RAPID COMMUNICATIONS

PHYSICAL REVIEW B VOLUME 32, NUMBER 10 15 NOVEMBER 1985

# Photoemission study of the antibonding surface-state band on Si(111)2×1

Per Mårtensson, Antonio Cricenti, and Göran V. Hansson

*Department of Physics and Measurement Technology, Linköping Institute of Technology, S-581 83 Linköping, Sweden*

(Received 29 July 1985)

Cleaved Si(111)2×1 surfaces of a heavily $n$-doped crystal have been studied with angle-resolved photoemission. A new surface state is observed at the Fermi level, only appearing close to the $\bar{J}$ points in the 2×1 surface Brillouin zone. The observed emission corresponds to the dispersion minimum of the antibonding band in the $\pi$-bonded chain model. The direct surface-state band gap is found to be 0.45 eV, in good agreement with results from absorption measurements. This indicates that excitonic effects are small in those measurements.

When silicon or germanium crystals are cleaved, the atoms on the surface rearrange into a 2×1 reconstruction. According to, e.g., the $\pi$-bonded chain model[1,2] of this reconstruction a filled bonding surface-state band is formed as well as an empty antibonding band. The energy dispersion of the bonding surface-state band on Si(111)2×1 has been studied previously using angle-resolved photoelectron spectroscopy.[3-5] Although the results from the different measurements are not in perfect agreement, they all support the $\pi$-bonded chain model.

Evidence for the existence of an empty antibonding state was first obtained in a photoconductivity measurement by Müller and Mönch[6] and in an optical-absorption measurement by Chiarotti, Nannarone, Pastore, and Chiaradia.[7] Further evidence has been obtained in experiments using techniques such as electron energy-loss spectroscopy,[8] photothermal displacement spectroscopy,[9] and polarization-dependent reflectivity.[10] Assuming that excitonic effects are small, the optical-absorption experiments give the value of the direct surface band gap. However, from the temperature dependence of energy-loss spectra[11] it has been suggested that excitonic effects cannot be neglected.

In a recent angle-resolved photoemission experiment on Ge(111)2×1 surfaces using highly $n$-doped Ge crystals, Nicholls, Mårtensson, and Hansson[12] have shown that it is possible to populate the antibonding surface-state band enough to make a direct observation in photoemission possible. From this experiment it is clear that, in the case of Ge, excitonic effects are weak in absorption measurements and that the position of the direct surface band gap is at the $\bar{J}$ point in the surface Brillouin zone (SBZ).

In this paper we present an angular-resolved photoemission study on cleaved highly $n$-doped Si crystals. The bonding and antibonding surface states have been observed simultaneously in the region around the $\bar{J}$ points in the 2×1 SBZ. The surface-state band gap is located at the $\bar{J}$ point, in agreement with the $\pi$-bonded chain model.[2] The measured value of the gap is in good agreement with the value obtained in absorption measurements,[6,9,10] implying that excitonic effects are not strong in those experiments.

Angle-resolved photoemission spectra were recorded in a UHV chamber at a pressure of $< 5\times10^{-11}$ Torr. Monochromatized 10.2-eV radiation from a hydrogen discharge lamp was used. The estimated combined energy resolution, determined by the analyzer voltages and the monochromator slit widths, was $\sim 50$ meV. A Si(111) rod, Sb doped ($\rho \sim 8$ m$\Omega$ cm, $N_D \sim 8\times10^{18}$ cm$^{-3}$), was cut into bars with a square cross section of 8×8 mm$^2$. The bars were cleaved along the $[2\bar{1}\bar{1}]$ crystal direction, and the distribution of the three possible domains on the surfaces was determined with photoemission and verified with low-energy electron diffraction (LEED) when the photoemission experiment was completed. Only areas that showed no multidomain spots in LEED and that were larger than the lightspot were used in the present experiment. The position of the Fermi level

