# The Si (100) surface. III. Surface reconstruction

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The potential, charge density, energy spectrum, and occupied surface density of states are calculated selfconsistently for two currently popular structural models of the stable  $2 \times 1$  reconstruction of the Si (100) surface. The features which emerge are discussed in terms of their relationship to the same features on the unreconstructed surface. We feel that comparison with uv photoemission data favors one model, the pairing model, over the other, the vacancy model.

### I. INTRODUCTION

That the (100) surface of silicon undergoes a reconstruction to a  $(2 \times 1)$  superlattice has been known for some time through low-energy-electrondiffraction studies.<sup>1</sup> A major theoretical problem is to understand how the reconstruction is related to the electronic and structural properties of the surface. Complicating this problem is the fact that the arrangement of atoms within the superlattice unit cell is not known, such determination being presently beyond the capability of low-energy-electron diffraction for semiconductors. Nonetheless, there are a limited number of plausible structural models for the reconstruction and we have chosen two of them, the pairing model<sup>2,3</sup> and the vacancy model,<sup>4</sup> to explore here.

Our aim in this work is to understand the similarities and differences between these two models and between these models and the unreconstructed Si (100) crystal which we studied in the first two papers in this series.<sup>5, 6</sup> A single set of geometric parameters was studied for each model, and while further refinement may be possible, we feel that the difference between the two models is sufficiently marked that, after comparison with experiment, one model (the pairing model) is strongly favored over the other model (the vacancy model).<sup>7</sup>

In Sec. II, we describe the arrangement of atoms in the two models we have studied. Section III lists those details of the calculation which are newly introduced because of the change of surface geometry. In Sec. IV, we describe the spatial form and the energy spectra of the states arising from broken bonds, relating them to what we found on the unreconstructed surface. Section V discusses some of the other surface states which arise. In Sec. VI, we describe the total charge density, and the density of states for both models. We compare the density of occupied states with experimental photoemission data and on this basis, choose between the two models.

#### **II. GEOMETRY OF THE SURFACE**

In order to make contact with the results of our earlier studies, it is convenient to recall the geometry of the ideal unreconstructed surface and to describe the two reconstruction models as distortions of or additions to the ideal structure. Atoms in the topmost four layers of the ideal Si (100) surface are arranged as in Fig. 1(a). Each surface atom (labeled 1) has two broken bonds: the reconstruction geometry in each of the proposed models is such that some or all of the broken bonds rebond, thereby lowering the energy of the surface.

In the pairing model proposed by Schlier and Farnsworth,<sup>2</sup> alternate rows of surface atoms move toward each other to form pairs, thereby rebonding *half* the broken bonds. This, at least, was the original suggestion and is the obvious conclusion based on a ball-and-stick model. As we shall discuss in Sec. IV, our results show that the bonding situation is actually more favorable than heretofore considered, and that all the bonds are rebonded. (The rebonding of the second pair is, admittedly, weak.) Levine<sup>3</sup> proposed that the pairing is such that all bonds, including the newly formed one between pairs of surface atoms, have the bulk bond length. In such case, the angle between the new bond at the surface and the back bonds between atomic layer 1 (the surface layer) and 2 (the next layer in) is very nearly equal to the tetrahedral angle 109° characteristic of the bulk. There is, however, significant distortion of the angle between these latter bonds and those between atom planes 2 and 3. This distortion, to 93°, raises the energy of the back bonds, causing back bond surface states to form. In Fig. 1(b), we show the position of atoms in the top four layers in the Levine geometry which we adopted for these calculations.

The other structural model of interest here is the vacancy model recently proposed by Phillips.<sup>4</sup> Alternating vacancies and atoms are located along

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FIG. 1. Orientation of the first four planes of atoms, as viewed from the vacuum looking normally into the bulk. Figure 1(a) depicts the ideal unreconstructed Si (100) surface. Successive planes of atoms are separated by  $\frac{1}{4}a$  where a = 5.43 Å. Nearest neighbors in a given plane are separated by  $a/\sqrt{2}$  and the bulk bond length is  $(\frac{3}{16}a^2)^{1/2} = 2.35$  Å. Circles of the same size, labeled by the same integer, are in the same plane parallel to the surface, with smaller circles, or higher numbers, indicating increasing distance from the vacuum. Figure (b) depicts the Schlier-Farnsworth-Levine geometry where rows of surface atoms move towards each other in a direction normal to the rows in such way that all bonds have the bulk bond length. Figure (c) depicts the vacancy model geometry where alternating vacancies and atoms are located along surface rows. The back bonds on the atoms in the topmost plane are 2.13 Å; all other bonds are bulk bond length.

