

Measurement of the Angle of Dangling-Bond Photoemission from Cleaved Silicon

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The surface state near the top of the valence bands on the cleaved (111) face of Si has been investigated by using angular-resolved photoemission spectroscopy at the photon energy 10.2 eV. Anisotropy, dispersion, and splitting are observed. The results are consistent with an appreciable admixture of S_2 character in this surface-state band.

Photoemission from the intrinsic surface state close to the top of the valence bands on the (111) face of Si has been observed recently in several laboratories.¹⁻³ This particular state, sometimes designated as the S_1 surface-state band, is thought to be composed primarily of p_z , or dangling-bond-type, orbitals, where the z axis is normal to the crystal surface.^{4,5} In this Letter, we report angular-resolved photoemission studies which have revealed detailed information on this surface state not attainable by conventional photoemission techniques. Our results demonstrate for the first time the energy dispersion of the surface-state band consistent with recent semiempirical tight-binding calculations. In the outer regions of the two-dimensional Brillouin zone, however, the surface state is observed to split. This and certain other features of the data, namely the energy location of the surface state and also the azimuthal dependence of the emission intensity, indicate that the dangling-bond surface state on cleaved silicon surfaces is more complicated than current models would suggest. The possibility of an appreciable admixture of the so-called S_2 surface state is advanced.

The measuring apparatus has been described elsewhere.⁶ Photons of energy 10.2 eV are incident normally upon the sample, and photoelectron energy spectra can be measured as a function of both the polar angle, θ , and the azimuthal angle, φ . Lightly doped p -type ($p \sim 2 \times 10^{14} \text{ cm}^{-3}$) silicon (111) samples were prepared by cleaving in ultrahigh vacuum of about 5×10^{-10} Torr. Measurements were taken on three separate cleaved surfaces and were found to be reproducible. Spectra will be referenced to initial-state energy relative to the clean-surface Fermi level, E_F , which was obtained from measurements on a Cu film evaporated on the Si surface in ultrahigh vacuum.

Figure 1(a) shows photoelectron spectra taken at $\theta = 25^\circ$ and $\varphi = 0^\circ$. (As will be indicated below, the origin of azimuth is chosen such that the plane $\varphi = 0^\circ$ contains the $[11\bar{2}]$ direction.) The

full curve was obtained on a freshly cleaved sample, and the dashed curve was obtained 10 days later on a contaminated surface. The dashed curve has been shifted toward the Fermi energy by +0.15 eV to correct for changes in band bending after contamination, thus bringing the bulk direct-transition peaks at about -1.9 eV and -3.2 eV into coincidence for the two spectra. An intense surface-state peak is observed at -1.15 eV which is ~ 0.3 eV lower than values previously reported for lightly doped samples.¹⁻³ For com-

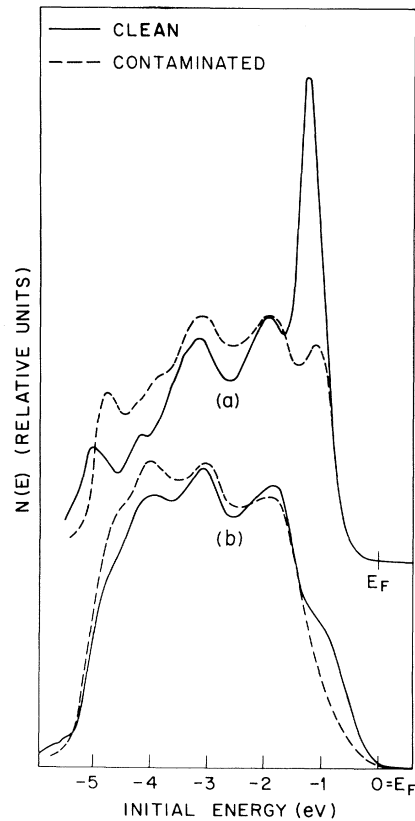


FIG. 1. Photoelectron energy spectra $N(E)$, measured on clean and contaminated (111) faces of Si: (a) angle-resolved spectra taken at $\theta = 25^\circ$ and $\varphi = 0^\circ$; (b) angle-averaged spectra using a 2π -sr collector.

