

Many-Body Calculation of the Surface-State Energies for Si(111)2×1

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The surface-state excitation energies for the Si(111)2×1 surface have been calculated in the *GW* approximation. The energy position and the dispersion of the occupied and empty surface states are in excellent agreement with photoemission and inverse-photoemission experiments. The calculated quasiparticle surface-state band gap, 0.62 eV, is 0.15 eV larger than the measured onset energy for electron-hole pair excitations. The possibility that excitonic effects are responsible for this difference is examined.

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The Si(111)2×1 surface is one of the most studied semiconductor surfaces. Its atomic structure has been analyzed by low-energy electron diffraction¹ (LEED) and medium-energy ion scattering² (MEIS). Its electronic structure has been explored through a variety of techniques including angle-resolved photoemission,³⁻⁵ inverse photoemission,⁶ differential reflectivity,⁷ electron-energy-loss spectroscopy,^{8,9} photothermal deflection spectroscopy,¹⁰ excite-and-probe photoemission,¹¹ and scanning tunneling microscopy¹² (STM). These experiments support the π -bonded chain model¹³ with a buckling of the surface-atom chain. Despite this extensive work, a fundamental question remains regarding the surface electronic structure. Namely, the possible role of large excitonic effects¹⁴ in the optical absorption remains an open question.

The electronic structure of Si(111)2×1 is dominated by a pair of highly dispersive π and π^* bands of surface states. These bands arise from the dangling bonds on the threefold-coordinated surface atoms (atoms 1 and 2 in Fig. 1). Along the chains, the dispersion of the bands is much larger than in the direction perpendicular to the chains. The π and π^* surface states lie well inside the bulk band gap over much of the surface Brillouin zone. This facilitates an accurate mapping of the surface-state dispersion.³⁻⁶ Transitions between the π and π^* surface states dominate the optical properties of the surface for

sub-band-gap radiation, and in STM experiments,¹² these states dominate the tunneling current for bias voltages less than ± 0.5 eV.

From photoemission⁵ and inverse-photoemission experiments,⁶ it is possible to infer an energy gap between the occupied and empty *single*-quasiparticle surface states of about 0.75 eV. On the other hand, in low-temperature optical-absorption experiments,⁷ the lowest energy for electron-hole *pair* creation is found to be 0.47 eV. While some of the differences (~ 0.15 eV) between these two energies may result from limited resolution in the inverse-photoemission experiment,⁶ it highlights the fundamental difference between one- and two-particle excitations: excitonic correlations. In view of the reduced dimensionality (quasi-one-dimensional π bands) one might expect enhanced excitonic effects for this surface. We have investigated the electronic structure of the Si(111)2×1 surface in two steps. First, we have calculated the quasiparticle surface-state energies based on a self-energy approach for the many-body correlations. The resulting bands agree well with photoemission experiments but yield a quasiparticle gap 0.15 eV larger than the optical gap. Second, the quasiparticle energies are incorporated into a model calculation of the surface optical absorption. The inclusion of excitonic effects in the optical absorption has a dramatic effect on the spectral shape and significantly improves the agreement with experiment. This suggests that the excitonic binding could be as large as 0.15 eV for this surface.

A prerequisite for a first-principles calculation of the electronic structure is an accurate set of atomic positions. The structural determination was made via total-energy minimization within the local-density-functional approximation (LDA). The total energy and forces were calculated using first-principles pseudopotentials and a supercell formalism. The calculations employed a plane-wave basis ($E_{\text{max}} = 10$ Ry) and a centrosymmetric supercell containing 24 atoms. The coordinates of the atoms in the innermost two layers of the slab were kept fixed at their bulk values. The structure obtained is indicated schematically in Fig. 1. The calculated structural

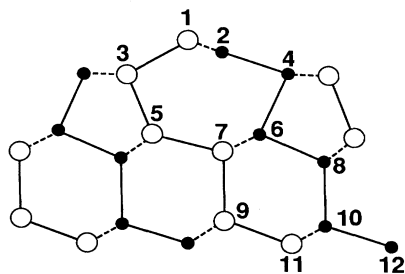


FIG. 1. Schematic side view of the π -bonded chain model. The surface atoms 1 and 2 form the π -bonded chains. The solid and open circles denote atoms in different (110) planes.

TABLE I. Structural parameters (in angstroms) obtained from (a) previous energy-minimization calculations (Ref. 15), (b) LEED (Ref. 1), (c) MEIS (Ref. 2), and present results. z_i is the coordinate of the i th atom along the surface normal (Fig. 1).

