

Surface States and Surface Bonds of Si(111)*

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A realistic smooth potential is constructed for the Si(111) surface both with and without relaxation of the surface atoms. In both cases, a single band of surface states whose charge is highly localized in "dangling bonds" is found in the energy gap. In the relaxed case, two new bands of surface states appear, lying 2.0–3.6 eV and 10.7–12.9 eV below the valence-band maximum, and localized in the back bonds of the surface atoms.

Previous theoretical studies of the surface states of real semiconductors fall into two general groups: complex band-structure calculations and tight-binding calculations. In the former, pseudo-plane-wave¹ or $\vec{k} \cdot \vec{p}$ ² Hamiltonians which give good bulk band structures are used to calculate decaying Bloch states in the band gap, and these are matched to exponential "vacuum" wave functions. This method cannot avoid an unphysical potential in the surface region which is bulk-like up to an arbitrarily positioned plane where it jumps discontinuously to a constant value. The latter calculations have used minimal basis sets with empirical matrix elements which give comparatively poor band structures and introduce unknown model-dependent approximations into the surface potential.³ The results reported here are based on a method previously introduced by the authors for exactly solving the Schrödinger equation for any potential in the last few atomic layers and nearby vacuum.⁴ Realistic potentials have been constructed for the Si(111) surface with the atoms in their ideal lattice positions and with the last atomic plane relaxed in the normal direction. In both cases, a single band of gap surface states is found which are highly localized in the surface and have an unmistakable dangling-bond shape. In the relaxed case, two additional bands of surface states within and below the valence band are found which are localized in the back bonds of the surface atoms and whose presence may explain recent inelastic scattering results.⁵ Preliminary results on the surface region charge of the bulk band states indicate that the potential for this case is essentially self-consistent.

Si cleaves on the (111) plane, and the unreconstructed or primitive structure is stable above 840°C. At lower temperatures, a 7×7 superstructure is observed for the clean surface, but as little as 0.04 monolayer of adsorbed Cl can stabilize the primitive structure.⁶ This indi-

cates that very small energies and atomic displacements separate these two structures, so that our results should also apply to the 7×7 surface. The ideal lattice positions were selected as plausible and expedient for our first calculations. However, evidence discussed below as well as arguments based on empirical structural chemistry suggest that the three back bonds of the surface atom be shortened. The "bond order" of these bonds increases from 1 to $\frac{4}{3}$ when the surface is formed, and the formula for bond order versus bond length indicates that the last atomic plane should move 0.33 Å inwards.⁷

The potential is constructed starting with a smooth model potential for the Si⁴⁺ ion which gives a self-consistent band structure fitting experimental optical gaps and valence bandwidths to state-of-the-art accuracy.⁸ The surface charge density is approximated for the unrelaxed structure by smoothly cutting off the three-dimensional bulk charge density. The cutoff function is adjusted to give charge neutrality in the surface region, and to yield the experimentally observed electron affinity⁹ when the total surface potential (including ionic, Hartree, and exchange-correlation contributions⁴) is calculated. For the relaxed structure, a hypothetical crystal is introduced with every sixth (111) plane displaced. The charge density for this crystal is synthesized using an atomic-charge form-factor curve fit to the bulk Si charge. This is then used as above, with the cutoff occurring past a displaced plane. Our construction builds a great deal of the known physical properties of Si and its surface into the potentials, but it is by no means a unique procedure. The correctness of any surface potential must ultimately be established through self-consistency. The potential is assumed to achieve its bulk value past the midpoint between the second and third atom planes (the "matching plane").

Schrödinger's equation is solved using around

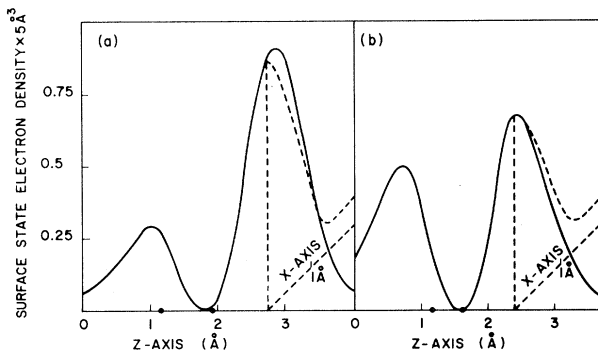


FIG. 1. Electron density in the "dangling-bond" (band 1) state at J , plotted along a line normal to the surface (z axis) and passing through a surface atom. Also shown is the density along a line in a plane parallel to the surface whose direction is between the two nearest-neighbor surface atoms. (a) Unrelaxed and (b) relaxed structure. The heavy dots on the z axis locate the atom planes, and the origin is at the matching plane (see text for definition). Note that average volume per valence electron in bulk Si is 5 \AA^3 .

