PHYSICAL REVIEW B VOLUME 12, NUMBER 4 15 AUGUST 1975

The Si(2 × 1) surface: A theory of its spectroscopy

J. A. Appelbaum and D. R. Hamann
Bell Laboratories, Murray Hill, New Jersey 07974

(Received 18 February 1975)

The metastable reconstructed form of the Si(111) surface produced by cleavage is studied. Modifications of Haneman's model for the detailed geometry of the reconstruction are proposed to explain recent spectroscopic measurements. In the modified model, the bonds between the first and second layers are alternately lengthened and shortened as first-layer atoms are raised and lowered. The results of detailed calculations for realistic models of unreconstructed surfaces with such bond-length modifications are reported. The dangling-bond surface states are found to be lower in energy, narrower in bandwidth, and more sp^3-like in shape for the raised atoms. A new band of surface states associated with the lengthened bonds is found to lie 0 to 4.0 eV below the valence-band maximum, and to have its density of states and shape consistent with the energy and azimuthal angular structure of surface-state photoemission in this range. Since both the dangling-bond and stretched-bond surface states will depend primarily on their local environment, a two-dimensional tight-binding picture is invoked to estimate the positions and widths of the hybridized surface-state bands on the 2×1 surface. These are shown to be consistent with infrared absorption and other measurements. While it explains the spectroscopy of the surface, the present model appears energetically unfavorable, and we propose that the steps invariably formed upon cleavage may be necessary to render it metastable.

I. INTRODUCTION

A large number of experimental studies have been undertaken to elucidate the electronic spectrum of the Si(111) 2×1 surface.[1] This surface, prepared only by cleavage, is a metastable precursor of the geometrically more complex but stable 7×7 form.

Until recently, the main focus of experimental and theoretical interest has been the surface states believed to exist within the absolute band gap of bulk Si. They have been studied extensively by band bending and threshold photoemission experiments, field-effect and chemisorption-modified surface-mobility studies, photoconductivity, and infrared-absorption measurements.

These experiments have had qualitative if not definitive theoretical interpretation in terms of a broken-bond surface-state band (predicted originally by Schockley)[2] that was expected to lie within the bulk band gap. This band was in turn assumed to split into two by potential modifications resulting from the 2×1 reconstruction of the surface.

This relatively satisfactory situation is complicated considerably by recent spectroscopic studies. These ultraviolet photoemission experiments, by Wagner and Spicer[3] as well as Eastman and Grobman,[4] indicated the presence of a large density of surface sensitive states 0.5 eV below the top of the bulk valence band which they interpret as dangling-bond surface states. These spectral features were shown to be characteristic specifically of the 2×1 reconstruction in studies by Rowe and Ibach,[5] whose measurements on both the 2×1 and 7×7 forms of Si(111) revealed significant differences between them.

Very recently, Rowe, Traum, and Smith,[6] using the new technique of angular photoemission, have found that the broad peak observed approximately 0.5 eV below the valence-band maximum (VBM) when all photoemitted electrons are collected, can be resolved by angular differentiation of the exiting beam into two peaks, one approximately 1.0 eV below VBM and the other somewhat higher in energy. The former peak was shown to have threefold rotation symmetry, unlike what one might expect from a dangling-bond state.

To the authors's knowledge, no satisfactory theoretical explanation exists for the occurrence of surface-state bands in the energy range 0.0 to -1.0 (referenced here and from now on to the valence-band maximum). While a number of theoretical calculations on ideal Si(111) 1×1 surfaces have indeed found that the dangling-bond surface-state band extends into this energy range,[7] recent self-consistent calculations by the authors[8] have shown these calculations to be in serious error. The primary cause for the excessive widths reported for the dangling-bond band is believed to be a poorly converged solution to Schrödenger's equation.

It is the purpose of this paper to study the electronic structure of the 2×1 form of Si(111), assuming a modified Haneman model of the surface reconstruction.[9] It will be shown that if explicit account is taken of the presence of two kinds of surface bonds, one shorter and the other longer than the ideal Si-Si single bond, the observed electronic spectrum can be understood theoretically.

The remainder of the paper will be organized as follows. In Sec. II, an explicit discussion of the Haneman model of surface reconstruction will be given. In Sec. III, the results of a number of self-consistent surface calculations on hypothetical Si(111) 1×1 surfaces will be presented together with arguments that allow us to understand the spectrum of the 2×1 reconstructed surface in terms of specific types of surface states. A final section will briefly consider the energetics of surface reconstruction.

II. HANEMAN MODEL

The analysis of the symmetry patterns seen by low-energy-electron diffraction (LEED) on carefully prepared and cleaved Si(111) surfaces reveal a 2×1 superstructure. Unfortunately, no dynamic analysis of LEED intensities exists at present that allows a unique specification of surface geometry. Haneman suggested[9] that the 2×1 reconstruction as well as a variety of others on semiconductor surfaces could be understood in terms of a buckling model in which alternate rows of surface atoms are raised and lowered. In subsequent work Haneman and co-workers[10] specialized the model to Si, and in so doing assumed as a working hypothesis that the surface distortions occurred in such a way as to maintain at constant length the bonds between first- and second-layer surface atoms (hereafter referred to as back bonds). This requires lateral displacements of atoms in the second plane.