	(a)	(b)	(c)	Present
$z_1 - z_2$	0.10	0.38	0.30	0.47
$z_3 - z_4$	-0.05	-0.07	-0.15	-0.05
$z_5 - z_6$	-0.08	-0.07	-0.10	-0.07
$z_7 - z_8$	0.30	0.20	0.27	0.28
$z_9 - z_{10}$	0.20	0.13	0.14	0.15

parameters, given in Table I, are similar to those predicted by earlier calculations,¹⁵ except that we find a larger surface-atom buckling which is in better agreement with experiment.^{1,2} The present calculations employ a larger supercell and a more complete plane-wave basis set than did the earlier work.

The minimum-energy direct gap between the π and π^* bands occurs at the J point of the surface Brillouin zone. This energy gap (E_g) is a consequence of the structural inequivalence of the two surface atoms in the unit cell. Atom 1 (in Fig. 1) is sp^3 coordinated and atom 2 is sp^2 coordinated. The surface-state band gap depends on the buckling, $b = z_1 - z_2$, of the surface chain. Increased buckling tends to increase the energy gap, with $dE_{g(\text{LDA})}/db \sim 0.4 \text{ eV/\AA}$. From energy minimization we find $z_1 - z_2 = 0.47 \text{ \AA}$ with an uncertainty of about 0.05 \AA . This translates into an uncertainty in $E_{g(\text{LDA})}$ of about 0.02 eV. The calculated buckling is about 0.1 \AA larger than that inferred from the LEED IV spectra.¹ Independent LDA structural calculations¹⁶ for $\text{Si}(111)2 \times 1$ also indicate a buckling (0.49 \AA) which is in excellent agreement with the present result.

The calculation of the electronic structure is based on the evaluation of the self-energy operator within Hedin's GW approximation.¹⁷ The self-energy Σ includes the effects of exchange and correlation on the single-particle excitation energies. In the GW approximation, Σ is taken to be the first term in a perturbation series involving the screened Coulomb interaction W and the electron Green's function G . This approach has been shown to yield bulk^{18,19} and surface²⁰ quasiparticle energies with an accuracy of about 0.1 eV. The calculational method has been described in detail elsewhere.¹⁸ In the present calculation the plasmon-pole ansatz, which extends the static dielectric matrix to nonzero frequencies, is applied to the symmetric inverse dielectric matrix in its *diagonal* representation rather than to each element of $\epsilon_{\mathbf{G},\mathbf{G}'}$ separately.²¹ We tested this method for bulk Si and found that it gave quasiparticle energies in good agreement with experiment and with those obtained using the generalized plasmon-pole ansatz.¹⁸ In the construction of the screened Coulomb interaction $W = \epsilon^{-1}v$, dielectric matrices $\epsilon_{\mathbf{G},\mathbf{G}'}(\mathbf{q})$ containing reciprocal-lattice vectors \mathbf{G} for which $|\mathbf{q} + \mathbf{G}| < 2.1 \text{ a.u.}$ were employed. This corre-

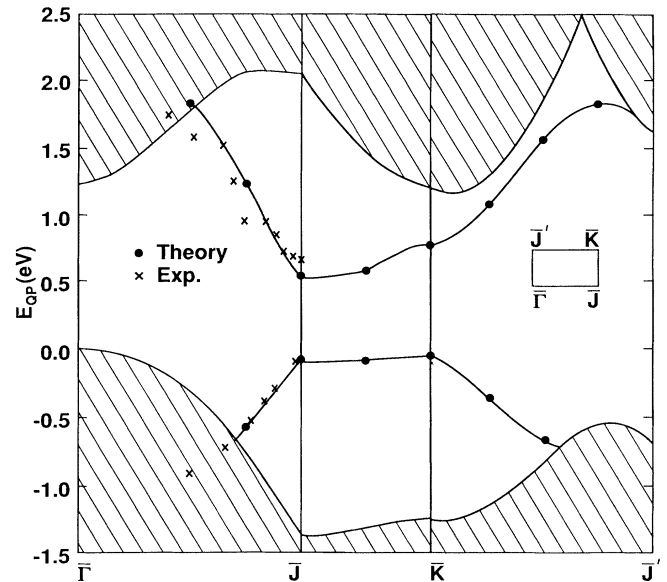


FIG. 2. Quasiparticle surface-state band structure for $\text{Si}(111)2 \times 1$ compared to photoemission (Ref. 5) and inverse-photoemission (Ref. 6) experiments.

sponds to matrices of order 640×640 . The dielectric function is calculated in the random-phase approximation. In the evaluation of the self-energy operator the sum over bands was truncated at the 500th band, and the required Brillouin-zone summation was performed with a weighted sum over seven \mathbf{q} points in the irreducible zone. We obtain the quasiparticle energies $E_{n\mathbf{k}}$ from Dyson's equation in first-order perturbation theory.