surface rows and double bonds are supposedly formed between atoms of the first and second layer. This would account for all the broken bonds. Our calculations do not support this bonding picture, however, and we shall discuss in Sec. IV the fact that the actual bonding situation is less favorable. In Fig. 1(c), we show the position of atoms in the top four planes of this model. In this figure, we have placed a half-filled layer of atoms (layer 0) on top of the arrangement depicted in Fig. 1(a) and have deleted the innermost atomic layer (layer 4). The half-filled layer of atoms is relaxed by 0.45 Å towards the bulk to give a bond length of 2.13 Å between atoms in the first and second layer.<sup>8</sup> This is in accord with the estimate of double bond length given by Pauling's formula.<sup>9</sup>

### **III. THEORETICAL METHODS**

The results we shall present were obtained by carrying out a self-consistent solution of the three-dimensional Schrödinger equation using Fourier series to handle the periodicity of the crystal in the two dimensions parallel to the surface and using numerical integration in the dimension normal to the surface. The interaction of a valence electron with a silicon ion core is represented by a local model potential. The interaction of the valence electrons among themselves is represented by the Hartree potential plus a local density functional term for exchange and correlation. Although this is the same method as that described by Appelbaum, Baraff, and Hamann<sup>5</sup> (referred to as I), some details of the calculation differ slightly because of the change in geometry and need to be cited.

The reconstructed surface, with its  $2 \times 1$  unit cell, gives rise to a surface Brillouin zone (SBZ) half the area of that for the unreconstructed surface. This SBZ is shown in Fig. 2. About twice as many reciprocal lattice vectors—71 instead of 30—are used in the expansion of the wave function to guarantee that it is as well represented in the  $2 \times 1$  calculation as it was in the  $1 \times 1$ . The spacing for the numerical integration in the normal direction remains unchanged.

The surface superlattice introduces a qualitatively new feature in this calculation. Every  $\vec{k}_{\mu}$  point in the 2×1 SBZ represents two different  $\vec{k}_{\mu}$  points in the SBZ of the undisturbed Si substrate. Thus scattering states which contain an incident Bloch wave associated with a single  $\vec{k}_{\mu}$  will contain reflected Bloch waves of that same  $\vec{k}_{\mu}$  and of its "partner"  $\vec{k}_{\mu}$ . Similarly, surface states will decay into evanescent Bloch states associated with two bulk  $\vec{k}_{\mu}$  points. The folded band structure as a function of perpendicular wave vector  $k_{\mu}$  is shown



FIG. 2. Surface Brillouin zone appropriate to the  $2 \times 1$  surface unit cell.

in Fig. 3 for  $\vec{k}_{\parallel}$  at four symmetry points of the 2×1 SBZ.

Neither of the two geometries considered changes changes the point group symmetry of the unreconstructed surface  $C_{zv}$ . The bands at symmetry points can therefore be labeled according to the irreducible representations of the group of the wave vector, which is also  $C_{2v}$  at each of the selected points. Many of the bands have degenerate states of several symmetries, but these do not mix. The  $2 \times 1 \Gamma$  and J' points include bands from inequivalent points in the  $1 \times 1$  zone, and these bands are labeled to indicate their origin. The  $2 \times 1 J$  and K points each represent pairs of equivalent  $\vec{k}_{\parallel}$  points in the  $1 \times 1$  SBZ.

The matching plane, which separates the bulk region from the surface, is, as before, located midway between the atom planes 2 and 3. Since the surface in the vacancy model is constructed by adding an ordered half monolayer array of atoms on top of the ideal surface depicted in Fig. 1(a), there are  $2\frac{1}{2}$  layers of atoms in the surface region in our vacancy model calculations while there are two full layers of atoms (as there were in our calculations of the unreconstructed surface) in our pairing model calculations.

As Levine pointed out, one feature of the pairing model is that the surface consists of alternate "pedestal" and "cave" regions, the pedestals being the built up regions where two surface atoms have moved closer to form a pair and the cave regions being holes opened up by the motion of two atoms previously nearest neighbors on the surface away from each other. The formation of caves means that the surface region—parts of the crystal where the charge density and potential differ from their bulk forms—extends somewhat further



FIG. 3. Si band structure in the direction normal to the surface for  $\mathbf{\hat{k}}_{\parallel}$  at four symmetry points in the surface Brillouin zone. Energies are measured relative to the valence-band maximum. Bands are labeled according to irreducible representations of the point group symmetry of the surface as listed in Table I. Bands at  $\Gamma$  and J' are labeled in lower case letters according to which of the inequivalent  $\mathbf{\hat{k}}_{\parallel}$  points of the 1×1 SBZ they correspond.

into the bulk than it did before the pairing took place. This results in the formation of some weakly split surface states whose charge is predominantly in the vicinity of the second to third layer bonds. While these states extend well inside the matching plane, their effect on the charge density in this region is small because of the approximate "completeness relation" obeyed by surface states and nearby bands of scattering states.<sup>10</sup> We expect to verify the insensitivity of the self-consistent potential to any residual disturbance in further study of this system by moving the matching plane.

