functions adjusting relative oscillator strength). With respect to the validity of the tight-binding results, the question thus arises, whether different curve-smoothing procedures applied to the present results (Fig. 6) could yield a similar "experimental" spectrum. To allow direct comparison (see also Table II) in Fig. 9, the "raw" calculated spectrum

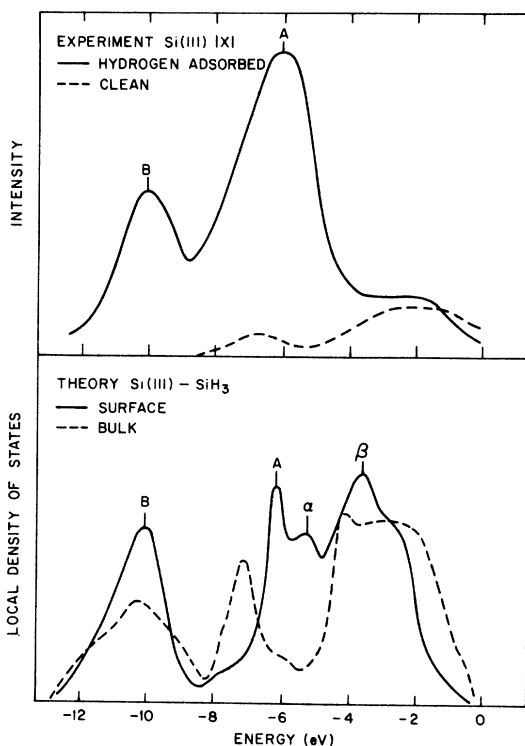


FIG. 9. Comparison of the calculated local density of states averaged over the two outermost layers in the Si(111)-SiH<sub>3</sub> trihydride phase with an experimental UPS spectrum of Ref. 7. The experimental spectrum was obtained from hydrogenation of a quenched 1×1 starting surface. The emission spectrum for the clean surface is indicated.

of the model trihydride phase is presented together with the experimental data of Ref. 7 obtained on a Si(111) 1×1 surface prepared as discussed before. While very good agreement is found for peak B at -9.8 eV, the comparison is less satisfactory for peak A. In particular, the structures at -5.0 and -3.5 eV, labeled  $\alpha$  and  $\beta$  are not resolved in the observed spectrum though some additional emission is found (see the spectrum for the clean 1×1 surface for comparison). It is difficult to answer how far broadening and/or matrix element effects could improve the correspondence. On the other hand, reasons for the discrepancy may be connected to details of the structural model used for the trihydride phase. If one accepts the basic idea of the trihydride structural model,<sup>7</sup> which based on the observed overall changes in the spectrum seems to be experimentally confirmed, not too much room is left for structural changes. In particular, to decrease the effective hydrogen-hydrogen interaction, bond distances need only to be changed slightly ( $\sim 0.1$  Å) to obtain perfect two-dimensional close packing. Bond-angle changes, however, may influence the hybridization of the silicon orbitals enough to alter the effective hydrogen-hydrogen interaction. No additional pseudopotential calculations for different structural models are undertaken since the basic spectral changes between the monohydride and the trihydride phases are well reproduced.

#### IV. CONCLUSIONS

The paper presents a study of possible structural models for hydrogen adsorption on Si(111) surfaces using a self-consistent pseudopotential technique. The calculations are done for two basically different structural models, the mono and trihydride phase. While the monohydride phase represents the "obvious" geometry for hydrogen chemisorption on Si(111),<sup>6,7</sup> the trihydride phase is somewhat unexpected, but has recently been proposed to account for spectral changes occurring after special thermal treatment of the silicon substrate.<sup>7</sup> The present calculations in fact yield results for the monohydride phase, which are in excellent agreement with experimental data obtained on hydrogenated surfaces starting with clean 7×7 surfaces. The drastic spectral changes occurring for hydrogen-adsorbed surfaces starting with 1×1 quenched surfaces are reasonably accounted for by the present calculations done for the trihydride structural model. While the actual agreement is less quantitative, minor changes in the structural model may improve it. The discrepancies are caused by the strong hydrogen-hydrogen interaction which plays

an important role in the trihydride phase containing a rather dense hydrogen monolayer. Neither the monohydride nor the trihydride results alone are able to explain the data obtained for hydrogen adsorption starting with freshly cleaved surfaces,<sup>3</sup> which approximately resemble an average of the two phases.

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<sup>1</sup>J. T. Law, *J. Chem. Phys.* **30**, 1568 (1959).

<sup>2</sup>G. E. Becker and G. W. Göbeli, *J. Chem. Phys.* **38**, 2942 (1963).

<sup>3</sup>H. Ibach and J. E. Rowe, *Surf. Sci.* **43**, 481 (1974); J. E. Rowe (unpublished).

<sup>4</sup>T. Sakurai and H. D. Hagstrum, *Phys. Rev. B* **12**, 5349 (1975).

<sup>5</sup>J. E. Rowe, *Surf. Sci.* **53**, 461 (1975).

<sup>6</sup>J. A. Appelbaum and D. R. Hamann, *Phys. Rev. Lett.* **34**, 806 (1975).

<sup>7</sup>K. C. Pandey, T. Sakurai, and H. D. Hagstrum, *Phys. Rev. Lett.* **35**, 1728 (1975).

<sup>8</sup>M. Schlüter, J. R. Chelikowsky, S. G. Louie, and

M. L. Cohen, *Phys. Rev. B* **12**, 4200 (1975).

<sup>9</sup>M. L. Cohen, M. Schlüter, J. R. Chelikowsky, and S. G. Louie, *Phys. Rev. B* **12**, 5575 (1975).

<sup>10</sup>S. G. Louie and M. L. Cohen, *Phys. Rev. Lett.* **35**, 866 (1975).

<sup>11</sup>S. G. Louie, M. Schlüter, J. R. Chelikowsky, and M. L. Cohen, *Phys. Rev. B* **13**, 1654 (1976).

<sup>12</sup>J. P. Walter and M. L. Cohen, *Phys. Rev. B* **4**, 1877 (1971).

<sup>13</sup>J. A. Appelbaum, H. D. Hagstrum, D. R. Hamann, and T. Sakurai, *Surf. Sci.* **58**, 479 (1976).

<sup>14</sup>H. Frotzheim, H. Ibach, and S. Lehwald, *Phys. Lett. A* **55**, 247 (1975).