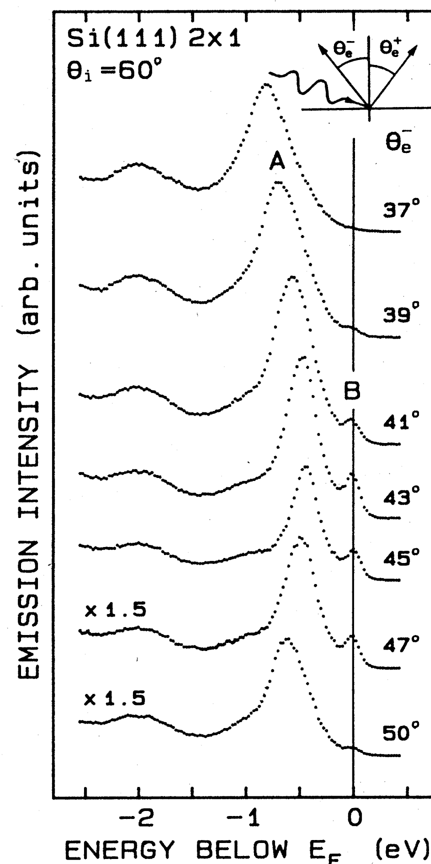


FIG. 1. Photoemission spectra recorded for various negative angles of emission ($\theta_e^-$) along the $\bar{\Gamma}$-$\bar{J}$ line in the 2×1 SBZ. The peak marked A corresponds to the bonding surface-state band ($\bar{J}$ at $\theta_e^- \approx 45°$) and the peak B to the antibonding band ($\bar{J}$ at $\theta_e^- \approx 43°$).



©1985 The American Physical Society

was determined to an accuracy of ±20 meV by photoemission from the metallic sample holder.

From high-resolution photoemission studies of the Si 2*p* core levels on Si(111)2×1,[13] it has been shown that for good-quality cleaves the Fermi level is pinned ~0.40 eV above the valence-band edge over a large range of doping concentrations. For highly *n*-doped samples the resulting band bending is ~0.71 eV. At the doping level used in the present experiment this corresponds to an estimated surface charge of 0.01 electrons per surface atom,[14] which is slightly more than the amount that could be detected very clearly on Ge(111)2×1.[12]

Figure 1 shows photoemission spectra recorded for various negative angles of emission ($\theta_e^-$, defined in the inset of Fig. 1) along the $\bar{\Gamma}$-$\bar{J}$ line in the 2×1 SBZ. The angle of incidence of the photons is $\theta_i = 60°$. The peak marked A corresponds to the bonding surface state and the peak B to the antibonding state. For $\theta_e < 35°$ there is negligible intensity near the Fermi level $E_F$. The strong localization in momentum space of structure B indicates that this structure cannot be due to localized defects.

In Fig. 2, we show the measured initial energy dispersion $[E_i(k_\parallel)]$ for the bonding and antibonding surface states together with the bands from a calculation by Northrup and Cohen.[2] The calculation was made for the energy-minimized geometry of the $\pi$-bonded chain model.

The measured dispersion for the bonding state band is nearly the same as was found in the earlier study by Uhrberg, Hansson, Nicholls, and Flodström.[3] The total dispersion is 0.8 eV in both experiments, while the experiments by Himpsel, Heimann, and Eastman[4] and by Houzay *et al.*[5] both gave a dispersion of 0.6 eV.

The peak position of the antibonding state is at the Fermi level, indicating that the antibonding state is responsible for the pinning of the Fermi level on this surface. The bonding peak has an initial energy of −0.45 eV at the $\bar{J}$ point and we estimate the value of the direct surface band gap to be approximately 0.45 eV. This is in good agreement with the band gap found in experiments with optical absorption by Chiarotti *et al.*[7] (0.46 eV) and Chiaradia, Cricenti, Selci, and Chiarotti[10] (0.45 eV), and with photothermal displacement spectroscopy by Olmstead and Amer[9] (0.47 eV). This implies that excitonic effects are quite small in those absorption measurements, in contrast to what was suggested by the temperature dependence of the energy-loss spectra according to DiNardo, Demuth, Thompson, and Avouris.[11]

In an inverse photoemission experiment Straub, Ley, and Himpsel[15] have found the position of the antibonding band at the $\bar{\Gamma}$ point to be ~0.8 eV above the Fermi level. Assuming that also in this experiment the Fermi level was pinned at the energy minimum of the antibonding band, the difference between the minimum energy position and the energy position at $\bar{\Gamma}$ is therefore 0.8 eV. This is in rough