In this paper, we shall be describing the surface density of states, a quantity which does not appear in I or II. The position dependent density of states is defined by<sup>11</sup>

$$\rho(r, E) \equiv \sum_{n \text{ occupied}} |\psi_n(r, E_n)|^2 \delta(E_n - E).$$
(3.1)

We find it convenient to summarize our results by presenting the integral of  $\rho$  over the surface region:

$$\rho(E) = \int_{\substack{\text{matching}\\\text{plane}}}^{\infty} dz \int_{\substack{\text{surface}\\\text{unit cell}}} dx dy \ \rho(r, E).$$
(3.2)

In evaluating (3.2) using a scheme based on a discrete sampling of states rather than a continuum, it is necessary to smooth the delta function in (3.1). We have replaced it by a Gaussian of unit area and a width appropriate to the sampling of states we used. This sampling, which comprises about 700 surface and scattering states, involves occupied states at all four symmetry points  $\Gamma$ , J, K, and J', in the SBZ (see Fig. 2). This is about twice as many as those used in the charge summation scheme which here, as in I, is based primarily on the two symmetry points  $\Gamma$  and K. That this sampling is well converged is demonstrated by the fact that an evaluation of (3.2), carried out by using only states at the symmetry points  $\Gamma$  and K, led to substantially the same results as exhibited here.

# **IV. BROKEN BOND SURFACE STATES**

We turn now to the first category of results, surface states which arise from broken bonds at the surface. These states are most easily discussed in terms of the simplest tight-binding picture according to which every silicon atom is regarded as contributing four tetrahedrally directed  $sp^3$  orbitals. Each orbital on a bulk atom is directed at a nearest-neighbor atom, is overlapped by the directed orbital on that neighbor, and forms a bond whose one-electron energy level is of the order of the average valence-band energy.<sup>12</sup> The antibonding combination of the neighboring directed orbitals forms a state typical of the lowest set of conduction bands, and therefore has a one-electron energy level appropriate to these. Surface atoms contribute some orbitals—the broken bonds which have no nearest neighbors at which to point, which are unable to take advantage of the attractive bonding potential between atoms. It is clear that to a first approximation these states should have an energy midway between the valence- and conduction-band averages, and thus in the band gap. These broken bond orbitals can be considered to give rise to the states we shall discuss here.

Let us first recall the results of I: Each surface unit cell for the unreconstructed surface contains two broken bonds, as shown in Fig. 4. These two bonds are equivalent to each other by symmetry (that is, there is a reflection which leaves the crystal unchanged but which interchanges the two broken bonds in a unit cell) and so the two orbitals combine to give two states, one of them even and one of them odd under this reflection. The even combination is the dangling bond surface state depicted in Figs. 6-9 of I, and the odd combination is the nonbonding bridge state depicted in Figs. 10-12 of I.

We pointed out in I that the dangling bond state, of  $sp_z$  type, had lower energy than the bridge state and was nearly filled, while the bridge state, of  $p_x$  type, was nearly empty. One point that we did not stress was that the even combination, the dangling bond, does have substantial charge behind the surface atom, as Figs. 6–9 of I make clear, and that this charge arises in part from the back lobes of the directed orbitals. This point will come up again below.

Next, consider the surface reconstructed according to the vacancy model. Each surface unit



FIG. 4. Broken bonds for the three surface models depicted in Fig. 1. All bonds are directed up out of the page as if they were tetrahedral orbitals attached to atoms whose back orbitals point down towards nearest neighbors.

cell now contains three atoms, two of which were on the surface before the third (central) atom was added. Two back orbitals on the added atom and one forward orbital on each of the two original surface atoms combine to form the two back bonds holding the added atom to the surface. These are similar to bulk bonds, but have a modified spectrum which will be discussed in Sec. V. The four broken bonds per unit cell are depicted in Fig. 4. Again, certain orbitals are symmetry equivalent to each other and can be expected to give rise to states which are even or odd with respect to the symmetries involved.

