Symmetry properties and band structure of surface states on the single-domain, hydrogen-chemisorbed Si(100)2×1:H surface

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The surface electronic band structure and symmetry of surface states on the Si(100)2×1:H (monohydride) surface have been studied with polarization-dependent angle-resolved photoemission. By using Si samples cut 4° off the (100) plane, tilting towards the [011] direction, a single-domain 2×1:H surface was obtained. Three dispersing hydrogen-induced surface-state or resonance bands were observed in the energy range 4.7-6.5 eV below the Fermi level. By using a linearly polarized light source, the symmetry properties of these structures were determined along the main symmetry axes of the surface Brillouin zone. Based on the observed symmetries and theoretical considerations, we attribute two of the H-induced structures to Si—H bond states, derived from the bonding (π_b) and antibonding (π_a) dangling bonds of the clean surface shifted down in energy ~4.5 eV by the hydrogen adsorption.

The hydrogen-chemisorbed Si(100) surface has been studied both theoretically and experimentally for several years as a model chemisorption system. Three different phases have been identified, with 1×1,[1] 2×1,[1,2] and 3×1 (Ref. 3) periodicities, respectively. The Si(100) 2×1:H (monohydride) phase appears to be the most well-defined and unambiguous of these three. The favored model (Ref. 4 and references therein) for this surface consists of a top Si layer arranged into symmetric dimers, with the H atoms saturating the Si dangling bonds, i.e., one H atom is bonded to each dimer atom, as illustrated in Fig. 1(a). The similarity to the dimer model for the clean Si(100)2×1 surface makes the monohydride surface particularly interesting.

Experimental studies of the electronic structure of the monohydride surface have mainly been performed with angle-integrated photoemission,[1,4−6] as well as electron-energy-loss spectroscopy (EELS),[2,7] and recently scanning tunneling microscopy (STM).[8] These techniques, however, are inadequate for studies of the surface-state band dispersions. Recently, the surface band structure of the monohydride surface was investigated with angle-resolved photoelectron spectroscopy (ARPES).[9] That study, however, was performed on the normally studied two-domain Si(100)2×1 surface, and the band structure of the H-induced states could only be mapped unambiguously along the diagonal [010] direction in the surface Brillouin zone (SBZ) [see Fig. 1(b)].

In the present experiment, we have studied the Si(100)2×1:H surface with ARPES, using Si(100) samples cut 4° off the (100) plane, tilting towards [011]. It is well known[10,11] that this vicinal surface, after careful annealing, forms terraces separated by steps with a height of two atomic layers, thereby giving a single-domain 2×1-reconstructed surface. The formation of this single-domain surface allowed us to measure the surface-state band dispersions along the main symmetry lines of the SBZ as well as studying the symmetry properties of the surface states in the mirror planes of the surface.

The ARPES experiments were performed in a ultrahigh vacuum (UHV) chamber with a base pressure of less than 2×10^{-10} Torr. The light source was a resonance lamp, giving a photon energy of 16.85 eV. Due to a deflection of the light in a osmium-coated mirror, a strong linear polarization in the horizontal plane was obtained. The angular and energy resolutions were better than $\pm 1°$ and ~200