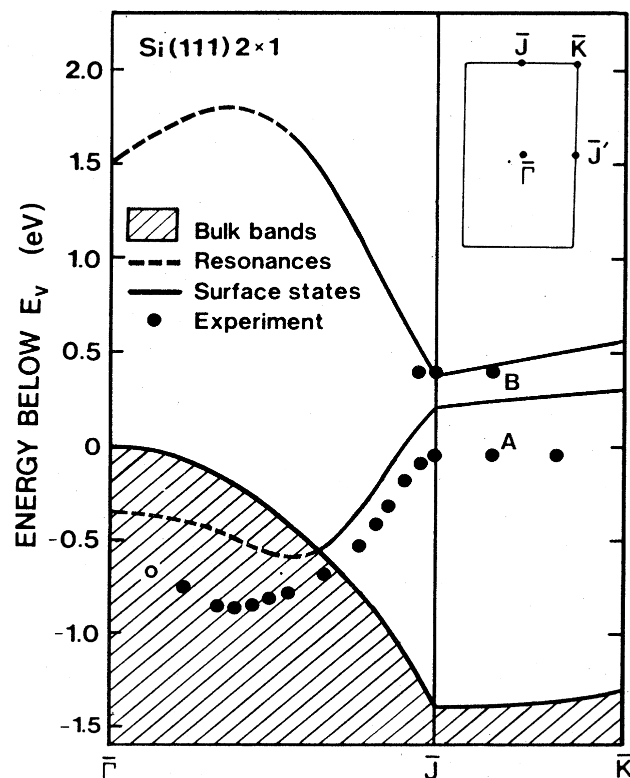


FIG. 2. Initial-state energy dispersions for the bonding (A) and the antibonding (B) surface states, along the $\bar{\Gamma}$-$\bar{J}$-$\bar{K}$ lines, and the corresponding calculated bands for the $\pi$-bonded chain model (Ref. 2). $E_F - E_v \approx 0.40$ eV (Ref. 13).

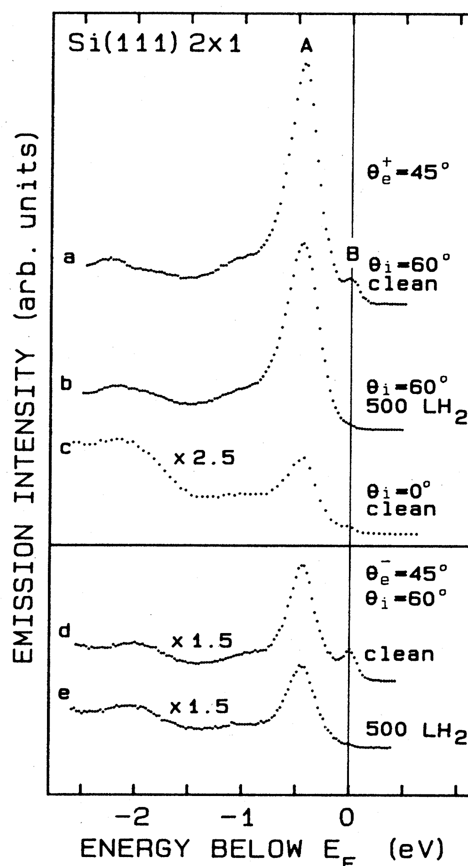


FIG. 3. Photoemission spectra recorded along the $\bar{\Gamma}$-$\bar{J}$ line in the 2×1 SBZ for positive (a,b,c) and negative angles of emission (d,e). Spectra b and e were measured after exposing the surface to 500 L $H_2$. Spectrum c was obtained for an angle of incidence $\theta_i = 0°$.

agreement with the value found for the $\pi$-bonded chain model, 1.15 eV.[2] The model predicts that the direct surface band gap is located at the $\bar{J}$ point, but the calculated value of the gap is only 0.25 eV.

Comparison of the present results with those obtained for Ge(111)2×1 (Ref. 12) shows that the electronic structures of cleaved Si and Ge surfaces are very similar not only for the bonding dangling-bond band but also for the antibonding band. There are, however, two minor differences that can be discussed. First, we find that the surface-state peaks on Si(111)2×1 generally are slightly broader than those on Ge(111)2×1. This combined with the difference in surface-state band gap (Si: ~0.45 eV, Ge: ~0.50 eV) makes the separation between the two surface-state peaks less clear on Si(111)2×1. Secondly, in the case of Ge there is a very large difference in the ratio between the emission intensities from the bonding and antibonding surface states for positive ($\theta_e^+$) and negative ($\theta_e^-$) angles of emission, respectively. The intensity ratio $I_A$:$I_B$ changes from 70:1 for positive to 1.5:1 for negative angles. Figure 3 shows that this difference is much smaller in Si. For positive angles of emission (Fig. 3, spectrum a) the ratio $I_A$:$I_B$ is 20:1, whereas for negative angles (Fig. 3, spectrum d) it is 10:1.

