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by

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Abstract

Using polarization dependent angle-resolved photoemission we show that a dominant structure in the spectra at a photon energy of 10.2 eV, earlier interpreted as a back-bond surface state, is due to direct transitions from the uppermost valence band. Direct transitions from the second highest valence band are also identified. The final state band for these transitions is found to have free-electron-like dispersion.

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The surface electronic structure of semiconductors has been studied extensively, both experimentally and theoretically, during recent years. In trying to determine the correct model for reconstructed semiconductor surfaces, not only the dangling-bond but also back-bond surface states are considered. For Si(111) 2x1 there is a dominant structure in the photoemission spectra originally reported by Rowe et al /1/, which has been discussed by many authors as a back-bond surface state /2/.

Using highly polarized synchrotron radiation, we show that this structure is due to a direct transition from the uppermost valence band to a final band with free-electron-like dispersion. Thus this structure should not be considered when comparing experimental with calculated surface state dispersions for different reconstruction models of the Si(111) 2x1 surface. We also report on another structure which corresponds to a direct transition from the second highest valence band to the same final band. For these two structures, the initial-state energy dispersions with momentum parallel to the surface, $E_i(\bar{k}_{//})$, compare favourably with calculated dispersions.

The experiments were performed in a VG ADES 400 spectrometer using synchrotron radiation from the DORIS II storage ring at HASYLAB, DESY /3/. Si(111) single crystals of p-type ($\varrho \sim 43\ \Omega\mathrm{cm}$) were cleaved in the UHV chamber at a pressure of $\sim 1\times10^{-10}$ Torr. In the 10.2 eV spectra the total energy resolution was $\lesssim 0.2$ eV. The initial energies have been referenced to the valence band maximum (VBM) by comparing the energy of the bulk structure A for 10.2 eV photon energy in Fig. 1a with that for Si(111) 7x7 as discussed elsewhere /4,5/.

The emitted electrons were analyzed in the $(1\bar{1}0)$ mirror plane with $\bar{k}_{//}$ in the $[11\bar{2}]$ azimuthal direction (same as in Ref. 1). Two different geometries were used in the measurements.

1. Normal light incidence ($\theta_i = 0^0$) with the polarization vector lying in the $(1\bar{1}0)$ mirror plane, parallel to the [112] direction. For emission angles (θ_e) between 0^0 and 10^0, $\theta_i = 15^0$ was used. This geometry will be referred to as the $\bar{A}_{//}$-case.

2. Both the analyzer plane and the crystal were rotated 90° azimuthally compared to geometry 1. Because of experimental limitations, $\theta_i = 15^{\circ}$ was chosen instead of $\theta_i = 0^{\circ}$. This makes the light polarized mainly perpendicular to the mirror plane. This geometry will be referred to as the $\bar{A}_{\perp}$ -case.

Fig. 1a shows a set of normal emission spectra for the $\bar{A}_{//}$-case in the photon energy range 10.2 - 21.2 eV. The spectra are dominated by a dispersive peak B with initial-state energies from 0.60 to 1.60 eV below the VBM.

Fig. 1b shows the calculated band structure for Si along the Γ-L line (dashed lines), obtained from a self-consistent field LAPW calculation /6/. Both valence band (VB) 2 and VB:s 3,4 (degenerate along Γ-L) lie in the region of experimental initial energies. The use of VB 2 as initial-band gives an experimental final band that is extremely steep, incompatible with any calculated or assumed free-electron final bands. This makes us exclude VB 2 as a possible initial-band for direct transitions in this case.

The degenerate VB:s 3,4 would give an experimental final band with a realistic dispersion, but the calculated band width is not large enough to contain all experimental initial energies. The calculated L_3' point energy is -1.15 eV in good agreement with other calculations /7/, while the lowest initial-state energy deduced from the 21.2 eV spectrum is -1.60 eV.

In a recent photoemission study by Himpsel et al. /8/ the L_3' point was found at -1.5 eV from normal emission data, where the L_3 point is probed at a photon energy of 21 eV. From our 21.2 eV spectrum we find the L_3' point energy to be -1.6 eV in close agreement with the earlier experiment.

In Fig. 1b we have introduced an experimental valence band (solid line) which is lowered with respect to the calculated band. The lowering is proportional to the distance from Γ so that the L_3' point energy is -1.60 eV. Using this experimental valence band we can plot the final band shown

by the dots in Fig. 1b. The dispersion of the obtained final band shows little resemblence to the calculated conduction bands. Instead, the dispersion is free-electron-like.