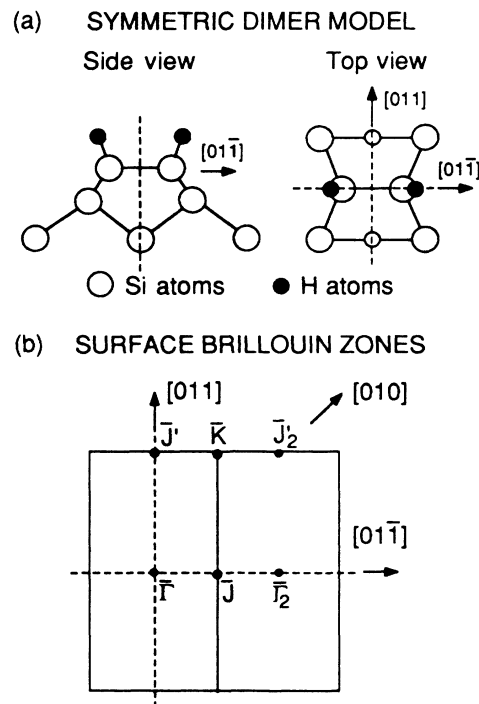(a)   SYMMETRIC DIMER MODEL

(b)   SURFACE BRILLOUIN ZONES

FIG. 1. (a) The symmetric dimer model for the monohydride surface. (b) The surface Brillouin zones of the single-domain Si(100)2×1:H surface in the repeated zone scheme. High-symmetry points are indicated in the figure. Mirror planes of the surface are indicated with broken lines.

meV, respectively. The Fermi-level (E_F) position was determined by photoemission from the metallic (Ta) sample holder.

The sample was an n^+-doped, mirror-polished Si single crystal ($\rho = 4$–$6 \, \text{m}\Omega \, \text{cm}$, As-doped, Wacker Chemitronic), cut $4°$ off the (100) plane, tilting towards the [011] direction. Before insertion into the vacuum chamber, it was cleaned using the etching procedure of Ishizaka and Shiraki.[12] In ultrahigh vacuum it was thoroughly out-gassed at 600–750 °C and then cleaned by step-wise heating up to 850 °C. After each annealing, the sample was cooled down slowly, i.e., in 2–3 min. After 2 min at 850 °C, a good single-domain 2×1 LEED pattern was obtained. The formation of regularly spaced double-layer steps was indicated by the characteristic splitting of the LEED spots, as described by Kaplan[10] and Bringans, Uhrberg, Olmstead, and Bachrach.[11] To maintain the clean surface, the sample was annealed for 30 sec at ~ 800 °C every second hour. No sign of contamination was seen in the ARPES spectra within this time period.

The hydrogen exposures were done with the Si surface facing a hot (~ 1700 °C) tungsten filament at a distance of ~ 9 cm, in order to chemisorb atomic hydrogen. The sample was cleaned by heating to ~ 800 °C just prior to the exposures. To produce the monohydride phase, exposures of H_2 of typically 500 L (1 L=1 langmuir=10^{-6} Torr sec) were done.[13] The sample was subsequently annealed to ~ 450 °C for 30 sec, which produced a good single-domain 2×1 LEED pattern, indicating the formation of the monohydride phase. This was confirmed in the ARPES spectra by the complete removal of the well-known dangling-bond band, present on the clean surface. The clean surface was restored by annealing at ~ 800 °C. In subsequent formations of the monohydride phase, the ARPES spectra were easily reproduced.

ARPES spectra were recorded in the [011], [010], and [01$\bar{1}$] azimuthal directions. The dispersions of H-induced states were also measured along the $\bar{J}'$-$\bar{K}$ and $\bar{J}$-$\bar{K}$ lines in

the SBZ. In most cases, the corresponding spectra from the clean Si(100)2×1 surface were also recorded. The hydrogen-induced peaks could then be identified by direct comparison. The symmetric dimer model has mirror planes in the [011] and [01$\bar{1}$] azimuthal directions (see Fig. 1). In order to explore the polarization dependence, and thereby the symmetries of the surface states in the mirror planes, two different geometries were used when recording normal-incidence spectra: (a) The electric field vector is *in* the plane defined by the [100] direction and the emission direction. This will be referred to as the $A_{\parallel}$ case. (b) The electric field vector is *perpendicular* to the same plane. This will be referred to as the $A_{\perp}$ case. Also spectra with a high angle of incidence ($\Theta_i = 60°$) were recorded with the $A_{\parallel}$ geometry.

