

Conduction-Band and Surface-State Critical Points in Si: An Inverse-Photoemission Study

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From measurements of the dispersion of the lowest two conduction bands in silicon by k -resolved inverse photoemission the energies of the $L\uparrow$ and $L\downarrow$ critical points were determined as 2.40 ± 0.15 and 4.15 ± 0.10 eV relative to the valence-band edge, respectively. A comparison with energies derived from photoemission and optical data reveals a large excitonic lowering of the E_1 transition by 0.5 ± 0.2 eV. The lowest unoccupied surface state on the Si(111) 2×1 surface at $\bar{\Gamma}$ is identified at 1.2 ± 0.1 eV.

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The bulk band structure of silicon is likely to be the most studied of all semiconductors.¹ Combining the information from photoelectron spectroscopy and optical measurements with an empirical nonlocal pseudopotential band-structure calculation, Chelicowsky and Cohen (CC) obtained what appeared to be a satisfactory and complete picture of the band structure of silicon up to about 5 eV above the valence-band edge.² They assigned, for example, energies (all referred to the valence-band edge E_V) of -1.23 eV ($L\downarrow$), 2.23 eV ($L\uparrow$), and 4.34 eV ($L\downarrow$) to the critical points at L that bracket the fundamental gap in Si. *Ab initio* calculations, on the other hand, gave critical-point energies in substantial disagreement with the empirical scheme of CC. The recent calculation of Wang and Klein³ which stands for many similar theoretical results arrives at energies of 1.46 and 3.66 eV for the $L\uparrow$ and $L\downarrow$ critical points, 0.8 and 0.7 eV lower than the empirical CC values.

This raises the fundamental question of to what extent the influence of the valence hole on the photoemission binding energies and the optical excitation energies can be neglected in what amounts to a single-particle interpretation of these one- and two-quasiparticle (electron and hole in the case of optical spectra) excitations. Hanke and Sham⁴ have recently treated the influence of the electron-hole interaction on the optical response of silicon rigorously. They are able to reproduce position and amplitude of the E_1 maximum in the ϵ_2 spectrum of Si satisfactorily provided that they allow for a nonlocal screening of the electron-hole interaction in the form of a momentum-dependent dielectric constant. The calculation yields an excitonic lowering of the E_1 edge, i.e., the onset of transitions from $\Lambda\downarrow$ to $\Lambda\uparrow$, by $\Delta E_x = 0.2$ eV compared to its "band-structure value," a result that amounts to a breakdown of the conventional interpretation scheme of optical data.

In this Letter we address the same problem by providing independent energies of the lowest two conduction bands of Si that were obtained by *adding* (not tak-

ing away) an electron to the system and comparing them with the combined results of photoelectron spectroscopy and optical data. The new energies were derived from normal-incidence, k -resolved inverse-photoemission measurements with variable photon energy performed on cleaved, well ordered Si(111) 2×1 surfaces with an energy and momentum resolution of 0.3 eV and 0.1 \AA^{-1} , respectively.⁵

Figure 1 shows a limited series of spectra obtained with the electron beam impinging perpendicularly onto the Si(111) surface ($k_{\parallel} = 0$). For each spectrum the energy distribution of the emitted photons was recorded for a given energy E_i of the primary electron beam. The zero of energy in the spectra of Fig. 1 corresponds to transitions to the Fermi level E_F as determined from the high-photon-energy cutoff in the spectrum of a Au film. We identify the two peaks around 2.5 and 4.2 eV with direct transitions into the two lowest conduction bands along the ΓL (i.e., $[111]$) direction in the Brillouin zone of Si. The momentum component perpendicular to the surface, k_{\perp} , was calculated with a free-electron initial-state dispersion with a value of $E_0 - E_V = -12.1$ eV for the inner potential.⁶ Thus, given the 5.34-\AA lattice constant of Si, transitions at L have a k_{\perp} value of 1.0 \AA^{-1} at an initial-state energy of 22.2 eV above E_V . Peak positions are plotted versus k_{\perp} in a reduced-zone scheme in Fig. 2 and the data are seen to cover approximately 60% of the ΓL dimension. The measured energy dispersion of the two bands agrees qualitatively with virtually all band-structure calculations: a dispersion that follows that of the highest valence band for the Λ_1 conduction band and a slight maximum about halfway between Γ and L for the band of Λ_3 symmetry. Minima at L define the $L\uparrow$ and $L\downarrow$ critical-point energies independent of the particular choice made for E_0 .

