

Crystal-Field Splitting and Charge Flow in the Buckled-Dimer Reconstruction of Si(100) 2×1

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The effect of the 2×1 reconstruction on the core-electron binding energies of the outermost Si(100) layers has been determined using high-resolution photoemission data. A previously unobserved 190-meV crystal-field splitting is resolved for the up-atoms of the asymmetric surface dimers, whose average core-level shift is -400 meV. The signal from the down-atoms is clearly identified and has a shift of $+220$ meV. These new findings indicate a charge flow of $\sim 0.05e$ from the subsurface to the surface layers, with a substantially larger difference of $\sim 0.34e$ between the up-atoms and down-atoms in the dimer.

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The reconstruction of the Si(100) 2×1 surface has received extensive theoretical [1-6] and experimental [7-14] investigation since its discovery more than three decades ago [15]. The majority of evidence points to a model where the outerlayer Si atoms form buckled-dimer pairs [2] and the subsurface atoms are significantly relaxed from their bulk positions [1]. In spite of the detailed *structural* characterization of this surface, there is no consensus regarding the interpretation of its *electronic* core-level photoemission spectrum. One model [16-19] assigns a component observed at negative-binding-energy shift (relative to bulk Si) to both the up-atoms and down-atoms of the surface dimers, allowing that it might be split by less than 200 meV [19]. Another model [20-22] posits the existence of two surface-related components, one above and one below the bulk-Si binding energy, corresponding to the down and up dimer atoms, respectively. Neither model considers subsurface components. The models differ markedly in their conclusions regarding the electron escape depths and the degree of charge transfer between the dimer atoms, factors which are essential for understanding the electronic character of this reconstructed surface.

Here, we report on core-level photoemission data from clean Si(100) 2×1 which resolve the contradictions of the earlier interpretations through three new observations. First, our analysis firmly establishes the existence of surface-related features both below *and* above the energy of the bulk-derived peak. Second, we resolve a splitting of the low-binding-energy feature into two components, which has its origin in the surface crystal field. Third, our data demonstrate that the surface-atom core levels exhibit *asymmetric* Doniach-Šunjić (DS) [23] line shapes by virtue of electronic excitations from the valence band into a nearby-surface state. From these results we conclude that the higher-binding-energy feature corresponds to the down-atoms and the split low-energy feature to the up-atoms of the surface layer. The sign and magnitude of these shifted surface components shed new light on how the surface charge is redistributed upon reconstruction. Furthermore, our observations of a crystal-field splitting and a DS line shape for the surface-atom core levels represent novel features in photoemission measurements from a semiconductor surface.

The data were obtained using the AT&T Bell Laboratories 6-m Toroidal Grating Monochromator (TGM) on beam line U4A of the National Synchrotron Light Source. The combined resolution of the TGM (~ 80 meV) and our 100-mm hemispherical electron energy analyzer (40 meV) was 90 meV. Clean surfaces of both *n*- and *p*-type Si(100), prepared by sputtering with 1-keV Ne⁺ followed by annealing at 900-1150°C, exhibited sharp two-domain 2×1 low-energy electron-diffraction patterns and showed no signs of contamination during our measurements.

Spectra from the $2p$ core levels taken with the sample at 77 K (see Fig. 1) illustrate the change in surface sensitivity with photon energy. Data taken at higher photon energies clearly exhibit the well-known feature at smaller binding energy associated with the surface dimers, labeled *S*. The asymmetric shape of the main component suggests that there is also a component at larger binding energy. The fact that the width of the bulk line remains large compared with the instrumental resolution even near the $2p$ threshold energy (i.e., at low surface sensitivity) and the fact that the bulk line shape is primarily Gaussian (see below), together indicate that the broadening is an inherent property of bulk Si arising largely from the production of phonons. This phonon width sets a fundamental limit on the effective resolution of Si $2p$ data, so that, regardless of how high the instrumental resolution, only the gross features can be seen by inspection.

As a first approach in identifying the components of the spectra in Fig. 1, we consider another surface-sensitive spectrum taken at $h\nu=130$ eV [see Fig. 2(a)] and take the negative second derivative of the raw data. The result [see Fig. 2(b)] clearly displays the unresolved *S'* component at larger binding energy. Note that the result of this procedure is highly reliable because no free parameters are involved. Unfortunately, the wings of the second derivative of the main line obscure the component *S*, so that no further information is obtained.

