

Surface Potential, Charge Density, and Ionization Potential for Si(111)—a Self-Consistent Calculation

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We report three fully self-consistent calculations of the ionization potential, charge density, and surface potential for the Si(111) surface in which the normal coordinates of the outer two planes of surface atoms were allowed to vary. The ionization potential, calculated to be 5.4 eV, and the Fermi energy (relative to the valence-band maximum), calculated to be 0.3 eV, are both relatively insensitive to surface geometry. This is not true of the surface-state bands, which are quite sensitive to surface geometry.

We should like to report the first fully self-consistent calculation of the potential and charge density at the surface of a semiconductor. The semiconductor chosen was Si, and the calculation was done for an unreconstructed (111) surface.

The authors recently reported a calculation of the surface states for the Si(111) surface¹ and their relationship to the assumed lattice relaxation of the outermost plane of surface atoms. The potentials upon which that analysis was based were empirically adjusted to yield the experimental work function and were not self-consistent. In the present calculation no adjustable surface parameters were used—rather the surface potential and charge density were iterated to self-consistency for three different surface geometries. Within the context of an unreconstructed surface these geometries correspond to assigning normal coordinate positions to the two outermost planes of surface atoms. The work function of Si as well as the position of the bulk Fermi energy with respect to the surface valence-band maximum are two important quantities that are predicted by such calculations in addition to the more detailed information contained in the surface charge density and potential.

The calculations were performed in the following manner: At any stage in the iteration the surface potential was calculated from the valence charge density obtained in the previous stage of iteration, assuming a fixed model potential for the Si⁴⁺ ion.² With this potential Schrödinger's equation was solved using ~ 30 surface reciprocal-lattice vectors for the continuum as well as surface states that contribute to the charge density. For both the method of calculating the potential and the procedures used in solving the Schrödinger equation the reader is referred to the authors' work on the Na(100) surface,³ except

for several improvements. These involved the use of the full Wigner interpolation formula for the exchange and correlation potential, and the inclusion, in solving Schrödinger's equation, of evanescent Bloch waves in the bulk region.

The summation scheme used to construct the charge density consisted of the following: A representative sample of \vec{k}_{\parallel} points in the two-dimensional Brillouin zone was chosen on the basis of a two-point surface variant of the Baldereschi summation scheme used for bulk semiconductors.⁴ At these two points, Γ at the zone center and J at the center of the zone edge, Schrödinger's equation was solved for all surface states lying below the Fermi energy and for ten continuum states per bulk valence band. The Fermi energy, which lies in the gap surface-state band for Si, was fixed by filling this band so that the Si surface was charge-neutral. This procedure locates the Fermi energy with respect to the bulk energy bands for the flat band condition (no long-range band bending or Schottky surface barrier).

The iteration loop in the self-consistent calculations was entered at the potential stage and typically took eight iterations to achieve self-consistency between input and output potentials of better than 50-meV rms error over the entire surface region. This region started ~ 1 a.u. on the vacuum side of the third plane of atoms and extended ~ 11 a.u. toward vacuum, at which point the surface charge density was one thousandth of its bulk value.

Of the three geometries studied, the first was chosen on the basis of empirical arguments from structural chemistry⁵ already elaborated upon in the context of the authors' previous work.¹ The second and third geometries represented our attempt to study the effects of changing the first-to-second layer spacing and moving the first and second layers rigidly inward. The qualitative

nature of the charge distribution in the three bands of surface states present for the first and third geometries is similar and little changed from our previous results.¹ The single band of gap surface states present for the second geometry is more strongly directed outwards from the surface atom than in the other cases. On the basis of a comparison of the theoretical location of the surface-state critical points and surface resonances⁶ with photoemission and energy loss spectra for the Si(111) 7×7 , the second geometry can be ruled out.⁷

