Chemisorption of hydrogen on the Si(100) surface: Monohydride and dihydride phases

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We present a systematic study of the clean and chemisorbed-hydrogen-covered Si(100) surfaces. Experimentally, we used HeI and HeII ultraviolet photoemission spectroscopy and were able to resolve important chemisorption features which had not been observed previously. We carried out electronic energy calculations using both empirical tight-binding and extended Hückel methods, from which we deduce a consistent interpretation of the spectra. It is found that the low-binding-energy surface states resulting from the asymmetric dimer-bond model are in good agreement with the experimental data, whereas one high-binding-energy surface state associated with the displacements of the subsurface atoms does not appear in the spectra. Hydrogen chemisorbing on the Si(100)-(2×1) surface forms a monohydride phase, and removes most of the surface states, except for the dimer bond and some of the backbonding states. Based on the theoretical and experimental results it is suggested that at high coverage the Si—H bonds of the dihydride phase rotate and depart from the tetrahedral directions. The occurrence of this phase on the other surfaces of silicon, and its possible connections with the observed spectral features, are extensively discussed.

I. INTRODUCTION

Hydrogen chemisorbed on the Si(100) surface at high temperature (~250 °C) preserves the (2×1) reconstruction, and also gives rise to a monohydridelike ultraviolet photoemission spectroscopy (UPS) spectrum. Upon lowering the temperature under continuing H exposure, the surface superstructure is destroyed, and concomitantly the UPS spectrum undergoes changes. Based mainly on these observations, Sakurai and Hagstrum¹ introduced the idea of a dihydride phase (i.e., two hydrogens bonded to a surface silicon, SiH₂) that forms on the Si(100) surface at room temperature. Recently, a study of the H vibration on the Si(111) surface by Wagner *et al.*² pointed out an important fact: In the early stages of adsorption H is capable of breaking the backbonds to form a SiH₂ complex.

Although the chemisorption of H on Si surfaces has been studied extensively in the past, a theoretical investigation of the dihydride phase is still lacking. Present understanding of the states associated with this phase does not go beyond the observed UPS features. Apart from the erosive action brought about by the formation of SiH₂, the interaction of H with the Si(100) surface is important because other surfaces also display a similar configuration, namely, they have a Si-Si bond with a dangling bond protruding from both ends. Therefore, a study of the Si(100) + H system, together with the recent experimental advances, is expected to contribute not only to our understanding of the dihydride phase, but also to give new insight into the UPS spectrum of other Si surfaces. The principal goal of this study is to present a unified treatment of the various hydrogen phases that may occur on this surface. Of particular interest are how the various binding structures affect the state distributions at the surface. For these reasons, starting from the clean Si(100) surface, we have carried out systematic experimental and

theoretical studies on the electronic structure of H chemisorbed on the Si(100)-(2 \times 1) and Si(100)-(1 \times 1) surfaces. Experimentally, we have investigated the distribution of occupied states at several temperatures by using HeI and HeII UPS spectroscopies. With the HeII we have identified some chemisorption states of crucial importance which were not resolved previously. Theoretically, to provide a comparison with the monohydride (SiH) and trihydride (SiH₃) phases on the Si(111) surface we have utilized the empirical tight-binding (ETB) method and the energy parameters introduced in conjunction with them.³ In previous ETB works the interaction among the chemisorbed H atoms, which happens to be significant for the H-H distances of relevance, was left out of consideration. To treat the H-H interactions properly we have also taken recourse to an extended Hückel type (EHT) approach, which has proven to be a reliable method for the H + Si(111) system.⁴ This way our results are double checked. The adsorbate-substrate systems have been treated by slabs (of \sim 30 layers) that are sufficiently thick to lead to convergent energies. To explore the effect of the geometry, such as the disorder of the substrate, large cluster calculations have also been covered under the same context. In view of the present results we reexamine previous works, both theoretical and experimental, and present a detailed discussion of the H phases occurring on the Si(100) surface. In connection with the monohydride and dihydride phases we also touch upon various questions remaining unanswered. The central result emanating from this study is that the electronic structure of the monohydride phase on the Si(100)-(2 \times 1) surface differs in many respects from that forming on the Si(111) surface. Depending upon the coverage, the orientations of the Si-H bonds in the dihydride phase may undergo a change. The salient feature in the electronic structure of this phase is the enhancement of the chemisorption states at ~ -5.0 eV below the maximum of the valence band.

II. EXPERIMENTAL RESULTS

All experiments were performed in an UHV system with a base pressure on the order of 10^{-10} mbar and equipped with a double-pass cylindrical-mirror analyzer for Auger electron spectroscopy (AES) and photoelectron spectroscopy and a four-grid low-energy electron diffraction (LEED) system. A differentially-pumped He discharge lamp delivered the HeI (21.2-eV) and HeII (40.8-eV) resonance lines running at 0.3 and 1 mbar, respectively. Whereas the kinetic energy distribution curves (EDC) using the He II line were taken at a pass energy of 50 eV, the pass energy was lowered to 25 eV while working with the HeI line. As a consequence, the resolution was 1.0 and 0.5 eV, respectively. The analyzer axis was in the plane of incidence of the uv light (grazing incidence) and formed an angle of about 50° with the sample normal. The EDC are given relative to the vacuum level.

