

Electronic excitations on Si(100)(2×1)

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Angle-resolved high-resolution electron-energy-loss spectroscopy has been used to study electronic excitations on both the clean and contaminated Si(100)(2×1) surfaces. Absorption edges on the clean surface were observed near 0.4 and 1.1 eV corresponding to transitions from the bulk valence band to the surface conduction band and to the bulk conduction band, respectively. The bulk-to-surface absorption edge was found to move both as a function of primary energy and angle of incidence. The resulting dispersion relationship can be explained without invoking phonon-mediated transitions. This implies that the minimum in the unoccupied surface state is at the Γ point, that the true unit cell is larger than the (2×1), and that the reconstruction of the surface is more extensive than a simple, asymmetric dimerization of the surface atoms. One of the more interesting results of this study is the absence of observable direct transitions from the occupied to the unoccupied surface state. Transitions from the occupied surface state to the bulk conduction band are, however, observed.

I. INTRODUCTION

This paper intends to present new, angle-dependent high-resolution electron-energy-loss spectroscopy (HREELS) data on the clean, reconstructed Si(100) surface for the purpose of better determining the detailed structure involved in the reconstruction of this surface. These data show the existence of an unoccupied surface state in the bulk band gap that has a minimum at the Γ point in the Brillouin zone. The implications of this observation in terms of the actual size of the unit cell and in terms of the details of the reconstruction will be discussed.

The Si(100) surface has been studied by a number of techniques including low-energy electron diffraction (LEED),¹⁻³ helium diffraction,⁴ angle-resolved photoemission,⁵ multiple-reflection infrared spectroscopy,⁶ ion-neutralization spectroscopy,⁷ and low-resolution electron-energy-loss spectroscopy.^{8,9} Early LEED investigations¹ showed that the surface was reconstructed to form a (2×1) superstructure, presumably reflecting the formation of dimer pairs on the surface. This dimerization would allow for the overlap of adjacent dangling bonds on the surface silicon atoms with a concomitant reduction of the total free energy of the system.

Later LEED investigations,^{2,3} have shown that the reconstruction is closer to a $c(2\times 4)$ structure under optimal circumstances. He-diffraction experiments indicate that $p(2\times 2)$ and possible $c(2\times 2)$ regions may also exist on the surface.⁴ The observation of this surface structure, and the results of theoretical calculations by Chadi¹⁰ and by Yin and Cohen,¹¹ indicate that the dimer formation is

accomplished by an asymmetric shift of adjacent Si atoms towards their common center (Fig. 1). Both symmetric and asymmetric dimerization should result in two surface states corresponding roughly to the bonding and the antibonding orbitals in a diatomic molecule.

Unlike the symmetric case,^{12,13} asymmetric dimerization should lead to an unoccupied surface state lying completely above the valence-band maximum (VBM). In the symmetric case a partially occupied band is predicted, but Himpsel and Eastman⁵ do not observe such a metal-like state on the Si(100)(2×1) surface. Furthermore, they have mapped the occupied surface state on Si(100)(2×1) which is totally below the VBM, having its maximum in energy at the Γ point (0.35 ± 0.15 eV below the VBM) and its minimum (0.85 eV below the VBM) at the J' point.

Calculations by Chadi¹⁰ have shown that the degree of dispersion of the unoccupied surface state is strongly dependent upon the geometric details of the dimerization. Therefore, a mapping of this state should provide information about the detailed reconstruction. Infrared studies by Chabal⁶ have shown the minimum energy gap between the VBM and the bottom of the unoccupied surface state to be approximately 0.4 eV. This is somewhat smaller than the value calculated by Chadi (0.68 eV) for the (2×1) structure,¹⁰ but is appreciably more consistent with the asymmetric than with the symmetric dimer model where the "unoccupied" surface state should actually disperse below the VBM.

HREELS provides a unique tool for investigating the dispersion of such unoccupied states. This technique has been used to study the vibrational spectra of such chemisorbed species as O, and dissociated H₂O on the Si(100)