thirty surface reciprocal-lattice vectors, which is equivalent to the basis used by Brust in a well-converged bulk calculation.¹⁰ The computer codes have been verified to reproduce conventionally calculated bulk band energies to within 0.1 eV, and are used to find evanescent bulk Bloch states as well as the surface region wave functions. Surface states are identified by finding energies at which the surface-region wave function can match decaying bulk solutions in value and slope over the entire (*internal*) matching plane to better than 1%. Attention has so far been focused on the center of the two-dimensional zone (Γ) and the center of its edge (J), since these are the first two points in a two-dimensional adaptation of the Kleinman-Phillips summation scheme for the charge density.¹¹

Using the procedure outlined above we have searched for the existence of surface states (at Γ and J) in the unrelaxed structure. We find a band of surface states lying in the absolute band gap between the conduction and valence band with $E_{\Gamma} = 0.61$ eV and $E_J = 0.03$ eV. ($E_{\Gamma_{25'}}$, the valence-band maximum, is the zero of energy.) Of particular interest is the nature of the wave functions in this band. In Fig. 1(a) the electron density in the state at J is plotted along a line normal to the surface plane and passing through a surface atom. Notice that the electron density is confined effectively to the surface region, that it has a large lobe at the cleavage plane, a null at the surface atom, and a secondary lobe be-

TABLE I. Energies E of the three surface bands for the relaxed structure at Γ and J , referenced to the valence-band maximum, and the fraction of the integrated electron density, α , in a region including only the first two planes of surface atoms and vacuum (see Fig. 2).

Band	Γ		J	
	E (eV)	α	E (eV)	α
1	0.88	0.678	0.04	0.766
2	-1.95	0.917	-3.55	0.855
3	-12.87	0.708	-10.67	0.725

hind the surface atom. The characterization of this state as a dangling bond appears amply justified. We believe that this is the first time that the connection between intrinsic gap surface states and the "dangling-bond" concept has been placed on a precise quantitative foundation.¹²

It should be mentioned that the surface states are quite sensitive to changes in the surface potential. For example, if the surface barrier is artificially moved in a few tenths of an angstrom without changing the electron affinity, the surface band is completely wiped out.

Turning to the study of the surface-state spectrum for the relaxed geometry, we find three bands of surface states. The band energies at Γ and J for these states are listed in Table I. Notice that while the topmost surface band lies in the absolute band gap of the crystal, the second and third bands overlap the bulk valence band.¹³ It should be emphasized that these are bona fide surface states, not resonances, and that they do not mix with the bulk valence bands because of symmetry.¹⁴

A comparatively straightforward interpretation can be given these states. Band 1 is the broken or dangling bond state. In Fig. 1(b) we have plotted the charge density for the state at J . While similar to the dangling-bond state for the unrelaxed potential, the ratio of the forward to back lobe is much closer to 1. This state is closer to a p_z than an sp^3 state, which is consistent with the contraction of the surface atom and the transformation of the sp^3 back bonds toward planar sp^2 bonds. It is worth noting that the higher energy state at Γ has more charge in the back than in the forward lobe (as seen in the planar average charge density in Fig. 2) and could be interpreted as a dangling antibond.

Experimental evidence for the dangling-bond surface band has existed for over 10 years.⁹ Re-

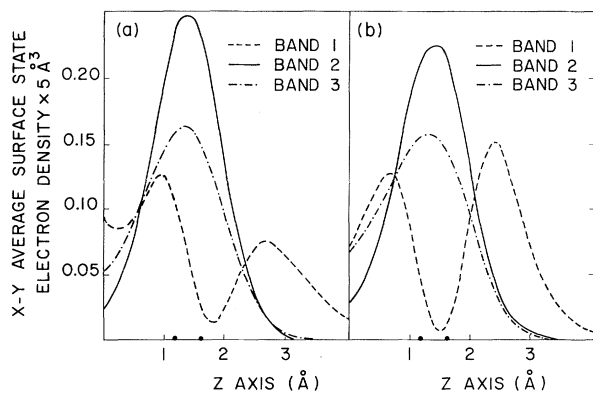


FIG. 2. Planar or x - y average charge density plotted along the z axis [(111) direction] for the (a) Γ and (b) J surface states for all three surface bands of the relaxed structure. The heavy dots on the z axis locate the atom planes and the origin is at the matching plane (see text for definition). Note that average volume per valence electron in bulk Si is 5 \AA^3 .

cent ultraviolet photoemission results¹⁵ comparing freshly cleaved and oxidized Si(111) surfaces have been interpreted as showing the surface state density to be peaked at -0.5 eV. This result cannot be directly compared with ours, since the electronic structure of the metastable 2×1 configuration obtained on cleavage may be significantly different from that of the equilibrium configuration studied here. In addition, these authors' assumption that the effect of oxidation on the surface density of states can be interpreted solely in terms of the density of surface states is not warranted.

The second band of states has most of its charge located on the back bonds between the first and second planes of surface atoms. This band forms in response to the more attractive potential on the contracted back bonds. It is doubly degenerate at Γ but only singly degenerate at J , implying that one component merges into the continuum somewhere between Γ and J . The third band, near the bottom of the valence band, is split from the valence band by the generally more attractive potential implied by bond contraction. Its charge lies along the bonds between the first and second as well as the second and third planes of atoms and is less localized than that of the middle bands.