Solely within the context of the present calculation a distinction between the three structures could be made on the basis of a comparison of the total surface energies for the three structures. While this has not as yet been done, a preliminary calculation of the forces on each of the two planes of surface atoms has been made using the Hellmann-Feynman theorem.^{8,9} There are, for geometries 1 and 3, forces on the surface atoms of ~ 0.05 (a.u.) pointing inward. (This is the force a harmonic oscillator with the mass of Si and a natural frequency of 60 meV would have when stretched 0.2 a.u.) The stretching of the first-to-second bond length for geometry 2 results in a force on the outermost surface plane of 0.15 inward, tending to argue against this geometry. Whether the net forces for geometries 1 and 3 are real or in the noise of the calculation (they correspond to differences in the fifth plane) cannot as yet be ascertained.

Listed in Table I are the ionization potential (IP), number of electrons per surface atom in the gap surface states (n_{ss}), and number of surface bands found for each geometry. Notice that the ionization potentials for the three geometries are almost identical, and agree well with the measured value of 5.15 eV for the Si(111) surface.¹⁰ This insensitivity of the IP to geometry change is consistent with the small variation of the IP of Si from face to face¹¹ and its relative insensitivity to large temperature and structural changes.¹²

The constancy of the IP for all three geometries implies that the dynamic effective surface charge—a concept recently discussed by a number of authors¹³—is negligible for long-wavelength phonon modes whose motion is normal to the Si(111) surface.

From a knowledge of the density of states for the dangling-bond surface band and the number of electrons in this band (dictated by charge neutrality) the position of the Fermi energy relative

TABLE I. For three different surface geometries, identified by giving the location of the second and first atomic layers relative to the third, we have listed the ionization potential (IP), electronic occupancy of the gap surface-state band (n_{ss}), and number of surface-state bands present. The geometric parameters corresponding to the ideal bulk lattice are 4.44 and 5.92.

| Geometry (a.u.) | IP (eV) | n_{ss} | No. of surface-state bands |
|--------------------|------------------|----------|----------------------------------|
| 4.44, 5.26 | 5.44 ± 0.05 | 0.7016 | 3 |
| 4.44, 5.56 | 5.46 ± 0.004 | 0.5834 | 1 |
| 4.24, 5.06 | 5.51 ± 0.07 | 0.6350 | 3 |

to the valence-band maximum was found to be 0.3 eV, in excellent agreement with experiment.¹⁰ This energy remained essentially constant for all three geometries, in spite of the 0.1 electron spread in occupancy number for the three bands.

For surface geometry 1, we have plotted in Figs. 1 and 2 contours of constant surface potential and valence charge density, on a plane which is normal to the (111) surface. This plane passes through a line connecting a surface atom with one of its nearest neighbors in the second plane of atoms. Since these calculations are based on a Si^{4+} model potential, we are dealing here with pseudopotentials and pseudocharge densities. It is our contention that the pseudocharge density is identical to the real charge density outside the ions, a fact which is supported by a self-consistent Si-atom calculation¹⁴ using our model potential in which a comparison was made between "pseudo" wave functions and Hartree-Fock wave functions outside the nodal region.

We first consider the potential plotted in Fig. 1. Along the lines connecting the Si atoms, indicated by the heavy dots, we notice the attractive bond potential responsible for the covalent bonding in Si. Above the Si atom at the surface there is present a residual attractive potential. It is this potential which is responsible for the localized dangling-bond surface states in the energy gap of Si. The reader should be aware of a certain amount of elliptical distortion in the vicinity of the atoms present in these contours. This results from a Gibbs phenomenon due to the truncation of the Fourier expansion of the potential parallel to the surface, and has no physical significance.