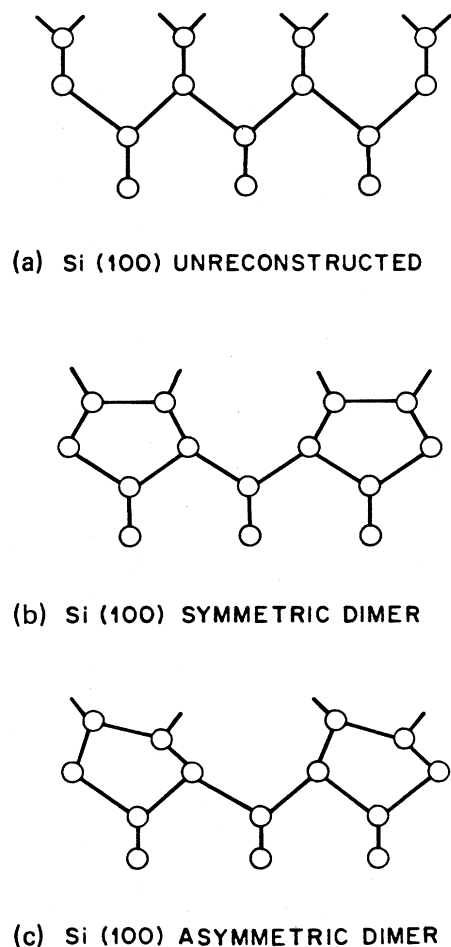


FIG. 1. Position of the Si atoms at the (100) surface is shown schematically for (a) the unreconstructed surface, (b) the symmetric dimer model, and (c) the asymmetric dimer model.

surface.¹⁴ Electron-energy-loss spectra (EELS) from the Si(100)(2×1) surface have been measured by Ibach and Rowe⁸ and more recently by Maruno *et al.*⁹ above about 1.4 eV with an energy resolution on the order of 0.5 eV (Ref. 9) or so. These authors found two features attributable to bulk-band transitions near the surface (E_1 and E_2 at about 3.5 and 5 eV, respectively) and three surface specific transitions; S_1 attributed to a “dangling-bond” state (near 1.7 ± 0.4 eV) and S_2 and S_3 (at 8.4 ± 0.8 and 14.7 ± 0.8 eV, respectively) that are assigned to transitions from back-bond surface states originating in subsurface strain.⁹ However, angle-resolved HREELS has not yet been used in investigations on this surface in the 0.5 to 1.5-eV loss-energy region.

II. EXPERIMENTAL

The experiments were performed in the Leybold-Heraeus combined HREELS—ESCA (electron spectroscopy for chemical analysis) system at the Center for Research in Surface Science (CRISS) of the Physics Department at Montana State University in Bozeman, Montana. This system contained a HREELS apparatus with a resolution of 6-meV full width at half maximum

(FWHM), as well as ESCA, LEED, and ion-bombardment equipment. During the experiment, a pressure in the mid 10^{-11} -Torr range was maintained in the experimental chamber. The sample was etched, loaded into the vacuum system, and then prepared *in vacuo* by alternately ion bombarding and heating to approximately 850°C. After several cycles, the LEED patterns showed a clear (2×1) structure on the surface. A definitive $c(2 \times 4)$ structure was never observed—possibly because of the low annealing temperatures. Prior to each EELS measurement, the sample was flashed briefly to 850°C to remove any residual adsorbates. The impurities observed using x-ray photoemission spectroscopy (XPS) were carbon, $\leq 2\%$ of a monolayer, and oxygen. During the HREELS experiments, the oxygen concentration was less than 1% of a monolayer after flashing the sample, but increased with time. In addition to hydrogen, the residual gas contained mainly H_2O and CO.

III. RESULTS

Figure 2 shows the HREELS spectrum from clean Si(100)(2×1) for specular reflection at an angle of incidence θ_i of 60° and a primary energy E_0 of 7 eV. Here, the resolution has been adjusted to be about 25-meV FWHM to increase the sensitivity. As can be seen, except for the specularly reflected beam there are no sharp peaks in the spectrum (barring the residual peak near 110 meV whose origin is still uncertain¹⁵) even when the scale is amplified 3000 times. This indicates the absence of gases adsorbed onto the surface. Two broad features can be observed starting at about 0.4 and 1.1 eV. The position of the edge near 0.4 eV was observed to be a function of primary energy. As shown in Fig. 3, the energy-loss threshold associated with this edge decreases with increasing primary energy down to a minimum value of about 0.2 eV at a primary energy above 7 eV. A similar variation was noted as a function of the angle of incidence, with the position of the edge decreasing in energy with increasing θ_i .

The edge near 1.1 eV was not observed to move as either a function of primary energy or angle of incidence, though it should be noted that conclusive measurements on this edge are significantly more difficult than on the lower-energy-loss edge because of the greater background.