In this paper we shall assume that there are no lateral distortions of the surface or second-layer atoms, only normal displacements. An important physical consequence of this assumption is that the back bonds are no longer of equal length; on the contrary, back bonds connecting raised (lowered) atoms are longer (shorter) than their ideal length. How does one explain the presence of two kinds of back bonds on the 2×1 surface? Our main argument is spectroscopic, and consequently indirect. By assuming both stretched and shortened back bonds we can offer a plausible picture of the experimentally measured spectrum of the Si(111) 2×1 surface.

We have been unable to construct simple chemical arguments that lead to this picture. This is perhaps not surprising, since it is impossible to prepare thermodynamically the 2×1 structure. Rather, a nonequilibrium shock wave, perhaps coupled with the presence of steps that invariably occur even in good cleaves, is necessary for its formation. Once annealed, the Si(111) reverts to a 7×7 structure or an impurity stabilized 1×1; the fact that the 2×1 is impossible to recover after annealing argues strongly that it is not easily rationalized chemically. A consideration of the energetics involved in the formation of the 2×1 structure will be deferred to Sec. IV.

The specific model adopted in this paper for the 2×1 is shown in Fig. 1. It corresponds to our having displaced uniformly inward the surface plane by 0.18 a.u. and then buckling this surface by alternatively raising and lowering rows of surface atoms by 0.48 a.u. This specific model in no way represents an optimized or best-choice model for the 2×1 reconstruction. Rather it represents a model whose spectral features we believe, on the basis of theoretical calculation to be described in Sec. III, resemble those measured.

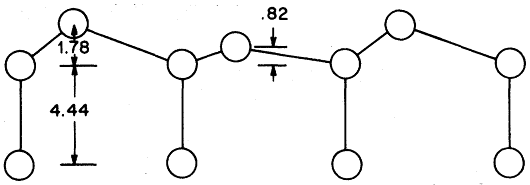

FIG. 1. Geometry of the Haneman model for the Si(111) 2×1 surface used in this paper is shown as viewed along a [100] direction. Distances are in a.u.

III. ELECTRONIC SPECTRUM—THEORY AND EXPERIMENT

Ideally, a fully self-consistent calculation of the Si(111) 2×1 surface analogous to that carried out by the authors for the relaxed Si(111) 1×1 surface[8] would be most suitable for making theoretical contact with the experimentally measured spectrum. In this paper we take a less-ambitious approach, calculating instead the self-consistent spectrum of a number of different hypothetical Si(111) 1×1 surfaces, each differing from the other by the position of the surface plane of atoms relative to the bulk. The methods used in these calculations have already been discussed by the authors. In each case we find one or more bands of surface states in the energy region of interest here (within 2 eV of the valence-band maximum). The spatial nature of the wave functions associated with these bands is in general highly localized, and we argue, associated with the local bonding environment of the surface atoms and influenced strongly by the band structure of the underlying bulk Si. Based on these observations the following strategy for studying the spectrum of the modified Haneman model of the 2×1 surface discussed in Sec. II is employed. We study the electronic spectrum of a 1×1 surface with an expanded surface layer in order to learn about the number and kind of surface states that result from the back bonds being stretched on the Si(111) 2×1 surface. Similarly, we study the spectrum of a contracted surface layer to learn about the surface states that result from back-bond contractions.

The electronic spectrum of the model 2×1 surface we wish to calculate should bear the following relationship to the spectrums of the two 1×1 surfaces discussed above. The center of gravity of the individual bands found on the 1×1 surfaces should be located, to zeroth approximation, at the same energies on the 2×1 surface. What is primarily different is the nature of the banding that takes place on the 2×1 compared with the 1×1 surface. We shall not attempt to calculate this banding, rather, we show that given the size of the banding on the 1×1 surface, that a plausible banding of the surface states on the 2×1 surface can be made consistent with all available experimental data. First, however, we consider the surface-state bands on the 1×1 surfaces.

The spectrum of the relaxed 1×1 surface (whose first- to second-layer interlayer spacing $d = 0.82$ a.u.) has already been discussed in some detail in the literature.[8] We are here most interested in the dangling-bond surface-state band whose energy at four key points in the surface Brillouin zone (SBZ) are listed in Table I. The location of these points in the SBZ are shown in Fig. 2. The significance of these four points can be seen by studying the expansion of $\epsilon_{\vec{k}_\parallel}$, the energy of the surface states, in a Fourier series.[11] Such an expansion is

$$\begin{aligned}\epsilon_{\vec{k}_\parallel} = \epsilon_0 &+ \epsilon_1(2\cos 2\pi k_1 + 4\cos\pi k_1 \cos\pi k_2)\\ &+ \epsilon_2(\cos 2\pi k_2 + 2\cos\pi k_2 \cos 3\pi k_1)\\ &+ \epsilon_3(2\cos 4\pi k_1 + 4\cos 2\pi k_1 \cos 2\pi k_2) + \cdots . \qquad (3.1)\end{aligned}$$