The Si(100) samples were cut from *p*-doped Si wafers with a conductivity of 40–70 Ω cm. Since the question of surface contamination in connection with atomic hydrogen adsorption is very important, much care must be taken on that problem: After a sputtering process mainly to reduce the carbon contamination, the sample was heated up to at least 900 °C removing the rest of the oxygen contamination. Subsequently, the sample was cooled down very slowly in order to establish a well-ordered 2×1 structure. All samples were checked by AES before and after the hydrogen exposures. The sample surface was considered "clean" with respect to oxygen and carbon contamination for an AES ratio of O(510 eV)/Si(92 eV) < 10⁻³ and C(272 eV)/Si(92 eV) < 4×10⁻³.

In order to demonstrate the sensitivity of UPS spectra on oxygen contamination and to show in which energy range the respective emission yield may interfere with hydrogen-induced features, we give in Fig. 1 a spectrum (curve a) taken after annealing up to 800° C (O/Si= 5×10^{-3}) with a remaining oxygen coverage of 0.04 monolayers as calibrated by the procedure described by Ibach *et al.*⁵ Curve b is obtained after annealing to only 600°C (O/Si= 2.5×10^{-2}). The strong peaks at -12.2 and -17.1 eV belong to an oxygen coverage of about 0.5 monolayers.



FIG. 1. He II UPS spectra for the Si(100) surface with different oxygen coverages. The curves are obtained after annealing the sample up to 800 (a) and 600 °C (b). The corresponding oxygen coverages are 0.04 and 0.5 monolayers, respectively.

Oxygen contamination during exposure to atomic hydrogen very likely occurs via water adsorption from the residual gas. It turns out that for low water coverages mainly the peak at -12.2 eV broadens to an asymmetric peak, whereas the high-binding-energy peak remains in its intensity and shape.

The Si surfaces were exposed to atomic hydrogen produced by dissociation of H₂ (99.999%) at a hot W ribbon, which was heated up to 2000 °C and placed about 5 cm in front of the sample. The H₂ exposure dosage given in langmuirs (1 L=10⁻⁶ Torr sec) (H₂ partial pressure in 1.3×10^{-6} mbars times exposure time in sec) was taken as a measure for the atomic hydrogen deposition rate. The temperature was measured by a thermocouple welded onto the frame of the sample holder. The temperature drop between frame and sample was taken into account by calibrating the thermocouple reading versus the sample temperatures measured by an infrared pyrometer. The heating periods usually lasted 2–3 min.

As already mentioned in the Introduction several groups have presented UPS data of hydrogen adsorbed on various Si surfaces. In the present paper we refer especially to the experiments and interpretations of Sakurai and Hagstrum¹ and focus our interest on systematic hydrogen exposures at different temperatures observed in the HeII discharge mode. Owing to the smaller contribution of secondary electrons to the valence-band emission yield as compared to HeI, a higher sensitivity for the electronic structure at energies far below the Fermi level is obtained. As the theoretical calculations will show, one expects distinctive structures in this energy range. Figure 2 shows for comparison UPS spectra taken for both excitations, HeI and HeII. They were obtained upon an exposure to 60 L H₂ keeping the sample at a temperature of about 250 °C. The LEED pattern maintained a 2×1 structure. Therefore, these spectra can be attributed to a "H-saturated" surface revealing the monohydride phase. It is characterized by a strong peak near -12 eV, which



FIG. 2. UPS spectra for the Si(100) surface taken for both excitations, He II and He I, and produced by the atomic hydrogen exposure holding the sample at 250 °C. The exposure dose amounts to 60 L H₂.

can be regarded as an enhancement of the peak at the same energy of clean silicon due to the hydrogen coverage. The peak at -10 eV is attributed to the adsorbed hydrogen, and its contribution is less in the monohydride than in the dihydride phase as shown below. Besides these peaks we see a further structure at $\sim -15 \text{ eV}$ in the He II spectrum. In this energy region it appears that features of the EDC are visible in He II, but hidden within the background of secondary electrons in He I. The AES ratio O/Si of this experimental run amounted to 5×10^{-4} .

In Fig. 3 we present a set of HeII curves obtained before and after exposure to 10^3 L H_2 at room temperature and measured after annealing to different temperatures. Curve a represents the clean Si spectrum, curve b is a spectrum accompanied by a 1×1 LEED structure and attributed to the dihydride phase. Whereas the shoulder near -7 eV is certainly due to Si states, probably the backbonding states, the peaks at -10.0 and -14.7 eV reflect the contribution from hydrogen chemisorption. A further remarkable change from the clean to the hydrogen-covered surface is the shift of the steep slope characterizing the valence-band maximum. As the sample is p-doped, the band bending gives only a small contribution. Furthermore, we must take into account that surface states, which can be observed as a small hump near the valence-band maximum,⁶ are deleted upon hydrogen adsorption. This process may also give rise to the shift mentioned above.

The monohydride phase should develop after heating up to 250° C.¹ We obtained a spectrum with five peaks located at -8.0, -9.2, -10.0, -11.5, and -13.9 eV (curve c in Fig. 3). Although the peaks at -9.2 and -10.0 eV are small, their energy positions are exactly reproducible. The obvious differences between this spectrum and the one in Fig. 2, we attribute to the monohydride phase, may be due to the different preparation procedures. In Fig. 2 the monohydride phase is built up at a characteristic hydrogen coverage while keeping the sample at the critical temperature of 250° C, whereas curve c in Fig. 3 was achieved starting with a fully hydrogencovered surface and gentle, stepwise heating to 250° C.