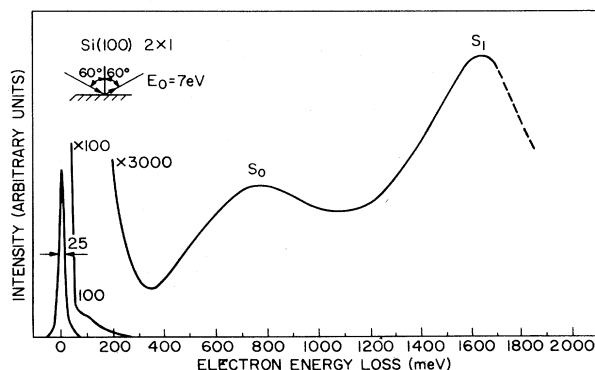


FIG. 2. HREEL spectrum from clean Si(100)(2×1) at specular reflection is shown for a primary energy of 7 eV and an angle of incidence of 60°.

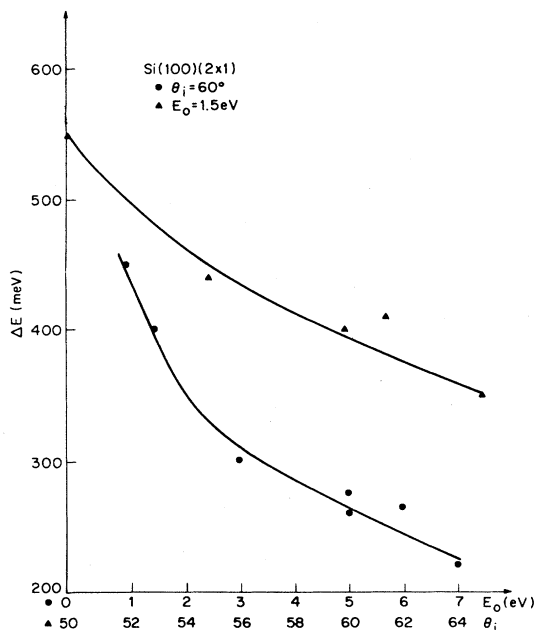


FIG. 3. Loss energy for the adsorption edge near 400 meV is shown as a function of primary energy and scattering angle.

This edge is most probably assignable to transitions from the bulk band. In addition, the maximum that is observed near 1.6 eV in Fig. 2 and 1.5 eV in Fig. 4 for the clean surface we identify with the feature labeled S_1 , of Ibach *et al.*⁸ and Maruno *et al.*⁹ Note also that the shoulder near 1.8-eV loss energy in Fig. 4 is discussed below. Two other features corresponding to the bulk interband transitions E_1 and E_2 may also be seen near 3.5 and 5 eV.

It is consistently noted that the presence of contamination on the surface suppressed the two broad features with

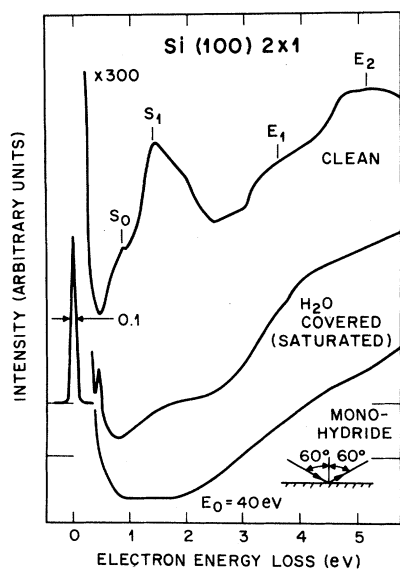


FIG. 4. EELS spectra from (a) the clean Si(100)(2×1) surface, (b) the water saturated Si(100) surface, and (c) the monohydride Si(100)(2×1):H are shown for specular reflection at a primary energy of 40 eV at $\theta_i = 60^\circ$.

edges near 0.4 and 1.1 eV. Figure 4 shows spectra for the surface saturated with H₂O and for the surface monohydride.¹⁵ As can be seen, both the feature whose edge is near 0.4 eV (which we will designate S_0) and the feature near 1.5 eV (S_1 , which is on a broad background due to bulk transitions) are reduced by these treatments. When the surface is saturated with H₂O, S_0 is extinguished and S_1 is appreciably reduced leaving only what is presumably pure bulk transitions from the vicinity of the surface. When the monohydride is formed,¹⁵ not only is S_0 extinguished, but no residual intensity is left in the vicinity of S_1 . Similar results are observed for the dihydride. These observations are consistent with the reduction in the density of states near the VBM seen in photoemission for Si(100)(2×1):H.⁵

After sputtering and a mild annealing of the clean surface to around 200°C to remove the argon, S_0 vanished and the intensity near S_1 resembled the intensity in Fig. 4(b). These results indicate that the first feature is not defect related. The second feature has both bulk and surface components as discussed in Sec. IV.

