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Electronic structure of Si(100)$c(4\times2)$ calculated within the *GW* approximation

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The electronic structure of the Si(100)$c(4\times2)$ surface has been calculated using a quasiparticle formalism in which the self-energy is evaluated in the *GW* approximation. The calculated surface state dispersions and band gaps are in good agreement with experiments. The results support the existence of correlated dimer buckling at room temperature. The equilibrium $c(4\times2)$ surface obtained from total-energy calculations is 0.14 eV/dimer lower in energy than the 2×1 symmetric dimer surface, exhibits a dimer buckling of 0.69 Å, and has a surface energy of 1.39 eV/(1×1).

Because of its technological importance as a substrate, the Si(100) surface has been studied thoroughly. Numerous experimental and theoretical techniques have been employed in attempts to determine its structure and electronic properties. It is known from scanning tunneling microscopy[1,2] (STM) and other experiments[3–11] that the basic reconstruction mechanism on Si(100) is dimerization, and that the ground state of the surface is the $c(4\times2)$ buckled dimer structure proposed by Chadi.[12] In this structure one atom in the dimer adopts a planar sp^2 configuration, while the other atom adopts a p^3 configuration as shown in Fig. 1. The direction of buckling alternates along the rows of dimers. The STM images appear to show the coexistence of buckled and symmetric dimers, with the buckled dimers often appearing near defects.[1,2] This observation raised the question of whether buckling is intrinsic or occurs as a response to defect strain fields. Wolkow[2] has shown, however, that the number of buckled dimers increases as the temperature is reduced and that for $T=120$ K the $c(4\times2)$ reconstruction occurs on most of the surface. This indicates that dimer buckling is, in fact, energetically favorable.[2] The appearance of rows of symmetric dimers on some parts of the surface can be attributed to rapid dimer switching between the two possible orientations of the dimer. A buckled dimer could appear to be symmetric if the dimer orientation switches more rapidly than the time required to scan across the dimer.[1]

At low temperatures the low-energy electron-diffraction pattern exhibits a $c(4\times2)$ diffraction pattern, and analysis of the temperature dependence of the intensity and width of the quarter-order features indicates that some $c(4\times2)$ ordering is present at room temperature.[11] Photoemission[4–7] and inverse photoemission[8] experiments performed at room temperature indicate the existence of two occupied and two empty dangling-bond surface states, thus demonstrating that $c(4\times2)$ or $p(2\times2)$ short-range order is present. It is shown here that the surface bands calculated for a $c(4\times2)$ buckled dimer model are in good agreement with photoemission spectra. This result supports the existence of correlated dimer buckling at room temperature. The electronic structure calculations were performed with the quasiparticle approach developed by Hybertsen and Louie,[13,14] and the $c(4\times2)$ surface atomic structure employed in the calculations was derived from first-principles total-energy calculations.

Many pseudopotential density-functional calculations have examined the energetics of dimer buckling.[15–21] In general, these calculations have found the buckled and symmetric dimer surfaces to be close in energy: the difference in energy is typically 0.1 eV/dimer or less. Dabrowski and Scheffler,[18] employing a well-converged plane-wave basis set, found the 2×1 buckled dimer surface to be lower in energy than the symmetric dimer surface by 0.10 eV/dimer. In calculations employing a local orbital basis set, Kruger and Pollmann[19] found the 2×1 buckled dimer surface to be lower than the symmetric dimer surface by 0.14 eV/dimer. Roberts and Needs[20] found that the $p(2\times2)$ buckled dimer surface is lower than the symmetric dimer surface by 0.09 eV/dimer. These results suggest that within the framework of density-functional theory dimer buckling is energetically favorable. The present total-energy calculations for the $c(4\times2)$ surface, discussed below, support this assertion.

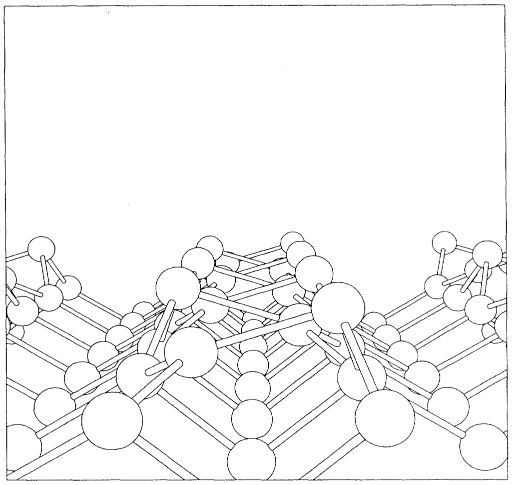

FIG. 1. Ball and stick model of the $c(4\times2)$ buckled dimer surface. The top three layers are shown. The vertical separation between the up and down atoms in the dimers is 0.69 Å.