FIG. 3. Set of He II curves obtained during thermal desorption of atomic hydrogen. Curve a, clean surface; curve b, H-saturated surface produced by an exposure of 10^3 L H at room temperature. The temperature at which the sample has been held for 1 min are 250 (c); 300 (d); and 400 °C (e).

Consequently, in the former procedure SiH_2 complexes are formed concomitantly by the impinging H atoms, but they are transformed subsequently to the monohydride by H_2 evolution, so that an equilibrium may be established between the monohydride and dihydride mixture. In the latter, a stable and regular monohydride phase should be produced without any mixture of the dihydride. Further heating to 300 and 400 °C (curves d and e in Fig. 3) clearly exhibits the shape of curve a again, which is in conformity with the fact that at around 400 °C hydrogen desorption takes place. It also reveals that the oxygen contamination stayed below a tolerable limit.

III. CLEAN Si(100)-(2×1) SURFACE

During the course of our study we noted that the features of the monohydride phase on the Si(100)- (2×1) surface have a close bearing on the states inherent to the clean surface. Therefore, we first present our results concerning the clean surface, which in turn brings a number of new aspects into view.

The symmetric dimer-bond formation⁷ was suggested long ago, but the observation of the superlattice gap between the surface-state bands⁸ has led to the consideration of the asymmetric (or ionic) dimer-bond model.⁹ Some experimental data, such as angle-resolved ultraviolet photoelectron spectroscopy^{8,10} (ARUPS) and work-function measurements,¹¹ favored the ionic dimer-bond formation on the Si(100) surface, and this fact was reinforced by the LEED (Ref. 12) and the self-consistent total-energy calculations.¹³ Calculated bands^{9, 14-16} associated with the asymmetric dimer bond were able to display the main aspects of the electronic structure, specifically the superlattice gap, though their energy positions have been a subject of dispute. The energy bands illustrated in Fig. 4 are calculated by using the reconstruction geometry proposed by Chadi.⁹ Here and in the rest of the paper the top of the valence band (VB) marks the zero of energy. The locations and dispersions of the surface-state bands in the fundamental gap region are in good agreement with the ARUPS data, but differ from that calculated by the selfconsistent pseudopotential method.¹⁴ On the other hand, the surface-related states in the VB are similar to the selfconsistent bands, though some differences are discernible. The dangling-bond band, S_u , is formed primarily from the $s + p_z$ orbitals of the up-surface silicon, whereas the contribution of the down atom becomes significant near the center of the surface Brillouin zone (BZ). This band has a width of 0.5 eV and is fully occupied. The empty band S_d is separated from S_u by a superlattice gap of ~ 0.6 eV, and is mainly associated with the down-surface silicon. The dispersion of this band along J-K-J' is found to be sensitive to the slab thickness, such that a thin slab of 13 atomic layers ended up giving a negative dispersion leading to a smaller superlattice gap. Therefore, it appears that a realistic superlattice gap can only be obtained by using a thick slab, as in fact was done here. In the underlying reconstruction model one distinguishes three different types of Si-Si bonds of relevance, namely the ionic dimer bond and two backbonds connecting the up and down atoms to the second layer, which in turn intro-



FIG. 4. Energy-band structure of the clean Si(100)- (2×1) with an asymmetric dimer bond. Heavy and dashed lines denote surface states and surface resonances. Shaded areas are the bulk states projected to the surface BZ. The inset delineates the irreducible part of the surface BZ with the symmetry point labeling previously adopted. Labeling of the surface states are explained in the text. The zero of energy marks the valence-band maximum.

duce several surface states, mostly resonances. Near the edge of the VB and at the center of the zone these resonances (some of them hybridize with S_{μ}) are expected to contribute to the ARUPS intensity at $\theta = 0^\circ$, and thus to the shoulder at ~ -1.0 eV. The upper lying peak observed near the J' point of the multidomain zone may also be attributed to these resonances.¹⁰ The S_b band, which is located just at the bottom edge of the VB along J-K-J' direction, is produced mainly by the second-layer Si s orbitals, and perhaps is connected with their displacement from the ideal positions. Similarly, bands near K at ~ -9 eV and also in the gaps along J'- Γ at ~ -8 eV are s-type states localized near the subsurface layer. The surface band labeled by S_{DB} (DB represents the dimer bond) originates from the surface Si s orbitals, and is therefore identified as s-type dimer-bond states. The resonances near the center of the surface BZ at ~ -9.5 eV are the stype backbonding states. In the energy region from ~ -6 to ~ -5 eV the resonance states (SP_b) along the K-J'- Γ direction are also localized at the backbonds. The p-type backbonding states (P_b) appear at K near -3.7 eV, and disperse to ~ -1.0 eV along the J'- Γ direction. The differences in the geometry of the backbonds impose the splitting. The *p*-type dimer-bond band,¹⁷ P_{DB} , occurs along the *J-K-J'* direction. The antibonding combinations of these states discussed above are located in the upper region of the optical gap (band labeled by P_a) and also in the conduction band.

