PHYSICAL REVIEW B VOLUME 36, NUMBER 11 15 OCTOBER 1987-I

Unoccupied surface-state band on Si(111) 2×1

P. Perfetti,* J. M. Nicholls,† and B. Reihl
IBM Research Division, Zurich Research Laboratory, 8803 Rüschlikon, Switzerland

(Received 24 February 1987)

Employing k-resolved inverse-photoemission spectroscopy, we have measured the dispersion of the unoccupied electronic surface-state band of cleaved single-domain Si(111) 2×1 along the $\bar{\Gamma}$-$\bar{J}$ and $\bar{\Gamma}$-$\bar{J}'$ symmetry directions. The energy dispersion and general shape of the measured surface-state band agree well with the calculated band of the π-bonded chain model.

Investigations of the reconstructed Si(111) 2×1 surface have in recent years focused on the question whether the π-bonded chain model, originally suggested by Pandey,[1] can describe the electronic and geometric properties better than any other model and in particular the buckling-type[2] models of atomic arrangement at the surface. Total-energy arguments favored the chain model theoretically,[1] while one of its first experimental supports came from angle-resolved photoemission measurements[3] of the occupied surface-state bands. Their energy dispersion could not be reconciled with the bands calculated within any plausible buckling model.[1] Soon afterwards, an improved experimental determination of the occupied surface-state dispersion[4] was shown to be in excellent agreement with the bands calculated,[5] employing pseudopotential total-energy calculations for the energy-minimized geometries of the π-bonded chain reconstruction of Si(111) 2×1. In the meantime, other techniques like optical reflectivity,[6] ion channeling,[7] and scanning tunneling microscopy[8] (STM) have lent strong support to the chain model and excluded the buckling models.[2] On the other hand, it has been concluded from low-energy electron diffraction (LEED) studies[9,10] that quite a large buckling within the π-bonded chains must be present in order to explain the experimental data.

Here, we present k-resolved inverse-photoemission measurements which allow determination of the energy dispersion $E(k_{\parallel})$ of an unoccupied surface-state band, corresponding to the antibonding surface-state band of the π-bonded chain model along the $\bar{\Gamma}$-$\bar{J}$ and $\bar{\Gamma}$-$\bar{J}'$ directions of the surface Brillouin zone (SBZ); $k_{\parallel}$ denotes the wave vector parallel to the surface. We find good agreement with the calculated antibonding-band dispersion of the energy-minimized π-bonded chain model.[5,11]

The π-bonded chain model predicts[1] a semiconducting Si(111) 2×1 surface with bonding and antibonding surface-state bands which have a large dispersion $E(k_{\parallel})$ along the $\bar{\Gamma}$-$\bar{J}$ direction of the SBZ, i.e., along the direction of the chains. This reflects the strong interaction of silicon dangling bonds within the chains, and causes the asymmetry observed in optical spectroscopy with light polarized parallel and perpendicular to the chains.[6] In these experiments, optical transitions from the occupied to the unoccupied surface states are monitored. A surface-state band gap of 0.45 eV occurring along the $\bar{J}$-$\bar{K}$ direction, i.e., the SBZ border line, is thus obtained. This number agrees with angle-resolved photoemission results[12] from a highly doped (n-type) Si sample in which the empty surface-state band is partially filled near the $\bar{J}$ point, pinning the Fermi level. Also recent photoemission experiments[13] in which the antibonding state is filled by laser pumping arrive at this figure of 0.45 eV which is, however, at variance with the value of 0.25 eV calculated.[5] In addition, I-V curves measured with the scanning tunneling microscope gave 0.45 eV as a tunneling gap which could be associated with the surface-state band gap.[8] The agreement between the optical-spectroscopy results and the values obtained by photoemission and tunneling spectroscopy suggest that excitonic effects play a minor role in the absorption process. Or, if they were present, their magnitude ought to be much smaller than the limit of accuracy in the various experimental techniques.[8,12,13] Recent electron-energy-loss spectroscopy[14] (EELS) and optical-absorption measurements[15] found a temperature dependence of the electronic transitions across the surface-state band gap, which could be identified with localized excitations with a strong electron-lattice interaction. However, these effects are also too small ($\sim$20 meV) compared to the band-gap energy, and their presence could not be clearly established in a comparison[15] between optical absorption and direct photoemission. In the present k-resolved inverse-photoemission experiment, we can therefore expect to obtain an unoccupied surface-state band dispersion with a minimum energy position at the $\bar{J}$ point, yielding a band gap consistent with those found by the other techniques. So far, only normal-incidence inverse photoemission[16,17] on Si(111) 2×1 has been performed, which showed the surface-state energy at $\bar{\Gamma}$ to be 0.9 above the Fermi level.