Three strong H-induced structures, denoted M_1, M_2, and M_3, were observed in the spectra. Their initial-energy dispersions are plotted in Fig. 2. A collection of spectra are shown in Figs. 3 and 4. The M_1 state is seen most strongly along the $\bar{\Gamma}$-$\bar{J}'$ line, dispersing downwards towards $\bar{J}'$ and extending into the bulk band gap towards $\bar{K}$. The M_2 state shows its strongest emission in the bulk band gap along the $\bar{J}'$-$\bar{K}$ and $\bar{J}$-$\bar{K}$ lines, but is observed over large parts of the SBZ. The appearance of M_1 and M_2 in the bulk band gap clearly show their surface-state

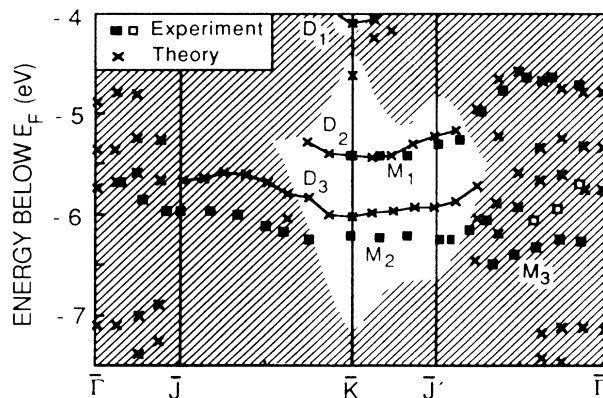
FIG. 2. Surface-band structure of the Si(100)2×1:H surface. Squares denote experimental points obtained in this work. Filled and open squares indicate strong and weak peaks, respectively, in the ARPES spectra. Crosses denote calculated points reproduced from Ref. 4, assuming that $E_F - E_V = 0.9$ eV. The shaded region is the projected bulk band structure (from Ref. 4).
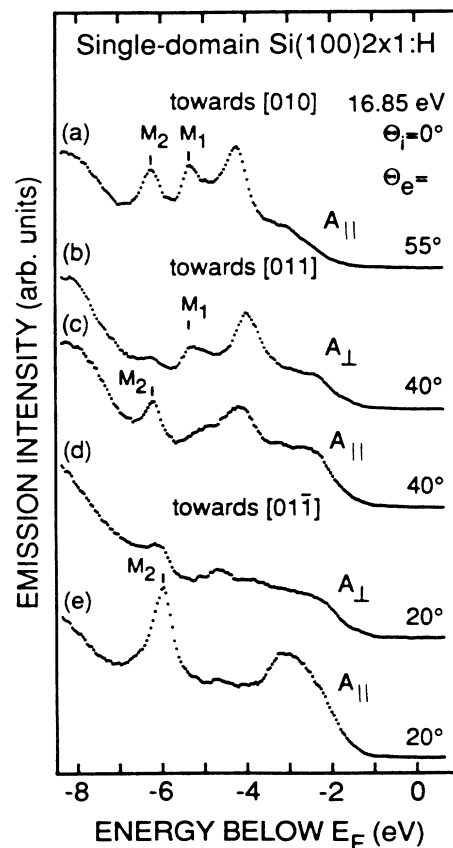

FIG. 3. ARPES spectra recorded with 16.85 eV photon energy. The recording geometries are indicated in the figure. The M_1 and M_2 peaks are shown near (a) $\bar{J}_2$; (b),(c) $\bar{J}'$; and (d),(e) $\bar{J}$ in the SBZ. The unlabeled peaks in the spectra are interpreted as bulk transitions.

nature. M_3 is a surface resonance that is only seen in the $\bar{\Gamma}$-$\bar{J}'$ direction. The broadness and asymmetry of the M_3 peaks [see Fig. 4, spectrum (c)] suggest that there are at least two components, one minor at slightly higher initial energy and one major at the peak positions indicated in Fig. 2.