Less attention has been given to the surface excited-state properties. This is natural because density-functional calculations commonly predict band gaps which are too small for semiconductors. To obtain the surface electronic structure from first principles one must include the energy dependence and nonlocality of the electron self-energy. In addition, one must perform the calculation for a realistic structure; i.e., the $c(4\times2)$ or $p(2\times2)$ buckled dimer surfaces. That is the objective of the present work.

To obtain the surface atomic structure, total-energy and force calculations[22,23] were carried out within the local-density approximation[24] (LDA) for the $c(4\times2)$ structure. These calculations were performed with first-principles pseudopotentials[25] and with a plane-wave basis set containing plane waves with kinetic energies up to 10 Ry. Three **k** points in the irreducible zone were employed in the Brillouin-zone summations. Atoms in the first 4 layers on each side of a 12-layer centrosymmetric supercell were relaxed while the 4 central layers were kept at bulk positions. The atomic coordinates predicted by these calculations are listed in Table I (see Fig. 2). The dimer buckling predicted for the $c(4\times2)$ structure is strikingly large: the up and down atoms of the dimer are separated by a vertical distance (Δz) of 0.69 Å. The dimer bond length (b) is 2.29 Å. These values may be compared with those obtained in tight-binding calculations,[3] $\Delta z = 0.63$ Å and $b = 2.35$ Å, and with those obtained in a previous LDA calculation[21] for the $c(4\times2)$ surface, $\Delta z = 0.54$ Å and $b = 2.27$ Å. We have also minimized the energy of the symmetric dimer surface with precisely the same procedure as used for the $c(4\times2)$ structure. The $c(4\times2)$ buckled dimer surface is found to be lower in energy than the symmetric dimer surface by 0.14 eV/dimer. The surface energy calculated for the $c(4\times2)$ surface is 1.39 ± 0.1 eV/(1×1).

TABLE I. Calculated structural parameters for the first four layers of the Si(100)$c(4\times2)$ surface. The numbering system refers to Fig. 2. Displacements from ideal 1×1 positions are given in Å.

	Δx	Δy	Δz
1	0.0	0.61	−0.04
2	0.0	−1.04	−0.74
3	0.0	1.04	−0.74
4	0.0	−0.61	−0.04
5	−0.08	0.10	−0.07
6	0.08	−0.10	−0.07
7	0.08	0.10	−0.07
8	−0.08	−0.10	−0.07
9	0.01	0.0	0.05
10	0.0	0.0	−0.19
11	−0.01	0.0	0.05
12	0.0	0.0	−0.19
13	0.0	0.0	0.04
14	0.0	0.0	−0.12
15	0.0	0.0	0.04
16	0.0	0.0	−0.12

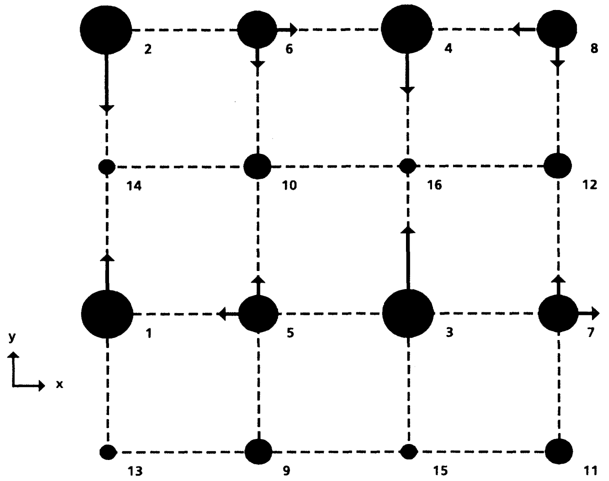

FIG. 2. Schematic top-view representation of the first four layers of the Si(100) surface. Atoms 1–4 reside in the topmost layer. Atoms 5–8, 9–12, and 13–16, reside in the second, third, and fourth layers, respectively. Arrows, not drawn to scale, indicate in-plane relaxations. The calculated displacements from the ideal positions are listed in Table I.

