RAPID COMMUNICATIONS

PHYSICAL REVIEW B VOLUME 27, NUMBER 4 15 FEBRUARY 1983

Experimental dangling-bond band on the Ge(111)-(2 × 1) surface

J. M. Nicholls, G. V. Hansson, R. I. G. Uhrberg, and S. A. Flodström
Department of Physics and Measurement Technology, Linköping Institute of Technology, S-581 83 Linköping, Sweden
(Received 18 November 1982)

The electronic structure of the cleaved Ge(111)-(2 × 1) surface has been studied with angle-resolved photoemission, with the use of photons in the energy range 7.4–11.6 eV. Similar to the Si(111)-(2 × 1) surface, the dominating structure in the emission corresponds to a highly dispersive dangling-bond surface state. The initial-state energy, as a function of momentum parallel to the surface $E_i(k_{\parallel})$ for this surface state, is presented along the $\bar{\Gamma}$-$\bar{J}$-$\bar{K}$-$\bar{\Gamma}$ lines in the (2 × 1) surface Brillouin zone.

Several studies of the electronic structure of the cleaved Ge(111) surface have been published,[1–3] but so far no angle-resolved photoemission results have been presented. In this paper we report on new angle-resolved photoemission measurements of germanium cleaved at room temperature. Similar to silicon, this surface has a (2 × 1) reconstruction. In the previous angle-integrated measurements on the Ge(111)-(2 × 1) surface, a broad dangling-bond surface state structure at approximately 0.7 eV below the Fermi level has been observed.

The corresponding dangling-bond surface state on silicon has recently been subject to a number of studies where angle-resolved photoemission spectroscopy has been used.[4–7] The dispersion of this dangling-bond surface state is now known in some detail. In analogy with the results on Si,[6,7] a highly dispersive dangling-bond band on the Ge(111)-(2 × 1) surface is found in the present study.

The angle-resolved spectra have been recorded along the different symmetry lines of the surface Brillouin zone (SBZ). Initial-state energy dispersions for the dangling-bond band along these lines are presented.

The cleave samples were made from a Ge(111) single-crystal rod of n type, $\rho \sim 60\ \Omega$ cm, cut into bars with a square cross section of 5 × 5 mm^2. On each bar three different cleavages could be made. During the cleavage procedure and while recording the spectra the pressure in the UHV chamber was below 7×10^{-11} Torr. The photoelectrons were excited by monochromatized radiation from a hydrogen discharge lamp. Photons in the energy range 7.4–11.6 eV were used. The emitted electrons were energy analyzed by a 180° spherical deflection analyzer, rotatable in the plane of the light incidence. The slit widths and the radius of the analyzer were such that a resolution ($\Delta E/E$) of 1.5% was obtained. Monochromator slits and analyzer voltages were set to obtain a combined resolution of ≤ 0.2 eV in the recorded spectra. The sample holder could be rotated azimuthally 200° around the normal of the sample, which allowed all nonequivalent directions of the (2 × 1) SBZ to be probed from the same cleave.

Angle-resolved spectra were recorded from single domain areas of the cleaved surfaces that were sufficiently larger than the lightspot to certify emission from one domain only. In most cases multidomain diffraction spots were observed in low-energy electron diffraction (LEED) near the edges of the crystal. The crystals were cleaved either towards the $[\bar{2}11]$ or the $[2\bar{1}\bar{1}]$ direction. The best cleaves were obtained when cleaving towards the $[\bar{2}11]$ direction, which in most cases produced cleaves with one domain covering the entire surface. The reproducibility in photoemission spectra between different cleavages was very high. To avoid contamination and other disturbances of the freshly cleaved surfaces, due to the LEED electron gun, photoemission was used to determine the distribution of domains. At the time that the photoemission measurements were completed, the surface was checked with LEED.

The Fermi level was determined with photoemission from the sample holder to an accuracy of ±0.05 eV. No significant shift of the Fermi level relative to the valence band was observed for different cleavages. The valence-band position has been determined in other studies to be at the Fermi level.[8]

In Fig. 1 spectra are shown that were recorded for various angles of emission along the $\bar{\Gamma}$-$\bar{J}$ line in the (2 × 1) SBZ, with a photon energy of 10.2 eV. The geometry of the (2 × 1) SBZ is indicated in Fig. 2. The dominating structure (A) in the photoemission spectra corresponds to the dangling-bond band. At high angles of emission, the dangling bond exhibits a sharp peak in the emission. At the angle $\theta_e = 42°$ corresponding to a $k_{\parallel}$ value slightly smaller than the value at the $\bar{J}$ point, the dangling-bond emission has a pronounced maximum in the intensity. At this point in the (2 × 1) SBZ there is also a minimum in the value of the full width at half maximum (FWHM) of 0.25 eV for the dangling-bond peak. For decreasing angles of emission, the peak position of the dangling bond is lowered in energy until it