In Fig. 2 we compare the calculated π and π^* surface-state quasiparticle energies with those measured by photoemission⁵ and inverse photoemission.⁶ The overall agreement between theory and experiment is better for the occupied states than for the empty states. This may be because the energy and momentum resolution obtainable in the inverse-photoemission experiment, which probes the empty-state energies, is not as good as that possible in photoemission. A recent analysis of the effects of the limited resolution in the inverse-photoemission experiment indicates that the true energy of the π^* state at J could be lower than that indicated in Fig. 2 by 0.15 eV.⁶ This would further improve the agreement between theory and experiment. The self-energy corrections, i.e., the difference between the quasiparticle energies $E_{n\mathbf{k}}$ and the LDA eigenvalues $\epsilon_{n\mathbf{k}}$, are plotted in Fig. 3. We find that the bulklike conduction-band states are shifted up relative to the bulklike valence-band states by about 0.6 eV. This shift is similar to that obtained in bulk calculations. On the other hand, the energy gap between the surface states is increased by a lesser amount, 0.35 eV. The corrections for the π band at $0.75\Gamma J$ and at J are very similar, as are those for the π^* band at these \mathbf{k} points. Thus, the dispersion obtained in the

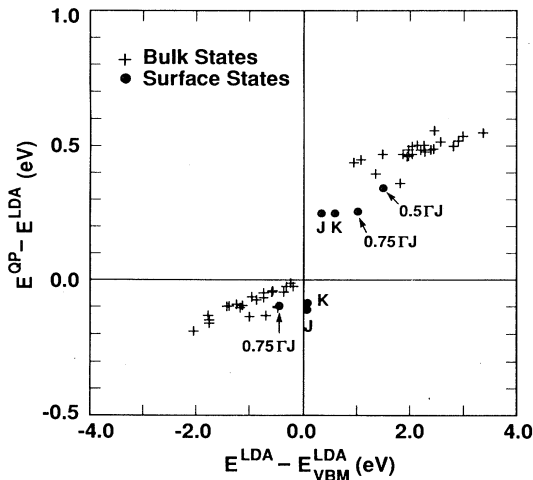


FIG. 3. Self-energy corrections to LDA eigenvalues for the surface and bulklike states of the twelve-layer slab representing Si(111)2×1. The corrections are referred to the value at the bulk valence-band maximum.

quasiparticle calculation is not very different from that obtained in LDA calculations.¹⁵

Comparisons between the calculated gap (0.62 eV) and the optical gap (0.47 eV) support the possibility that excitonic effects of order 0.1 eV could be present in the optical data. A first-principles calculation of the absorption including excitonic correlations requires a consistent treatment of the one- and two-particle Green's functions and is beyond the scope of this work. Nevertheless, it is possible to estimate the effect of the electron-hole interaction on the surface optical absorption. To do this, we calculate the exciton energy spectrum and wave functions with the calculated surface-state band structure and with a model electron-hole interaction. From this we obtain the optical-absorption spectrum.

The i th exciton wave function $A_i(\mathbf{k})$ satisfies a secular equation of the following form:²²

$$E_g(\mathbf{k})A_i(\mathbf{k}) + \sum_{\mathbf{k}'} V(\mathbf{k}, \mathbf{k}')A_i(\mathbf{k}') = E_i A_i(\mathbf{k}').$$

$E_g(\mathbf{k})$ is the calculated quasiparticle energy gap between the π and π^* states,²³ and E_i is the energy of an electron-hole pair excitation. $V(\mathbf{k}, \mathbf{k}')$ is taken to be of the following form:

$$V(\mathbf{k}, \mathbf{k}') = (2\pi e^2 / \epsilon q A) e^{q^2/4\beta^2} [1 - \text{erf}(q/2\beta)].$$

Here, $q = |\mathbf{k} - \mathbf{k}'|$, ϵ is the effective medium static dielectric constant (taken to be 6.5), A is the surface area, and β is related to the localization perpendicular to the surface of the surface-state wave function. This interaction follows from the assumption that the surface-state wave functions may be written²⁴ as

$$\psi = e^{i\mathbf{k}\cdot\rho} e^{-\beta^2 z^2}.$$

Once the A_i and E_i are determined, we may calculate

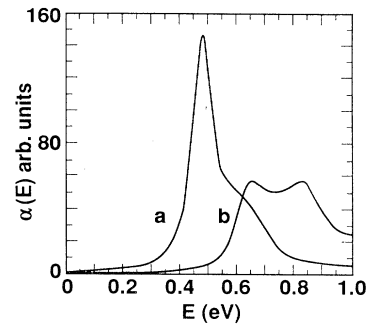


FIG. 4. Optical-absorption coefficient calculated curve a , with $\epsilon=6.5$, and curve b , without excitonic interactions. The δ function in the expression for $\alpha(E)$ has been replaced by a Lorentzian of half-width 40 meV.