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There are two symmetry operators involved,  $\sigma_v$  (reflection in the x axis so that y - -y) and  $\sigma_v$ . (reflection in the y axis), giving rise to four types of states,  $A_1$ ,  $A_2$ ,  $B_1$ , and  $B_2$ , whose parity under the two reflections is given in Table I. Referring to Fig. 4, the obvious combinations of equivalent broken bonds are

$$\begin{split} \phi_{a} &= 2^{-1/2} (|1\rangle + |4\rangle); A_{1}, \\ \phi_{b} &= 2^{-1/2} (|1\rangle - |4\rangle); B_{1}, \\ \phi_{c} &= 2^{-1/2} (|2\rangle + |3\rangle); A_{1}, \\ \phi_{d} &= 2^{-1/2} (|2\rangle - |3\rangle); B_{2}. \end{split}$$

$$(4.1)$$

However, the two states of  $A_1$  symmetry undergo a further mixing for reasons we shall discuss below. The actual combinations which correspond most closely to the four bands of broken bond surface states produced in our calculations are

$$\begin{aligned} &|\pi_{b}\rangle = 2^{-1/2}(\phi_{a} + \phi_{c}) = \frac{1}{2}(|1\rangle + |2\rangle + |3\rangle + |4\rangle); A_{1}, \\ &|\pi_{a}\rangle = 2^{-1/2}(\phi_{a} - \phi_{c}) = \frac{1}{2}(|1\rangle - |2\rangle - |3\rangle + |4\rangle); A_{1}, \\ &|1_{br}\rangle = \phi_{d} = 2^{-1/2}(|2\rangle - |3\rangle); B_{2}, \end{aligned}$$

$$\begin{aligned} &|2_{br}\rangle = \phi_{b} = 2^{-1/2}(|1\rangle - |4\rangle); B_{1}. \end{aligned}$$

$$(4.2)$$

The labeling denotes  $\pi$ -bonding,  $\pi$ -antibonding, first-layer bridge, and second-layer bridge. Let us discuss these states.

Referring to (4.1) and Fig. 4, it is clear that  $\phi_d$  would be a bridge state and  $\phi_c$  a dangling bond situated, relative to the newly added surface atom, in exactly the same way as the bridge states and dangling bonds were situated relative to the surface atoms in I. In Fig. 5, we show the charge density for the one band of gap surface states

TABLE I. Parities of states under  $\sigma_v$  and  $\sigma_{v'}$ .

	$\sigma_v (y \rightarrow -y)$	$\sigma_{v'} (x \rightarrow -x)$
$A_1$	1	1
$A_2$	-1	-1
$B_1$	1	-1
$B_2$	-1	1

having  $B_2$  symmetry as calculated at two symmetry points,  $\Gamma$  and K in the SBZ. Not only is the charge density almost the same as that of the bridge state in I but its average band energy and bandwidth (see below) are virtually the same. The state is clearly  $\phi_d$ , a first-layer bridge.



FIG. 5. Contour plot of the charge density for the gap surface state of  $B_2$  symmetry for  $k_{\parallel} = \Gamma(a)$  and at  $k_{\parallel} = K(b)$  on a plane normal to the surface passing through a row of newly added surface atoms in the vacancy model. In this and in all subsequent charge contour plots, charge densities are in  $10^{-3}$  atomic units. Atom sites are indicated by dots.

The states  $\phi_a$  and  $\phi_b$  would be second-layer bridges joining the left atom in one unit cell to the right atom in the next. However, because of the back lobe on each broken bond, each of these states would have a lesser—but still not negligible—amount of charge under the added surface atom in the same unit cell. For  $\phi_a$ , the  $A_1$  even symmetry would enhance the charge under this atom, while for  $\phi_b$ , the  $B_1$  symmetry would give a node there. In Fig. 6, we exhibit the charge density for the band of gap surface states of  $B_1$  symmetry and it is clear that this second-layer bridge is  $\phi_b$  of (4.1).

The two states of  $A_1$  symmetry,  $\phi_a$  and  $\phi_c$ , would both have substantial amplitude below the added surface atom because they each have two lobes of the same sign there. In the symmetric combination  $|\pi_b\rangle$ , all four back lobes have the same sign and there is enhanced charge in the attractive region behind the surface atom. A state of much lowered energy will result, which is why the further mixing occurs. In Fig. 7, we show the charge density for this  $\pi$ -bonding state calculated at the symmetry point K. Its energy at  $\Gamma$  and J' would



FIG. 6. Contour plot of the charge density for the gap surface state of  $B_1$  symmetry for  $\vec{k}_{\parallel} = K$  on a plane normal to the surface and passing through the newly added surface atoms and their back bonds.

be expected to be lower, which would put the state in the valence band at these symmetry points. We do find scattering resonances at the expected energies in the valence bands of  $A_1$  symmetry at  $\Gamma$  and at J', but of course no bona fide surface state can exist there at these energies.

In the antisymmetric combination  $|\pi_a\rangle$ , the four back lobes cancel in pairs, reducing the charge in the attractive region behind the added atom. This, and the antibonding nodal structure, both of which are evident in Fig. 8, raise the energy of the  $\pi$ antibonding state.