After exposing the Si(111)2×1 surface to 500 L (where 1 L = $10^{-6}$ Torr sec) of hydrogen in the presence of a hot filament no emission from the antibonding surface state could be observed, whereas the bonding surface-state peak was only slightly reduced (see Fig. 3, spectra b and e). After this exposure, the surface still exhibited a clear 2×1 pattern in LEED. To reduce the bonding surface-state peak by half an exposure of ~2000 L of hydrogen was needed.

When the angle of incidence of the photons was changed to $\theta_i = 0°$, the intensities from both surface structures on the clean surface almost completely vanished (see Fig. 3, spectrum c), indicating the $p_z$ character of the two surface states.

In a previous study of the surface-state band structure on Si(111)2×1, in which crystals with low $p$-doping levels were used,[3] only emission from the filled dangling-bond band could be seen. The present results thus show that a large portion of the surface charge giving rise to the band bending on highly $n$-doped surfaces can be attributed to filling of the empty surface-state band. The fact that we have not seen any defect-related (angle insensitive) pinning states could be due to small matrix elements for transitions from such states or to low concentration of defects on the surfaces studied. The Fermi level has been reported to be pinned at $\sim E_v + 0.40$ eV also for $p$-doped crystals.[13] It therefore seems that defect-related states are necessary to explain the pinning of $E_F$ near the top of the surface-state band gap for $p$-doped crystals.

In conclusion, a new surface state at the Fermi level is observed on the cleaved surfaces of heavily $n$-doped Si crystals. This structure corresponds to the antibonding surface state predicted by the $\pi$-bonded chain model. The direct surface-state band gap is found to be 0.45 eV, in good agreement with the value obtained in previously reported absorption measurements.

We wish to thank Dr. J. M. Nicholls for valuable discussions, and Wacker-Chemitronic, Gesellschaft mit beschränkter Haftung for kindly supplying the crystals. This work was supported by the Swedish Natural Science Research Council.

[1] K. C. Pandey, Phys. Rev. Lett. **47**, 1913 (1981); **49**, 223 (1982).
[2] J. E. Northrup and M. L. Cohen, Phys. Rev. Lett. **49**, 1349 (1982).
[3] R. I. G. Uhrberg, G. V. Hansson, J. M. Nicholls, and S. A. Flodström, Phys. Rev. Lett. **48**, 1032 (1982).
[4] F. J. Himpsel, P. Heimann, and D. E. Eastman, Phys. Rev. B **24**, 2003 (1981).
[5] F. Houzay, G. Guichar, R. Pinchaux, G. Jezequel, F. Solal, A. Barsky, P. Steiner, and Y. Petroff, Surf. Sci. **132**, 40 (1983).
[6] W. Müller and W. Mönch, Phys. Rev. Lett. **27**, 250 (1971).
[7] G. Chiarotti, S. Nannarone, R. Pastore, and P. Chiaradia, Phys. Rev. B **4**, 3398 (1971).
[8] J. E. Rowe, H. Ibach, and H. Froitzheim, Surf. Sci. **48**, 44 (1975).
[9] M. A. Olmstead and N. M. Amer, Phys. Rev. Lett. **52**, 1148 (1984).
[10] P. Chiaradia, A. Cricenti, S. Selci, and G. Chiarotti, Phys. Rev. Lett. **52**, 1145 (1984).
[11] N. J. DiNardo, J. E. Demuth, W. A. Thompson, and P. Avouris, Phys. Rev. B **31**, 4077 (1985).
[12] J. M. Nicholls, P. Mårtensson, and G. V. Hansson, Phys. Rev. Lett. **54**, 2363 (1985).
[13] F. J. Himpsel, G. Hollinger, and R. A. Pollak, Phys. Rev. B **28**, 7014 (1983).
[14] E. S. Yang, *Fundamentals of Semiconductor Devices* (McGraw-Hill, New York, 1978).
[15] D. Straub, L. Ley, and F. J. Himpsel, Phys. Rev. Lett. **54**, 142 (1985).