For a surface band lying strictly within a band gap, such expansions are believed to be strictly if not rapidly convergent when applied to the energy. Using the four points $\vec{k}_\parallel = J$, Γ, $\frac{3}{4}K$, $\frac{1}{2}J$ one can simply show that ϵ_0, the energy-band center, is

$$\epsilon_0 = \tfrac{1}{16}(\epsilon_\Gamma + 3\epsilon_J + 6\epsilon_{J/2} + 6\epsilon_{3K/4}) + \mathcal{O}(\epsilon_7) , \qquad (3.2)$$

so that the band center is located very accurately from the four key points. Using (3.2), one finds $\epsilon_0 = 0.0795$.

Examination of the charge distribution of this surface band shows that, in tight-binding terminology, it is more like a p_z than an sp^3 orbital. This can be attributed to the fact that the first and second layer in the relaxed geometry are approaching a coplanar graphite structure, and there is little energy to be gained from s-p hybridization for the broken bond.

This surface has additional bands of surface states, with the next lowest in energy lying 1.7–4.9 eV below the VBM. This band of states consists of back-bonding surface states, resulting from the contracted and consequently strengthened bonds between the first- and second-surface layers; we shall have only a little to say about this state here.

TABLE I. Energies of the dangling-bond surface band at $\vec{k}_\parallel = \Gamma$, J, $\frac{3}{4}K$, and $\frac{1}{2}J$ are listed for both the relaxed and expanded 1×1 surface geometries. Energies are in a.u., and the valence-band maximum is at 0.0662.

$\vec{k}_\parallel$	Expanded	Relaxed
Γ	0.0756	0.0955
J	0.0561	0.0666
$\frac{3}{4}K$	0.0597	0.0747
$\frac{1}{2}J$	0.0639	0.0882

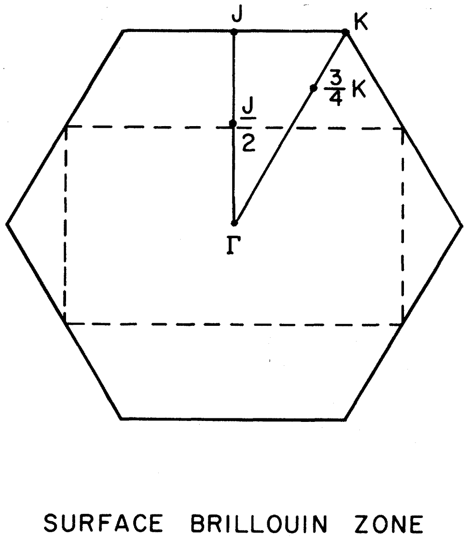

FIG. 2. Hexagonal surface Brillouin zone is shown for the (111) 1×1 surface together with the rectangular unit cell for the 2×1 reconstructed surface.

Turning now to the surface which has an expanded geometry, with a surface plane spacing $d = 1.78$, we find two bands of surface states within 2.0 eV of the VBM. One band is clearly dangling-bond-like, and quite narrow, with energies at the four key $\vec{k}_\parallel$ points listed in Table I. Notice that this band has dropped relative to its position for the relaxed geometry and that its band center is now at $\epsilon_0 = 0.0616$. The charge distribution in this band has changed as well, becoming nearly sp^3-like. The less-than-tetrahedral angle of the back bonds apparently promotes s-p hybridization despite the lack of a bond potential. The other band, which lies considerably lower in energy, is a back-bond surface state. It exists as a *bona fide* surface state at Γ, $\frac{1}{2}J$, and K, and as a sharp resonance at J. The spatial nature of this band is clearly seen in Figs. 3–6, where we have plotted contours of constant charge density for both Γ surface state and the J resonance on planes perendicular (Figs. 3 and 4) and parallel (Figs. 5 and 6) to the (111) surface. The orientation of these planes was such that the perpendicular plane passed through a row of surface atoms, a row of second-plane atoms, and the bonds between them, while the parallel plane passed through the midpoints of those same bonds. The back-bonding character of these states is immediately apparent.