The inverse-photoemission experiments were performed in a two-chamber vacuum system described elsewhere.[18] Electrons from a custom-built electron gun impinged on the sample surface at a polar angle θ with respect to the surface normal. The beam divergence was better than 3°, resulting in $\Delta k_{\parallel} < 0.1$ Å^{-1}. Outcoming photons were filtered and monitored at an isochromat energy of $h\nu = 9.5$ eV with a Geiger-Müller counter. The total-energy resolution (electrons and photons) was 0.35 eV as determined from the 90%-to-10% Fermi-level onset of an inverse-photoemission spectrum from a polycrystalline Ta foil. This foil could easily be interchanged with the Si sample, and was used to periodically check the Fermi level which defines the energy zero, $E_F \equiv 0$. Essential in the present investigation was the single-domain character of the Si(111) 2×1 surface. We used the identical cleavage device as in Refs. 4 and 12. The $\langle 111 \rangle$-oriented Si rods (p doped, ~ 0.3 Ω cm) were cleaved along the $\langle \bar{2}11 \rangle$ direction in a vacuum better than 1×10^{-10} Torr to produce flat 4×5-mm^2 surfaces. In eight out of ten cleavages, LEED exhibited a sharp single-domain 2×1 pattern with low background intensity over the whole surface. LEED was also used to set the azimuthal orientation for the k-resolved inverse-photoemission measurements, i.e., polar-angle changes along or parallel to the π-bonded chains, which are the $\bar{\Gamma}$-$\bar{J}$ and $\bar{\Gamma}$-$\bar{J}'$ directions of the SBZ, respectively.

Two among several reproducible sets of k-resolved inverse-photoemission data taken as a function of θ are presented in Figs. 1 and 2. At normal incidence ($k_\parallel = 0$), we note an emission feature at 0.9 eV above the Fermi level, which could be quenched by exposing the clean Si(111) 2×1 surface to hydrogen activated by a hot filament, until a 1×1 LEED pattern was obtained (solid versus dashed curves in Fig. 1). Such behavior, characteristic of surface states in general,[18] has been observed for Si(111) 2×1 before.[16,17] Presented here are measurements of the dispersion of this surface-state feature along the $\bar{\Gamma}$-$\bar{J}'$ direction in Fig. 1 and along the $\bar{\Gamma}$-$\bar{J}$ direction in Fig. 2. To obtain a better determination of the surface-state peak positions, we have performed difference curves of the clean and hydrogen-covered spectra which are shown as solid and dashed curves, respectively (only in Fig. 1 for clarity). The surface-state peak positions obtained in this manner are shown as vertical bars in Figs. 1 and 2. The uncertainty in the vertical-bar positions is ± 0.05 eV, except for the 15° and 20° curves in Fig. 1, where it is ± 0.1 eV. While we observe a rather small energy dispersion of 0.2 eV along $\bar{\Gamma}$-$\bar{J}'$, we find a stronger dispersion of about 1 eV along $\bar{\Gamma}$-$\bar{J}$, similar to the differences observed along these two directions for the occupied surface-state band.[4] The minimum-energy position of 0.25 eV is found for $\theta = 45°$ corresponding to the $\bar{J}$ point of the SBZ at $k_\parallel = 0.82$ Å^{-1}. Around this critical point, the surface-state feature exhibits the strongest spectral intensity (cf. Fig. 2) as long as it falls within the projected bulk band gap.[5] For $\theta < 30°$, the feature approaches the bulk bands and is less pronounced, as it becomes a surface resonance for

