[9]See, for example, L. W. Swanson and L. C. Crouser, Phys. Rev. 163, 15 (1967).
[10]F. G. Allen, J. Phys. Chem. Solids 19, 94 (1961).
[11]A. F. Yatsenko, Phys. Status Solidi (a) 1, 333 (1970).
[12]L. F. Wagner and W. E. Spicer, Phys. Rev. Lett. 28, 1381 (1972).
[13]From Wagner and Spicer's data, we approximate $V(x) = 0.6\exp[-x/(10.9\ \text{Å})]$. Thus $F = dV/dx(x=0) = 5.495\times10^{-2}$ V/Å. This corresponds to what would be a 0.648-V/Å external field, using $\epsilon = 11.8$ for Si.
[14]E. Kisker, A. H. Mahan, and B. Reihl, Phys. Lett. 62A, 261 (1977).

Experimental Evidence for One Highly Dispersive Dangling-Bond Band on Si(111) 2 × 1

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Angle-resolved photoemission data along the $\bar{\Gamma}$-$\bar{J}$ symmetry line in the surface Brillouin zone of the Si(111) 2×1 surface show that there exists only one dangling-bond band. This fact removes the experimental basis for the introduction of electron correlation effects for the Si(111) 2×1 surface. The dangling-bond band shows a large positive energy dispersion, which favors the recently suggested π-bonded chain model instead of the widely considered buckling model.

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In this Letter we present new angle-resolved photoemission results which provide evidence for the existence of *one* dangling-bond surface-state band on the Si(111) 2×1 surface. This dangling-bond band shows a large positive initial-state energy dispersion along the $\bar{\Gamma}$-$\bar{J}$ symmetry line in the 2×1 surface Brillouin zone (SBZ). This result is in agreement with measurements, in which the dispersion relations along the $\bar{\Gamma}$-$\bar{J}$ and $\bar{\Gamma}$-$\bar{K}$ symmetry lines in the 2×1 SBZ for both the dangling-bond and the back-bond surface-state bands were obtained.[1]

The initial-state energy dispersion relation for the dangling-bond band presented here is in disagreement with a recent photoemission study,[2] where the existence of *two* dangling-bond bands along the $\bar{\Gamma}$-$\bar{J}$ symmetry line was suggested. Our results are also in qualitative disagreement with calculated dispersion relations obtained from the buckling model,[3-6] which has so far been the most widely accepted model for the 2×1 reconstruction of the Si(111) surface.

Experimentally determined dangling-bond bands along the $\bar{\Gamma}$-$\bar{J}'$ symmetry line[7,8] have failed in providing conclusive comparison with the calculations, since the buckling model gives bands with small dispersion, and the experiments have not been consistent concerning the magnitude of the dispersion. Experiments which present results along the $\bar{\Gamma}$-$\bar{J}$ or $\bar{\Gamma}$-$\bar{K}$ symmetry lines[6,9] have indicated a dangling-bond band with a large positive dispersion from $\bar{\Gamma}$ to $\bar{J}$ and $\bar{K}$, respectively. A new "π-bonded chain model" proposed by Pandey[10] gives a single dangling-bond band with a positive dispersion from $\bar{\Gamma}$ to $\bar{J}$. The dispersion relation obtained from this chain model is similar to the experimental dispersion presented here, and is also consistent with the existence of only one experimental dangling-bond band.

Angle-resolved photoemission spectra were measured in a UHV chamber at a pressure of 5×10^{-11} Torr. The photoelectrons were excited with use of monochromatized 10.2-eV radiation from a hydrogen discharge. The electrons emitted were energy analyzed by a 180° spherical deflection analyzer rotatable in the plane of light incidence. Monochromator slits and analyzer voltages were set to give a combined energy resolution of ≤ 0.15 eV in the recorded spectra.

The samples were made from a Si(111) single crystal of p type ($\rho \sim 43\ \Omega$ cm), cut into bars with a square cross section of 5×5 mm^2. The Si(111) bars were cleaved in UHV and on each bar three different cleavages could be made.

Angle-resolved spectra were obtained from both single and multidomain cleavages.[11] In contrast to some earlier reports,[8] we have found a very high degree of reproducibility of the electronic structure for different cleavages. For surfaces with more than one domain, the spectra are con-

cerning the dangling-bond peak just superpositions of the contributions from the different domains. In fact, we use the photoemission spectra to check the domain distribution over the surface, and use low-energy electron diffraction as an additional tool to confirm the surface domain assignment after the photoemission studies. The Fermi-level (E_F) reference was obtained by photoelectron emission from the Mo sample holder to an accuracy of ± 0.05 eV.