parison, we show in Fig. 1(b) angle-averaged spectra taken on a separate cleaved surface by using a 2π -sr collector with essentially the same geometry as that used by Wagner and Spicer.¹ Our angle-averaged results are very similar to theirs for lightly doped samples in that the surface-state structure is more of a broad Gaussian-like shoulder centered at about -0.85 eV compared to their value of -0.9 eV. These results for the "clean" surface were obtained after a number of angular-resolved measurements; hence the surface states are somewhat weaker than previously reported by other workers.¹⁻³ A result apparent in Fig. 1, and of importance to workers interested in the use of photoemission spectroscopy in the study of surface rather than bulk properties, is that the ratio of surface to bulk features can be greatly enhanced by judicious choice of the angle of collection. The optimum angle, however, is not a simple extremum like $\theta = 0^\circ$ or 90° , but appears to be determined by the specific material and electronic states under investigation.

A sequence of photoelectron energy spectra for polar angles in the range $\theta = 15^\circ$ to 65° is shown in Fig. 2; the azimuthal angle in these spectra was kept constant at $\varphi = 0^\circ$. We note that the intensity of the surface-state peak varies dramati-

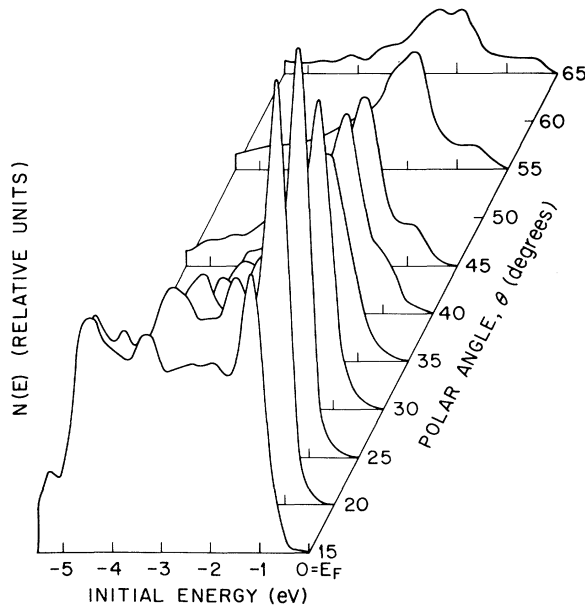


FIG. 2. Angle-resolved photoelectron energy spectra taken on a clean (111) 2×1 Si surface at a sequence of polar angles. The azimuthal angle was kept constant at $\varphi = 0^\circ$.

cally with θ , reaching a maximum at about $\theta = 20$ – 25° . (Expressed as a fraction of the total emission, the maximum of the surface-state emission occurs nearer $\theta = 30^\circ$.) The surface-state peak also moves to lower energies as θ is increased. It has been shown by Smith, Traum, and Di Salvo⁷ that results like these can be used to plot two-dimensional band structures, since, if E is the measured kinetic energy of a photoelectron, the quantity $(2mE/\hbar^2)^{1/2} \sin\theta$ is the component of its wave vector parallel to the surface, k_{\parallel} . The results of Fig. 2 indicate a surface-state band in which the energy decreases with increasing k_{\parallel} . This sign of the dispersion is consistent with the semiempirical band calculations of Pandey and Phillips⁵ which predict that the bands for both the S_1 and S_2 surface states have their maxima at $\Gamma(k_{\parallel} = 0)$ and fall smoothly on moving away from Γ .

A feature of the spectra *not present* in the calculations⁵ is the splitting of the surface-state peak which takes place for θ greater than about 35° . A shoulder emerges on the high-energy edge of the main surface-state peak, and then moves toward the Fermi energy as θ is increased further. The energy dispersion of this weaker feature with k_{\parallel} is therefore in the *opposite* sense to that of the main peak. One possibility is that the weak splitoff peak is a consequence of the 2×1 superlattice of the reconstructed surface of cleaved Si.