The dispersion relation for these four bands of states is presented in the lower part of Fig. 9, which interpolates between the symmetry points using the interpolation formula Eq. (4.1) of I. This ignores the fact that some of the indicated cross-ings are forbidden by symmetry, and therefore that there are really small (and ignorable) hybridization gaps except at the allowed  $B_1 - B_2$  crossings.<sup>5</sup>

The interesting features of the surface-state spectrum for this model are these: The first-lay-



FIG. 7. Contour plot of the charge density for the lower-energy-gap surface state of  $A_1$  symmetry in the vacancy model, at  $\hat{k}_{\parallel} = K$ , on a plane normal to the surface passing through the newly added surface atoms and their back bonds.

er bridge has essentially the same dispersion relation as the bridge state in Fig. 5 of I. (Interchange J and J' points there because the bridge here, in the added atom layer, is now oriented along yrather than along x.) The second layer bridge, like the first layer bridge, has a nearly one-dimensional dispersion relationship but one which depends on  $k_x$  rather than  $k_y$ . Its energy is lower and its bandwidth is slightly less than half that of the first layer bridge. The flat  $\pi$ -bonding and  $\pi$ antibonding states, separated by 1.5 to 2 eV, also have smaller bandwidths than the dangling bond state in the unreconstructed surface. The narrowing of three of the four bands is connected with the smaller number of unit cells per x length of reconstructed surface, since a smaller change in xdirection kinetic energy is achieved by sweeping  $k_x$  from  $\Gamma$  to J. The fourth band, whose dispersion depends only on  $k_y$ , is unaffected.

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Distributing four electrons among these bands partially fills the bridge bands and leaves the Fermi energy pinned at midgap, at about 0.5 eV. Since only one  $\pi$ -bonding band exists while there are two back bonds per added surface atom, the effective bond order of the first to second layer bonds is 1.5 rather than 2 as proposed.<sup>4</sup> The re-



FIG. 8. Charge density for the higher-energy gap state of  $A_1$  symmetry at  $\vec{k}_{\parallel} = J$ .

maining electrons from the broken bonds are shared by the two bridge bonds. The unsaturated bonding represented by these partially filled bonds is manifestly unstable. The most geometrically favorable distortion of the assumed geometry would be to pair atoms in the surface half-layer in the y direction. This would split the  $1_{br}$  bond into occupied bonding and unoccupied antibonding parts. Unfortunately, it would still leave one electron in a partially filled band  $(2_{br})$ , and would produce a  $2 \times 2$  structure instead of the observed  $2 \times 1$ . Another alternative—pairing the second layer atoms in the x direction—preserves the  $2 \times 1$ structure but fails to achieve bond saturation. While it would lower the J to K portion of the  $2_{br}$ bond, it would raise the J' to  $\Gamma$  portion which has a node between these atoms. No additional splittings could be produced, and a partially filled band would remain. We conclude that bond counting alone does not suffice to predict saturated bonding. The required distortions from their basic tetrahedral directions are simply too great to allow all the bonds of the first- and second-layer atoms to be completed.

Let us next consider the surface reconstruction according to the pairing model. The unit cell and broken bonds in it are also depicted in Fig. 4. Before reconstruction, the four broken bonds would already be combined into a dangling bond and a bridge state on each of the two atoms in a unit cell. The two dangling bonds would be equivalent to each



FIG. 9. Dispersion relation for surface states near the absolute gap as calculated for the pairing model and the vacancy model. Energy is measured from the valence-band maximum. Dotted curves are resonances and the hybridization gaps at symmetry-forbidden crossings are omitted for clarity.

Г		J		 K		J'			
Label	(Energy)	Label	(Energy)	Label	(Energy)	Label	(Energy)		
B <sub>1</sub>	0.65	$B_1$	0.85	$B_1$	0.01	$B_1$	-0.15		
$A_1$	0.11	$A_1$	0.18	$A_1$	-0.45	$A_1$	-0.54		
$oldsymbol{A}_2$	-1.03	$B_2$	-2.62	$B_2$	-1.94	$A_2$	-2.26		
$B_1$	-5.06	$A_1$	-12.21	$B_1$	-3.12	$A_2$	-2.85		
$B_1$	-10.09			$B_2$	-3.18	$B_2$	-3.91		
				$A_2$	-3.72	$B_1$	-6.95		
				$B_2$	-4.00	$oldsymbol{A}_2$	-8.46		
				$B_1$	-7.24	$B_2$	-8.48		
				$A_1$	-9.28	$A_1$	-9.36		
				$B_2$	-10.21	$B_2$	-10.68		
Pairing model									
$B_2$	2.20	$\boldsymbol{B}_2$	2.36	$A_1$	0.48	$\boldsymbol{B}_1$	1.09		
$B_1$	1.23	$A_1$	0.76	$oldsymbol{B}_2$	-0.05	$A_1$	0.45		
$A_1$	0.76	$B_1$	-0.11	$\boldsymbol{B}_1$	-0.29	$B_2$	-0.07		
$B_1$	-10.63	$A_1$	-0.58	$A_1$	-0.97	$B_1$	-2.86		
-		$A_1$	-8.33	$A_2$	-3.04	$A_1$	-5.63		
		$A_1$	-12.14	$A_1$	-3.09	$A_2$	-8.43		
		-		$B_2$	-3.32	$B_1$	-8.47		
				$B_2$	-3.66	$A_1$	-10.36		
				$B_1$	-3.82	-			
				$A_1$	-5.46				
				$\vec{B_1}$	-8.62				
				$A_1$	-10.38				
Vacancy model									

