pearance of surface states near E_F. Curves *b* are shifted by these changes in band bending so as to subtract bulk emission.[11] Ge and GaAs show bands of intrinsic surface states about 0.9 ± 0.2 eV wide centered at about 0.7 and 1.05 eV below E_F, respectively, i.e., at about 0.75 and 0.5 eV below the valence-band maxima E_v. For Ge, a tail of surface states extends essentially up to E_F, while for GaAs there appears to be a gap (~ 0.3 ± 0.1 eV) just below E_F in which the optical density of surface states is very small.[12] For GaAs, the amplitude of surface-state emission appeared to decrease with time faster than might be expected for gas exposure with $p \sim 3 \times 10^{-10}$ Torr. The surface-state emission intensity shown in Fig. 2 was measured about 15 min after cleaving and decreased by about a factor of 4 within the next 45 min.

For Si, the shape of our optical density of states of intrinsic surface states near E_F is similar to the hyperbolic-cosine-like curve (one of several models) which Allen and Gobeli[1] concluded was consistent with their studies of work function and photothreshold versus doping, and which has been used by others.[3,13] If we normalize our optical density of states to contain about one occupied surface-state electron per surface atom, out resulting number of surface states within ~ 0.1 eV of E_F is roughly $\frac{1}{4}$ that previously reported.[1,2] This might be due to our crude assumptions such as constant matrix elements or might simply be due to inaccuracies in the shape of our ODS near E_F, since the charged surface states involved in reported work-function measurements[1,2] are roughly $\lesssim 1\%$ of the total number of surface states.

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[11]The amplitudes of curves *b* in Figs. 1 and 2 were scaled so as to be about equal to curves *a* at ~ 2–3 eV below E_F; this scaling assumes that essentially all of the emission from ~ 2–3 eV below E_F is bulk emission. Slight changes in the relative amplitude of curves *b* will not significantly change our surface-state emission curves *c*.

[12]This 0.3-eV gap was determined from data for $h\nu = 20$ eV, for which the photon band-pass broadening $\Delta h\nu$ was less. The gap shown in Fig. 2 is narrowed by about $\frac{1}{2}\Delta h\nu$ or ~ 0.2 eV, and also the width of the optical density of states is broadened by ~ 0.3 to 0.4 eV.

[13]Ref. 4, p. 120.

Observation of a Band of Silicon Surface States Containing One Electron Per Surface Atom*

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We have studied the energy distribution of electrons photoemitted from surface states on the cleaved (111) face of a 0.001-Ω-cm *n*-type Si crystal. We find a 1.8-eV-wide surface band with a peak at 1.1 eV and a shoulder at 0.5 eV below the Fermi energy containing about 8×10^{14} electrons/cm^2, i.e., approximately one electron per surface atom. The strong peak lies below the valence-band maximum at the surface. The surface nature of this structure is confirmed by its disappearance when exposed to vacuum contamination at 10^{-10} Torr or to oxygen.

Information about surface states on silicon can be inferred from an analysis of work function and photoelectric threshold measurements as shown by the pioneering work of Allen and Gobeli,[1] whose techniques have been refined by Fischer.[2] Eden[3] has identified photoemission from the sili-

con band gap with surface states. This Letter[4] describes the observation on silicon of a 1.8-eV-wide surface-electron band having a density comparable to one electron per surface atom. The surface nature of this structure is confirmed by its disappearance when exposed to ultrahigh vacuum contamination or to oxygen. Eastman[5] has also obtained similar results on lightly doped Si, Ge, and GaAs.

A 0.001-Ω-cm ($N_D = 10^{20}$ cm^{-3}) arsenic-doped silicon crystal has been cleaved along a (111) plane with a tungsten-carbide blade and an annealed copper anvil in an ultrahigh (10^{-11} Torr) vacuum chamber. Energy distribution curves (EDC's) are obtained by the ac method[6] using a hemispherical retarding potential analyzer. A copper photoemitter, interchangeable with the silicon, is used as a Fermi-energy reference.

EDC's from the freshly cleaved Si are shown in Fig. 1. Four pieces of structure are apparent. Peaks C and D, whose initial- and final-state energies vary with photon energy, are from well-known bulk-state direct (k-conserving) transitions.[7] Peaks A and B, whose initial-state energies do not change are identified with surface electrons.[8] Four cleaves have been made, all of which follow the same pattern: A surface structure is observed which disappears when exposed to contamination. Since some details of this pattern depend upon the nature of the cleave and the type of contaminant, the cleaves will be identified separately.