The meaning of the charge density for the surface state at Γ needs no elaboration; this is not

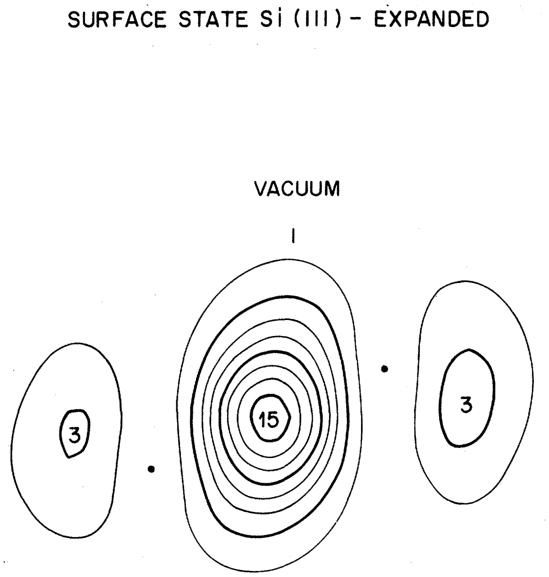

FIG. 3. Contour plot of the charge density for the back-bond surface state at $\vec{k}_{\|}=\Gamma$ (on the expanded surface) is shown for a plane normal to the (111) surface and passing through surface atoms (heavy dots), second plane atoms, and the bond between them. Charge densities are in a.u. and have been scaled by 10^3.

true of the corresponding resonance at J. This resonance lies in a band of continuum states whose energy extends from $\simeq -0.039$ to 0.022. In Fig. 7 we have plotted the contribution of a state in that band to the charge in the surface region as a function of the energy E of that state. Notice the strong asymmetrical peak near the top of this band. For comparison we have plotted the analogous charge for the ideal or undisplaced surface geometry for which we have also done a self-consistent calculation. This curve peaks near midgap, is comparatively broad, and smoothly approaches its zero-value asymtotes at the band extrema.

To represent the charge in the resonance we have summed over three states at energies 0.0090, 0.0168, and 0.0213. These energies span the resonance, correspond in the bulk to wave vectors normal to the surface of 0.75, 0.85, and 0.95 $(\pi\sqrt{3}/a)$, respectively, and were available in the course of doing our self-consistent calculation.

The physical origin of this state is easily found. By expanding the surface plane outward we have stretched the back bonds from the first to second layer. This in turn has weakened them, causing the spectral weight in the band associated with this bond to shift upward in energy. This same band supplied the spectral weight for the back-bond surface states that occur for the relaxed geometry. In that case, however, the bonds are strengthened by the assumed surface distortions, and a surface state is split off the bottom of the band. The back-bond surface-state band is quite broad, ~4.0 eV, so that the spectral character of the band can only be revealed by plotting a density of states for the band. This is done by truncating the expansion (3.1) at ϵ_3 and fitting it to $\epsilon_{\vec{k}_{\|}}$ calculated at $\vec{k}_{\|}=\Gamma$, J, $\frac{1}{2}J$, and K, ignoring the resonant character of J. This leads to values for ϵ_i of $\epsilon_0=0.0119$, $\epsilon_1=0.0121$, $\epsilon_2=-0.0116$, and $\epsilon_3=0.0034$. With $\epsilon_{\vec{k}_{\|}}$ now fixed through (3.1), a numerically converged density of states can be obtained (see Fig. 8) by sampling the SBZ with a dense mesh of $\vec{k}_{\|}$ points. The critical-point structure is quite simple here, consisting of a logarithmic singularity at J and steps at the band extrema K and J. The critical point at J will clearly be the dominant spectral feature for this band.

Given the results just discussed for the various 1×1 surfaces, what can be said about the 2×1 surface? Clearly, both dangling-bond and back-bond surface states can be expected on the 2×1 surface. The difference between the dangling-bond surface states for the two 1×1 geometries is presumably a measure of the splitting of this band of states by the 2×1 reconstruction.

The presence of two types of dangling-bond states, one p_z-like and associated with the relaxed atoms, the other sp^3-like, and associated with the expanded atoms, changes the nature of the banding of these states compared to what is to be expected from the 1×1 calculations.

Of equal if not greater importance to the dangling bond as well as other states is the change in both the translational and point-group symmetry of the

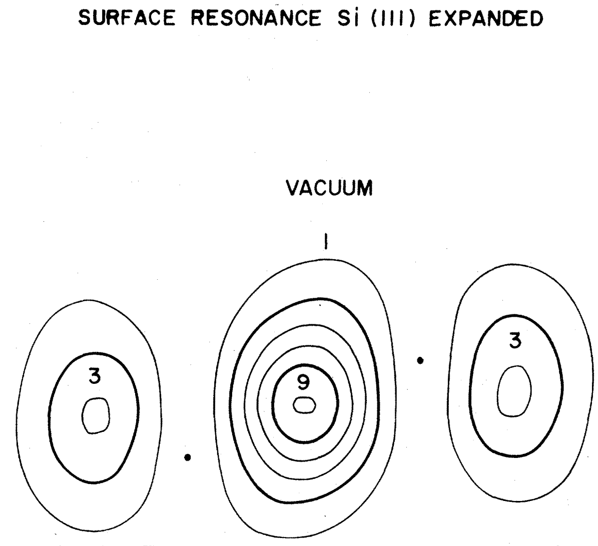

FIG. 4. Contour plot of the charge density for the $\vec{k}_{\|}=J$ surface resonance (see text for definition) on the expanded surface is shown for a plane normal to the (111) surface and passing through surface atoms (heavy dots), second plane atoms, and the bond between them. Charge densities are in a.u. and have been scaled by 10^3.