The two symbols in Fig. 2 refer to n -type samples (As doped, $N_D = 2.6 \times 10^{19} \text{ cm}^{-3}$) and to p -type samples (B doped, $N_A = 3 \times 10^{19} \text{ cm}^{-3}$), respectively. The heavy doping was chosen to reduce the effect of band bending on the spectra and the agreement in final-state

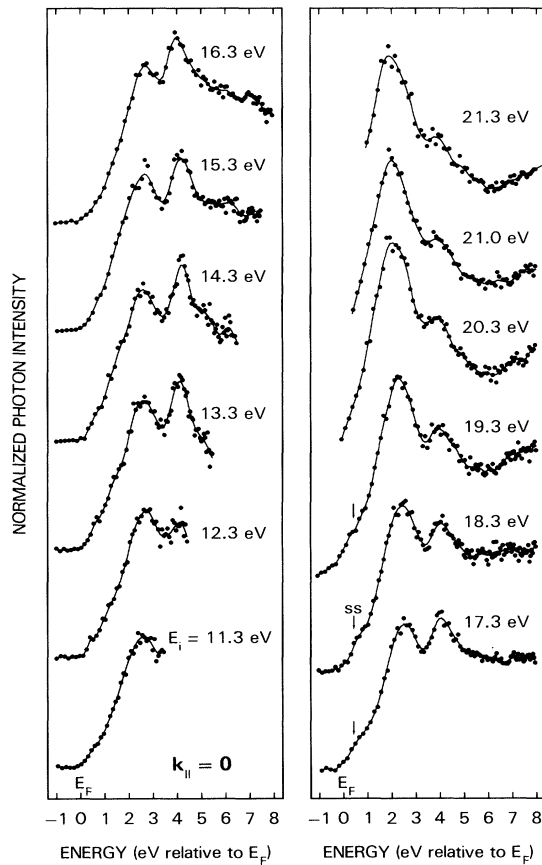


FIG. 1. Inverse-photoemission spectra at normal incidence for a range of initial electron energies E_i .

energies for the two samples excludes band bending as a source of systematic error in the band dispersion of Fig. 2.

Values between 0.32⁸ and 0.48 eV⁹ have been quoted for the Fermi-level pinning position relative to the valence-band edge, E_V , on the Si(111) 2×1 surface. We base our analysis on the most recent value of 0.40 ± 0.03 eV,¹⁰ and obtain the following uncorrected energies (relative to E_V) for the lowest two conduction-band critical points at L : $L_1^c = 2.50 \pm 0.10$ eV and $L_3^c = 4.15 \pm 0.10$ eV. The error reflects variations in the peak positions of a total of six samples (± 0.07 eV) and a ± 0.08 -eV uncertainty in the spectrometer calibration.

We have also measured the dispersion of the Λ_1^c and Λ_3^c bands perpendicular to ΓL at a point corresponding to $k_{\perp} = 0.78 \text{ \AA}^{-1}$ by taking spectra at off-normal angles for k_{\parallel} along $(01\bar{1})$ (see Fig. 3). The dispersion in this direction, which is parallel to the LW symmetry line, is comparatively small (see inset of Fig. 3), as would be expected for k vectors perpendicular to the $[111]$ direction near the surface of the Brillouin zone.¹¹ Taking the finite momentum resolution of the spec-

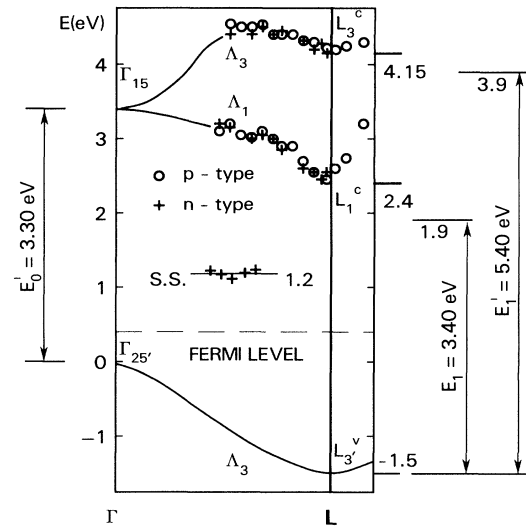


FIG. 2. Energy dispersion of conduction-band states along ΓL as derived from inverse-photoemission data. The Λ_3^c band is from Ref. 6, and optical transition energies appropriate for $T=300$ K are from Ref. 7. Data points marked S.S. correspond to an empty surface state on the Si(111) 2×1 surface.

trometer into account we make allowance for this dispersion by lowering L_1^c to 2.40 ± 0.15 eV. The second peak in Fig. 3 does not disperse measurably.

