

$n(\vec{r})$ to be the total electron density; however, if we had incorrectly used only the valence electron density in Eqs. (10) and (11) the results would have been similar to those obtained from Eq. (12). Thus we see that by using the total electron density in G_{xc} the influence of the core electrons on XC is properly accounted for.

The validity of the VP theory is established by the success of its predictions for Li and Na where there is little doubt about the values of χ_h/χ_0 since $r_s \lesssim 4$, and where χ has been measured directly.¹⁰⁻¹² Furthermore, for K and Rb the VP predictions for χ differ from the dHvA values by at most 5% and the existence of spin-wave measurements removes the ambiguity in the dHvA method. If we consider the fact that the calculations have been done in the spherical-cell approximation this level of agreement suggests the correctness ($\pm 5\%$) of recent calculations of χ_h/χ_0 for $r_s \lesssim 5$. Unfortunately, for Cs there are only the dHvA results which admit two plausible values of χ/χ_0 (1.76 and 2.24). Our calculation indicates strongly that the higher value is correct, but this is dependent upon the spherical-cell approximation for calculating m_s (and $\gamma[\vec{r}; n]$) and upon the use of χ_h/χ_0 for $r_s \lesssim 5.6$ where the calculations are most uncertain. Therefore, measurements of χ that could distinguish between the two plausible dHvA values would be very helpful in furthering our understanding of XC effects in the range $4.5 \lesssim r_s \lesssim 5.6$.

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Si(111):SiH₃—A Simple New Surface Phase

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Photoemission spectra show that atomic hydrogen reacts near room temperature with Si(111)1×1 to form a trihydride phase, Si(111):SiH₃. The new phase, clearly to be distinguished from the monohydride Si(111):H obtained from Si(111)7×7, has been identified by theoretical calculation of the photoemission spectrum. Formation of Si(111):SiH₃ suggests that the vacancies that exist on clean Si(111)7×7 are disordered on Si(111)1×1.

In several recent studies chemisorption of oxygen^{1,2} and hydrogen^{3,4} on various semiconductor surfaces has been investigated by energy-loss, ion-neutralization, and ultraviolet-photoemission spectroscopies (UPS). For each of the surfaces studied it was concluded that the adsorbate atom

forms bonds with surface atoms of the equilibrium clean surface. For the particular case of atomic hydrogen adsorbed to the annealed Si(111)7×7 surface, theory^{5,6} and experiment⁴ agree in suggesting that the H atoms bond to the single dangling orbital per Si atom to form what we

shall call the monohydride phase represented by Si(111):H.

In this paper we report the first observation and interpretation of another hydrogenated surface phase of Si(111) in which SiH₃ radicals are attached to the dangling orbitals of Si(111). We represent this trihydride phase by Si(111):SiH₃. Its electronic energy levels are strikingly different from those of Si(111):H.

The monohydride and trihydride surfaces are produced by hydrogenation of different clean starting surfaces. That for Si(111):H is the annealed and well-ordered Si(111)7×7. This is achieved by the removal of approximately 1000 monolayers by sputter etching, annealing at 600°C for about 10 min, and cooling to room temperature. The starting surface for the production of Si(111):SiH₃ displays a 1×1 low-energy-electron diffraction (LEED) pattern in which the relative intensity of background to diffraction spot is greater than in the 7×7 pattern. The 1×1 surface is achieved from the clean 7×7 surface by heating to 800°C for 10 min followed by quenching to room temperature.⁷ Although others have achieved this surface at room temperature by specific impurity stabilization,⁸ inspection of our sample by Auger-electron spectroscopy revealed no impurity signals distinguishable above noise level (1/2000 of the principal Si signal at 91 eV). Moreover, as judged by both LEED patterns and UPS spectra, we have alternately produced the 1×1 and 7×7 surfaces at room temperature over tens of cycles.⁷

Hydrogenation was achieved⁴ by dissociation of H₂ to 2H at the heated W filaments in our sputtering apparatus. The sample is inserted into a metal sphere inside which it is surrounded by, but shielded from, four W filaments. We cannot specify the H arrival rate as such but can specify the constant pressure of H₂ (3.0×10⁻⁶ Torr), the constant temperature at which the filaments are held during the exposure (1710°C), and the exposure time. Proximity to the hot filaments raises the temperature of the sample to about 150°C in a few minutes.