To calculate the electronic structure we have employed the GW approximation in which Σ, the self-energy operator, is approximated by the first term in a perturbation series involving the Green function (G) and the screened Coulomb interaction ($W = \varepsilon^{-1} V_{\mathrm{Coulomb}}$). The Green function is obtained in a quasiparticle approximation employing LDA wave functions. This has proven to be a good approximation in previous calculations for both bulk[13] and surface[27] systems. The dynamic dielectric matrix (ε^{-1}) is obtained by applying a plasmon pole ansatz to the eigenvalues of the static dielectric matrix.[26] The large size of the unit cell, which has 48 atoms, precludes a direct calculation of the static ε^{-1} such as those performed for the Ge(111)1×1:As (Ref. 27) and Si(111)2×1 surfaces.[28] Instead, an approximation introduced by Hybertsen and Louie[14] was employed to calculate the dielectric matrix. In this approach one obtains the dielectric matrix directly from the crystalline charge density. Although approximate, this method predicts quasiparticle energies for bulk systems which are within 0.1–0.2 eV of the complete calculations. In addition to the charge density, the static dielectric constant of the material (ε_0) is required. For bulk Si, $\varepsilon_0 = 12$, but in the vacuum, $\varepsilon_0 = 1$. We therefore take ε_0 to be a function which interpolates between these two values: $\varepsilon_0(z) = 6.5 + 5.5\tanh[(z_0 - z)/\lambda]$, where z_0 is 1 Å outside the surface and $\lambda = 1.5$ Å. Test calculations were performed with a constant value for ε_0 (equal to 10) and very similar quasiparticle energies were obtained. For example, the surface-state gap at J_2' changed by only 0.02 eV. Thus, as found in previous work,[29] the quasiparticle energies are not sensitive to the precise form of $\varepsilon_0(z)$. In the evaluation of the matrix elements of the self-energy operator the sum over conduction bands included 1000 bands and the weighted sum over **q** points included four special points in the irreducible $c(4\times2)$ Brillouin zone. The size of the dielectric matrices is limited by a cutoff in momentum space: $|\mathbf{q}+\mathbf{G}|<2.2$ a.u.

The surface-state band structure is obtained in two steps. Initially, the dispersions for the surface-state bands are obtained within LDA for many $\mathbf{k}$ points along the $\Gamma J_2'$ direction of the surface Brillouin zone indicated in Fig. 3. For $\mathbf{k}$ points in this direction, the energies are equal in the two domains normally present on Si(100).[4,5] Quasiparticle energies are then calculated within the GW approximation for a few $\mathbf{k}$ points. The difference between the quasiparticle energies and the LDA eigenvalues is primarily an increase in the gap between occupied and empty surface states by about 0.5 eV. Relative to the valence-band maximum, the occupied states are shifted down in energy by 0.15 eV, and the unoccupied states are shifted up by 0.33 eV. The width of the surface bands is changed by less than 0.1 eV. The approximate band structure obtained by applying these shifts to the LDA eigenvalues is shown in Fig. 4 along with photoemission data. The two occupied π and two empty π^* bands of surface states are derived from the four dangling bonds in each $c(4\times2)$ unit cell. The overall agreement between theory and angle-resolved photoemission experiments for the occupied states is very good and thus provides support for the $c(4\times2)$ structural model. In particular, the width of the π bands obtained for the $c(4\times2)$ structure (0.71 eV) is within 0.05 eV of the experimental value. In contrast the π bandwidth obtained for the 2×1 symmetric dimer surface (0.95 eV) is ~0.2 eV larger than experiment. The reduction in π bandwidth found for the $c(4\times2)$ structure results from an increased separation of up atoms in adjacent dimers compared to the corresponding separation for 2×1 dimer surfaces.

A proper treatment of electron correlation is essential in order to obtain accurate values for the surface-state band gaps. The quasiparticle calculations predict gaps which are 0.5 eV larger than obtained from LDA eigenvalues and are within about 0.2 eV of the various experimental values. For example, the calculated direct band gap at the J_2' point is 0.87 eV. This compares well with an experimental value of 1.0 eV which may be inferred from a combination of photoemission[4,7] and optical spectroscopy experiments.[30] The minimum surface-state band gap measured by scanning tunneling spectroscopy[31] is 0.9 eV. This value may be compared with the 0.7 eV minimum indirect gap obtained in the quasiparticle calculations. The minimum energy of the π^* band is 0.3 eV above the valence-band maximum (VBM). Optical absorption experiments[30] indicate that the minimum energy of the π^* bands is 0.4–0.5 eV above the VBM. The 0.1–0.2-eV difference between the theory and experiment is consistent with the expected accuracy of the calculations.