More insight into peak positions throughout the entire spectrum can be gained by deconvolution [24]. A virtue of deconvolution is that no assumptions about the location or shape of the component lines or about the nature of the background are required; only the functional form of the broadening is needed. This procedure is particular-

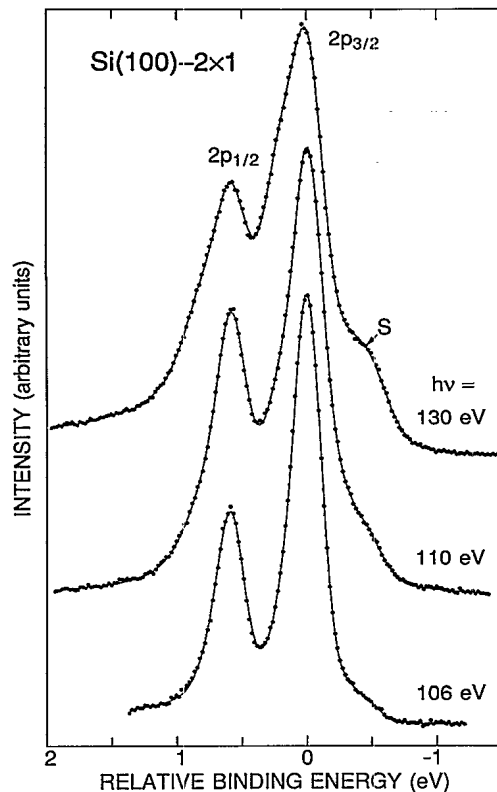


FIG. 1. Si 2p photoemission spectra from a Si(100)2 \times 1 surface at 77 K obtained with photon energies from 106 to 130 eV. The inelastic background has been subtracted.

ly well suited here because phonons, which impart a well-defined Gaussian smear, provide the dominant source of linewidth. A major pitfall of deconvolution lies in the amplification of noise frequencies which lie within the bandpass of the broadening function. The resulting small oscillations are, however, readily identified in the flat region of the spectrum and provide a useful indication of the size of the smallest significant feature. In fact, an objective criterion which we use in this work for assessing the validity of the deconvolved spectrum is provided by the residuals obtained when the spectrum is reconvolved with the broadening function and subtracted from the original data. If the Gaussian width used in the deconvolution is less than that inherent in the data, the residuals consist of only statistical fluctuations; if the width is greater, the residuals exhibit low-frequency oscillations.

In Fig. 2(c) we show the deconvolute of the data shown in Fig. 2(a). The location and intensity of the component S' is now well defined and in excellent agreement with the second derivative in Fig. 2(b). The important new result, however, is that *the surface-dimer component S is split into two lines*. To confirm that this is not an artifact of a given data set, we have similarly analyzed ten independent data sets taken with photon energies ranging from 110 to 140 eV. All show this splitting, as well as the component S' , at larger binding energy and, equally important, all exhibit residuals (as described above) which

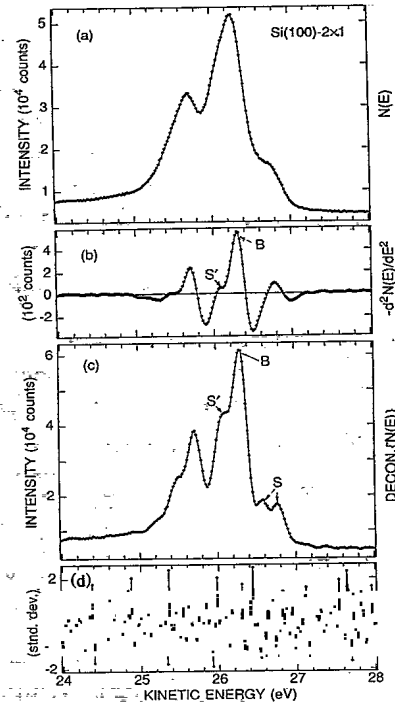


FIG. 2. Analysis of a 130-eV Si 2p spectrum from a Si(100)2 \times 1 surface. Only the 2p_{3/2} components are labeled. (a) Original data. (b) Negative second derivative of data. (c) Iterative deconvolution of data. (d) Residuals of the deconvolution (see text). S and S' denote surface, B denotes bulk.

are purely statistical; see Fig. 2(d). Furthermore, the intensities of S and S' decrease as the escape depth increases, identifying them both as surface features.