The UPS spectrum of the clean 1×1 surface, shown as the lowest curve in Fig. 1, is similar to that of the 7×7 surface,⁴ except that the valley at $E - E_{\text{vac}} \approx -10$ eV is shallower. In the UPS measurements all photoemitted electrons are detected using a four-grid analyzer. In the early stages of the H exposure, near 2-min exposure time, two peaks at $E - E_{\text{vac}} \approx -10$ and -12 eV (labeled C and D in Fig. 1) appear. In this spec-

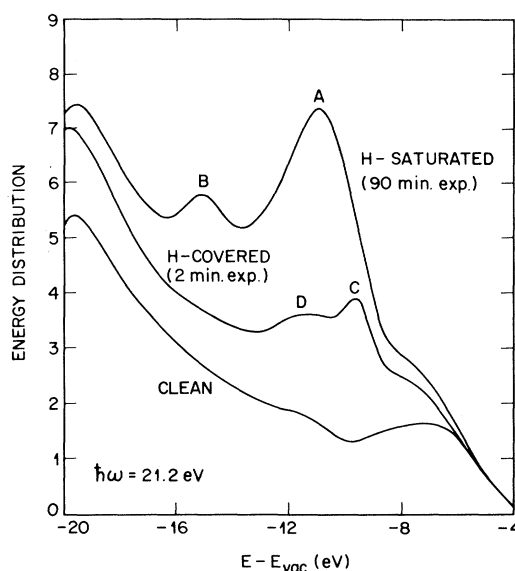


FIG. 1. UPS spectra of clean Si(111)1×1 and surfaces derived from it by exposure to atomic hydrogen near room temperature.

trum the H-related structure is similar to that in the UPS spectrum of Si(111):H,⁴ but is weaker and is smeared out or broadened. Continued H exposure, however, changes the spectrum dramatically with the complete disappearance of peaks C and D and the appearance of two new peaks at $E - E_{\text{vac}} \approx -11$ and -15 eV (A and B in Fig. 1). For the same generation rate of atomic hydrogen the exposure time required to produce the terminal spectrum associated with H saturation (90 min) is approximately 6 times longer than that needed to saturate the 7×7 surface (15 min). The LEED pattern of this new H-saturated surface is 1×1.

Thermal-desorption experiments showed Si(111):SiH₃ to be quite stable in that heating to 700°C for 30 sec was required to recover the UPS spectrum of the clean 1×1 surface. During thermal desorption the intensities of peaks A and B in the spectrum decrease monotonically without the reappearance of peaks C and D. This indicates that the first stage of H exposure when the C and D peaks are seen differs fundamentally from the subsequent exposure that produces peaks A and B.

To interpret the new spectrum we have calculated photoemission spectra for several plausible models.⁶ The only model which gives good agreement with the new experimental spectrum is Si(111):SiH₃. The theoretical photoelectron distribution, including secondaries and effective

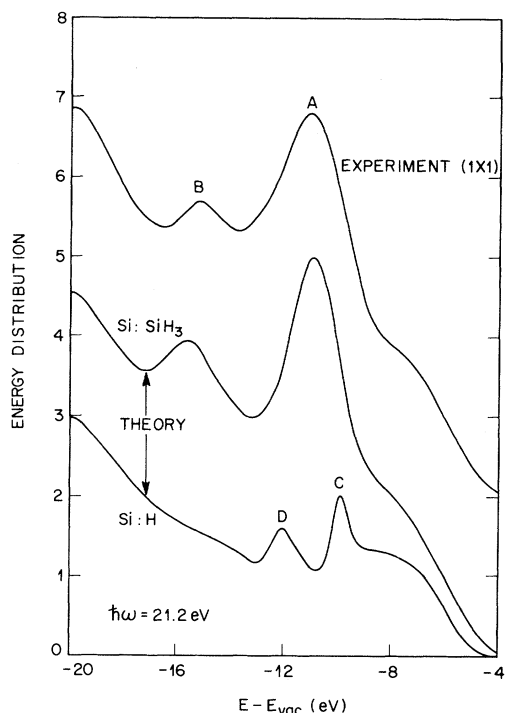


FIG. 2. UPS spectra for the trihydride (top curve) compared with the theoretical spectrum (center). The top curve is shifted up by 2 units for clarity. The lowest curve shows the theoretical spectrum for Si(111):H. The theoretical spectra are broadened by a Lorentzian of half width 0.3 eV. The ionization potential was taken to be 5.0 eV.

oscillator strengths,^{6,9} is shown in Fig. 2 (center curve). The experimental distribution for the trihydride is shown at the top and the theoretical spectrum for the monohydride⁶—the experimental spectrum is almost identical⁴—at the bottom.

The theoretical spectrum for Si(111):SiH₃ was calculated using the same Si-H interaction parameters as were derived from molecular data (SiH₄ and Si₂H₆) and which fitted the spectrum of Si(111):H very successfully.⁶ However, in the trihydride phase, the SiH₃ radical is relatively free to rotate around the Si-Si bond with the substrate. In the ideal or staggered configuration the charge distributions of the two nearest H atoms, which are only 1.4 Å apart, overlap considerably, and give rise to a repulsive force¹⁰ between them due to the Pauli exclusion principle. A repulsion also arises from Coulomb interaction between H atoms that carry a negative charge because of the electronegativity difference¹⁰ between Si and H. The energetically most favorable configuration of H atoms is obtained when each SiH₃