TABLE II. Surface state energies in eV and symmetry labels.

other and would give rise to a pair of states which are even and odd under  $\sigma_{v}$ . The same is true for the two bridge states. Thus, the basic description of the states of the unreconstructed surface referenced to a double size unit cell is

$$\begin{aligned} |\pi_{b}\rangle &= \frac{1}{2}(|1\rangle + |2\rangle + |3\rangle + |4\rangle); A_{1}, \\ |\pi_{a}\rangle &= \frac{1}{2}(|1\rangle + |2\rangle - |3\rangle - |4\rangle); B_{1}, \\ |\sigma_{b}\rangle &= \frac{1}{2}(|1\rangle - |2\rangle - |3\rangle + |4\rangle); A_{1}, \\ |\sigma_{a}\rangle &= \frac{1}{2}(|1\rangle - |2\rangle + |3\rangle - |4\rangle); B_{1}. \end{aligned}$$
(4.3)

The  $\pi$  states, bonding and antibonding, are even and odd combinations of the left and right dangling bond state, while the  $\sigma$  states, bonding and antibonding, arise from the bridge states.

This symmetry classification remains valid as the surface reconstructs by having the two atoms move towards each other. The even and odd dangling bond states,  $|\pi_b\rangle$  and  $|\pi_a\rangle$ , which were degenerate, now split, although the splitting is small because the potential in the region occupied by the dangling bond is not greatly altered by the reconstruction. The even and odd bridge states are much more affected by the reconstruction: The state  $|\sigma_b\rangle$  has large charge density in the attractive region between the paired surface atoms and its energy is greatly lowered. When the reconstruction is such that the two surface atoms have a bulk bond separation, the attractive potential is much like that in the bulk bonds and the one-electron energy level of the state should be like that of the bulk bonds, namely an average valence-band energy. As a matter of fact, the  $|\sigma_b\rangle$  state does not have an independent identity in our calculations: there are surface states and resonant scattering states of the  $|\sigma_{b}\rangle$  form all through the valence-band energy range. A tabulation of all the surface states which occur in our calculation is given in Table II. Those of  $|\sigma_b\rangle$  form are at -12.21 eV (J), -9.28 eV (K, shown in Fig. 10), and -9.36 eV (J'). The other  $\sigma$  state,  $|\sigma_a\rangle$ , has a node in the attractive bonding region. Its charge is in the repulsive region opened up by the caves and it has markedly higher energy, like a bulk antibonding state. We expect it is spread throughout the conduction band.

In Figs. 11 and 12, we show the charge distribution for  $|\pi_b\rangle$  and  $|\pi_a\rangle$  calculated at a representative point in the SBZ. The relation between these states and the dangling bond states of I is evident. The spectra of these states are shown in the upper part of Fig. 9. The  $\pi$  states must hold two electrons, and we find that the  $|\pi_b\rangle$  band is almost completely occupied, and the  $|\pi_a\rangle$  band is almost empty. This indicates that the pairing geometry has done more to repair the broken bonds than just rebond the two pointing towards each other (in the ball-and-stick model sense) as originally pro-



FIG. 10. Charge density for a typical  $\sigma$  bonding state in the pairing model, that at  $\vec{k}_{\parallel} = K$ , E = -9.3 eV, on a plane normal to the surface passing through the paired surface atoms.

posed.<sup>2</sup> It has in fact resulted in the (nearly) complete rebonding of all the broken bonds. While the presence of two occupied bonding bands per surface pair could be called a double bond on the basis of simple counting, we hesitate to do so. The average splitting of the bonding and antibonding and antibonding antibonding splitting of 4.4–4.8 eV in bulk Si.<sup>13</sup> If we take these numbers as a rough measure of bonding strength, we conclude that the  $|\pi_b\rangle$  band contributes considerably less than the 40% additional strength associated with the Si double bond.<sup>14</sup>

We expect the extra bonding contributed by  $|\pi_b\rangle$ to shorten the pair bond slightly from the assumed single bond length. This would further separate the  $|\pi_a\rangle$  and  $|\pi_b\rangle$  bands to give a semiconducting surface instead of the slightly semimetallic surface presently found. It would also raise these bands slightly. (Note that the average  $|\pi\rangle$  state in the pairing model has a spectrum similar to, but higher in energy than, the dangling bond from which it is derived. Much of this rise in energy occurs because the surface atoms, in their motion towards each other, have been moved closer to the bulk in order to maintain the back bonds at the same length. Table I of Ref. 6 indicates that the inward motion of the surface atoms alone, without reconstruction of the surface, raises the energy of the dangling bond.)