To be able to calculate the initial-state energy dispersions $E_i(\bar{k}_{//})$, for direct transitions we have introduced the free-electron band corresponding to the $\bar{G}_{111}$ reciprocal lattice vector. This "primary cone" band has been fitted in energy to the experimental points. This gives the bottom of the free-electron bands at -12.1 eV. We have also assumed the lowering of VB:3 and 4, as described above, in the whole mirror plane.

We will now compare experimental with calculated $E_i(\bar{k}_{//})$ dispersions for direct transitions from VB:s 3 and 4 to the free-electron final band at a photon energy of 10.2 eV. Since angle-resolved photoemission spectra have been measured for both the $\bar{A}_{\perp}$ and $\bar{A}_{//}$ cases it is possible to use symmetry selection rules to determine the parity of the initial-states with respect to the mirror plane /9/.

Spectra obtained for the $\bar{A}_{\perp}$-case are shown in Fig. 2. There is one dominating structure C, dispersing downwards with increasing emission angle, and having maximum intensity around $\theta_e = 20^{\circ}$. This structure was originally reported by Rowe et. al. /1/. Both the dispersion (filled and open circles in Fig. 4) and intensity variations are in good agreement with the results in Ref. 1. This is the structure that has so far been interpreted as a surface state in the literature.

For the $\bar{A}_{\perp}$-case the initial-state should have odd parity which corresponds to the upper valence band, i.e. VB 4 /10/. The calculated $E_i(\bar{k}_{//})$ dispersion using this initial band is shown by the dashed line in Fig. 4. We find good agreement between experiment and calculation for both energy position and dispersion.

In the spectra for the $\bar{A}_{//}$-case (Fig. 3) in which even initial bands should be probed structure C is not observed. Instead we find the structure B which first disperses downwards to a local minimum in initial energy at ~20°, then upwards to a local maximum at ~40° and finally moves downwards again at higher emission angles. The experimental E_i ($\bar{k}_{//}$) dispersion is plotted in Fig. 4 as filled and open squares. The calculated dispersion using VB 3, which has even parity /10/, is shown by the dashed-dotted line in Fig. 4. Also, in this case the energy position and the general shape of the dispersion are well reproduced by the calculation. The energy positions of structures B and C coincide for transitions on the Γ-L line in the [11$\bar{1}$]-direction. This occurs for both the experimental and calculated dispersions at $\bar{k}_{//} \sim$ 0.7 $Å^{-1}$ (see Fig. 4).

A surface state interpretation of structures B and C is definitely ruled out by the significant changes in $E_i(\bar{k}_{//})$ dispersions with photon energy found in the photon energy range investigated (10.2, 13.0, 15.0 and 17.0 eV). Also for the higher photon energies the calculated dispersions are in good agreement with experiment /11/.

The polarization dependence and the good agreement with calculated dispersions make us interpret both structures B and C as direct transitions from the two highest valence bands to a free-electron-like final band. Our interpretation of structure C gives a natural explanation of the three-fold emission pattern observed /1,4/ instead of the 2x1 symmetry expected for a surface state. The sensitivity of structures B and C to contamination was found to be far less than for the dangling-bond surface state /4/.

In the present experiment the dangling-bond surface state is observed as a weak structure dispersing towards the valence band edge. Emission from the dangling-bond is suppressed for both the $\bar{A}_{//}$ and $\bar{A}_{\perp}$ cases because of the angles θ_e used (0° and 15° resp.). In our case the [11$\bar{2}$]-direction corresponds to the $\bar{\Gamma}$-$\bar{K}$ line in the 2x1 surface Brillouin-zone.

In summary, we have shown that our experimental results lead to the identification of the well-known "back-bond surface state" as instead being due to direct transitions from the uppermost valence band to a free-electron-like final band. The L_3' point in the valence bands was found at -1.6 eV, which is as much as 0.4 eV lower than in most energy band calculations.

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REFERENCES

1. 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).

2. It is described in practically every recent review article on surface states on semiconductors, see e.g. D.E. Eastman, J. Vac. Sci. Technol. 17, 492 (1980) and references 12, 13 and 27-30 therein.

3. C.A. Feldmann, R. Engelhardt, T. Permien, E.E. Koch and V.Saile, Nucl. Instrum. Methods 208, 785 (1983).

4. G.V. Hansson, R.I.G. Uhrberg and J.M. Nicholls, Surf. Sci. 132, 31 (1983).

5. In this paper we have used E_F-E_V = 0.59 eV for Si(111) 7x7. See F.J. Himpsel, Th. Fauster and G. Hollinger, Surf. Sci. 132, 22 (1983).