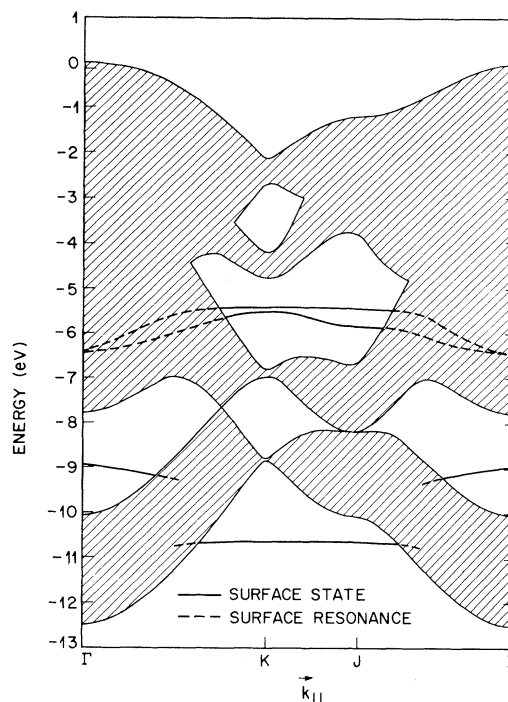


FIG. 3. Surface energy bands of Si(111):SiH₃. Points in the hexagonal surface Brillouin zone are denoted by Γ (zone center), J (edge center), and K (corner). The zero of energy is taken at the valence-band maximum 5 eV below the vacuum level.

radical is rotated by 30° from the ideal or staggered configuration. In this geometry H atoms attached to adjacent Si atoms are as far apart from each other as possible for a fixed Si-H bond length. The minimum H-H distance for these atoms is 2.2 Å, compared to 2.4 Å for H atoms bonded to the same Si atom and 3.8 Å in Si(111):H. Thus we expect a small interaction V_{HH} between the nearest neighbor H orbitals, at 2.2 Å, and the next nearest neighbors at 2.4 Å. In the present calculation both these interactions have been taken to be 0.5 eV. Self-consistent pseudopotential calculations⁵ of Si(111):H also suggest that the interaction between chemisorbed H orbitals may reverse sign and become repulsive at distances ≥ 1.5 Å.

The surface energy bands of Si(111):SiH₃ are shown in Fig. 3 together with the allowed (shaded) and forbidden regions of bulk states. The two very narrow and highly localized surface bands near -6 eV arise from the hydrogen *s* and silicon *p_x* and *p_y* orbitals in the surface plane. Though these surface bands merge into the continuum to form surface resonances (dashed lines,

Fig. 3) they are still very localized. Peak A in the UPS spectrum of Fig. 2 arises from these bands. The lower two bands, which are responsible for peak B of Fig. 2, arise mainly from the s orbital of H and the s and p_z orbitals of Si.

The most uncertain quantity in our calculation is the H-H interaction V_{HH} . We have studied the effect of varying V_{HH} on the UPS spectrum in considerable detail.⁶ With V_{HH} fixed, rotation alone has almost no effect on the spectrum due to the highly localized nature of H orbital. With $V_{HH}=0$ the energy separation of peaks A and B increases by about 0.5 eV and peak A is somewhat broadened. When $V_{HH}=-0.5$ eV the broadening is rather large but all of these changes are small relative to the differences between the spectra of Si(111):H and Si(111):SiH₃. They are large enough, however, considering the improved agreement with experiment, for us to estimate $V_{HH}=0.5 \pm 0.3$ eV.

The existence of Si(111):SiH₃ is quite unexpected and gives support to the surface vacancy model¹¹⁻¹³ for clean Si(111)7×7. Though the trihydride phase is energetically more favorable than the monohydride since the Si-H bond is about 50% stronger than the Si-Si bond, its formation requires the breaking of Si-Si bonds to remove the first silicon layer. A plausible mechanism for the formation of Si(111):SiH₃ emerges if we assume the vacancy model for clean Si(111)7×7 and that these vacancies also exist on the 1×1 surface but are disordered there. Filling of the valley at $E - E_{vac} \approx -10$ eV in the UPS spectra in going from clean 7×7 to 1×1 surface can be successfully explained by this model.⁶ Since about 27% of the surface atoms are missing in the outermost Si layer,¹¹ vacancy disordering will produce vacancy clusters within which some H adsorption to the three dangling orbitals of Si atoms in the second layer can occur. The release of energy in the formation of these bonds can contribute to the removal of Si atoms at the edges of the vacancy cluster which can, with further bonding to incident H, be desorbed as SiH₄ or Si₂H₆. This mechanism leads to the eventual removal of almost the entire surface mono-

layer of Si permitting the formation of Si(111):SiH₃ by the adsorption of the three H atoms per Si atom in what was second layer.¹⁴ We believe the desorption model for the production of Si(111):SiH₃ is supported by the relatively large amount of H required to produce it, the sequential appearance of the photoemission spectra of Si(111):H and Si(111):SiH₃ on adsorption, and the simple decay of the Si(111):SiH₃ spectral features on thermal desorption. Though we believe our identification of Si(111):SiH₃ to be conclusive we suggest that LEED analysis and infrared detection of both bond-bending and bond-stretching modes would provide crucial tests of our structural model.

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