To obtain quantitative information about the location, amplitude, and width of these components, a least-squares analysis with a suitable model function is required. We initially restricted the model functions to a superposition of spin-orbit doublets whose $p_{3/2}$ and $p_{1/2}$ components have the same intensity ratio, splitting, and natural linewidth. Independent Gaussian widths were assigned to the bulk and surface components. Significantly, attempts to fit the data with Voigt function lines were unsuccessful because the decaying energy-loss tail cannot be adequately represented by the usual techniques, e.g., by a loss proportional to the integral of the line spectrum or to excitations across the band gap. Even adding two weak components with shifts greater than that of S' did not improve the fit significantly. However, a surface state just above the valence band in surface-sensitive 2p absorption edge spectra of Si(100)2 \times 1 [20] provides a loss mechanism for the surface atoms that quantitatively accounts for the shape of this tail. The process is formally identical to that in bulk graphite, where photoemission of a core electron causes excitations from the valence band into a narrow excitonic state just above the valence band [25]. As shown in Ref. [25], the resulting line shape is close to the DS form, even when there is a small gap between the band edge and the narrow empty state. The intensity of the resulting photoemission line is augmented

by the loss tail, which becomes an integral part of the line.

For completeness we note that the bulk component of the Si spectrum may well be inhomogeneously broadened by unresolved contributions from the perturbed near-surface layers. The shape of this component has an important effect only on the intensity of S' , which cannot be determined with confidence.

With this model function, we have applied least-squares fitting to assess previous models for the Si(100)2×1 surface. Following Refs. [16–19], which assume a single, possibly split, surface component at smaller binding energy, we obtain an rms error of 5.2 standard deviations between the fit and the data, compared to a value of 1.0 expected for an optimum fit. Adding a second component with Voigt line shape at S' , as suggested in Refs. [20–22], reduces the rms error to 2.6. Letting this component have an asymmetric DS line shape drops the rms error to 1.28, but the residuals still show an unacceptable oscillatory misfit at the low-binding-energy component. This misfit is removed by following the results of the deconvolution and splitting the $2p_{3/2}$ component of S into a doublet with equal intensity. The resulting fit has a substantially improved rms error of 1.11.

To present the results of this last fit most clearly, we show only the $2p_{3/2}$ components of the spectrum in Fig. 3. For comparison, the corresponding deconvolved spectrum from Fig. 2(c) is shown above. The agreement is striking.

From the analysis of data taken at photon energies between 106 and 140 eV we obtain the following numerical results. The spin-orbit splitting is 602 ± 6 meV and the spin-orbit ratio is 0.53 ± 0.03 , in very good agreement with the value of 608 meV [26] and the theoretical ratio of $\frac{1}{2}$. The lifetime width is 95 ± 25 meV, in reasonable accord with the value of 80 meV [26]. The bulk Gaussian width, obtained by subtracting the instrumental resolution in quadrature from the total Gaussian width, is 235 ± 10 meV in the most surface-sensitive spectra and drops to ~ 160 meV in the most bulk-sensitive ones. The latter value is in satisfactory agreement with the bulk-phonon width of ~ 140 meV obtained from x-ray photoelectron spectroscopy (XPS) data [26]. The larger width of the surface-sensitive data is most likely due to the fact that the signal in these spectra comes largely from the first four subsurface layers, which are also affected by the reconstruction [2]. Changes in both the binding energies and the vibrational properties [5] of these layers will broaden the bulk line in the surface-sensitive spectra. The surface-phonon width is ~ 260 meV, and the singularity index for S' is 0.22, while that of S is much smaller, ~ 0.02 . The value for S' is larger than that in graphite [25] because the occupied density of states in Si rises much faster at the band edge than that of graphite.

Casual inspection of our results does not allow a distinction to be made between the two models described above. The split components of S could represent either

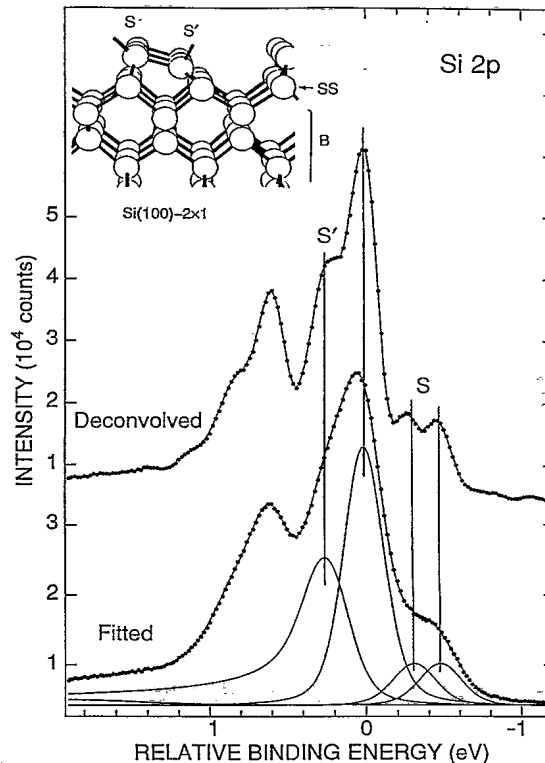


FIG. 3. Least-squares fit to data in Fig. 2(a), compared with the deconvolution of those data in Fig. 2(c). For clarity, only $2p_{3/2}$ components of the fit are shown. Inset: Schematic view of Si(100)2×1 reconstruction.