6. P.E.S. Persson, unpublished.

7. C.S. Wang and B.M. Klein, Phys. Rev. B24, 3393 (1981) and references therein.

8. F.J. Himpsel, P.Heimann and D.E. Eastman, Phys. Rev. B24, 2003 (1981).

9. J. Hermanson, Solid State Commun. 22, 9 (1977).

10. H. Becker and U. Gerhardt, Phys. Rev. B19, 2189 (1979).

11. R.I.G. Uhrberg et al, to be published.

FIGURE CAPTIONS

Fig. 1 a) Normal emission spectra from Si(111) 2x1 for various photon energies. Structure A was used to determine the valence band maximum. Structure B corresponds to a direct transition from the degenerate valence band 3,4.

b) Calculated band structure for silicon along the Γ-L symmetry line (dashed lines). The experimental final band for structure B (full circles) was obtained using the experimental valence-band (full line). The final band is approximated by the $\bar{k} + \bar{G}_{111}$ free-electron band.

Fig. 2 Photoemission spectra for different emission angles for the $\bar{A}_\perp$-case. Structure C corresponds to a direct transition from the uppermost, odd parity, valence band.

Fig. 3 Photoemission spectra for different emission angles for the $\bar{A}_{//}$-case. Structure B corresponds to a direct transition from the second highest, even parity, valence band.

Fig. 4 Experimental $E_i(\bar{k}_{//})$ dispersions for structure C (filled and open circles corresponding to strong and weak structures) and structure B (filled and open squares). The calculated dispersion for direct transitions from the odd and even parity valence bands (dashed and dashed-dotted lines) are in close agreement with experimental dispersions.

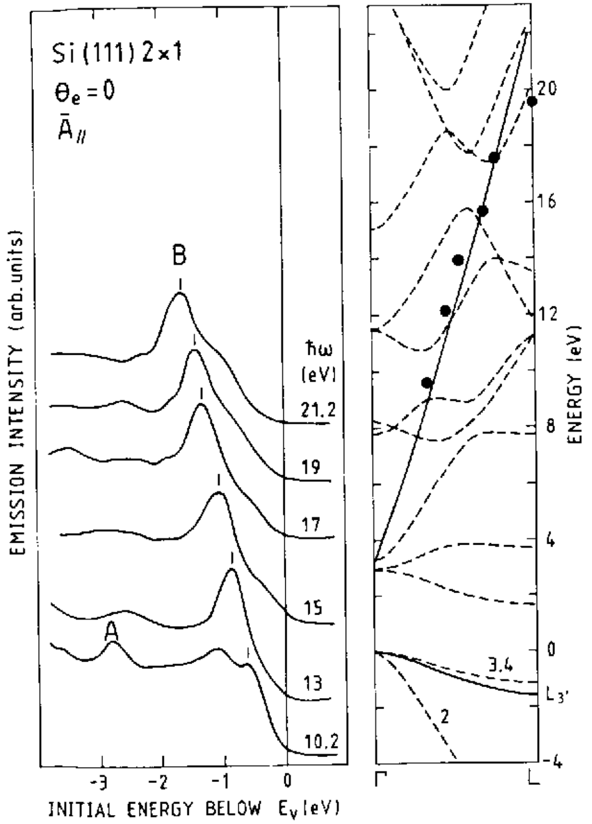
Si (111) 2×1
θe = 0
Ā//
B
A
ħω (eV)
21.2
19
17
15
13
10.2
-3
-2
-1
0
INITIAL ENERGY BELOW Ev (eV)
EMISSION INTENSITY (arb. units)
20
16
12
8
4
0
-4
3.4
2
L3'
Γ
L
ENERGY (eV)

Fig. 1 a. b.