FIG. 11. Charge density for the pairing model  $\pi$ -bonding state at  $\hat{k}_{\parallel} = K = -0.45$  eV, on a plane normal to the surface passing through the paired surface atoms.



FIG. 12. Charge density for the  $\pi$  antibonding state at  $\vec{k}_{\parallel} = K$ , E = 0.01 eV.

The surface Fermi level shown in Fig. 9 was determined by putting two electrons in these bands. It has been experimentally located by Rowe at  $0.2 \pm 0.2 \text{ eV}$ ,<sup>15</sup> although the recent core electron excitation results of Koma and Ludeke,<sup>16</sup> in which an unoccupied surface state peak appears 1.0 eV below a feature which is at or slightly below the conduction band edge at 1.1 eV, suggests that the Fermi level lies near Rowe's<sup>15</sup> lower limit. This is consistent with our results of  $E_F = 0.05$  eV for the pairing model, and is inconsistent with our result for the vacancy model.

# V. BACK-BOND SURFACE STATES

The surface states discussed in the last section are not the only ones present in either model of the reconstructed surface. Back bonds in both models are sufficiently different from bulk bonds that they too give rise to surface states.

In the vacancy model, the two back bonds holding the added atom to the crystal are shorter than any other bonds in the crystal and so the potential is more attractive in these bonds than anywhere else in the crystal. The charge forming these bonds tends to be lower in energy and much of it is con-

tributed by surface states which lie below the bands from which they are derived. Among the states collected in Table II, this type occurs at  $-10.09 \text{ eV} (\Gamma)$ , -8.33 and -12.14 eV (J), -3.82, -8.62, and -10.38 eV (K, shown in Fig. 13), and -2.86, -5.63, and -8.47 eV (J'). There are also states whose charge is maximum in the plane between the second and third layer and whose energy lies above the band from which they arise at -10.36 eV (J') and -10.38 eV (K, shown in Fig. 14). The energy which pushes this state out of the top of the band may be associated with the distortion of angle between the back bonds on the surface atom and those in the next deeper layer. The remaining deep states in Table II are weakly split from narrow bands and have no discernable significance.

In the pairing model, the back bonds and the pair bond almost form the perfect tetrahedral angle of  $109^{\circ}$  about the surface atom. However, the bond angles about the second layer atoms are significantly distorted, the angle between the back bond and the nearest second to third layer bond being 93°. The distortion would be expected to



FIG. 13. Charge density for a back bond state in the vacancy model at  $\vec{k}_{\parallel} = K$ , E = -10.4 eV.



FIG. 14. Charge density for second to third-layer bonding state in the vacancy model at  $\vec{k}_{\parallel} = K$ , E = -5.5 eV.

raise the energy of the back bonds. Ten of the surface states listed in Table II are associated with back bonds. Those at -1.03 (shown in Fig. 15) and -10.09 eV ( $\Gamma$ ), -1.94 and -3.18 eV (K), and -2.85 and -6.95 eV (J') have energies split off above the nearest bands of the same symmetry. Most of these are highly localized states, and they contribute around half the charge in the pair bond regions. Other, at -2.62 eV (J), -7.24 and -10.21 eV (K), and -8.46 eV (J') have their energies split below adjacent bands, but these are in general only weakly localized. The predominant trend is upward. This can be regarded as a physical manifestation of the empirical "bond-bending" force, which tends to oppose the pairing. The energy increase of the back bonds, however, is considerably smaller than the energy decrease of the



FIG. 15. Charge density for a back bond state in the pairing model at  $\vec{k}_{\parallel} = \Gamma$ , E = -1.03 eV. This figure, unlike all the others shown, is not periodic in the direction parallel to the surface, because the plane of the back bonds, when extended, cuts different unit cells in different locations.

 $|\sigma_b\rangle$  state caused by pair bond formation.

Additional surface states occur in internal band gaps which have their charge primarily behind the second atom layer. These are predominantly split from narrow bands, which often spawn surface states in the presence of weak disturbances. The disturbance involved in this case is probably the "pedestal-cave" arrangement,<sup>3</sup> but we do not believe that the existence of such surface states has any significant physical consequences. The states are at -5.06 eV ( $\Gamma$ ), -3.12, -3.72, and -4.00 eV (K), and -2.26, -3.91, -8.48, and -10.68 eV (J').