In Fig. 1 is shown a series of angle-resolved photoemission spectra for different angles of electron emission (θ_e). The azimuthal angle has been chosen such that the electron momentum parallel to the surface ($\bar{k}_{\parallel}$) is directed along the $\bar{\Gamma}$-$\bar{J}$ symmetry line in the 2×1 SBZ. In these spectra, there is one dominating structure denoted A which corresponds to the dangling-bond surface state. The initial-state energy position at $\bar{\Gamma}$ ($\theta_e = 0$) is ~0.75 eV below E_v. The valence-band edge, E_v, has been obtained by comparing

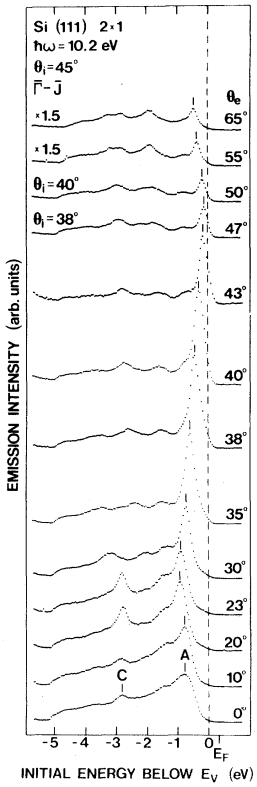

FIG. 1. Angle-resolved photoemission spectra for different electron emission angles (θ_e) along the $\bar{\Gamma}-\bar{J}$ symmetry line in the 2×1 SBZ. Peak A corresponds to the dangling-bond surface state. All displayed spectra are reproductions of the original ones showing the correct relative intensities.

the position of the bulk structure C for normal emission with the position of C for the Si(111) 7×7 surface.[1] This gives $E_F - E_v \approx 0.36$ eV.

The initial-state energy position for the dangling-bond peak moves downwards slightly from normal emission to $\theta_e \approx 23°$, which corresponds to ~0.5 of the $\bar{\Gamma}$-$\bar{J}$ distance. From its minimum the initial-state energy position disperses rapidly upwards to reach its highest energy 0.10 eV below E_v at the $\bar{J}$ symmetry point ($\theta_e = 47°$). For emission angles $\theta_e > 47°$ the surface state disperses downwards, showing symmetry in energy position around the $\bar{J}$ point. The dispersion relation for the dangling-bond band along the $\bar{\Gamma}$-$\bar{J}$ symmetry line is shown in Fig. 2, where the 2×1 SBZ appears in the inset. For $\bar{k}_{\parallel}$ values close to $\bar{\Gamma}$ we have drawn the dispersion with a dashed line, indicating an uncertainty in the peak positions. This uncertainty is due to the existence of a back-bond surface state which is close to or degenerate in initial-state energy with the dangling-bond state near $\bar{\Gamma}$.[1]

The existence of *two* flat dangling-bond bands has been suggested from photoemission experiments[2]; one band lying 0.7 eV below E_v with strong emission intensity near $\bar{\Gamma}$, and the other 0.15 eV below E_v with strong emission intensity near $\bar{J}$. However, the intensity variations in the emission from the two bands proposed was such that it appeared as if there was one strong peak dispersing from −0.7 eV at $\bar{\Gamma}$ to −0.15 eV at $\bar{J}$.

In Fig. 3 we show three spectra for $\theta_e = 23°$, 35°, and 47°, respectively, with an extended energy scale. The spectrum for $\theta_e = 23°$ shows the

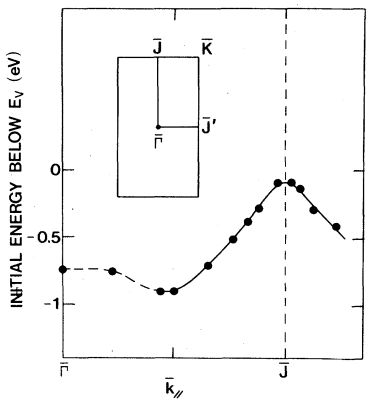

FIG. 2. Initial-state energy dispersion for the dangling-bond band along the $\bar{\Gamma}-\bar{J}$ symmetry line in the 2×1 SBZ, as obtained from the energy positions of peak A in Fig. 1. Also shown is the 2×1 SBZ with the symmetry points indicated.