IV. CONCLUSION

The intensity maximum S_1 , seen near 1.5-eV loss energy is assignable to transitions from the occupied surface-state maximum near Γ to the conduction-band minimum⁸ [also near Γ for the reconstructed Si(100) surface, unlike the pure bulk which has an indirect gap]. This assignment is reasonable on the basis of energetics because the band gap is 1.1 eV and the occupied surface state is approximately 0.35 eV (Ref. 5) below the VBM leading to a predicted transition at (1.45 ± 0.15) -eV loss energy. Similarly, the shoulder at higher loss energies is attributed to transitions either originating away from the Γ point or terminating deeper in the conduction band. The edge near 1.1-eV loss energy is due to indirect transitions from the bulk band structure.

The feature S_0 is most likely assignable to indirect transitions from the valence-band maximum (at the Γ point) to the unoccupied surface state in the gap. Unless the Fermi energy is pinned below the VBM, this is the only energetically allowed assignment for a relatively clean, defect-free surface. For the Fermi energy to be pinned below the VBM, a large number of acceptor states must exist on the surface. No such states were observed by Himpsel and Eastman,⁵ in fact, they estimated that the Fermi level was 0.35 ± 0.15 eV above the VBM. This observation, together with our measurements and those of Chabal *et al.*⁶ indicate that, on the clean Si(100)(2×1) surface, E_F may be pinned at the very bottom of the unoccupied surface band or states. As there are more than 10^{14} of these states per cm², no appreciable occupation of this band can occur without disturbing local charge neutrality and consequently setting up very large local-field gradients. For this reason, "metallic" surface states have not been observed with HREELS, infrared spectroscopy,⁶ or photoemission spectroscopy.⁵

In Fig. 5 we show the loss energy of the edge of the first broad feature as a function of the parallel component of the scattering vector for specular reflection

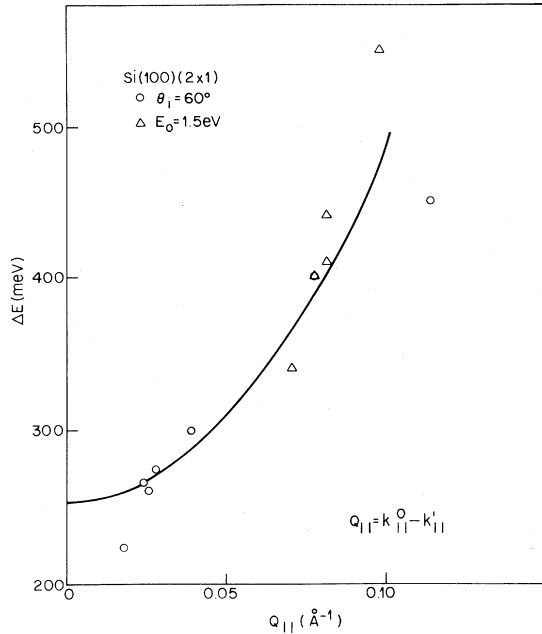


FIG. 5. Loss energy for the adsorption edge near 400 meV is shown as a function of the parallel component of the scattering vector, $\vec{Q}_{||} = \vec{k}_{||}^0 - \vec{k}_{||}^1$. Although there is considerable scatter in the points, they indicate a dispersion curve similar to the one shown.

$$Q_{||} = (2mE_0/\hbar^2)^{1/2} \sin\theta_i [1 - (1 - \Delta E/E_0)^{1/2}]^{-1},$$

where E_0 is the primary energy, ΔE is the loss energy, and θ_i is the angle of incidence. As can be seen, this edge shows an appreciable dispersion over a rather narrow range of the Brillouin zone. Most importantly, the minimum ΔE occurs at the Γ point ($\vec{Q}_{||} = \vec{0}$). As the VBM occurs at the Γ point and as the unoccupied surface-state minimum is expected to occur at the J' (or K) point for both the symmetric and the asymmetric dimer (2×1) structures,¹⁰ two possible explanations of the data need to be explored.

In the first case [Fig. 6(a)] it is assumed that the excitations are phonon assisted⁶ and that the difference in the scattering momenta between the $\Gamma \rightarrow J'$ distance (0.41 \AA^{-1}) and $Q_{||}$ ($\leq 0.12 \text{ \AA}^{-1}$) is made up by a phonon of wave vector $\vec{q} \cong \vec{Q}(\Gamma \rightarrow J') - \vec{Q}_{||}$. In this case, part of the dispersion seen in Fig. 5 could be accounted for by the energy of the phonon and part by the curvature of the VBM in the vicinity of the Γ point and the curvature of the unoccupied surface-state minimum near J' .