Figure 5 illustrates the local density of states (LDOS). The UPS spectra^{8,18} are reproduced by taking E_{F} - $E_V \cong 0.4$ eV, which also aligns the bulk peaks at about -7.0 eV. The S_u peak is contributed mainly by the up atom, whereas the lower part of the valence band is seen to have equal contributions from both surface atoms. In our population analysis this is recognizable by the 0.45 electron excess charge on the up-silicon atom (0.25 electron of which is transferred from the down atom, and the rest is taken from the subsurface atoms), so that the dimer bond becomes ionic and hence a surface dipole moment develops. In addition to the S_d and S_u peaks, P_{DB} , P_b , S_{DB} , and SP_b states are revealed by comparison of bulk and surface densities of states in Fig. 5. Since the S_b states are mainly localized at the subsurface layers, the corresponding LDOS structure does not occur in Fig. 5, but is intensified in the LDOS of the second layer. It can be seen that the UPS features^{8,18} illustrated by curves a and b in Fig. 5, such as the two peaks at the upper edge of the VB, are reproduced by the theoretical state densities. In the He II spectrum (curve c) the S_{μ} states are merged in the valence band and appear as a small hump near the VB maximum, so they are not as pronounced as in the HeI spectra (curves a and b). This can be explained by the fact that the HeII spectrum delivers comparably smaller resolution for *p*-type surface states. Our experimental and theoretical results suggest that the triangular-shaped UPS structure¹⁹ at ~ -2.7 eV is produced by the $P_{\rm DB}$ dimerbond states, p-type backbonding states (P_b) , and bulk states as well. It appears that the HeII spectrum puts emphasis on the dimer-bond states, which are clearly resolved in the ARUPS.¹⁰ The previous spectra fail to give any indication concerning SP_b and S_b states, which seemingly contribute to the broad, high-binding-energy peaks of the He II spectrum. However, neither of the UPS spectra gives any indication about the strong S_{DB} peak at ~ -8 eV, which was reproduced in several calcula-tions.^{9,15,16} Thus we raise the question whether the UPS technique has been sufficiently adequate to resolve the high-binding-energy features. In particular, this part of



FIG. 5. Calculated LDOS at two outermost silicons of the clean Si(100)-(2×1) surface with the shaded area illustrating the contribution of the up atom. Shown by the dotted line is the LDOS at two silicons located at the middle of the slab. Curves a and b are the photoemission spectra (hv=21.2 eV) reproduced from Refs. 8 and 18. Curve c is the He II spectrum.

the spectrum may be obscured by the secondary scattering in the HeI, or the emission may be restrained by matrixelement effects. In this respect, a further investigation of the intrinsic surface states, by using for example a different photoemission technique that emphasizes s-type states, is expected to elucidate the spectrum, and also to reveal worthwhile information concerning the surface geometry. Apart from the UPS data additional information concerning the intrinsic surface states can be obtained from surface photovoltage measurements²⁰ and electron-energy-loss spectra (EELS).^{21,22} As previously noted¹⁵ the superlattice gap between S_u and S_d bands is in good agreement with the value of the indirect gap deduced by Mönch et al.²⁰ In the EELS spectrum Rowe and Ibach²¹ observed three surface-related features at 1.7 ± 0.4 , 8.4 ± 0.8 , and 14.7 ± 0.8 eV. By assuming a single final state they attributed these features to the transitions from the dangling and backbonding surface states. Recently, the angle-resolved EELS spectrum by Maruno $et al.^{22}$ confirmed the previous EELS data. As illustrated in Fig. 6, the low-energy EELS feature can be ascribed to the transitions from the filled surface band, S_{μ} , to the empty band, P_a , lying ~1.5 eV above the VB. Based on the present results we tentatively assign the following transitions to result in the high-energy peaks in the EELS spectrum. For the ~ 8.0 -eV transition the initial state might be either the SP_b states at ~ -6.0 eV, or more favorably, $S_{\rm DB}$ states. Then the corresponding final states should be empty gap states: either P_a or S_d . The 14.0-eV transition is somewhat unexpected. If such a transition exists it should occur from the high density of states of the S_b band at the bottom edge of the VB.

Before concluding this section, mention should be made that the agreement between our results and the ARUPS data—that is one of the best obtained so far^{23} and even



FIG. 6. Tentative interpretation of the EELS spectra by using the LDOS at two outermost silicons of the clean Si(100)- (2×1) surface. The numbers in parentheses denote the transition energies taken from Ref. 21.