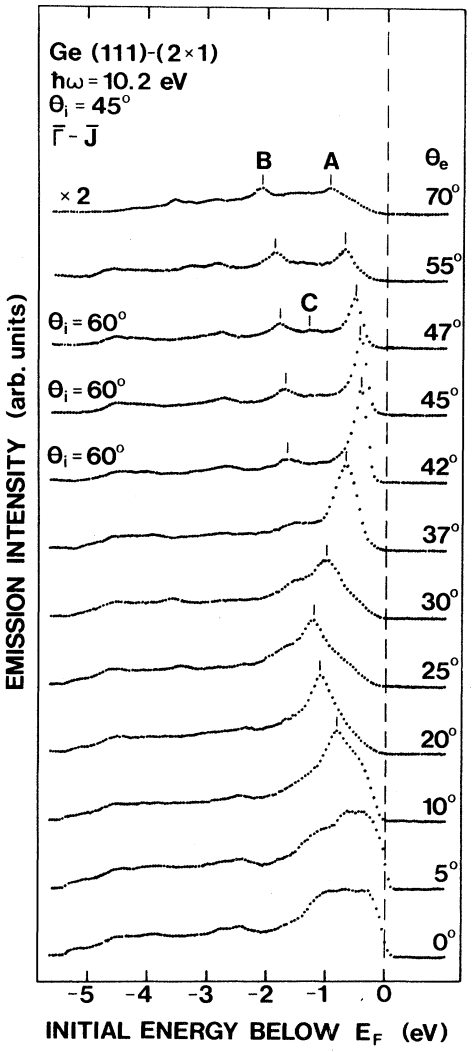

FIG. 1. Angle-resolved photoemission spectra for various angles of emission (θ_e) along the $\bar{\Gamma}$-$\bar{J}$ line in the (2×1) SBZ. Peak A corresponds to the dangling-bond surface state, and the peak marked B to a bulk-derived structure. All spectra are shown with correct relative intensities.

goes through a minimum. Close to normal emission ($\theta_e \leq 10°$) it is difficult to determine the position of the dangling-bond structure. For these angles of emission the dangling-bond band is a surface resonance within the projected bulk band structure. The intensity of the emission is also reduced near the normal direction.

In Fig. 2 the initial energy for the dangling-bond band is plotted versus the momentum vector parallel to the surface ($k_{\parallel}$) along the $\bar{\Gamma}$-$\bar{J}$ direction. Photoemission spectra were recorded for three different photon energies. There is good agreement between the initial-state energy dispersions for the different photon energies, which is a necessary criterion for a true surface state. In Fig. 2 the dangling-bond band

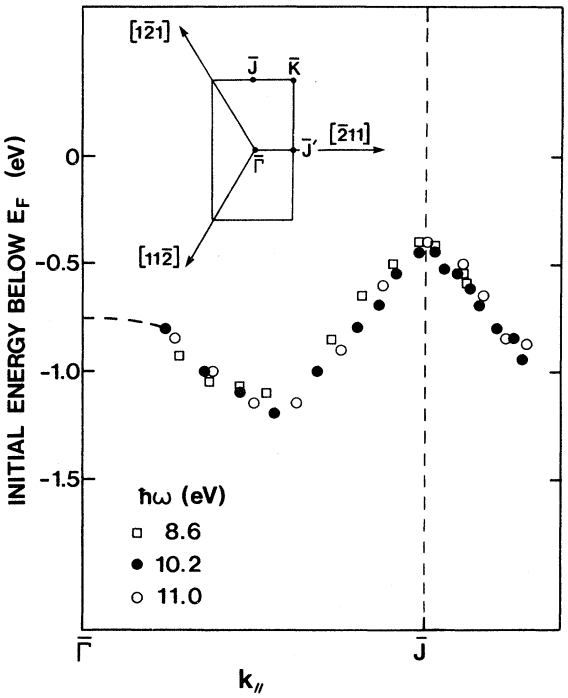

FIG. 2. Initial-state energy dispersions for the dangling-bond band along the $\bar{\Gamma}$-$\bar{J}$ line in the (2×1) SBZ. The geometry of the (2×1) SBZ is also indicated in the figure.