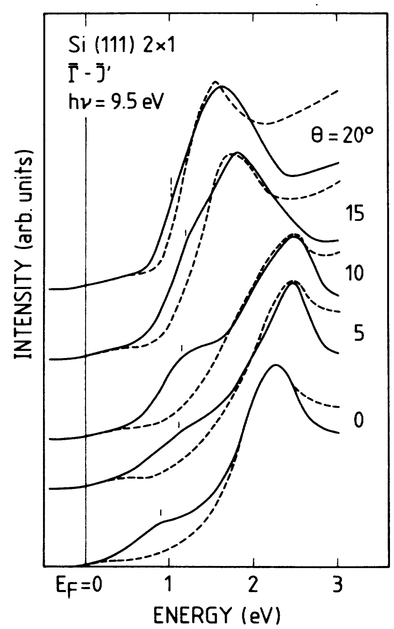

FIG. 1. k-resolved inverse-photoemission spectra at $h\nu = 9.5$ eV as a function of polar angle θ along the $\bar{\Gamma}$-$\bar{J}'$ direction. Solid curves are from the clean Si(111) 2×1 surface. Dashed curves are from the Si(111)-H 1×1 surface produced by exposing the clean surface to about 600 L of hydrogen activated by a hot filament. The peak positions of the surface-state emission are indicated by vertical bars obtained from the difference curves of the clean and hydrogen-covered spectra. The uncertainty is ± 0.05 eV for the 5° and 15° spectra, and ± 0.1 eV for the 0°, 15°, and 20° spectra.

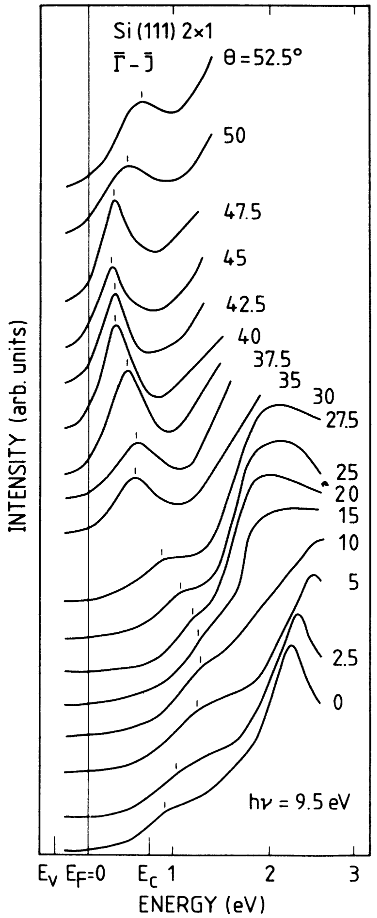

FIG. 2. k-resolved inverse-photoemission spectra at $h\nu = 9.5$ eV as a function of θ for the $\bar{\Gamma}$-$\bar{J}$ direction. The peak positions (vertical bars) are again obtained from difference curves of the clean and hydrogen-covered (not shown) spectra. Their uncertainty is ± 0.05 eV except for the 0°, 2.5°, and 5° spectra where it is ± 0.1 eV. Note the stronger energy dispersion of about 1 eV of the surface-state emission. See text for details.

$k_{\|} < 0.6 d_{\bar{\Gamma}-\bar{J}}$ in agreement with the calculations.[5] The maximum energy position, 1.22 eV above the Fermi level, also appears in this $k_{\|}$ region (see the $\theta = 10°$ spectrum in Fig. 2, which corresponds to $k_{\|} = 0.27 d_{\bar{\Gamma}-\bar{J}}$). The spectral feature at higher energies, e.g., at 2.33 eV in the normal-incidence spectrum, corresponds to the bulk L_1^c critical point discussed in detail elsewhere.[17]

The $E(k_{\|})$ dispersion curves of the surface-state features in Figs. 1 and 2 are plotted in Fig. 3 where strong features are marked as solid dots and weaker features by open circles. The solid line represents the calculated surface-state band of Pandey[11] using the π-bonded chain model for a fully energy-optimized geometry. We have chosen these theoretical results, since they were done for both symmetry directions $\bar{\Gamma}-\bar{J}$ and $\bar{\Gamma}-\bar{J}'$. The agreement with our experimental dispersion curves is quite good. Slightly better agreement between theory and experiment may be obtained for the $\bar{\Gamma}-\bar{J}$ direction if the calculated band of Northrup and Cohen[5] is used.