Turning to the surface charge density shown in Fig. 2, we note that the strongly covalent nature

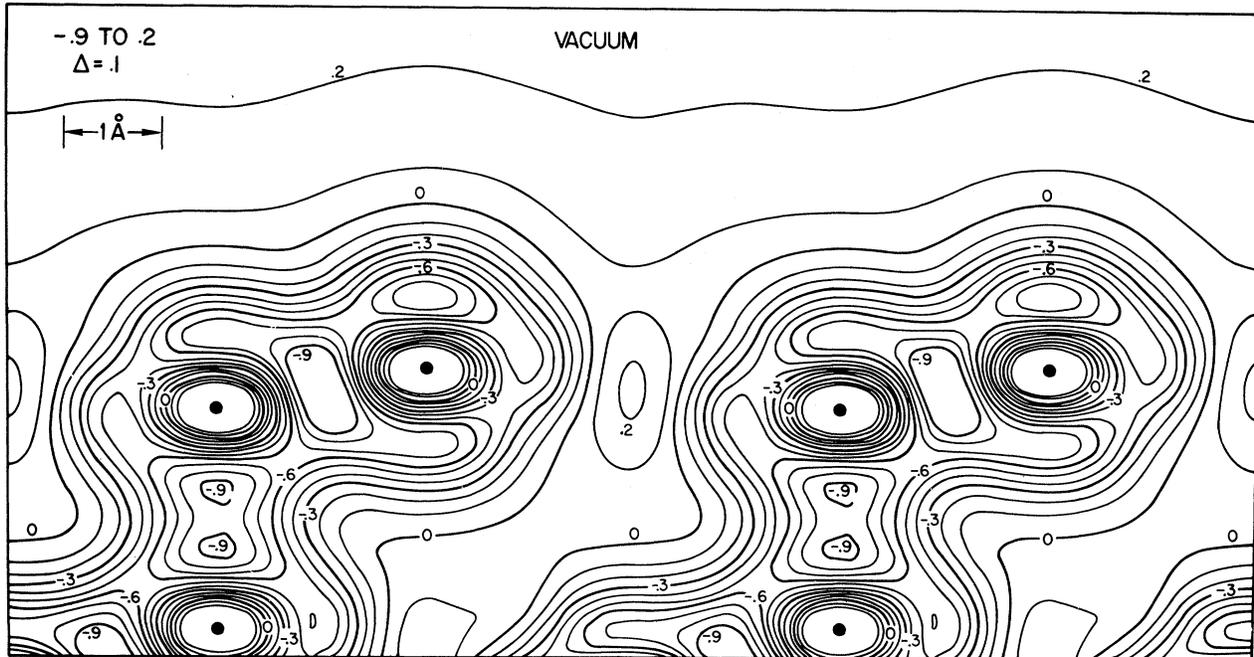


FIG. 1. Contours of constant surface potential plotted on a plane normal to the Si(111) surface and passing through a line connecting a surface atom with one of its nearest neighbors in the second plane of atoms. The heavy black dots locate the centers of Si atoms. The energy units are hartrees, the contours are spaced 0.1 hartree apart, and the scale is placed so that the valence-band maximum falls at +0.06 hartree.

of the bulk charge distribution persists undiminished at the surface. The outermost charge density contour (which is $\frac{1}{6}$ the average bulk density

of 30 in these units) extends well below the second plane of surface atoms, forming a channel into the interior of the crystal. One can specu-