A maximum in the three-dimensional density of conduction states lies at 2.9 ± 0.1 eV.¹² An unresolved contribution of this maximum to the spectra of Fig. 1 brought about by umklapp processes involving many reciprocal-lattice vectors could, in principle, reduce the measured dispersion of the Λ_1^c band and thus raise the energy of the minimum at L above the true position of L_1^c . Modeling this situation by two peaks with a width of 0.8 eV (full width at half maximum) placed at 2.9 and 2.0 eV, respectively, showed that even a 30% contribution of the density of states to the spectra does not affect the measured peak positions due to direct transitions near L . The opposite situation—a density-of-states peak modulated in its position by a direct transition—is most unlikely. The energy would be off by 0.5 eV and the rapid variations in the relative cross sections of the two peaks in Fig. 1 are characteristic of direct transitions rather than of density-of-states features. The final energies for the L critical points from inverse photoemission are thus $E(L_1^c) = 2.40 \pm 0.15$ eV and $E(L_3^c) = 4.15 \pm 0.10$ eV.

Rather than comparing the new critical-point energies with band-structure calculations let us examine our results in the light of the accurately known optical transitions involving critical points along Λ . To this end we augment the experimental band-structure scheme of Fig. 2 by adding the Λ_3^c valence band as

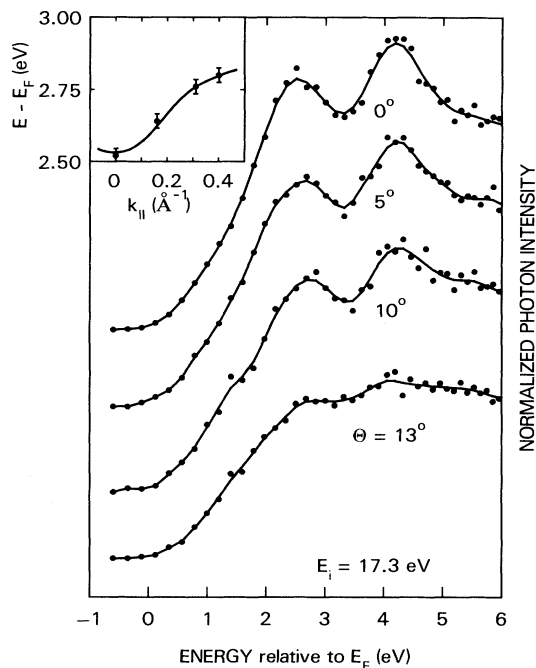


FIG. 3. Inverse-photoemission spectra for off-normal incidence with k_{\parallel} along $(01\bar{1})$ and $k_{\perp} = 0.78 \text{ \AA}^{-1}$. The inset shows the dispersion of the lower peak with k_{\parallel} .

determined in angle-resolved photoemission⁶ with an L_3^v end point that is the average of the energies in Himpsel, Heimann, and Eastman¹³ and Ref. 6, and by placing Γ_{15} at 3.30 eV in accordance with the direct optical gap of Si ($E_0' = 3.30 \text{ eV}$).⁷

E_1 and E_1' mark the onset of optical transitions from Λ_3^v to Λ_1^c and Λ_3^c near and including the critical points at L , respectively.¹² The E_1' end-point energy (3.9 eV; see Fig. 2) is only insignificantly lower than L_3^c when the combined error of initial and final states ($\pm 0.2 \text{ eV}$) is taken into account. It is apparent, however, that the E_1 excitation energy falls short of the corresponding energy difference as obtained from photoemission and inverse-photoemission data by $0.5 \pm 0.2 \text{ eV}$. This discrepancy, when ascribed to an excitonic lowering of the $L_3^v \rightarrow L_1^c$ optical transition, is in essential agreement with the 0.2-eV lowering of the E_1 threshold attributed by Hanke and Sham to the electron-hole attraction.⁴ Alternatively, our new data require a reinterpretation of the optical absorption near Γ rather than L .