better than that obtained by the self-consistent pseudopotential calculations-must be viewed as the justification of the ionic dimer-bond model, rather than the confirmation of a particular geometry proposed in Ref. 9. First of all, within the ETB framework the transfer of charge among the surface atoms is not (of course, cannot unambiguously be) reflected to the energy parameters. Otherwise, to keep the same superlattice gap the up atom must be raised further. This leads to a longer dimer bond. Secondly, the bulk energy parameters are customarily scaled when the first- and second-neighbor distances d deviate from their ideal bulk values. We found that some of the surface features depend (though not strongly) on the type of the scaling. For example, as compared to the d^{-2} scaling²⁴ used in this study exponential scaling²⁵ of energy parameters (as inferred from the extended Hückel method) gives rise to a narrower band for the filled surface states. At this point it is worthwhile to discuss a different model of reconstruction, and specifically its implications on the surface electronic structure. Recently, Yang et al.²⁶ carried out extensive LEED-intensity calculations for a variety of most likely configurations, and arrived at an asymmetric dimer-bond geometry in which surface atoms are displaced not only along the [001] and [100], but also along the [010] direction. Since the ionic dimer bond was also retained in this new model, overall features of the electronic structure calculated therein (such as the superlattice energy gap and the surface states in the valence band), can expectantly be viewed to be similar to that presented in Fig. 4. However, striking differences are recognized near the top of the VB, where a backbonding state appears between \hat{S}_d and S_u . Moreover, the width of the filled surface band, S_u , recedes and *p*-type dimer-bond states, P_{DB} , disappear. As far as these changes are concerned, the reconstruction model put forward by Yang et al.²⁶ leads to the theoretical one-electron states which are apparently at variance with the ARUPS bands,^{8,10} in spite of the fact that their model yields calculated LEED profiles which are, as compared to previous models, in better agreement with the experimental data. In regard to the position and the width of S_{μ} , another point of controversy is the band structure calculated by Ihm et al.¹⁴ using the self-consistent pseudopotential method. Even though they used the same surface atomic configuration as we used in the present study,⁹ their filled surface state band S_u occurred 0.8 eV too high in energy and had a larger width as compared to the ARUPS bands. Mazur and Pollmann¹⁵ sought the source of the disagreement in the method, and claimed it was due to the Si pseudopotential used in the calculations of Ihm et al.¹⁴ These discrepancies point to fundamental questions as to how precisely one can predict the surface atomic configuration by using the current one-electron theories at hand, such as band structure and total energy calculations, etc., and to what extent their predictions should be compared with the experimental data, such as ARUPS, LEED, etc. However, we shall bear in mind the possibility that on the theoretical side one has not converged to the most likely surface structure vet. Nevertheless, a worthwhile conclusion drawn from this discussion is that the ionic dimer-bond formation is essential to the electronic structure of the Si(100)- (2×1) surface, and the ETB, being quite sensitive to the surface structure, is capable of yield-ing the fundamental aspects of the spectrum.

IV. $Si(100)-(2 \times 1) + H$ SYSTEM (MONOHYDRIDE PHASE)

Appelbaum et al.²⁷ performed a self-consistent calculation of the monohydride phase on the Si(100)-(2 \times 1) surface by using an atomic configuration in which each surface Si was bonded to H along the fourth tetrahedral direction and also formed a symmetric dimer bond with the nearest-neighbor surface silicon. While they were not able to reconcile the calculated chemisorption states with the existing UPS spectrum,¹ they attributed the disagreement to a different (2×1) reconstruction form that may occur upon chemisorption. Based on the LEED data, we explored the electronic structure of the Si(100)- (2×1) + H system in several possible atomic configurations consisting of asymmetric or symmetric dimer bonds with various H-Si-Si bond angles. Aside from shifts of the peak positions and changes in the peak intensities the salient features of the surface electronic structure remained unaltered in all cases. Here we concentrate particularly on a bonding model (which is essentially the same as that employed by Appelbaum et al.²⁷) because recent experimental data have provided evidence for the appropriateness of this model. That the LEED pattern of the Si(100)-(2 \times 1) surface became pronounced and the half-order spots were intensified upon the chemisorption of H implies that the distortions at the subsurface bonds of the clean surface are relieved and the ionic dimer structure is probably reconstructed to a covalent dimer.²² Additional evidence emerges from the work-function measurements by Koke and Mönch¹¹ to support the above surface structure. Furthermore, the HeII spectrum presented in Fig. 3 was capable of resolving additional chemisorption features, which can easily be reconciled with the calculated state densities. In what follows we briefly discuss the electronic structure.

In Fig. 7 it is observed that upon the formation of the monohydride most of the localized states of the clean surface are removed, and henceforth new states of different character are produced. The 1s state of the free H atom has a binding energy of 13.6 eV, so it can hybridize with Si states throughout the VB. However, strongly localized states are split from the bulk states, and can be identified with their Si orbital component. In the s-orbital region of the VB the band at the bottom edge originates from the similar band of the clean surface (see Fig. 4), and mixes with the H s orbital. The s-type SiH band (D_5) is formed by the bonding combination of Si s and H s orbitals and lies at about -8.0 eV in the gap near the K point of the surface BZ. It should be recalled that for the monohydride phase on the Si(111) surface chemisorption states of similar character were found at about -7.0 eV. *p*-type SiH bands, D_2 and D_3 , are split because of two hydrogens in the surface unit cell which interact with each other via Si-Si bonds. The D_1 band appears in the small upper gap at the K point, and displays the same orbital character. The antibonding SiH states occur in the optical gap, but their position should not be so precise because of the



FIG. 7. Energy-band structure of the chemisorbedhydrogen-covered Si(100)- (2×1) surface with a symmetric dimer bond between two surface silicons. The lengths of all the Si–Si bonds at the surface are taken as the same as in the bulk, and the subsurface atoms are assumed to lie in their ideal position. The Si–H bond is taken to be 1.48 Å long, and lies close to the fourth tetrahedral direction. Heavy lines denote strongly localized SiH states. Closed circles are SiH resonances. Resonance states of the Si dimer bond and Si backbonds are shown by open circles. The zero of energy is set to coincide with the top of the valence band.

inadequacy of the ETB method in describing the conduction-band states. As a matter of fact, these states are pushed toward the edge of the conduction band in the EHT calculation. Also shown in the figure along the ΓJ and $\Gamma J'$ directions are the bulklike states with comparably small H contribution. These demonstrate that to a large extent the s orbital of H diffuses into the VB states. States shown by open circles at the upper part of the VB are the Si resonances localized at the dimer bond and backbonds, indicating the fact that these intrinsic states pertain to the dimerization and persist even after the chemisorption of H.