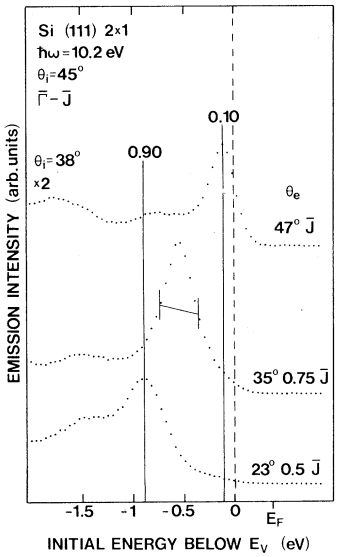

FIG. 3. Spectra showing the initial-state energy position and width of the dangling-bond surface-state peak (A) at three $\bar{k}_{\parallel}$ points on the $\bar{\Gamma}-\bar{J}$ symmetry line. The $\bar{k}_{\parallel}$ points correspond to the minimum ($\theta_e = 23°$), intermediate ($\theta_e = 35°$), and maximum ($\theta = 47°$) initial-state energy positions. The FWHM (0.4 eV) of the surface state at the intermediate energy position is much smaller than the energy difference between maximum and minimum peak positions (0.8 eV).

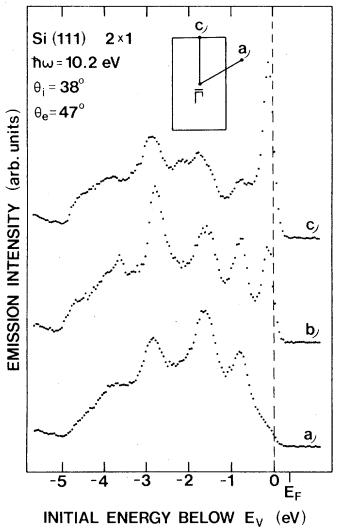

FIG. 4. The dangling-bond peak position is found at -0.75 eV for an electron emission angle of 47° in an azimuthal direction 60° from the $\bar{\Gamma}-\bar{J}$ symmetry line, as shown in spectrum a. At the $\bar{J}$ symmetry point the dangling-bond peak is found at -0.10 eV, spectrum c. Spectrum b which was obtained from a multidomain surface shows two dangling-bond peaks which are just the superposition of the dangling-bond peaks corresponding to the two $\bar{k}_{\parallel}$ points a and c in the 2×1 SBZ in the inset.

lowest initial-state energy position for the dangling-bond state. The spectrum for $\theta_e = 47°$ shows the peak position at $\bar{J}$ and for $\theta_e = 35°$ the peak has an intermediate energy position. The full width at half maximum (FWHM) for the peaks at $\theta_e = 23°$, 35°, and 47° are 0.5, 0.4, and 0.3 eV, respectively. If one assumes the existence of two flat bands, the peak for $\theta_e = 35°$ would then be due to the superposition of the peaks at 0.90 and 0.10 eV below E_v. From the FWHM's and the separation between these two peaks it is clear that such a superposition results in a *two*-peak structure.

In the spectrum for $\theta_e = 47°$, there is a weak peak on the low-energy side of the dangling-bond peak at about 0.75 eV below E_v. A shoulder at approximately this initial-energy position was observed near the $\bar{J}$ point in Ref. 2 and was there interpreted as being due to the lower-lying dangling-bond band. Having studied the intensity variation of this peak with different surface conditions, we conclude that the appearance of the peak in our spectra is due to multidomain effects. If more than one 2×1 domain is present on the surface, we will get a superposition of the dangling-bond emission from the $\bar{\Gamma}$-$\bar{J}$ symmetry line and a direction 60° from that line in the SBZ. Spectrum a in Fig. 4 was obtained for an electron emission angle $\theta_e = 47°$ along an azimuthal direction 60° from the $\bar{\Gamma}$-$\bar{J}$ line. In this spectrum the dangling-bond peak is observed at -0.75 eV, which is the same position as for the additional peak near $\bar{J}$ (see spectrum c). Spectrum b in Fig. 4 was obtained on a sample where the multidomain effect was large, giving rise to two peaks of about the same intensity at -0.10 and -0.75 eV. This spectrum also shows that the two peaks with an energy difference of 0.65 eV, which is less than the difference between the maximum and minimum energy positions of the dangling-bond band, appear to be well separated and cannot possibly give rise to a single peak at an intermediate initial-state energy. The choice of a light incidence angle (θ_i) of 38° has made the -0.75 eV peak near $\bar{J}$ appear as separated from the -0.10 eV peak. For $\theta_i = 50°$ the emission intensity of the -0.10 eV peak increases by a factor of 1.4 making the -0.75 eV peak appear as a shoulder on the low-energy side of the dangling-bond peak, with a shape similar to that of the spectrum near $\bar{J}$ in Ref. 2. Experimental data have thus shown that there exists only one dangling-bond band, with a bandwidth of 0.8 eV along

the $\bar{\Gamma}$-$\bar{J}$ symmetry line.