# VI. TOTAL CHARGE AND SURFACE DENSITY OF STATES

The densities of occupied states in the surface regions (including 2 and 2.5 atom layers for the pairing and vacancy models, respectively) were calculated using (3.2) and a sampling of about 700 surface and scattering states. The sample points were smoothed with the Gaussian  $\exp(-3.4\epsilon^2)$ , and we verified that the sample was well converged for this smoothing. The results from both models are compared to the photoemission spectrum at<sup>17</sup>  $\hbar\omega = 21.1$  eV in Fig. 16. A smooth background of estimated secondaries has been subtracted from the data, and the curves are aligned on the basis of surface Fermi energy. We believe that the device of calculating the density of states spatially



FIG. 16. Calculated surface region density of states compared to  $\hbar\omega = 21.1$  eV photoelectron density from Ref. 15, with estimated secondaries subtracted.

integrated over the first few atomic layers gives a reasonable approximation to the escape depth weighting operative in the 21-eV photon energy range.

The most immediately apparent difference between the data and either theoretical density of states is the strong suppression of emission from the s-band region (below -8 eV). This is common to all surfaces, and is presumably a matrix element effect. Major differences in the spectrum of the (100) surface from the others studied in Ref. 15 show up primarily in the p-band region, 0 to -5 eV. Most distinctive are the rapid rise in emission below threshold, the symmetric triangular peak at -2.5 eV, and the shoulder at -4 eV. These are fit much better by the pairing model than the vacancy model. The peak at -7 eV, while not a unique feature of the (100) surface, is well reproduced by the pairing model, but split by the vacancy model. We believe that this comparison constitutes substantial evidence that the pairing geometry is, within minor refinements, the correct one.

To identify the physical origin of features in the spectrum of the pairing model, we calculated the density of states (3.1) at several individual points within the surface region. In Fig. 17, curve (a)



FIG. 17. Calculated local density of states at three points in the surface region for the pairing model: (a), above one of the surface atoms; (b) in the center of the rebonded pair; and (c) in the center of a back bond.



FIG. 18. Contour plot of the total charge density for the pairing model on a plane normal to the surface passing through the paired surface atoms and atoms in the fourth layer. Atoms in the second and third layer are out of the plane of the paper.

gives the result at a point 0.73 Å above one of the displaced surface atoms; curve (b), at the center of the bridge bond between two surface atoms; and curve (c), at the center of the back bond. The surface enhancement in the 0-1-eV range is due to



FIG. 19. Contour plot of the total charge density for the pairing model on a plane normal to the surface and cutting perpendicularly through the center of the bond between two surface atoms.



FIG. 20. Contour plot of the total charge density in the vacancy model on a plane normal to the surface passing through the newly added surface atom and its nearest neighbors.

spectral weight from the broken bonds pulled down by the formation of the  $|\pi_b\rangle$  band, and weight in the back bonds pushed up by the bending distortion. The bulklike peak at -7 eV also gets a large contribution from the back bond and is 0.3 eV higher than the bulk peak given by our pseudopotential. The spectrum at the pair bond is highly peaked at -2.5 and -9.5 eV, quite unlike the bulk. The total charge density in the pair bond is shown in Figs. 18 and 19, and is not discernably different from that of a bulk bond in the closed contour region. We believe its spectrum is different because angular misalignment keeps it from hybridizing strongly with neighboring bonds.

The total charge density for the vacancy model is shown in Figs. 20 and 21. On the assumption that charge close to the bonding region is approximately cylindrically symmetric about the bond direction, one can compare the amount of charge in the "double bonds" behind the surface atom (Fig. 20) with the single bonds (see Fig. 21) of the bulk crystal. Counting charge within the contour numbered 65, the ratio is about 3:2, which is consistent with our earlier observation that the occu-



FIG. 21. Contour plot of the total charge density for the vacancy model on a plane normal to the surface passing through the newly added surface atom at right angles to the nearest neighbors.

pied  $|\pi_b\rangle$  state is only able to supply half the charge needed to produce a double bond. It is interesting to note that the charge profile shown in Fig. 21 bears a strong resemblance to that of the unstable unreconstructed surface shown in Fig. 15 of I.

#### CONCLUSION

We have presented the results of realistic selfconsistent calculations of the Si (100) surface, which is perhaps the simplest possible stable reconstructed surface of a tetrahedrally bonded semiconductor. Although the arrangement of atoms in the  $(2 \times 1)$  unit cell has not been previously determined, the Fermi energy and occupied density of states we calculate for the pairing model of the reconstruction are in reasonable agreement with what is observed, while our calculation of these quantities for the vacancy model is not.

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