In Fig. 8 we present calculated state densities together with the HeII UPS spectrum and several other spectra found in the literature. For the sake of comparison the LDOS and the UPS spectrum of the Si(111) + H monohydride are also illustrated on the same figure. Since the band bendings upon hydrogenation are not clearly known, experimental curves are aligned with respect to the peak at 7 eV below the VB maximum. The triangular-shaped structure of the LDOS is produced by the dimer-bond states ($P_{\rm DB}$) at ~2.4 eV and also by the backbonding states (P_b) at ~ -2.5--3.0 eV. This structure disappears at the LDOS of H alone. Interestingly, such a structure is not seen at the LDOS of the Si(111) + H system. The UPS spectrum by Himpsel and Eastman⁸ gives



FIG. 8. Calculated state densities for the Si(100)- $(2 \times 1) + H$ system (monohydride phase) and related spectra. The LDOS at H and surface silicons is shown by heavy lines. The curve by dashed-dotted line corresponds to a similar system except the dimer bond is elongated by ~10%. The curve by dotted line has the same normalization and illustrates the LDOS at H and outermost silicon of the ideal Si(111) + H system. Curves a and b are the photoemission spectra ($h\nu = 21.2$ eV) reproduced from Refs. 1 and 8. Curve c is the HeII spectrum taken from the Si(100) surface, which was first hydrogenated at room temperature and subsequently heated up to 250 °C. Curve d is the HeI spectrum of the Si(111) + H system reproduced from Ref. 3.

some indication about the P_b and P_{DB} states, whereas the original spectrum by Sakurai and Hagstrum¹ fails to resolve them not only for the hydrogenated surface, but also for the clean surface. In the HeII curve, the shoulder near the VB maximum is identified as the dimer-bond states. The first lowest-binding energy peak must be produced by the emission from the P_b and D_1 states. The two-peak pronounced density of states of p-type SiH states $(D_2 \text{ and } D_3)$ becomes less intense, but broader as compared to the monohydride phase occurring on the Si(111) surface. The HeI UPS spectra^{1,8} confirm this conclusion, but fail to resolve two peaks. These two structures are clearly observable in the HeII spectrum. Based on his high-exposure (18000 L) UPS spectrum Fujiwara²⁸ pointed out two H-related structures at the energy range of p-type SiH states. The other peak at ~ -7.0 eV is mainly produced by the bulk states and partly by the D_4 resonances. The broad peak near -9.5 eV (below E_V) in the HeII spectrum is associated with D_5 and/or D_6 bands. This information is apparently obscured in the HeI spectrum.¹ However, the HeII spectrum does not display a peak as sharp as D_5 seen in the LDOS, perhaps due to matrix-element effects. In the angle-resolved EELS spectrum,²² p-type SiH states become observable by a transition at 8.5 ± 1.0 eV, and show no dispersion. The high-energy transition (at 14.0 ± 0.2 eV) of the clean surface stays intact after the formation of the monohydride phase, and hence confirms our interpretation in Sec. III. The broad structure in curve c near -12 eV may be assigned as the initial state for the high-binding-energy transition.

Our population analysis shows that ~ 0.3 electron is transferred from the Si surface to the chemisorbed H. Since most of the charge is supplied by the surface silicons, one consequently expects that the dimer bond becomes softer and longer. We have explored such a possibility by using a model in which the symmetric dimer bond is taken to be $\sim 10\%$ longer than the bulk value. The LDOS corresponding to this configuration shows that the space between the D_2 and D_3 peaks of *p*-type SiH states becomes larger, and in this respect the agreement between the theory and experiment becomes even better (see Fig. 8). The high-binding-energy region of the state density preserves, however, its original shape, even after the elongation of the dimer band.

V. $Si(100)-(1 \times 1) + 2H$ SYSTEM (DIHYDRIDE PHASE)

The most relevant spectral observation pertaining to this phase is that the low-binding-energy feature at about -5.0 eV becomes intenser and broader, and on the contrary the feature at -7.0 eV recedes.¹ As for the bonding structure, one may have customarily thought that two H atoms attaching to each surface Si form Si-H bonds along tetrahedral directions. The LDOS shown by curve a in Fig. 9 is based on this geometry, and confirms the above observation, namely that the low-binding-energy



FIG. 9. Calculated state densities for the Si(100)- $(1 \times 1) + 2H$ system (dihydride phase). Curve a is the LDOS at two H and surface Si with $V_{H-H}=0$. The dotted curve is the LDOS at H and surface Si of the monohydride phase on the ideal Si(111) surface. Curves b and c are the same as curve a, except that V_{H-H} is assumed to be 1.0 and -1.0 eV, respectively. Curve d is the same as curve a, except that one of the Si-H bonds is in the surface plane, the other is perpendicular to it. State densities depicted by curves a-d are calculated by the ETB method. Curve e is calculated by using the EHT method and has the atomic configuration of curve d. Curve f is the HeI spectrum reproduced from Ref. 1, and curve g is the HeII spectrum.