By comparing spectra recorded with different geometries, interesting polarization-dependent effects are observed. This is illustrated in Fig. 3. The recording geometry for each spectrum is indicated in the figure. All angles are referred to the [100] direction, *not* the surface normal. Spectra (b) and (c) are recorded in the mirror plane in the [011] direction. The emission angles are chosen so that the H-induced peaks at -5.3 and -6.2 eV are probed close to $\bar{J}'$ in the SBZ. We observe that the M_1 state is only seen with the $A_\perp$ geometry, whereas M_2 is only seen with the $A_\parallel$ geometry. In spectrum (a), recorded in the [010] direction (i.e., *not* in a mirror plane), we observe *both* M_1 and M_2 with the $A_\parallel$ geometry near $\bar{J}_2$, in the second SBZ. In spectra (d) and (e), the M_2 peak is seen near $\bar{J}$ in the [01$\bar{1}$] direction. Also in this mirror plane, M_2 is observed with high intensity only when using the $A_\parallel$ geometry. The small M_2 peak seen in the $A_\perp$ spectrum is most likely due to the nonperfect linear polarization. The M_3 resonance is seen in Fig. 4, spectrum (c), which is recorded with $\Theta_i = 60°$. By comparison to spectrum (d) ($\Theta_i = 0°$), we see that it has a strong dependence on the z component of the electric field vector of the light, indicating a strong p_z character.

The dependence of the M_1 and M_2 states on recording geometry in the [011] and [01$\bar{1}$] directions can be explained by the selection rules imposed by the mirror-plane symmetry.[14] The electronic initial states must have a definite parity with respect to the mirror planes: even or odd. The requirement for even final states for electrons

emitted in the mirror plane then means that only even initial states will be observed with the $A_\parallel$ geometry and, conversely, only odd states will be observed with the $A_\perp$ geometry. Thus, we conclude that the M_1 state is odd and M_2 is even under reflection in the mirror plane containing the [011] direction. Similarly, M_2 must also be even with respect to the mirror plane containing the [01$\bar{1}$] direction. In the [010] direction, the selection rules are relaxed and we see both states in the same spectrum.

These experimental results are very similar to the theoretical results of Appelbaum *et al.*[15] in their pseudo-potential calculation of the electronic structure of the monohydride surface. In the calculated local density of states, they found two H-induced states, derived from the dangling-bond states of the clean surface, at energies 4.5 and 3.0 eV below E_V and with even and odd symmetry, respectively, with respect to the mirror plane containing the [011] direction. This agrees well with our experimental results, except that the calculated energy positions are too high by 1.0–1.5 eV. The bonding and antibonding dangling-bond states are expected to have A_1 symmetry (completely symmetric) and B_1 symmetry (odd under reflection in the mirror plane containing the [011] direction), respectively.[16] The present study shows that M_2 has A_1 symmetry. M_1 can have either A_2 (odd under reflection in both mirror planes) or B_1 symmetry, but B_1 is favored based on the interpretation of M_1 as derived from the antibonding dangling bond.

The surface band structure of the Si(100)2×1:H surface was calculated by Ciraci, Butz, Oellig, and Wagner[4] using empirical methods. Their results (in the indicated energy range) are plotted in Fig. 2, assuming an energy difference between E_F and the valence-band maximum (E_V) of 0.9 eV.[17] The main features of the calculated band structure are the D_2 and D_3 bands, corresponding to strongly localized states associated with the Si—H bonds. We observe that the similarity between the experimental and theoretical bands is very strong. It is clear that M_1 is associated with D_2 and M_2 with D_3, although there are differences in the absolute energy positions of M_2 and D_3; D_3 is ~0.3 eV above M_2. Also the M_3 resonances appear to be reproduced in the calculation, but they are ~0.5 eV too high. The calculated states that would correspond to M_3 were described as bulklike states with small H content. Ciraci *et al.*[4] also reported a third H-induced state, D_1, at 3.2 eV below E_V near $\bar{K}$. Comparing spectra from the clean and monohydride surfaces, we observe a broad intensity increase on the monohydride surface in this region of the SBZ that may be associated with D_1.