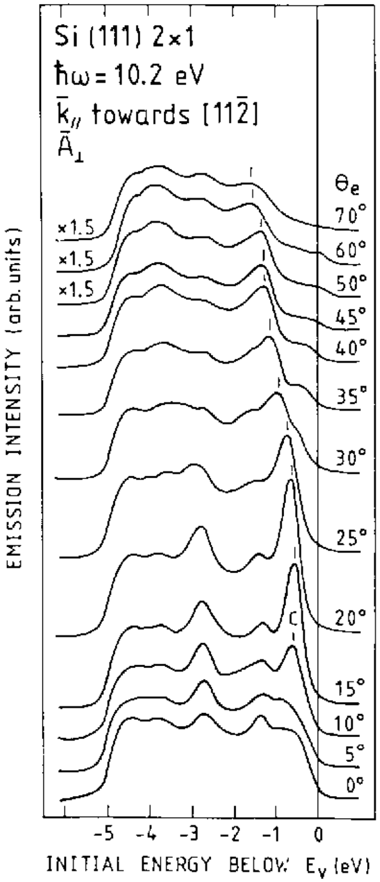
Si (111) 2×1
ħω = 10.2 eV
k̄// towards [11$\bar{2}$]
Ā⊥
θe
70°
60°
50°
45°
40°
35°
30°
25°
20°
15°
10°
5°
0°
×1.5
×1.5
×1.5
C
-5
-4
-3
-2
-1
0
INITIAL ENERGY BELOW Ev (eV)
EMISSION INTENSITY (arb. units)

Fig. 2

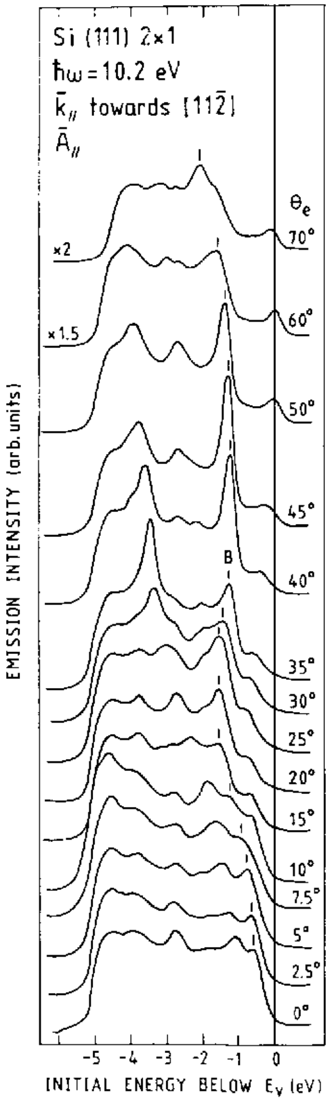
Si (111) 2×1
$\hbar\omega = 10.2$ eV
$\bar{k}_{\parallel}$ towards $[11\bar{2}]$
$\bar{A}_{\parallel}$
Θ_e
70°
×2
60°
×1.5
50°
45°
B
40°
35°
30°
25°
20°
15°
10°
7.5°
5°
2.5°
0°
EMISSION INTENSITY (arb. units)
-5 -4 -3 -2 -1 0
INITIAL ENERGY BELOW E_V (eV)

Fig. 3

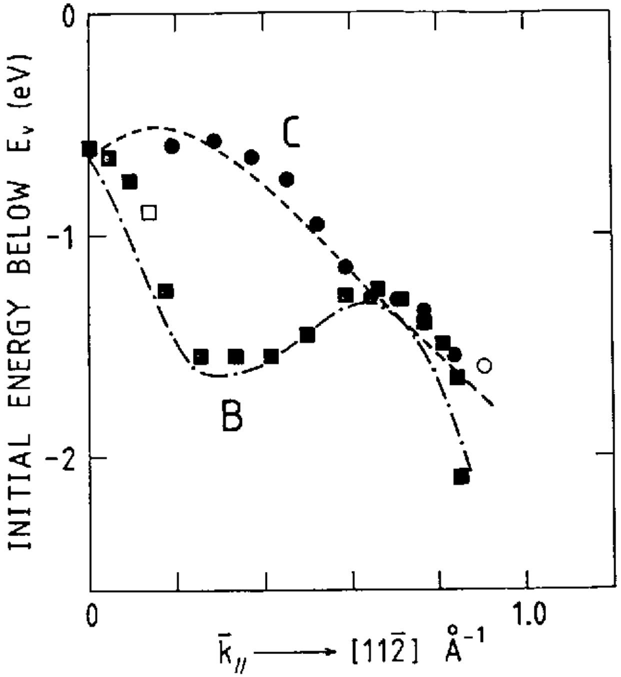
0
-1
-2
INITIAL ENERGY BELOW E_v (eV)
C
B
0
1.0
$\bar{k}_{\parallel} \longrightarrow [11\bar{2}]$ Å^{-1}

Fig. 4