is seen to have the symmetry of the (2×1) SBZ, as the dispersion is symmetric around the $\bar{J}$ point. With a minimum in initial energy ($E_i = -1.2$ eV) at about half the distance $\bar{\Gamma}$-$\bar{J}$ and a maximum ($E_i = -0.4$ eV) at the $\bar{J}$ point, the dangling-bond band has a total bandwidth of 0.8 eV. The dangling-bond dispersion of the Ge(111)-(2×1) surface is very similar to the dangling-bond dispersion on the Si(111)-(2×1) surface,[7] though the minimum is somewhat more pronounced on Ge.

Close to $\bar{\Gamma}$ the dispersion is uncertain (hatched line, Fig. 2) as there are several other structures at about the same initial energy as that of the dangling bond. To determine the value of the initial-state energy of the dangling bond at $\bar{\Gamma}$, spectra were recorded at normal emission for several photon energies, both for a clean as well as a contaminated surface. Furthermore, the $\bar{\Gamma}$-$\bar{J}'$ directions of the SBZ were probed. In these directions it was possible to reach the $\bar{\Gamma}$ point in the neighboring SBZ, where the dangling-bond band is situated in the band gap of the projected bulk bands. The energy position for the dangling-bond state found at $\bar{\Gamma}$ in the second SBZ is approximately −0.75 eV.

The dangling-bond surface state was checked for sensitivity to contamination (see Fig. 3, spectrum b). The surface was exposed to 8000 L of hydrogen (1 L = 10^{-6} Torr sec) in the presence of a hot filament. Spectra shown were recorded along the $\bar{\Gamma}$-$\bar{J}$ line,

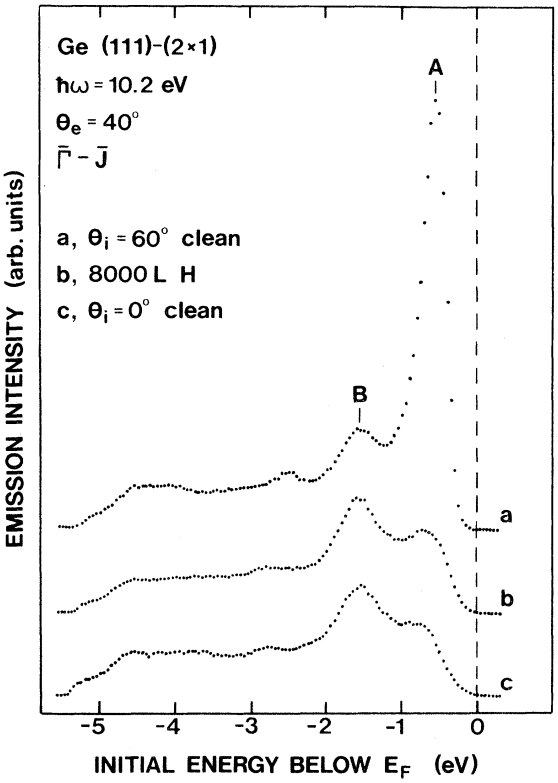

FIG. 3. Photoemission spectra for $\theta_e = 40°$ along $\bar{\Gamma}$-$\bar{J}$, for three different conditions. Spectrum a corresponds to a clean sample, in b the surface was exposed to 8000 L of hydrogen in the presence of a hot filament, and in c the incidence of the light was perpendicular to the surface for a clean sample.

$\theta_e = 40°$. The dangling-bond state is seen to be very sensitive to contamination and it is considerably reduced in intensity while, e.g., the bulk-derived structure marked B is not affected at all. Due to the p_z character of the dangling bond, the component of the electric field vector normal to the surface is the most efficient to excite the electrons to be emitted. In Fig. 3, spectrum c, where the incidence of the light was perpendicular to the surface, the emission is seen to be very much reduced compared to spectrum a.