From the above discussion it is clear that surface states are sensitive to relaxation and that a direct measurement of that relaxation is highly desirable. Low-energy electron-diffraction measurements on the 1×1 Si(111) surface have been

made⁶ but no dynamic analysis of the data is yet available.¹⁶ Lacking definitive evidence, there are two additional arguments which can be put forth which strongly support the relaxed over the unrelaxed structure.

First, we have been able to demonstrate a high degree of self-consistency for the relaxed surface potential. Precisely the opposite was true for the unrelaxed structure. The reason for this failure can be understood as follows: From a calculation of the charge density of the Bloch waves in the surface region one finds that the surface band needs to contain somewhat more than one electron for charge neutrality. Because of the highly extended nature of these states there is a very large dipole potential produced, so that the new potential we calculate from the charge density implied by the old potential no longer supports surface states in the gap and self-consistency cannot be achieved. Because of the contraction of the dangling-bond surface states brought about by the tightening of the back bonds this difficulty does not come up in treating the relaxed structure.

Second, the surface-state bands provide a natural explanation for the structure at 2 and 14 eV seen in the inelastic energy-loss spectrum for Si(111) reported by Rowe and Ibach.⁵ This structure, which disappears progressively with oxidation, could be interpreted as one-electron surface-state to conduction-band transitions.

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¹⁶Florio and Robertsom (Ref. 6) have performed a kinematic analysis of their data and arrived at a $0.16\text{-}\text{\AA}$ contraction of the outermost layer. Considering the serious difficulties associated with making such a kinematic analysis we believe that this result is at best suggestive that the surface has undergone some contraction.

Feasibility of Nuclear Polarization of ${}^3\text{He}^{++}$ Ions by Electron-Transfer Processes

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Preliminary results are reported of an experiment confirming the feasibility of a Lamb-shift source of polarized ${}^3\text{He}^{++}$ ions. Such a source is under construction and will be used for the axial injection of ions into a cyclotron.

The source to be briefly described is the outcome of various theoretical and practical studies made at Birmingham University since 1962 into the possibility of axially injecting a beam of polarized ${}^3\text{He}^{++}$ into a cyclotron. Consideration of the successful Lamb-shift sources for hydrogen ions¹ led to the idea² of a ${}^3\text{He}$ ion source based on the same principle. A beam of polarized ${}^3\text{He}^{++}$ ions can be achieved using the following sequence of processes: (a) the production of a beam of ${}^3\text{He}^+$ ions, containing a certain fraction of ions in the $2S$ metastable state; (b) the polarization of the electron spin state of the ${}^3\text{He}^+(2S)$ ions by electric-field quenching of unwanted components to the short-lived ${}^3\text{He}^+(2P_{1/2})$ state; (c) the partial transfer of electron polarization to nuclear polarization through hyperfine coupling; (d) the subsequent ionization of the ${}^3\text{He}^+(2S)$ ions to ${}^3\text{He}^{++}$ with discrimination against ionization of the unpolarized background beam of ${}^3\text{He}^+(1S)$.

The magnitude of nuclear polarization of the final ${}^3\text{He}^{++}$ beam depends mainly on the ratio of the electron capture cross sections σ_{21^*} and σ_{21} in process (a) and also on the ratio of the two electron-loss cross sections σ_{1^*2} and σ_{12} in process (d). Here 2 refers to the doubly ionized and 1 to the singly ionized atom, with 1^* denoting the metastable state.

Since no experimental information was available on the above cross sections in the energy region considered (about 30 keV for the optimum cyclotron injection energy), an experiment was performed to establish the combined effect of processes (a) and (d). The experiment deter-

mined the fraction of the final ${}^3\text{He}^{++}$ beam resulting from electron loss by the ${}^3\text{He}^+(2S)$ component, and also the overall efficiency of both the electron-transfer processes.

A sketch of the experimental arrangement is shown in Fig. 1. Both electron-transfer processes took place in canal-shaped gas targets GT_1 and GT_2 operating at pressures low enough to avoid multiple collisions. The required

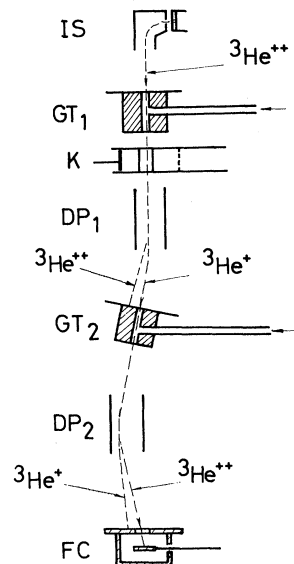


FIG. 1. Sketch of the experimental arrangement for investigation of electron-transfer processes with incident ${}^3\text{He}^{++}$ ions showing ion source (IS), gas targets (GT_1 and GT_2), electrostatic deflection plates (DP_1 and DP_2), microwave cavity (K), and Faraday cup (FC).