In the second case [Fig. 6(b)] no phonon mediation is assumed to occur. However, it is assumed that the unoccupied surface-state minimum is at the Γ point rather than at the J' point as predicted for the (2×1) structure. This picture is closer to Chadi's calculation for the (4×2) structure¹⁰ where the lowest empty state is calculated to be only 0.48 eV above the VBM and to be essentially at its minimum at the Γ point. [We note that the calculated dispersion of the occupied surface states for this (4×2) structure does not fit the photoemission data as well as that for the (2×1) structure. Possibly this discrepancy

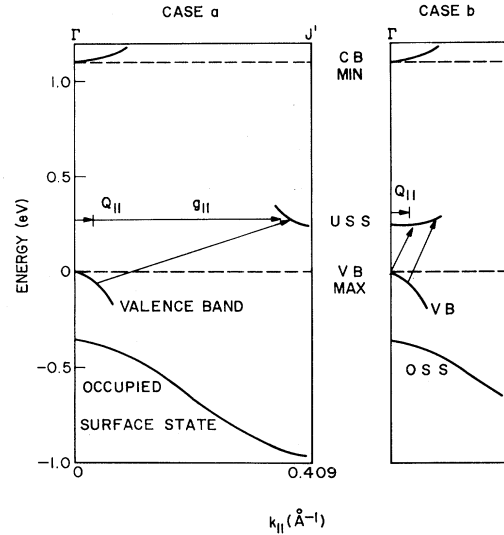


FIG. 6. Schematic representation of case (a) phonon-mediated transition between Γ and J' and case (b) transitions near Γ in the absence of phonon mediation.

could be remedied by a model with features intermediate between those used in the existing (2×1) and (4×2) calculations.] In this case, the dispersion in Fig. 5 would be accounted for by the curvature of the unoccupied surface band at the Γ point with a contribution from the curvature of the VBM.

These two different cases make significantly different assumptions about the electronic (and, therefore, the geometric) structure of the clean Si(100) surface. Our data support the second case, with the minimum in the unoccupied surface state at the Γ point, for the following reasons: (i) The dispersion seen in Fig. 4 is much too large ($\sim 0.25 \text{ eV}$) to be attributed to phonons alone,¹⁶ and (ii) the comparable intensities just above the two absorption edges near 0.4 and 1.1 eV indicate that similar mechanisms produce these features. As the intensities just above 1.1 eV are clearly attributable to near-direct bulk transitions (the presence of the surface producing a direct gap) with no phonon mediation, the absorption edge near 0.4 eV can also be explained without invoking a phonon-mediated mechanism.

An interesting result of this investigation is the apparent absence of direct transitions between the occupied surface state observed by Himpsel and Eastman⁵ and the unoccupied surface state in the gap. Such transitions should begin at about 0.6- or 0.7-eV loss energy, and may be hidden by stronger transitions from the VBM to the unoccupied surface state. However, it is probable that such a transition is essentially forbidden on the Si(100)(2×1) surface because of the symmetry of the occupied and unoccupied states, respectively. At the Γ point, even for the asymmetric configuration, the occupied state of the surface dimer will have approximately π_z symmetry while that for the unoccupied state will have π_z^* symmetry. Assuming momentum conservation and a Coulombic scattering mechanism, the allowed transitions will have a node in intensity when the scattering vector is along the surface normal where the parallel component of

the scattering vector $Q_{\parallel} = k_{\parallel}^0 - k_{\parallel}^i$ is zero. This point will be considered in more detail in a subsequent paper.¹⁷

In conclusion, our data indicate that for the clean, reconstructed Si(100) surface, the unoccupied surface state in the bulk band gap has its minimum at the Γ point at about 0.25 ± 0.05 eV above the valence-band maximum. This observation implies that neither the simple symmetric nor asymmetric dimer models with a (2×1) unit cell correctly describe the reconstruction of this surface. If the asymmetric dimer model is essentially correct, then a larger unit cell, possibly involving a "secondary reconstruction"⁴ with displacement of the underlying Si atoms, exists on the surface. The fact that such a larger superstructure is not ordinarily observed with LEED and associated techniques most probably indicates that imperfect

long-range order exists, except under optimal sample preparation conditions. Finally, it should be noted that our observations do not exclude the possibility that some radically different atomic arrangement exists on the clean, reconstructed Si(100) surface.

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