feature is intensified. The calculated surface features here are realistic only at low coverages of SiH2. However, the energy parameter $V_{\text{H-H}}$ representing the interaction between the two H atoms on the adjacent cells (which are only 1.42 Å apart from each other) becomes significant at full coverage, but is neglected in the ETB Hamiltonian. To investigate the effect of the H-H interaction the LDOS shown by curves b and c are calculated by the tentative values of $V_{\text{H-H}} = 1.0$ and -1.0 eV, respectively. In the presence of the attractive interaction the increased dispersion of the prominent p-type SiH band leads to the two well-separated peaks in disagreement with the experiment. The repulsive interaction that seems to be favorable from the total electronic energy²⁹ point of view inverses the dispersion of this band, and causes the main peak to become broader. However, the LDOS calculated by the EHT method, wherein the H-H interaction is taken into account properly, deviates drastically from the spectrum, and consequently casts doubts on the appropriateness of the tetrahedrally coordinated dihydride phase at full coverage. Moreover, on the basis of our population analysis and the electronegativity arguments, as well as in view of the observed shift³⁰ of the Si 2p core level caused by the chemisorption of H, the work function is expected to increase when the monohydride changes to the tetrahedrally oriented dihydride phase. The experimental data,¹¹ on the other hand, show a different trend. For low coverage of SiH₂ the work function increases slightly, whereas increasing coverage causes the work function to decrease. This behavior of the work function may be interpreted to imply that one of two Si-H bonds attached to the same surface Si rotates as the SiH₂ coverage increases. The driving force for this rotation may be the repulsion between closely lying hydrogens as substantiated by the self-consistent total-energy calculation.²⁹ Among various possibilities, a binding structure consisting of two Si-H bonds, one is perpendicular to the surface, the other lies in the surface and in a plane bisecting the backbonds, can be proposed. This structure is found to comply with the experimental data, and is reminiscent of the dangling bonds reforming on the ideal Si(100) surface as well.³¹ Furthermore, the proposed binding structure is consistent with the Fourier-transform spectrum by Chabal et al.³² The perpendicular and parallel SiH bonds lie in different environments, so they should have different eigenfrequencies.

The LDOS of the rotated dihydride phase is calculated by using the ETB and EHT methods, and is presented in Fig. 9 by curves d and e, respectively. Obviously, both state densities are almost identical, and give a good account of the UPS spectrum. The small peak or the shoulder of the LDOS at ~ -4.0 eV is associated with the parallel bond, and should correspond to the lowbinding-energy shoulder of the HeII curve. The prominent peak coincides with the major peak of the HeII curve. The broadening of the single, predominant peak in curve a can be understood in terms of the splitting of the t_2 level which occurs when a similar bond rotation is imposed on the SiH₄ molecule. The angle-resolved EELS spectrum²² taken from the dihydride phase resolved a peak associated with the SiH state displaying a higher dispersion as compared to the monohydride phase. Assuming a flat final state, the dispersion in question can also be explained by the broadening due to the Si—H bond lying in the surface. In the high-binding-energy region of the HeII spectrum the broad peak is associated with *s*type SiH states seen in the LDOS. It should be noted that the emission from these states is obscured in the HeI spectrum.

In concluding this section it is worthwhile to stress that the present results do not rule out the occurrence of the tetrahedrally coordinated SiH₂ complex leading to a slight increase of the work function at the initial stage of the room-temperature chemisorption. The Si-H bond lying in the surface plane and occurring at a advanced stage of chemisorption does not have any bearing on the unconventional bonding of H put forward by Appelbaum *et al.*³³

VI. DISCUSSION AND CONCLUSIONS

(i) Present experimental data and calculated electronic structure as well show that the monohydride phase formed on the Si(100)-(2×1) surface differs from the monohydride phase of the Si(111) surface. Because of two hydrogens, each attached to a surface silicon of the (2×1) unit cell, the major H peak at ~ -5.0 eV split and gives rise to additional structures in the spectra. The dimer bond connecting two surface silicons induces p-type Si resonances at the upper region of the VB and also s-type SiH states at about -8 eV. The former feature is then characteristic of the clean, as well as the hydrogenated surface in the form of the (2×1) reconstruction. While the experimental data can be interpreted to justify the atomic configuration (i.e., symmetric and possibly elongated dimer bond) the feature corresponding to s-type SiH states remains to be searched by different electronemission techniques. It should be recalled that the monohydride and trihydride phases³⁴ on the Si(111) surfaces have been shown to display states of similar character at -7.0 and -10.0 eV, respectively.