the optical absorption:²²

$$\alpha(E) = \sum_i \left| \sum_{\mathbf{k}} A_i(\mathbf{k}) p(\mathbf{k}) \right|^2 \delta(E - E_i).$$

In this equation $p(\mathbf{k})$ is a component of the matrix element of the momentum operator between the π and π^* surface states.

Results for α are shown in Fig. 4 for light polarized along the chains. Curve b corresponds to the complete neglect of the electron-hole interaction. In this case $\alpha(E)$ exhibits two peaks. The peak at lower energy corresponds to the creation of noninteracting electron-hole pairs with \mathbf{k} near the J point, and the upper peak corresponds to the saddle-point singularity in the joint density of states at the K point. Curve a corresponds to an exciton spectrum calculated with parameters (ϵ and β) chosen to give a binding energy of 0.13 eV for the lowest-energy exciton. This exciton is responsible for the peak in the optical absorption shown in curve a . The oscillator strength in the saddle point is largely eliminated. This shift in oscillator strength results from the nearly

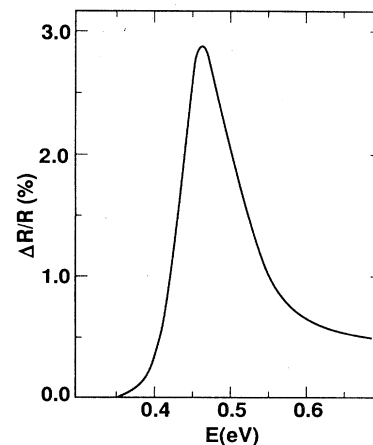


FIG. 5. Experimental differential reflectivity (after Ref. 7).

one-dimensional nature of the band structure near the edge (JK) of the surface Brillouin zone (see Fig. 2). The experimental differential reflectivity, which is closely related to a , has been measured by Ciccacci *et al.*⁷ and is shown in Fig. 5. It is clear that the absorption spectrum (curve b), obtained by neglecting the electron-hole interaction, cannot explain the data shown in Fig. 5. Spectrum a , which corresponds to an exciton binding energy of 0.13 eV, is more consistent with the data. We surmise that excitonic effects must be invoked to explain the optical properties for Si(111)2×1.

The present results are also in excellent agreement with excite-and-probe photoemission experiments¹¹ where the peak separation (0.5 eV) indicates the pair-creation energy, just as in the optical absorption. However, two other experiments seem to support the possibility that the excitonic binding energy is negligible. Photoemission²⁵ from heavily n -doped Si(111)2×1 shows a peak attributed to the π^* band just 0.45 eV above the π band. In principle, this experiment is a single-particle probe of the gap. However, two physical effects may lead to a reduced quasiparticle gap. First, the presence of carriers leads to band-gap renormalization beyond that included in the present calculation. Second, the buckling of the chain may be reduced locally around the extra electron in the π^* band, and this may lead to localization of the electron in a region of reduced buckling and band gap. The gap measured by the STM spectroscopy¹² is about 0.5 eV. The STM results imply that the excitonic binding energy is much less than 0.1 eV, provided tip-sample interactions are negligible. A more detailed analysis of both of these experiments is required to assess compatibility with our present results.

In summary, we have calculated the quasiparticle surface-state dispersion for the Si(111)2×1 surface within the GW approximation. The atomic structure was determined from LDA energy minimization and agrees with experiment. The calculated dispersion is in excellent agreement with photoemission data. Based on our analysis of the features in the absorption spectrum, we assert that excitonic effects are important for a qualitatively correct description of the optical absorption on this surface.

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²³In the region of \mathbf{k} space which contributes to the low-energy optical absorption the quasiparticle energy gap differs from the LDA energy gap by an essentially rigid shift of 0.35 eV (see Fig. 3). Thus the shape of the optical absorption is not significantly affected by the self-energy correction, but the peak position is shifted.

²⁴We take $\beta=0.05(a_B)^{-1}$ to yield an exciton binding energy of ~ 0.1 eV for $\epsilon=6.5$. Our conclusions do not depend on the details of the form of ψ or on the precise value of β .

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