the up-atoms and down-atoms of the dimer (so that S' is due to subsurface atoms) or the crystal-field splitting of the up-atoms alone (in which case S' is due to the down-atoms). This dilemma is resolved by the line-shape analysis because a good fit was obtained only when S' was assigned the DS line shape, i.e., this component must be associated with the *surface* atoms in which core ionization can cause excitations into the surface state. The fact that the S' component lies at higher binding energy and has a much larger singularity index than S implies that S' corresponds to the down-atoms, which have lost charge to S and are the major source of the empty-surface state. The splitting of S must then be due to the surface crystal field. We note that crystal-field splitting of the core levels of surface atoms has not been previously reported, but the possibility has certainly been anticipated [27]. The splitting is large and thus observable in the Si(100)2×1 surface because a substantial amount of charge is donated to the dangling bond of the (S) up-atom, as proposed in Ref. [2]. The absence of a measurable splitting in the down-atoms is consistent with this interpretation.

Our result is also gratifying from the point of view of the escape depth, which is determined from the fractional intensity of S (assumed to arise from half of the surface atoms). For Si $2p$ electrons at kinetic energies of ~ 30 eV, we obtain a value of $\sim 3.6 \text{ \AA}$, in accord with an ex-

trapolation of theoretical work [28] that agrees well with experimental escape depths measured at XPS energies. Furthermore, our value is consistent with an escape depth of $\sim 3 \text{ \AA}$ [29] obtained for 30-eV electrons from Si(111) adsorbed with Cl. (See also the discussion in Ref. [49] of Ref. [22].)

What are the implications of this assignment on charge redistribution? The results of adsorbate-induced shifts of Si $2p$ surface core levels [30] indicate a shift of 1.8 eV per electron. Using this calibration, and the average shift of -400 meV for the up-atoms and $+220 \text{ meV}$ for the down-atoms, gives an effective charge difference between the up and down dimer atoms of $\sim 0.34e$. This value is only half as large as the theoretical estimate of $0.7e$ [2], confirming the importance of the intra-atomic Coulomb correlation energy [31]. The combined average shift of S and S' is -90 meV , corresponding to a net transfer of $\sim 0.05e$ from the subsurface to the dimer atoms. Assuming the source of this charge to be the immediate subsurface layer, its shift would certainly be too small to resolve, but it would contribute both to the width of the bulk line and to the intensity of S' , which is generally greater than the total intensity of the crystal-field doublet.

In summary, we report the crystal-field splitting of the up-atoms of the surface dimers of the Si(100) 2×1 surface, as well as the binding energies of the down-atoms and a limit on the shift of the subsurface layer. The difference in binding energy of the buckled surface dimers corresponds to a charge transfer of $0.17e$. Charge flow from subsurface layers to the dimers is no larger than $0.05e$. Our observation of a crystal-field splitting for surface-atom core levels is a new result in photoemission measurements. The magnitude of the splitting of the up-atoms in the Si(100) 2×1 buckled dimers clearly calls for further theoretical study. Finally, our finding that the Si $2p$ photoemission lines from surface atoms are asymmetric and well represented by the Doniach-Šunjić function should be of utility in future studies of semiconductor surfaces.