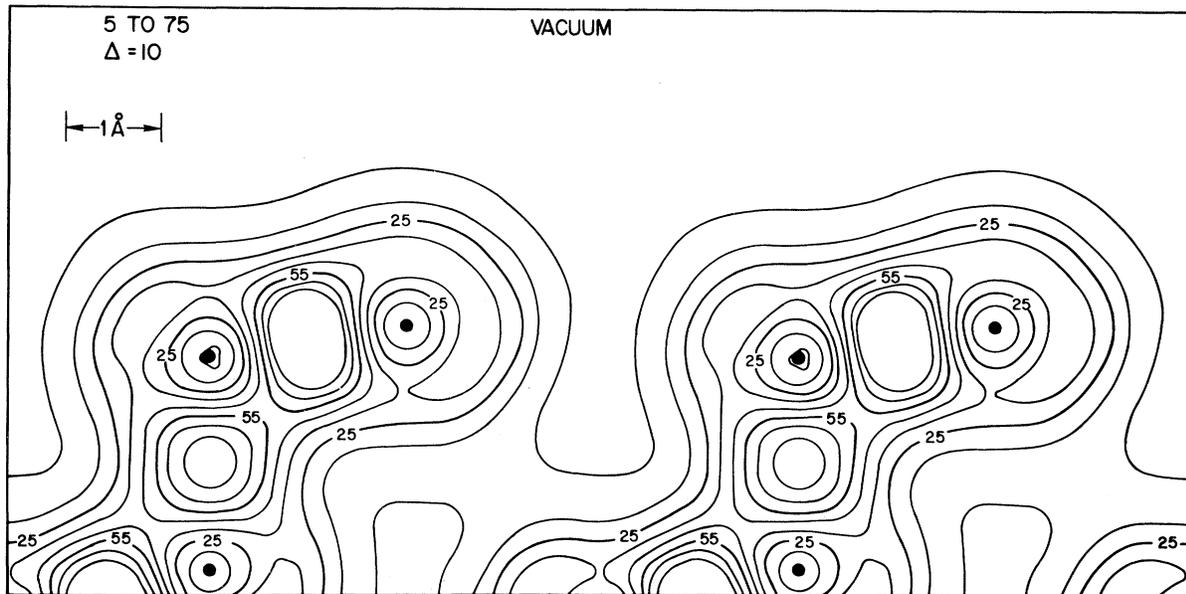


FIG. 2. Contours of constant charge density plotted on a plane normal to the Si(111) surface whose orientation is indicated in the caption of Fig. 1. The heavy dots locate the centers of Si atoms. The units of charge density are 10^3 a.u., with contours every 10 units apart.

late that interstitial migration of impurities from the surface into the bulk proceeds along these channels. One might have expected the surface-region electrons to have more metallic character, and to have a far less corrugated charge distribution on the basis of Smoluchowski's smoothing argument.¹⁵ Bulk Si is fairly free-electron-like in the sense that the average gap is only $\frac{1}{4}$ of the appropriate free-electron Fermi energy, and the surface electrons experience even less ion potential. It is clear, however, that such arguments do not describe the results. One final point needs to be made. Note the prominent buildup of bond charge between Si atoms in the surface region in response to the attractive potential seen in Fig. 1. The charge density in the center of the band is almost twice what one would obtain from a superposition of pseudoatom charge densities. At the corresponding point above the surface atom, however, the charge is 20% lower than given by such a superposition. This latter effect arises because the dangling-bond surface-state band need be occupied by only $\frac{7}{10}$ of an electron per surface atom to neutralize the surface; as a consequence that bond is unsaturated and the site above the surface atom is expected to be chemically active. In this picture, then, chemically reactive sites are revealed as regions of attractive potential at which there has been incomplete charge buildup. Work is currently underway to study the bonding of ordered overlayers to this surface.

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Verification of the Metal-Rich Surface Model for the Oxidation of Sr, by Auger-Electron Spectroscopy*

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The oxidation of strontium has been studied by Auger-electron spectroscopy. It is found that the surface of Sr remains metallic during oxidation, in support of recent photoemission experiments. A model based on the large electrostatic or Madelung energy of "ionic" metal/adsorbate systems is suggested that explains the phenomena.

The kinetics of the oxygen adsorption/oxidation process for the alkaline-earth metals is of considerable interest because of the gettering capabilities¹⁻⁴ of these metals and the low work function of their oxides.⁵ Recently, the authors applied the technique of ultraviolet photoelectron spectroscopy (UPS) to a study of the oxidation of

Sr.⁶⁻⁸

In interpreting data from these studies we viewed the oxidation process, in a manner similar to that of a number of early workers,¹⁻⁴ as occurring in three states: first, oxygen chemisorption with rapid movement of the oxygen ions below the surface; second, oxide nucleation and