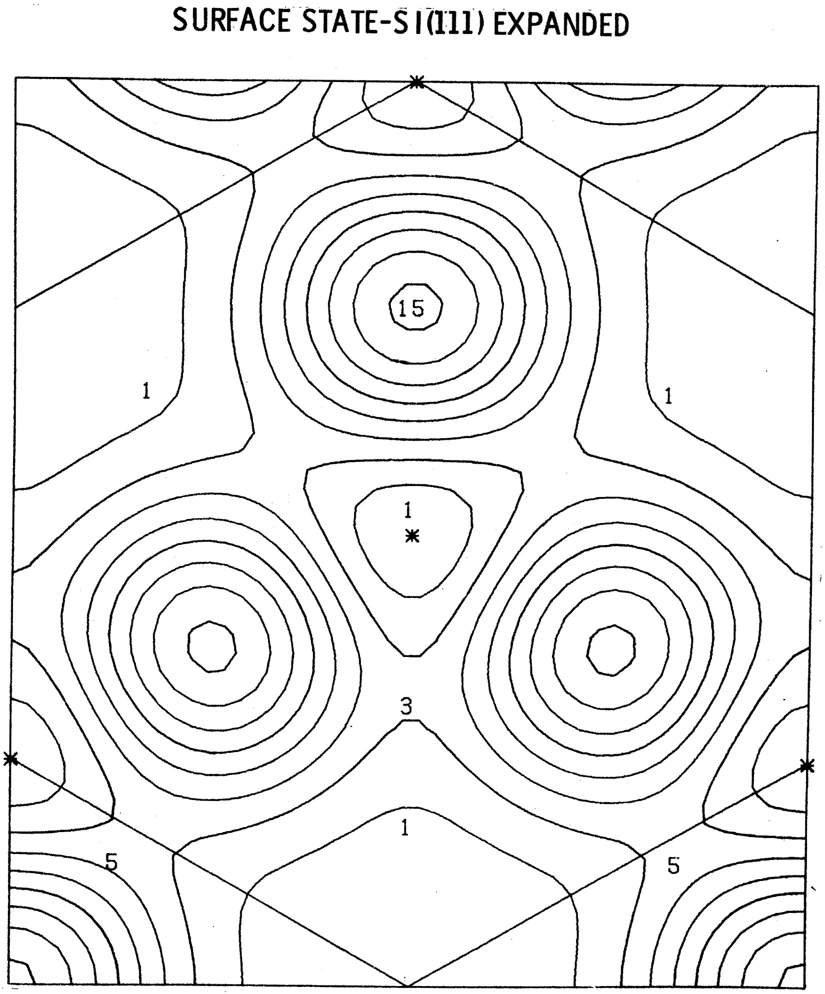

FIG. 5. Contour plot of the charge density for the $\vec{k}_\parallel = \Gamma$ surface state on the expanded surface shown for a plane parallel to the (111) surface and passing midway between the first and second atom planes. Charge densities are in a.u. and have been scaled by 10^3. The light lines frame the real-space hexagonal unit cell for the surface.

surface. This allows mixing states with different $\vec{k}_\parallel$'s in the 1×1 SBZ that are now equivalent in the new 2×1 SBZ. In Fig. 2 we have drawn in the 2×1 SBZ as a dotted rectangle whose area is one-half the original hexagonal zone. The new set of reciprocal-lattice vectors added by the reconstruction is $\{\vec{G}_\parallel + \vec{J}\}$, where $\{\vec{G}_\parallel\}$ is the original set of reciprocal-lattice vectors.

On the left-hand side of Fig. 9 we have plotted the location of the bands of surface states for both types of 1×1 surfaces. On the right-hand side of Fig. 9 we have indicated the changes that are necessary in the banding of these surface states in going from the 1×1 to the 2×1 surface. These changes are needed so that the following experimental facts are adequately explained:

(i) A band gap in the surface-state band of ~ 0.3 eV as derived from the Chiarotti *et al.*[12] experiments.

(ii) A surface Fermi level of ~ 0.35 eV, derived from band-bending and surface-mobility studies.[13,14]

(iii) A photoconductivity threshold of ~ 0.5 eV, assumed to measure the distance between the bottom of the upper unoccupied p_z dangling bond band and the VBM.[15]

(iv) A dangling-bond-like band of occupied states extending from 0.15 eV above VBM to ~ 0.5 eV below—obtained from photoemission and angular photoemission studies.[3-6]

(iv) A surface-state approximately 1 eV below the VBM having a threefold rotational pattern as revealed by angular photoemission.[6]

Can these changes be rationalized in general quantum-mechanical terms? We believe they can in the following way. The banding of the p_z dangling-bond state on the 2×1 surface proceeds at right angles to the reconstruction through identical p_z bonds (hereafter referred to as resonant banding) but along the reconstruction by nonresonant hopping through the sp^3 states at lower energy. An analogous statement can be made about the sp^3 dangling bonds.