Cleave No. 1 remained at 3×10^{-12} Torr, as measured on a Redhead[9] gauge, for 2 months with only a slight decrease in the amplitude of peaks A and B. However, exposure to a spontaneous

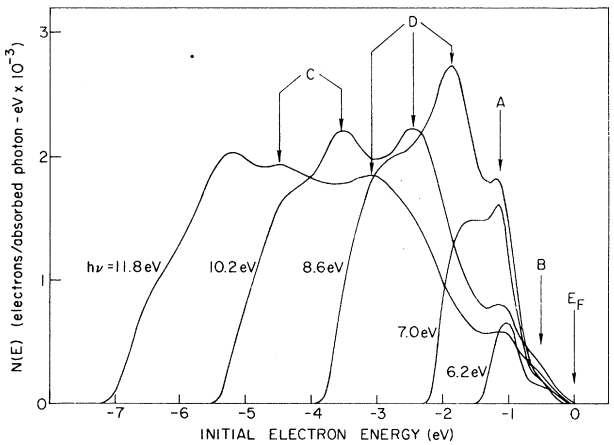

FIG. 1. EDC's for various photon energies on freshly cleaved Si (cleave No. 4) showing surface peaks A and B, and valence-band direct transitions C and D.

1×10^{-10}-Torr leak caused this structure to reduce to a small residual amount. After the leak, cleave No. 2 at 1×10^{-10} Torr began changing immediately. The fresh and contaminated EDC's from this cleave are presented in Fig. 2. Suspected contaminants are oxygen from H_2O or CO_2 after cleave No. 1 and hydrocarbons after cleave No. 2.[10] Cleaves No. 3 and No. 4 were intentionally exposed to oxygen in order to control the changing process.

A careful analysis of Fig. 2 yields the band-bending picture for the freshly cleaved silicon shown in Fig. 3(a). The surface distribution obtained in the following discussions is given on the same energy scale in Fig. 3(b) for comparison. Observe in Fig. 2 that the work function[11] and the extrapolated valence-band upper edge shifted 0.6 eV lower in energy with contamination. There is little or no band bending represented by the contaminated EDC since the extrapolated upper valence-band edge falls below the bulk position of the valence-band maximum. Contamination has apparently terminated dangling bonds in a natural way, neutralizing a negative surface charge, thus straightening bands which were initially bent upward 0.6 eV.

The 0.2-eV shift of peaks C and D while the band bending changed 0.6 eV indicates that many electrons escape from behind the band-bending region. To first order the electron escape depth is estimated to be 12 Å. This is obtained, and

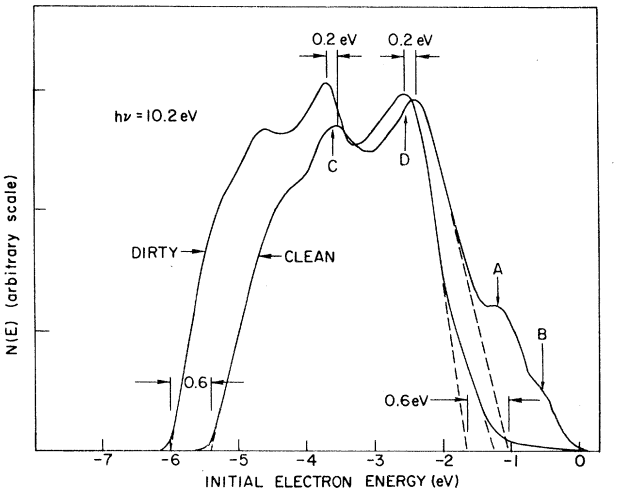

FIG. 2. Comparison of Si EDC's from cleave No. 2 before and after vacuum contamination at 10^{-10} Torr. Note that band bending causes the work function (left edge) and the extrapolated high-energy edge of the valence-band structure to shift 0.6 eV while the position of the bulk peaks, C and D, shift only 0.2 eV.