An interesting example of surface umklapp scattering of a bulk peak is seen in Figs. 4(a) and 4(b). The direct bulk transition at -1.4 eV (structure B) in the normal emission spectrum (b) is scattered by a surface reciprocal lattice vector to $\bar{\Gamma}$ in the second SBZ in the [01$\bar{1}$] direction [$\bar{\Gamma}_2$ in Fig. 1 (b)], as seen in spectrum (a). The assignment of peak B to a direct bulk transition is clear from the results of the previous ARPES study of the two-domain Si(100) surface.[9] The B peak at $\bar{\Gamma}_2$ must then be surface-umklapp-scattered emission from the direct transition at $\bar{\Gamma}$, since it lies in the projected bulk band gap of the 1×1 SBZ. The intensity of the scattered peak is
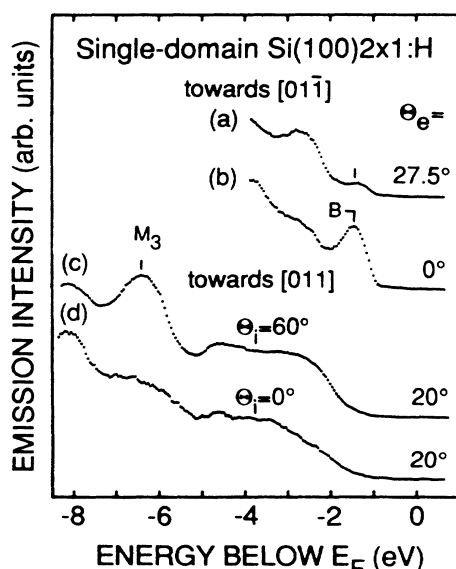

FIG. 4. ARPES spectra recorded with 16.85 eV photon energy and the $A_\parallel$ geometry. The angles of incidence for spectra (a) and (b) are 0° and 20°, respectively. The B peak is shown at (a) $\bar{\Gamma}_2$ and (b) $\bar{\Gamma}$. Spectrum (c) shows the M_3 resonance.

~20% of the normal-emission peak. A similar, but fainter, peak is seen near $\bar{\Gamma}$ in the second SBZ in the [011] direction. In other parts of the SBZ, no structures are seen at this initial energy.

Comparing our experimental results to previous photoemission experiments on the monohydride surface, we find a very good agreement with the recent ARPES experiment on the two-domain 2×1:H surface.[9] The main difference is a shift in the Fermi-level position by ~0.6 eV, which is caused by the big difference in doping of the samples used in the two studies. The M_3 resonance was not observed in the [010] direction with 21.2-eV photon energy, but with 16.85 eV an overlap between M_2 and an apparent bulk peak was observed, causing a strong enhancement of the emission. The bulk peak could be followed to the same energy position at $\bar{\Gamma}$ as M_3. This is consistent with the interpretation of M_3 as a bulklike state.

Recently, the clean Si(100)2×1 and the 2×1:H surfaces were studied with STM by Hamers, Avouris, and Bozso.[8] On the monohydride surface, occupied states were observed at the H-atom positions with a sample bias of −2 V. It was suggested that these states are Si−H bond states derived from the antibonding dangling-bond band. However, as shown in this study, the main H-induced structure associated with the antibonding dangling bond is the M_1 band. The highest-energy position of this band is 4.7 eV below E_F and it should, therefore, not be visible in the STM images. In fact, no H-induced

structures are observed at all in the energy range 0-(−2) eV in the ARPES spectra. The problems with interpreting the STM images in terms of the H-induced electronic states have been discussed in a more recent article by Hamers, Avouris, and Bozso.[18] From the localization of the tunneling to the H-atom positions, it was concluded that Si-H states are primarily involved, and it was suggested that these states originate from hybridization between the H $1s$ orbitals and the Si valence band. While this explanation is entirely reasonable, we conclude that there is no structure in the calculated surface density of states[4] or in the ARPES spectra, that corresponds to these tunneling states.

In summary, the hydrogen-chemisorbed Si(100)2×1:H surface has been studied with polarization-dependent angle-resolved photoemission. Three strong hydrogen-induced surface states or resonances were observed. Two of them correspond to the Si−H bonds and are derived from the bonding and antibonding dangling bonds on the clean Si(100)2×1 surface. The symmetries of these H-induced states are A_1 and B_1, respectively, similar to the dangling-bond states. The experimental results are in good agreement with theoretical predictions, with respect to band dispersions and symmetry properties.

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