The resonant banding leads to two relatively narrow p_z and sp^3 bands (~ one-third of their 1×1 bandwidth since only one of three equivalent 1×1 banding directions has been taken into account) that are

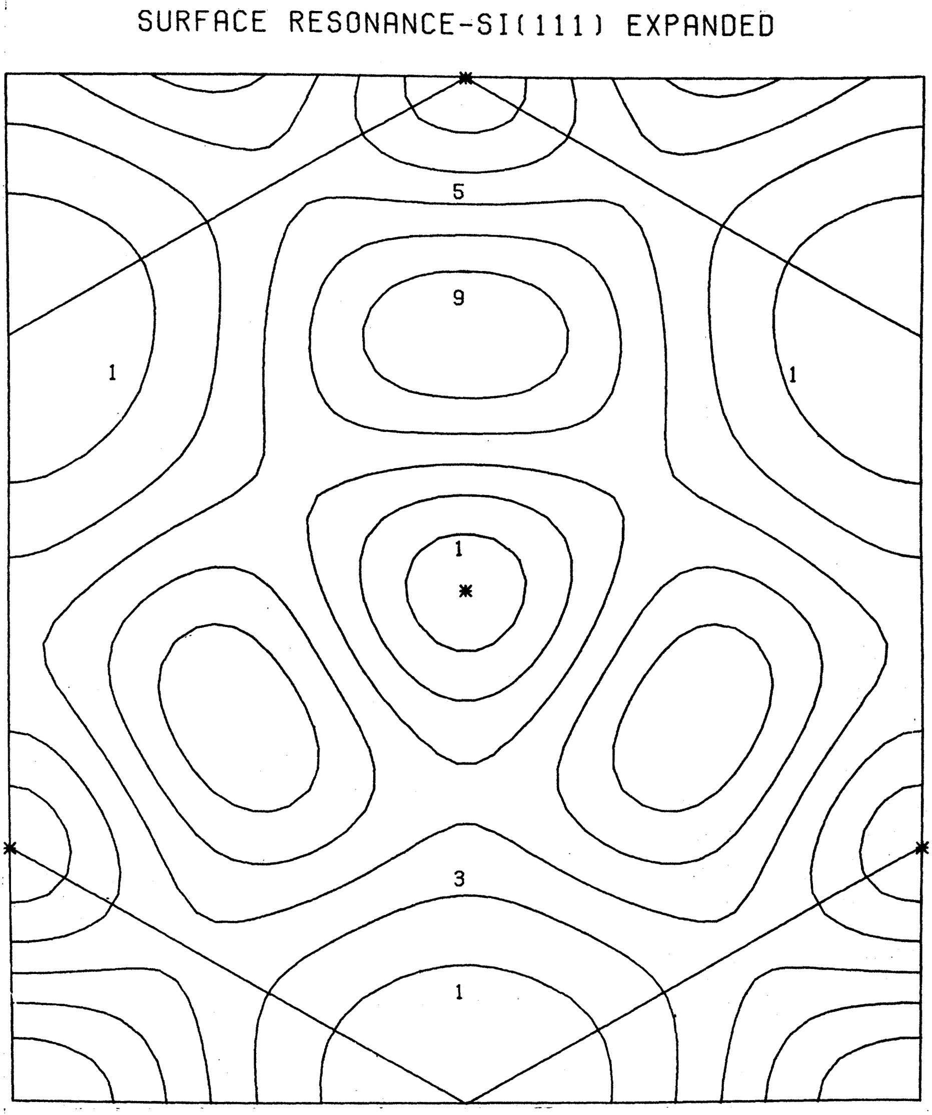

FIG. 6. Contour plot of the charge density for the $\vec{k}_{\parallel} = J$ surface resonance (see text for definition) on the expanded surface shown for a plane parallel to the (111) surface and passing midway between the first and second atom planes. Charge densities are in a.u. and have been scaled by 10^3. The light lines frame the real-space hexagonal unit cell for the surface.

nonoverlapping. The nonresonant banding causes the sp^3 and p_z bands to repel, maintaining or enlarging the gap present between the two bands when only resonant banding is included. The above arguments make plausible the shift in the dangling-bond bands.

In addition to the above changes, the sp^3 dangling bond is expected to broaden by interaction with the continuum states as well as the stretched back-bond surface states, which, because of the lowered surface point group symmetry can now hybridize with the dangling-bond states. This may account for its increased width on the 2×1 surface compared to what it had on the 1×1 surface. What of the back-bond states? The banding of the back-bond surface states, both the stretched as well as the contracted states, should behave analogously to the dangling bonds, except that they overlap a continuum band which can always serve as a source of resonant states for banding. As a consequence, a clearcut shift in the banding of these states is difficult to predict. We have shown them in more or less the same location on the 2×1 as on the 1×1, allowing only for a small ~0.1-eV shift in the critical-point structure for consistency with experiment.