A point of *strong disagreement* with the semiempirical calculations concerns the energy location of the surface state. The main surface-state peak of Fig. 2 is found to fall almost exactly halfway in energy between the S_1 and S_2 surface-state bands in the Pandey and Phillips calculation.⁵ We therefore advance the suggestion that the observed peak is not a pure S_1 dangling-bond-type state as previously assigned¹⁻³ but is a hybrid of the S_1 and S_2 states, whose precise proportions could vary with k_{\parallel} . The need to consider both the S_1 and S_2 states might serve also to explain the splitting at higher θ . Presumably the other surface states³ at lower energies (not considered in this paper) are also hybrids of the Pandey-Phillips solutions (S_1, S_2, S_3).

The azimuthal dependence of the surface-state emission intensity at $\theta = 30^\circ$ is represented in Fig. 3(a) by the open circles connected by a dashed line. This is a radial plot of the emission in the initial energy range -1.7 eV to E_F , a window which spans the surface-state peak, taken prior to contamination. The azimuthal dependence of the emission from below -1.7 eV is also indicat-

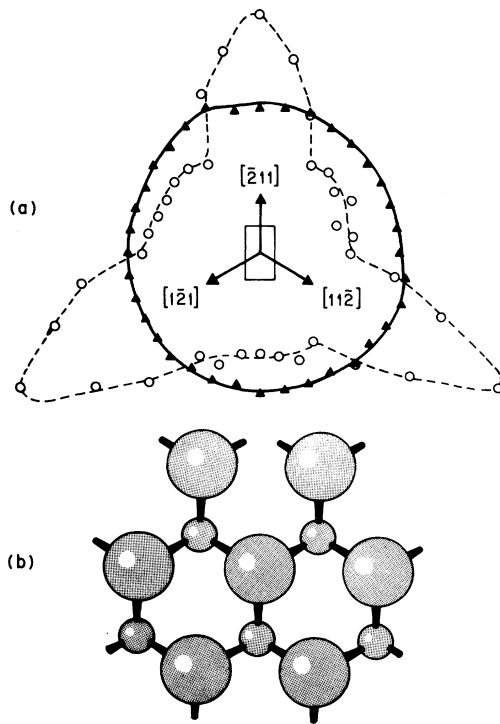


FIG. 3. (a) Radial plots of the azimuthal dependence of the photoemission intensity at $\theta = 30^\circ$. The surface-state emission intensity (i.e., emission in the energy window -1.7 eV to E_F) is represented by the open circles connected by a dashed line; the filled triangles connected by a full line represent, on a 10 times reduced scale, the remainder of the photoemission intensity from -5.4 eV to -1.7 eV; the shape and crystal orientation of the sample are shown at the center of the plot. (b) Orientation with respect to (a) of the outermost or first-layer (large circles) and second-layer (small circles) atoms of the unreconstructed (111) face of Si. The z axis or [111] direction points out of the figure.

ed in Fig. 3(a). It is seen that the surface-state emission is quite anisotropic and displays three sharp lobes centered about planes containing the $\langle 211 \rangle$ directions. The orientation of the photoemission lobes with respect to the crystal structure is illustrated further by comparing the data of Fig. 3(a) with Fig. 3(b) which shows the disposition of the outermost or first layer (large circles) and second layer (small circles) of atoms in the absence of surface reconstruction.

Liebsch⁸ has recently shown that anisotropies such as those observed can arise as a consequence of low-energy-electron-diffraction-type

multiple-scattering effects in the final state of the optical transition which gives rise to the photoelectron. Gadzuk,⁹ on the other hand, has proposed that the azimuthal dependence reflects the angular dependence of the atomic orbitals which comprise the initial states, the emission tending to be more intense along the directions in which the lobes of the orbitals point. In this picture, photoemission from the S_1 states, or p_x -like dangling-bond orbitals, would have cylindrical symmetry about the surface normal. The S_2 state is composed primarily of sp^n orbitals ($2 < n < 3$) centered on the first-layer atoms and pointing into the crystal along the back-bond directions, and similar sp^n orbitals centered on the second-layer atoms pointing outward from the surface along the back bonds. It is to be noted that the lobes of these second-layer orbitals point in the same azimuthal directions as the lobes in the observed photoemission intensity. In principle, the first-layer orbitals could also be included but they point into the crystal and have a threefold azimuthal lobe symmetry which points opposite to the observed directions. If the Gadzuk picture is appropriate, therefore, the azimuthal results tend to support the suggestion made above that the observed surface state is not of pure S_1 character, but has an appreciable S_2 content.

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