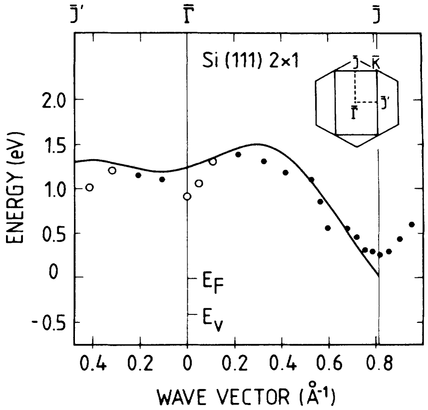

FIG. 3. Plot of the experimental energy dispersion of the surface-state emission from Figs. 1 and 2 (solid dots and open circles). Note the symmetric shape of the data plot around the $\bar{J}$ point. The solid line represents the energy dispersion calculated within the π-bonded chain model (from Pandey, Ref. 11). The inset shows the 1×1 and 2×1 surface Brillouin zones. Also indicated is the position of the valence-band edge $E_V = E_F - 0.40$ eV (from Ref. 19).

The experimentally derived unoccupied surface-state band is 0.25 eV above the Fermi level at $\bar{J}$ (cf. Fig. 3). The occupied surface-state band at $\bar{J}$ was determined[4] to be at $E_V - 0.1$ eV, where E_V denotes the valence-band edge measured[19] to be $E_F - E_V = 0.40$ eV. Altogether this could result in a surface-state band gap at $\bar{J}$ of 0.75 eV, a figure which is 0.3 eV higher than the optical-transition energy[6] and the value obtained by photoemission from highly doped silicon.[12] In this context, we note that the band gaps calculated within the local-density scheme [0.25 eV for the π-bonded chain model of Si(111) 2×1; Refs. 5 and 11] are normally underestimated, and direct comparison with experiment is not possible.[20]

Owing to our limited energy and $k_{\|}$ resolution of 0.35 eV and 0.1 Å^{-1}, respectively, we cannot completely rule out that the surface-state peak at $\bar{J}$ may be closer to E_F than actually measured in Fig. 2. However, we believe that part of this discrepancy is real and compare with the analogous inverse-photoemission[21] study of Ge(111) 2×1 where the surface-state band gap at $\bar{J}$ is deduced to be 0.15 eV larger than the 0.5 eV derived from optical-reflectivity[22] and direct-photoemission[23] measurements. Also in the case of GaP(110), inverse-photoemission results[24] for the minimum surface-state position at the $\bar{X}$ point arrive at a gap energy about 0.5 eV larger than the optical gap when combined with photoemission findings.[25] For strongly doped SrTiO$_3$, a comparison between direct and inverse photoemission[26] gives a band gap which is 1.5 eV larger than the optical gap.

Discrepancies of up to 0.5 eV between optical excitation energies and the corresponding energy difference as obtained from direct and inverse photoemission have also been derived for the unoccupied critical-point energies in bulk silicon[17] and attributed to a possible excitonic lowering of the optical transition. However, from temperature-dependent experimental as well as theoretical studies,[12,14,15] it seems that excitonic effects involved in energy absorption across the band gap are rather small. They are of the order that they cannot be determined from a comparison of absorption energies with the energy differences between the filled surface-state band found in direct photoemission and the empty band found with inverse photoemission.

In EELS (Ref. 14) and STM (Ref. 8) experiments, for example, it has been shown that empty electronic states may be present within the surface-state band gap for cleaves with high defect density. Such so-called extrinsic surface states could, in principle, pin the Fermi level, whereby the unoccupied surface-state dispersion would move to higher energies. On cleaves of good quality, it has been shown though that the Fermi level is pinned by the unoccupied surface-state band, independent of doping,[12] and this is most likely the case for the surfaces in the present study.

Finally, we note that the discrepancy found for the surface-state band gap may reflect the response of the electronic system to the photohole or additional electron in photoemission and inverse photoemission, respectively. The associated screening energies by which the ionization energy of an occupied level and the affinity energy of an unoccupied level will be altered are not accounted for in the one-electron calculations for the ground-state properties of semiconductors, although recently a controversy has arisen how big the energy deviations may be in the different approximations used within the local-density calculations (Ref. 20 versus 27).

In summary, inverse photoemission gives good agreement between the measured energy dispersion of the unoccupied surface-state band on Si(111) 2×1 and the dispersion calculated for the π-bonded chain model with respect to its overall shape, bandwidth, and energy position. Discrepancies up to 0.3 eV between the surface-state band gaps obtained by comparing direct and inverse photoemission with optical spectroscopy indicate the possible existence of relaxation effects. A continued theoretical and experimental effort is needed for a complete understanding of such effects.