In summing up, the following picture of the spectroscopy of the 2×1 reconstruction emerges. An occupied band of dangling-bond states whose nature is sp^3-like on the raised atoms and p^z-like on the lowered atoms accounts for the surface-sensitive spectral feature from 0 to -0.5 eV (we reference the VBM to 0.0). The preponderance of charge in this band resides in the sp^3-like states above the raised atoms. This has the effect of making the surface of the 2×1 Si(111) ionic, which may explain the ability of Ibach to observe surface phonons of the 2×1 surface but not on the 7×7.[16]

The spectral features ~1.3 eV below the Fermi

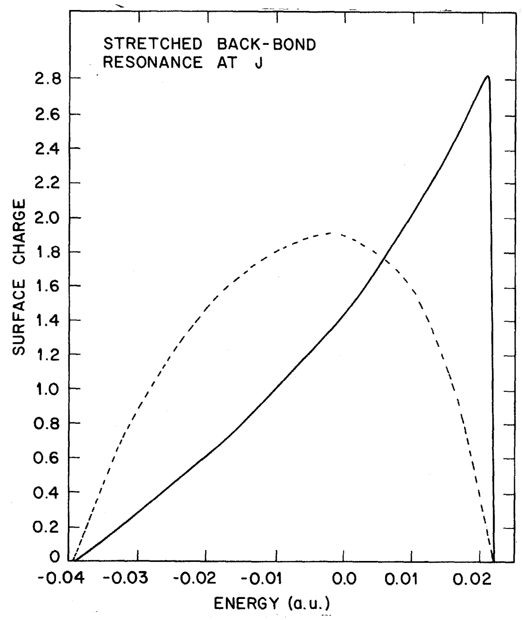

FIG. 7. Surface charge density in a bulk band at $\vec{k}_{\parallel}=J$ is plotted vs energy (in a.u.) for a surface with an expanded geometry (solid line) and an ideal geometry (dashed line). The valence-band maximum here is 0.0662.

level are accounted for by stretched back-bond surface states. This would imply that the initial state in the angular photoemission studies is the determining factor in the symmetry pattern observed by Rowe, Traum, and Smith.[6] Studies at different photon energies are clearly called for to establish this point experimentally. The unoccupied surface state band observed in the Chiarotti *et al.* infrared experiments and in band-bending experiments is predominantly p_z-like.

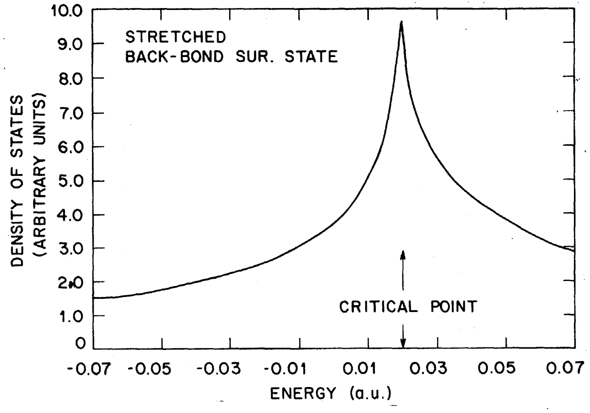

FIG. 8. Density of states, arbitrary units, is plotted vs energy (a.u.) for the stretched backbond surface state.

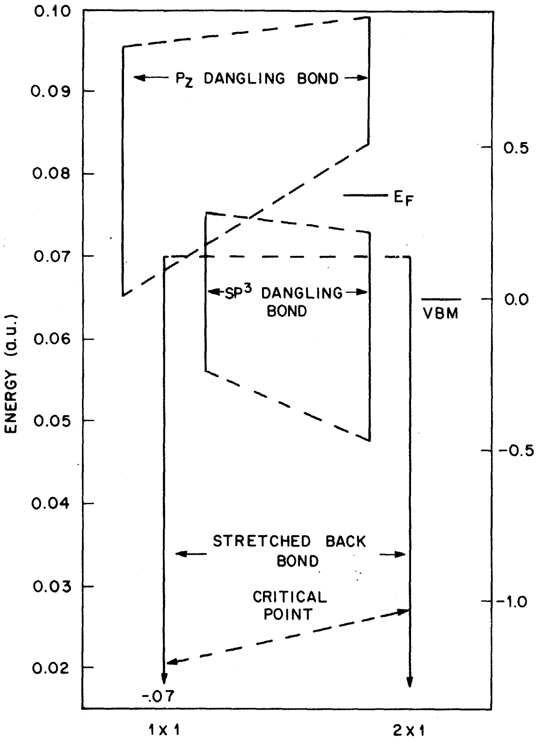

FIG. 9. Schematic diagram of the energies of the dangling and backbond surface states on the hypothetical 1×1 surfaces is shown together with the requisite changes necessary in these states in going to the 2×1 surface. E_F is the surface Fermi level, and VBM the valence-band maximum. Energies are listed in both atomic and Ev units, and the later are zeroed at the VBM.