Along the line $\bar{J}$-$\bar{K}$ in the SBZ, the dangling-bond band exhibits a sharp peak with a high intensity of the emission. In Fig. 4 the dangling-bond dispersion along the $\bar{\Gamma}$-$\bar{J}$-$\bar{K}$-$\bar{\Gamma}$ lines is plotted. From $\bar{J}$ to $\bar{K}$ the dangling bond of the Ge(111)-(2×1) surface has a negative dispersion (0.15 eV), whereas for the Si(111)-(2×1) surface the dispersion is positive (0.1 eV). Consequently, the maximum in initial energy of the occupied dangling-bond band occurs at the $\bar{J}$ point for Ge while it is at the $\bar{K}$ point for Si.[7]

The dispersion along the $\bar{\Gamma}$-$\bar{K}$ line is similar in shape to the dispersion along $\bar{\Gamma}$-$\bar{J}$. There is a rapid dispersion through a sharp minimum ($E_i = -1.2$ eV)

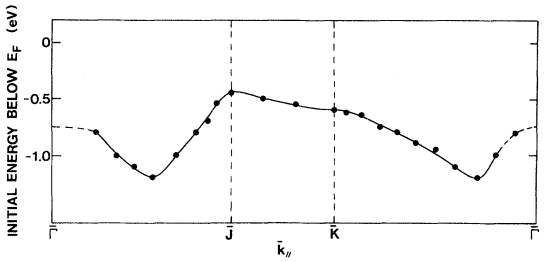

FIG. 4. Initial-state energy dispersion for the dangling-bond band along the $\bar{\Gamma}$-$\bar{J}$-$\bar{K}$-$\bar{\Gamma}$ lines in the (2×1) SBZ, obtained with 10.2-eV photon energy.

at about one third of the distance to the $\bar{K}$ point. The $\bar{\Gamma}$-$\bar{K}$ line in the (2×1) SBZ can be probed along two nonequivalent directions in the bulk, e.g., $[2\bar{1}\bar{1}]$ and $[\bar{2}11]$. The intensity of the emission is then markedly different for both the dangling-bond and the bulk-derived features in these two cases. In the $[2\bar{1}\bar{1}]$ direction, the dangling bond is the dominating structure (especially for low angles of emission), whereas in the $[\bar{2}11]$ direction the dangling-bond emission is smaller and the bulk-derived structures are more pronounced.

In Fig. 1 a minor structure is apparent at $E_i = -1.3$ eV, marked C ($\theta_e = 47°$). A corresponding structure is likewise observed for Si.[5,7] Several explanations have been proposed for the origin of this structure on the Si(111)-(2×1) surface. It has been suggested that this structure is due to multidomain effects.[7] For the Ge(111)-(2×1) surface this is not a possible interpretation, since the energy position of the dangling bond on domains rotated by ±120° from the main domain is 0.3 eV higher than the structure C. The question then remains, whether this structure corresponds to a second surface state band or to some other surface effect.

Recently, a new model for the (2×1) reconstruction on Si has been proposed, the π-bonded chain model.[9] A calculation for the energy minimized geometry of this π-bonded chain model[10] generates a dangling-bond band in very good agreement with the dominating surface state contribution in a previous photoemission study on Si.[7] The (2×1) reconstructions on the cleaved surfaces of Si and Ge are believed to be similar, and the experimental data are also very similar. Consequently, there is good reason to believe that the π-bonded chain model would apply to the Ge(111)-(2×1) surface as well. However, no theoretical results have yet been published on the π-bonded chain model that explains the extra structure (C in Fig. 1) that appears near the $\bar{J}$ point for the (2×1) reconstructed surfaces of both Si and Ge.

ACKNOWLEDGMENT

This work was supported in part by the Swedish Natural Science Research Council.

[1]D. E. Eastman and W. D. Grobman, Phys. Rev. Lett. 28, 1378 (1972).
[2]J. E. Rowe, Solid State Commun. 17, 673 (1975).
[3]T. Murotani, K. Fujiwara, and M. Nishijima, Phys. Rev. B 12, 2424 (1975).
[4]F. Houzay, G. M. Guichar, R. Pinchaux, and Y. Petroff, J. Vac. Sci. Technol. 18, 860 (1981).
[5]F. J. Himpsel, P. Heimann, and D. E. Eastman, Phys. Rev. B 24, 2003 (1981).
[6]R. I. G. Uhrberg, G. V. Hansson, J. M. Nicholls, and S. A. Flodström, Surf. Sci. 117, 394 (1982).
[7]R. I. G. Uhrberg, G. V. Hansson, J. M. Nicholls, and S. A. Flodström, Phys. Rev. Lett. 48, 1032 (1982).
[8]G. W. Gobeli and F. G. Allen, Phys. Rev. 137, A245 (1965).
[9]K. C. Pandey, Phys. Rev. Lett. 47, 1913 (1981).
[10]J. E. Northrup and M. L. Cohen, Phys. Rev. Lett. 49, 1349 (1982); (private communication).