We are grateful to A. Baratoff for helpful discussions, and G. Chiarotti and M. Morelli for their interest and support. We thank M. Tschudy for his expert technical assistance.

---

[*] Permanent address: Istituto di Struttura della Materia, Consiglio Nazionale delle Richerche, Via E. Fermi 38, 00044 Frascati, Italy.

[†] Present address: Royal Institute of Technology, Material Science, 10044 Stockholm, Sweden.

[1] K. C. Pandey, Phys. Rev. Lett. **47**, 1913 (1981); **49**, 223 (1982).

[2] D. Haneman, Phys. Rev. **121**, 1093 (1961); Adv. Phys. **31**, 165 (1982).

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

[4] R. I. G. Uhrberg, G. V. Hansson, J. M. Nicholls, and S. A. Flodström, Phys. Rev. Lett. **48**, 1032 (1982).

[5] J. E. Northrup and M. L. Cohen, Phys. Rev. Lett. **49**, 1349 (1982).

[6] P. Chiaradia, A. Cricenti, S. Selci, and G. Chiarotti, Phys. Rev. Lett. **52**, 1145 (1984).

[7] R. M. Tromp, L. Smit, and J. F. van der Veen, Phys. Rev. Lett. **51**, 1672 (1983).

[8] R. M. Feenstra, W. A. Thompson, and A. P. Fein, Phys. Rev. Lett. **56**, 608 (1986); J. A. Stroscio, R. M. Feenstra, and A. P. Fein, *ibid.* **57**, 2579 (1986).

[9] R. Feder and W. Mönch, Solid State Commun. **50**, 311 (1984).

[10] F. J. Himpsel, P. M. Marcus, R. Tromp, I. P. Batra, M. R. Cook, F. Jona, and H. Liu, Phys. Rev. B **30**, 2257 (1984).

[11] K. C. Pandey, Physica **117&118B**, 761 (1983).

[12] P. Mårtensson, A. Cricenti, and G. V. Hansson, Phys. Rev. B **32**, 6959 (1985).

[13] J. Bokor, R. Storz, R. R. Freeman, and P. H. Bucksbaum, Phys. Rev. Lett. **57**, 881 (1986).

[14] N. J. DiNardo, J. E. Demuth, W. A. Thompson, and P. H. Avouris, Phys. Rev. B **31**, 4077 (1985).

[15] F. Ciccacci, S. Selci, G. Chiarotti, and P. Chiaradia, Phys. Rev. Lett. **56**, 2411 (1986).

[16] B. Reihl, in Trieste International Symposium on Surface Spectroscopy of Adsorbates, Miramare-Trieste, Italy, 1984 (unpublished).

[17] D. Straub, L. Ley, and F. J. Himpsel, Phys. Rev. Lett. **54**, 142 (1985); Phys. Rev. B **33**, 2607 (1986).

[18] B. Reihl, Surf. Sci. **162**, 1 (1986).

[19] F. J. Himpsel, G. Hollinger, and R. A. Pollak, Phys. Rev. B **28**, 7014 (1983).

[20] M. Lannoo, M. Schlüter, and L. J. Sham, Phys. Rev. B **32**, 3890 (1985); R. W. Godby, M. Schlüter, and L. J. Sham, Phys. Rev. Lett. **56**, 2415 (1986).

[21] J. M. Nicholls and B. Reihl (unpublished).

[22] S. Nannarone, P. Chiaradia, F. Ciccaci, R. Memeo, P. Sassaroli, S. Selci, and G. Chiarotti, Solid State Commun. **33**, 593 (1980).

[23] J. M. Nicholls, P. Mårtensson, and G. V. Hansson, Phys. Rev. Lett. **54**, 2363 (1985).

[24] P. Perfetti, T. Riesterer, M. Tschudy, and B. Reihl, Surf. Sci. **189/190**, 556 (1987).

[25] F. Sette, P. Perfetti, F. Patella, C. Quaresima, C. Capasso, M. Capozi, and A. Savoia, Phys. Rev. B **28**, 4882 (1983).

[26] B. Reihl, J. G. Bednorz, K. A. Müller, Y. Jugnet, G. Landgren, and J. F. Morar, Phys. Rev. B **30**, 803 (1984).

[27] O. Gunnarsson and K. Schönhammer, Phys. Rev. Lett. **56**, 1968 (1986).