By reinterpreting the experimental data in Ref. 2 as being due to a single dangling-bond band with a large positive dispersion, one obtains a unified picture of the dangling-bond dispersion along the $\bar{\Gamma}$-$\bar{J}$ line. The energy positions of -0.75 eV at $\bar{\Gamma}$ and -0.10 eV at $\bar{J}$ reported here are in good agreement with -0.70 eV at $\bar{\Gamma}$ and -0.15 eV at $\bar{J}$ from Ref. 2. We have though obtained a larger value for the total bandwidth (0.8 eV compared with 0.55 eV). This difference is due to the fact that we observe a minimum in the initial-state energy position for $\bar{k}_{\parallel}$ values for which no data are presented in Ref. 2.

The suggested existence of *two* dangling-bond bands led to the consideration of electron correlation effects for the Si(111) 2×1 surface.[12,13] Including correlation effects for the 2×1 buckling model leads to a splitting of the dangling-bond band into *two* spin-polarized bands with negative dispersion. The experimental evidence of *one* dangling-bond band presented here removes the experimental basis for introducing correlation effects for the Si(111) 2×1 reconstructed surface.

After establishing the one-electron band picture of the Si(111) 2×1 dangling bond and its large positive dispersion, a reevaluation of the buckling model seems necessary. A larger positive disperison for the dangling-bond band is expected for a reconstruction where the dangling bonds overlap more strongly than can be obtained with the buckling model. The π-bonded chain model recently suggested by Pandey[10] gives such an increase in overlap, and the resulting dispersion shows reasonable agreement with the results presented here concerning shape and bandwidth. Along the $\bar{\Gamma}$-$\bar{J}'$ line we find a dangling-bond band with very small dispersion, and at the $\bar{K}$ point the initial-state energy is about 0.1 eV higher than at the $\bar{J}$ point. These results are also consistent with the calculated bands for the chain model.

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[1]R. I. G. Uhrberg, G. V. Hansson, J. M. Nicholls, and S. A. Flodström, in Proceedings of the Fourth European Conference on Surface Science, Münster, 1981, edited by K. Müller (to be published in Surface Science).

[2]F. J. Himpsel, P. Heimann, and D. E. Eastman, Phys. Rev. B 24, 2003 (1981).

[3]K. C. Pandey and J. C. Phillips, Phys. Rev. Lett. 34, 1450 (1975).

[4]S. Ciraci and I. P. Batra, Solid State Commun. 18, 1149 (1976).

[5]M. Schlüter, J. R. Chelikowsky, S. G. Louie, and M. L. Cohen, Phys. Rev. B 12, 4200 (1975).

[6]G. V. Hansson, R. Z. Bachrach, R. S. Bauer, D. J. Chadi, and W. Göpel, Surf. Sci. 99, 13 (1980).

[7]F. Houzay, G. M. Guichar, R. Pinchaux, and Y. Petroff, J. Vac. Sci. Technol. 18, 860 (1981).

[8]A. W. Parke, A. McKinley, and R. H. Williams, J. Phys. C 11, L993 (1978); A. W. Parke, A. McKinley, R. H. Williams, and G. P. Srivastava, J. Phys. C 13, L369 (1980).

[9]J. E. Rowe, M. M. Traum, and N. V. Smith, Phys. Rev. Lett. 33, 1333 (1974); M. M. Traum, J. E. Rowe, and N. V. Smith, J. Vac. Sci. Technol. 12, 293 (1975).

[10]K. C. Pandey, Phys. Rev. Lett. 47, 1913 (1981).

[11]The cleavages described as single-domain surfaces exhibited one domain over an area larger than 3×3 mm^2 which is a factor of 4 larger than the light spot. Multidomain diffraction spots were always observed near at least one of the crystal edges.

[12]R. Del Sole and D. J. Chadi, Phys. Rev. B 24, 7431 (1981).

[13]J. E. Northrup, J. Ihm, and M. L. Cohen, Phys. Rev. Lett. 47, 1910 (1981).