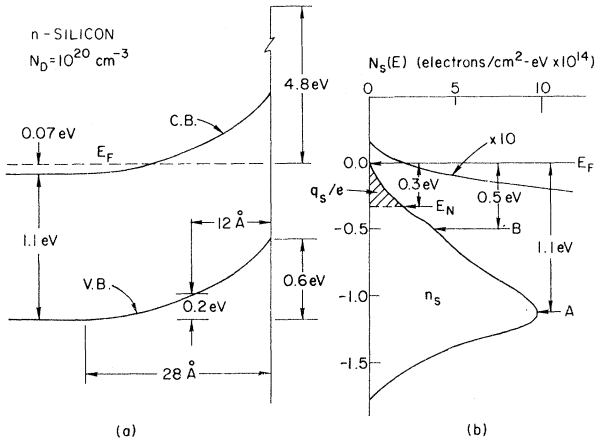

FIG. 3. (a) Band-bending picture obtained in the text, compared with (b) the surface-electron energy distribution. The shaded region illustrates the portion of the distribution responsible for the negative surface charge.

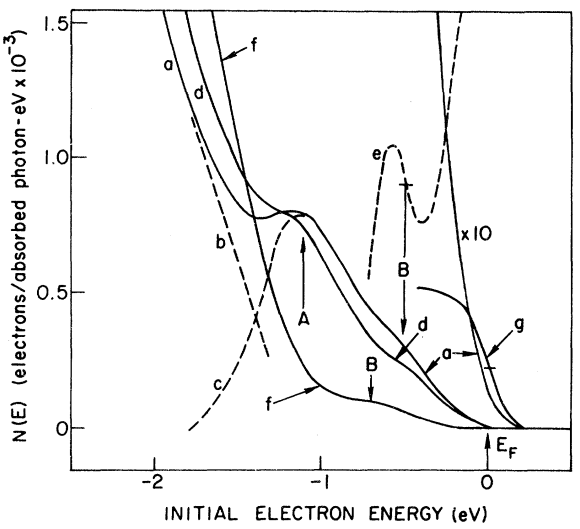

FIG. 4. Details of the upper edge of the EDC's for cleave No. 4 at $h\nu = 10.2$ eV. *a*, $\frac{1}{2}$ h after cleave; *b*, extrapolated upper edge of peak *D*; *c*, estimated surface-electron distribution obtained by subtracting curve *b* from *a*; *d*, EDC after 9 days at 1×10^{-11} Torr; *e*, location of peak *B* from inflection point in derivative EDC; *f*, result of exposure to 800 Langmuirs of oxygen; *g*, upper edge of EDC for reference Cu shutter used to determine the Fermi-energy zero.

verified with a computer calculation, by noting that the bands bend 0.2 eV at a depth of 12 Å.[12] This shows the advantage of using heavily doped *n*-type Si. The valence-band sturcture comes at the lowest possible energy leaving the widest possible energy window for observation of the surface-electron energy distribution.

The determination of the surface-electron energy distribution, Fig. 3(b), is illustrated for cleave No. 4 at 10.2 eV photon energy in Fig. 4. The extrapolated upper valence-band structure, *b*, is subtracted from the freshly cleaved EDC, *a*, to obtain curve *c*. The stronger peak, *A*, falls 1.1 eV below the Fermi energy while peak *B* appears as a subtle shoulder at -0.5 eV. The EDC, and hence the actual density of states, tails exponentially from about -0.4 eV through the Fermi energy, as can be seen by the expanded curve *a*. The resolution-broadened Fermi-Dirac distribution at the upper edge of the reference Cu EDC, curve *g*, is shown for comparison. After 9 days at 1×10^{-11} Torr the EDC has shifted to curve *d*, partially distorting peak *A* and sharpening peak *B*. The location of peak *B* can be fixed accurately from the inflection point in a derivative EDC, curve *e*.[13] Upon exposure to 800 Langmuirs of oxygen, a continuous change to curve *f* occurred. Peak *A* could be followed until it became obscured by the valence band. Peak *B*, reduced in amplitude, shifted 0.2 eV lower in energy, and sharpened into a clear shoulder.

It is of interest to estimate the surface-electron density associated with peaks *A* and *B* on the freshly cleaved surface. There are four valence-band electrons distributed over an energy range of 12.5 eV for each of the 5×10^{22} cm^{-3} bulk atoms. At 10.2 eV the valence-band part of the EDC is 4.3 eV wide, and the ratio of surface to bulk emission is 0.096. Assuming matrix elements are the same for surface and bulk transitions and using the 12-Å escape-length estimate determined above one obtains

$$n_s = 4(5\times10^{22})(4.3/12.5)0.096(12\times10^{-8}) \approx 8\times10^{14} \text{ electrons/cm}^2 \quad (1)$$

for the surface electron density. This is meant to be a first-order estimate only.