The model for the dangling-bond surface states should be contrasted with that of Haneman, who also envisage two kinds of dangling-bond states. One p_z-like and similar to our p_z state, the other s-like, which is not the same as what we find. The presence of an s-like dangling bond in the absolute band gap we find energetically quite unreasonable, considering the s, p splitting of atomic Si, ~6 eV. To our knowledge, no discussion of stretched back-bond surface states exists in the literature.

IV. 2×1 ENERGETICS

In this final section we should like to make some comments concerning the energetics of formation of the 2×1 surface structure. We begin first with the ideal 1×1 structure. The shortening of back bonds on an ideal Si(111) 1×1 surface can be rationalized on empirical grounds using Pauling's bond-order–bond-length argument.[17] This argument presumably also applies to the stable 7×7 structure, where the existence of surface states arising from shortened bonds has been experimentally confirmed.[5] Its quantum-mechanical justification we believe lies in the energy gained when the back-bond surface-state band is formed below and drawing weight from a fully occupied bulk band, effectively lowering the energy of the surface. This is achieved with little change in the energy of the dangling-bond electrons, which shift little in going from the ideal to the relaxed surface. Stretched back bonds, on the other hand, are expected to be energetically unstable, since they result in a back-bond surface band lying above and drawing weight from a fully occupied bulk band, effectively raising the energy of the 1×1 surface. Unlike for the relaxed case, however, the dangling-bond states drop significantly in energy, compensating partially for the loss of back-bond energy. It is unlikely, however, that this would be enough to reverse the conclusion that stretched bonds on 1×1 Si(111) do not correspond to the lowest energy state of that surface.

How does one rationalize the stretched bond on the 2×1 structure? Some additional energy is gained on the 2×1 by transferring charge from the dangling bond states above the relaxed back bond to those above the stretched bonds. The energetics of the 2×1 is then as follows. Energy is gained (compared with the ideal 1×1 surface) by forming the back-bond surface states and occupying the dangling bond states above the stretched bond. Energy is lost by stretching the back bonds. The net result is (from the empirical metastability of the 2×1 surface) a surface that is energetically unstable relative to the ideal 1×1 surface. More than being unstable, the surface is thermodynamically inaccessible once the 2×1 reverts to the 7×7 structure. (This structure is energetically separated from the 1×1 by at most a few tenths of an eV, as shown by its reversible transition to the 1×1 at 875 °C.[18]) It is formed only by cleavage, and the energy that stabilizes it may have its origins in the presence of cleavage steps, usually present in concentrations greater than (2–3)% in even good cleaves.[19]

ACKNOWLEDGMENTS

The authors wish to acknowledge useful conversations with J. E. Rowe and M. Traum.

---

[1] For a review of the experimental literature through 1973 the reader is referred to an article by W. Mönch [Solid State Phys. 13, 241 (1973)] and to M. Henzler and J. Clabes [in *Surface Physics of Crystalline Materials*, edited by Blakely (Academic, New York, to be published)].

[2] W. Shockley, Phys. Rev. 56, 317 (1939).

[3] L. F. Wagner and W. E. Spicer, Phys. Rev. Lett. 28, 1381 (1972).

[4] D. E. Eastman and W. D. Grobman, Phys. Rev. Lett. 28, 1378 (1972).

[5] J. E. Rowe and H. Ibach, Phys. Rev. Lett. 32, 421 (1974); and J. E. Rowe, H. Ibach, and H. Froitzheim, Surf. Sci. (to be published).

[6] J. E. Rowe, M. Traum, and N. V. Smith, Phys. Rev. Lett. 33, 1335 (1974).

[7] See review article by J. O. Jones [in *Surface Physics of Semiconductors and Phosphors*, edited by C. C. Scott and C. E. Reed (Academic, London, 1974)].

[8] J. A. Appelbaum and D. R. Hamann, Phys. Rev. Lett. 31, 106 (1973); 32, 225 (1974).

[9] D. Haneman, Phys. Rev. 121, 1093 (1961).

[10] A. Taloni and D. Haneman, Surf. Sci. 10, 215 (1968).

[11] A. Baldereschi, Phys. Rev. B 7, 5212 (1973); J. C. Phillips, Comments Solid State Phys. 5, 115 (1973); and S. L. Cunningham, Phys. Rev. B 10, 4988 (1974).

[12] G. Chiarotti, S. Nannarona, R. Pastore, and X. Chiaradia, Phys. Rev. B 4, 3398 (1971).

[13] F. G. Allen and G. W. Gobeli, Phys. Rev. 127, 150 (1962).

[14] M. Henzler, Phys. Status Solidi 19, 833 (1967).

[15] See W. Mönch, Ref. 1, pp. 256–258.

[16] H. Ibach, Phys. Rev. Lett. 27, 253 (1971); and private communication.

[17] L. Pauling, *The Nature of the Chemical Bond*, (Cornell U. P., Ithaca, New York, 1960), 3rd ed.

[18] J. V. Florio and W. D. Robertson, Surf. Sci. 24, 173 (1971).

[19] M. Henzler, Surf. Sci. 36, 109 (1973).