(ii) It emerged from the self-consistent pseudopotential calculations¹³ that the total energy of the $Si(100)-(2\times 1)$ surface with a symmetric dimer bond is lower than that of the ideal surface by 1.5 eV per dimer bond. When H saturates the dangling bonds the charge is transferred from the surface silicons, and consequently the energy of the dimer bond is expected to reduce. Therefore, the activation barrier which forms SiH₂ from the Si(100)-(2×1) + H system is estimated to be smaller than 1.5 eV. However, once the atomic hydrogen is available on the surface the empirical total-energy arguments³⁵ suggest that the breaking of the dimer bond which produces the tetrahedrally coordinated dihydride from the Si(100)-(2 \times 1) + H system is energetically favorable, and should relieve an energy of ~ 6.0 eV per dimer. The desorption energy of H from the monohydride phase of the Si(100)-(2 \times 1) surface can be estimated to be ~ 2.5 eV by taking the binding energy of the Si-H bond as 3.5 eV and the dissociation energy of H_2 as 4.5 eV. This value is in good agreement with the experimentally determined desorption energy.³⁶ On the other hand, the desorption of the H₂ molecule from the closely lying SiH₂ complexes is found to require an energy

of ~ 1.5 eV. When the weakness of the dimer bond upon H chemisorption is taken into consideration, this desorption energy may even increase slightly. Two different desorption energies corresponding to the monohydride and dihydride phases may induce two well-defined peaks³⁷ in the desorption curve of H. As a matter of fact, the desorption spectrum³⁸ obtained from the Si(111) surface exhibited two peaks which were attributed to different binding structures of H. As proposed by Wagner et al.² the monohydride and dihydride phases may coexist on the Si(111) surface, but their weights are determined by the surface temperature. Under this context we emphasize that the low-energy desorption feature observed on the hydrogenated Si(111) surface should have a close connection with the reformation of the Si-Si dimer bonds upon the H evolution. Also, the answer to the question as to why the dihydride phase is stable below $\sim 150 \,^{\circ}\text{C}$ and how the interplay between monohydride and dihydride takes place can be sought from the relatively low desorption energy of H from SiH₂.

(iii) On the basis of the experimental data, as well as the calculated state densities, it is proposed that the tetrahedrally coordinate SiH bonds of the SiH₂ complex on the Si(100)-(1×1) surface rotate at high coverage. Further investigation of this binding geometry by the self-consistent total-energy calculations is highly desirable.

(iv) We carried out calculations by using clusters to simulate the amorphous environment, and also our arguments concerning the formation energy of the SiH₂ complex suggest that the dihydride phase can also occur in the amorphous silicon. Since the dominant feature of this phase is broad and overlaps with that of the monohydride phase, the UPS spectrum³⁹ cannot easily be interpreted to rule out the occurrence of the SiH₂ complex in the hydrogenated amorphous silicon.

(v) It emerges from our calculations that the locations of strongly localized SiH states mainly depend on the bond order and on the symmetry of the underlying Si surface. It is also interesting to note that the monohydride phase on the cluster without a ring structure is found to yield s-type SiH states at about -7.0 eV.

(vi) The room-temperature UPS spectrum obtained from the Si(110) + H surface⁴⁰ is found to be reminiscent of the spectrum associated with the dihydride phase on the Si(100)-(1×1) surface. Both Si surfaces, namely Si(110)-(1×5) and Si(100)-(2×1), can be considered similar, except that the former displays a chain structure. By examining the evaluation of the room-temperature and high-temperature spectra of the hydrogenated Si(110) surface we cannot find any strong argument against the interpretation in which one foresees both SiH and SiH₂ coexisting on this surface at room temperature.⁴¹ In this regard the study of the H vibration on the chemisorbedhydrogen-covered surface by using the high-resolution EELS or Fourier-transform infrared spectroscopy is expected to provide useful information. It should be noted that previously the chemisorption features of the roomtemperature UPS spectrum were attributed to unconventionally bonded hydrogens³³ that would certainly induce vibrational features different from the conventionally bonded hydrogen.

(vii) The UPS spectrum of the Si(111)-(7 \times 7) surface at room temperature and at intermediate H exposure did not exhibit a chemisorption feature at -7.0 eV. This was attributed to the absence of the H-H interaction via back-bonds at low coverages.⁴² We calculated the electronic structure of the Si(111)- (3×3) + H (i.e., ~0.1 monolayer coverage of H) and of the Si(111)-(1 \times 1) + H (full coverage), and found that even the low coverage of H induces s-type SiH states (at \sim 7.0 eV) with a lessening degree of localization. Motivated by the fact that the vibration spectrum of H on the Si(111)-(7 \times 7) surface provides evidence on the occurrence of the SiH₂ complex,² and that the state density illustrated in Fig. 9 is similar to the UPS spectrum in question, we suggest that the intermediate phase forming on the Si(111)- (7×7) surface at room temperature should have a connection with the dihydride phase. It appears that at higher H exposures the monohydride prevails over the dihydride phase.

In summary, in spite of the fact that hydrogen is the simplest atom and readily forms bonds with silicon, the interaction of this atom with silicon surfaces and the resulting binding structure are seen to be rather complicated. It is seen that the surface symmetry plays an important role in the binding structure. The HeI spectrum alone is not capable of revealing all the interesting features of the electronic structure. Additional information was conveyed by the HeII spectrum. Presently, the chemisorption states lying at the upper part of the valence band are well understood, whereas some of the highbinding-energy states of the clean and H-covered Si(100) surface are not observed yet, and clearly more remain to be done experimentally. The dihydride phase occurring on the Si surfaces is seen to display interesting features. As interpreting the spectrum one should keep in mind the possibility that this phase already exists in varying amounts depending on the temperature and exposure.

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