Consider a simple model of the Si (111) cleavage plane in which one filled and one empty surface state for each of the 7.85×10^{14} cm^{-2} broken bonds gives charge neutrality. In order to have 0.6-eV band bending, Poisson's equation requires that $q_s/e = 2.8\times10^{13}$ cm^{-2} additional states be filled in order to give the required negative surface charge. Thus one expects a total of $n_s = 8.13\times10^{14}$ electrons/cm^2. The agreement of the above rough estimate with this value is satisfying.

This model is consistent with several other observations:

(a) A two-dimensional free-electron band containing 8×10^{14} electrons/cm^2 would be 2.1 eV

wide, in first-order agreement with the observed 1.8 eV. The peaked structure and low density of states at the Fermi energy, however, indicate a considerable perturbation from a free-electron picture. Compare this with bulk Si where the valence band has nearly its free-electron width, but perturbations act to form structure and a gap.

(b) Oxygen exposure ties dangling bonds, removing some of the surface states to lower energy. The remaining surface states have less overlap, which in turn causes the structure to sharpen as observed in Fig. 4, curves d and f.

(c) The shaded portion of Fig. 3(b) represents the electron density, $q_s/e = 2.8\times10^{13}$ cm^{-2}, responsible for the surface charge. In lightly doped silicon this charge would be negligible and the Fermi energy would fall at the neutral level, E_n, 0.3 eV lower as shown. This is in agreement with (i) the position of peak A, 0.8 eV below E_F, observed by Eastman,[5] (ii) the observation of Eden[3] for high-resistivity p-type Si that the surface distribution extends uniformly up to the Fermi energy, and (iii) the measurements of work function versus doping done by Allen and Gobeli[1] and by Fischer.[2]

(d) Chiarotti *et al.*[14] observed a peak at $h\nu = 0.46$ eV by comparing cleaved Si optical absorption before and after exposure to oxygen. This peak could correspond to transitions from peak B to a high density of empty states just above the Fermi energy. The sharpness of the peak, however, is not consistent with the structure shown in Fig. 3(b). Band-to-band absorption would have obscured peak A.

(e) Cleave No. 3 was bad and propagated at an unusual angle. Peak B was not found in that surface distribution. This suggests that the absence of peak B in Eastman's[5] data could be a result of the details of the cleaves.

(f) The conduction band, which could not be seen in the freshly cleaved EDC's because of band bending, was resolved after cleave No. 2 when the bands straightened. It appeared as a resolution broadened δ function occurring at the Fermi-energy zero.

The quantum yield of photoemitted electrons in electrons per absorbed photon above 8 eV is approximately 10^{-2} for the valence-band electrons, 10^{-3} for surface electrons, and 10^{-7} for conduction-band electrons. The weak output from the conduction band could be attributed to a small residual band bending or to weak matrix elements for intra-conduction-band transitions.

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[8]Calcott (Ref. 7), whose peak No. 11 corresponds to peak A, incorrectly identifies this as indirect transitions from the valence-band maximum. This suggestion is unlikely since the density of valence-band states reaches a minimum there. The change with contamination also tends to rule out a bulk process.

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[10]A residual gas analysis of another 1×10^{-10}-Torr leak in the same vacuum chamber shows 5% H_2, 1% He, 6% CH_3, 15% CH_4, 2% H_2O, 1% Ne, 26% CO or N_2, 10% Ar, and 34% CO_2. A 300-fold increase in the rate of contamination indicates a large increase in the partial pressure or a change in the type of the dominate contaminant. In fact cleave No. 1 followed a similar pattern to cleaves No. 3 and No. 4 which were exposed to oxygen: A large oxygen peak developed about 5.6 eV below the Fermi energy. No new structure appeared after cleave No. 2. Apparently the first contaminant was H_2O or CO_2 while hydrocarbons from the leak sealant dominated after cleave No. 2.

[11]The work function did not follow the band bending after cleaves No. 1, No. 3, and No. 4.

[12]G. W. Gobeli and F. G. Allen, Phys. Rev. 127, 141 (1962), estimate the escape depth to be 25 Å. This value was obtained from yield measurements near threshold and is not inconsistent with our value at higher energy.

[13]Second derivative of the I versus V curve. See L. W. James, R. C. Eden, J. L. Moll, and W. E. Spicer, Phys. Rev. 174, 909 (1968).

[14]G. Chiarotti, S. Nannarone, R. Pastore, and P. Chiaradia, Phys. Rev. B 4, 3398 (1971).