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- [1] J. A. Appelbaum and D. R. Hamann, *Surf. Sci.* **74**, 21 (1978).
- [2] D. J. Chadi, *Phys. Rev. Lett.* **43**, 43 (1979).
- [3] M. T. Yin and M. L. Cohen, *Phys. Rev. B* **24**, 2303 (1981).
- [4] P. Krüger, A. Mazur, J. Pollmann, and G. Wolfgarten, *Phys. Rev. Lett.* **47**, 1468 (1986).
- [5] A. Mazur and J. Pollmann, *Surf. Sci.* **225**, 72 (1990).
- [6] I. P. Batra, *Phys. Rev. B* **41**, 5048 (1990).
- [7] J. J. Lander and J. Morrison, *J. Chem. Phys.* **37**, 729 (1962).
- [8] T. P. Poppendieck, T. C. Ngoc, and M. B. Webb, *Surf. Sci.* **75**, 287 (1978).
- [9] M. J. Cardillo and G. E. Becker, *Phys. Rev. B* **21**, 1479 (1980).
- [10] W. S. Wang, F. Jona, and P. M. Marcus, *Phys. Rev. B* **28**, 2049 (1983).
- [11] R. M. Tromp, R. G. Smeenk, F. W. Saris, and D. J. Chadi, *Surf. Sci.* **133**, 137 (1983).
- [12] B. W. Holland, C. B. Duke, and A. Paton, *Surf. Sci.* **140**, L269 (1984).
- [13] R. J. Hamers, R. M. Tromp, and J. E. Demuth, *Phys. Rev. B* **34**, 5343 (1986).
- [14] B. S. Swartzentruber, Y.-W. Mo, M. B. Webb, and M. G. Lagally, *J. Vac. Sci. Technol. A* **63**, 2901 (1989).
- [15] R. E. Schlier and H. E. Farnsworth, *J. Chem. Phys.* **30**, 4 (1959).
- [16] C. U. S. Larsson, A. S. Floodstrom, R. Nyholm, L. Inccia, and F. Šenf, *J. Vac. Sci. Technol. A* **5**, 3321 (1987).
- [17] R. D. Bringans, M. A. Olmstead, R. I. G. Uhrberg, and R. Z. Bachrach, *Phys. Rev. B* **36**, 9569 (1987).
- [18] D. H. Rich, A. Samsavar, T. Miller, H. F. Lin, T.-C. Chiang, J.-E. Sundgren, and J. E. Green, *Phys. Rev. Lett.* **58**, 579 (1987).
- [19] D. H. Rich, T. Miller, and T.-C. Chiang, *Phys. Rev. B* **37**, 3124 (1988).
- [20] F. J. Himpsel, P. Heinmann, T.-C. Chiang, and D. E. Eastman, *Phys. Rev. Lett.* **45**, 1112 (1980).
- [21] R. McGrath, R. Cimino, W. Braun, G. Thorton, and I. T. McGovern, *Vacuum* **38**, 251 (1988).
- [22] F. J. Himpsel, F. R. McFeely, A. Taleb-Ibrahimi, J. A. Yarmoff, and G. Hollinger, *Phys. Rev. B* **38**, 6084 (1988).
- [23] S. Doniach and M. Šunjić, *J. Phys. C* **3**, 285 (1970).
- [24] P. H. van Cittert, *Z. Phys.* **69**, 298 (1981). The method was modified by smoothing each correction to avoid the buildup of noise. Tests with artificial data show that our methodology reliably resolves lines with a 2:1 intensity ratio in data with a signal-to-noise ratio of 50 in the peaks, provided the line separation exceeds $\frac{2}{3}$ of the Gaussian width. For two peaks with 1:1 intensity ratio (as is the case here) our approach is even more sensitive.
- [25] P. M. Th. M. van Attekum and G. K. Wertheim, *Phys. Rev. Lett.* **43**, 1896 (1979).
- [26] U. Gelius, L. Asplund, E. Basilier, S. Hedman, K. Helenelund, and K. Siegbahn, *Nucl. Instrum. Methods Phys. Res., Sect. B* **1**, 85 (1984).
- [27] D. E. Eastman, F. J. Himpsel, and J. F. van der Veen, *J. Vac. Sci. Technol.* **20**, 609 (1982).
- [28] D. R. Penn, *Phys. Rev. B* **13**, 5248 (1976).
- [29] J. F. Morar, U. O. Karlsson, J. A. Yarmoff, D. Rieger, F. R. McFeely, and F. J. Himpsel, BNL National Synchrotron Light Source Annual Report, 1986 (unpublished), p. 135.
- [30] F. J. Himpsel, B. S. Meyerson, F. R. McFeely, J. F. Morar, A. Taleb-Ibrahimi, and J. A. Yarmoff, in "Photoemission and Absorption Spectroscopy of Solids and Interfaces with Synchrotron Radiation," "Enrico Fermi" Course CVIII, edited by M. Campagna and L. Rosei (North-Holland, Amsterdam, to be published).
- [31] M. Schuluter, in *Chemical Physics of Solid Surfaces and Heterogeneous Catalysis*, edited by D. A. King and D. P. Woodruff (Elsevier, New York, 1988), p. 37.