Finally, we observe at $E_F + 0.8 \text{ eV}$ a shoulder in the spectra of freshly cleaved surfaces (Fig. 4) that has the characteristics of a surface state, i.e., it disappears upon contamination and shows no dispersion with k_{\perp} (Fig. 2). The energy of this empty surface state, when

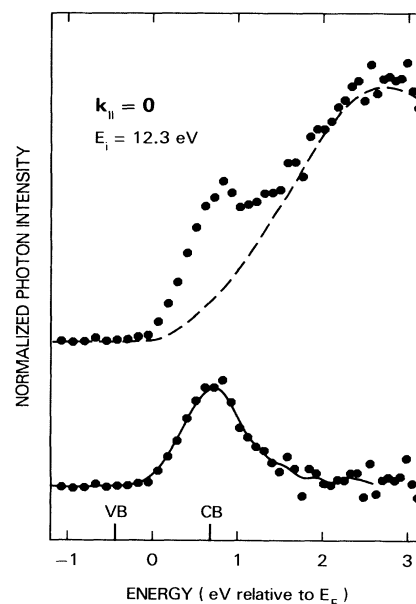


FIG. 4. Inverse-photoemission spectra of Si(111) 2×1 that show the lowest unoccupied surface state 0.7 eV above E_F . The dashed line represents the spectrum after contamination.

combined with that of the corresponding occupied state at $E_F - 1.1 \text{ eV}$,¹⁴ yields for the surface-state gap at $\bar{\Gamma}$ $1.9 \pm 0.1 \text{ eV}$. This is in good agreement with values calculated on the basis of the π -bonded chain model for the reconstruction of the Si(111) 2×1 surface: 2.0¹⁵ and 1.8 eV.¹⁶

In conclusion, we find evidence for strong electron-hole interaction in the E_1 but not the E_1' optical transition in Si. The excitonic lowering of at least 0.3 eV is comparable in magnitude to core exciton binding energies and renders obsolete the description of this transition in terms of an independent-particle picture.

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¹See, e.g., J. C. Phillips, in *Solid State Physics: Advances in Research and Applications*, edited by H. Ehrenreich, F. Seitz, and D. Turnbull (Academic, New York, 1966), Vol. 18, p. 56.

²J. R. Chelikowsky and M. L. Cohen, *Phys. Rev. B* **14**, 55 (1976).

³C. S. Wang and B. M. Klein, *Phys. Rev. B* **24**, 3393 (1981).

- ⁴W. Hanke and L. J. Sham, Phys. Rev. B **21**, 4656 (1980).
- ⁵Th. Fauster, D. Straub, J. J. Donelon, D. Grimm, A. Marx, and F. J. Himpsel, to be published.
- ⁶R. I. G. Uhrberg, G. V. Hansson, U. O. Karlsson, I. M. Nicholls, P. E. S. Persson, S. A. Flodström, R. Engelhardt, and E. E. Koch, Phys. Rev. Lett. **52**, 2265 (1984).
- ⁷*Physics of Group IV Elements and III-V Compounds*, edited by O. Madelung, Landoldt-Börnstein: Numerical Data and Functional Relationships in Science and Technology, Group 3 Vol. 17a (Springer-Verlag, Berlin, 1982), p. 45.
- ⁸F. G. Allen and G. W. Gobeli, Phys. Rev. **127**, 150 (1962).
- ⁹C. Sebenne, D. Bolmont, G. Guichar, and M. Balkanski, Phys. Rev. B **12**, 3280 (1975).
- ¹⁰F. J. Himpsel, G. Hollinger, and R. A. Pollak, Phys. Rev. B **28**, 7014 (1983).
- ¹¹E. O. Kane, Phys. Rev. **146**, 558 (1966).
- ¹²W. B. Jackson, S.-J. Odeh, C. C. Tsai, and J. W. Allen, Phys. Rev. Lett. **53**, 1481 (1984).
- ¹³F. J. Himpsel, P. Heimann, and D. E. Eastman, Phys. Rev. B **24**, 2003 (1981); the L_3^v energy was corrected for $E_F - E_V = 0.40$ eV from Ref. 9.
- ¹⁴R. I. G. Uhrberg, G. V. Hansson, J. M. Nicholls, and S. A. Flodström, Phys. Rev. Lett. **48**, 1032 (1982).
- ¹⁵K. C. Pandey, Physica (Utrecht) **117&118B**, 761 (1983).
- ¹⁶J. E. Northrup and M. L. Cohen, Phys. Rev. Lett. **49**, 1349 (1982).