The two unoccupied states at the J_2' point, π_1^* and π_2^*, are separated by 0.84 eV. Inverse photoemission experiments[8] indicate the existence of two such bands, but with a measured peak separation of 0.6–0.7 eV at this point. Considering the necessarily limited momentum resolution in inverse photoemission experiments, and the corresponding difficulties in determining the bottom of a highly dispersive band, the theory and experiment are in good agreement. As seen in Fig. 4, the unoccupied surface-states bands have minima at Γ and J_2'. This result is consistent with inverse photoemission[8] and with the angle-resolved photoemission experiments performed on surfaces which were heavily doped n-type.[32] Such doping creates states which are apparently derived from the π^* bands at the Γ and J_2' points, and photoemission from these states is detected in the experiment. These states

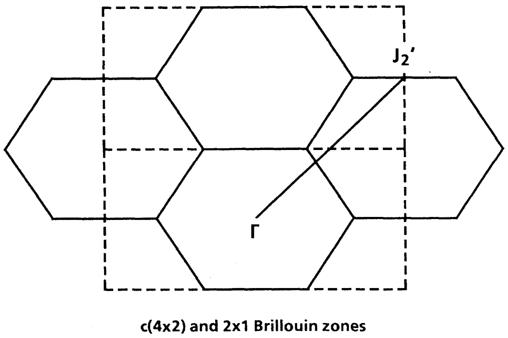

FIG. 3. The Brillouin zone for the $c(4\times2)$ cell is indicated by the solid lines. The Brillouin zone for the 2×1 cell is indicated by dashed lines. The surface state dispersion is calculated along the line Γ-J_2'.

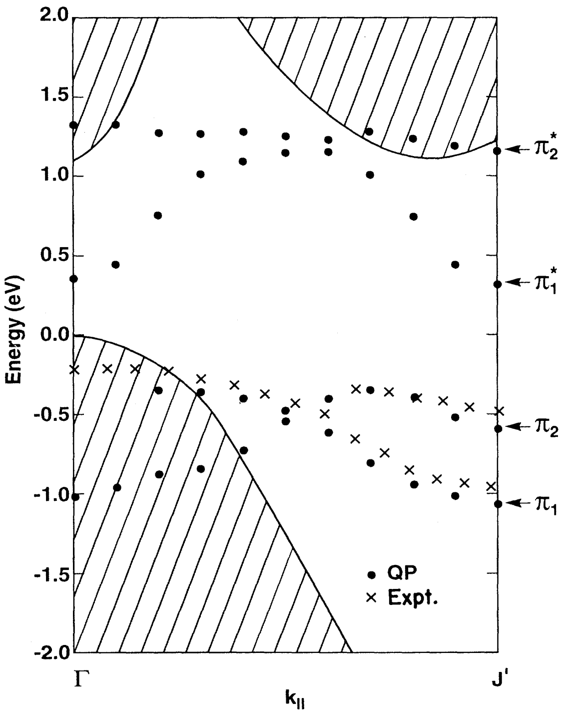

FIG. 4. Calculated dangling-bond surface-state quasiparticle energies are compared with results of angle-resolved photoemission experiments. The valence-band maximum is located at $E=0$. The two bonding (π) and two antibonding (π^*) bands of surface states arise from the four dangling bonds in each $c(4\times2)$ unit cell. The shaded region corresponds to the 1×1 bulk projected band structure. Experimental results are taken from Johansson *et al.* (Ref. 7).

are presumably localized by coupling to the dimer buckling.

Finally, it is important to note that the photoemission results discussed above are obtained for a surface at room temperature. Therefore, the agreement between these data and the electronic structure calculations suggests that the $2\times$ anticorrelation of dimer buckling along a row persists up to $T\sim300$ K. One may therefore speculate that dimer switching occurs sequentially as a *domain boundary,* where two adjacent dimers are buckled in the same sense, migrates along a dimer row. This mechanism could allow dimer switching to occur at low temperatures without completely destroying the $2\times$ anticorrelation of the buckling. A defect, such as an impurity atom or missing dimer, breaks the translational invariance of the total energy with respect to a movement of the domain boundary, and therefore may impede its movement. This mechanism could explain why long dimer rows, which have no defects to impede domain boundary migration, often appear to be symmetric.

In summary, the calculated surface energy for the $c(4\times2)$ structure is significantly lower than that of the symmetric dimer surface, and the surface electronic excitation spectrum calculated within a quasiparticle self-energy approach is in good agreement with experiments.

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