Direct Photoemission Study of the Antibonding Surface-State Band on Ge(111)2×1

J. M. Nicholls, P. Mårtensson, and G. V. Hansson
Department of Physics and Measurement Technology, Linköping Institute of Technology, S-581 83 Linköping, Sweden
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The cleaved Ge(111)2×1 surface of a heavily n-doped crystal has been studied with angle-resolved photoemission. A new partly filled surface-state band is observed at the Fermi level, only appearing close to the $\bar{J}$-$\bar{K}$ line in the 2×1 surface Brillouin zone. The observed emission corresponds to the dispersion minimum of the antibonding band in the π-bonded chain model. The direct band gap between the surface-state bands is found to be 0.5 eV, in good agreement with results from absorption measurements.

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It has been suggested for a long time that the existence of filled and empty surface states within the bulk band gap pins the Fermi level on several semiconductor surfaces. With angle-resolved photoemission it has been possible to map the filled surface-state bands on, for example, the cleaved (111)2×1 surfaces of silicon and germanium.[1-4] Evidence for the existence of empty surface-state bands (apart from the pinning of the Fermi level) has so far been obtained more indirectly, in experiments such as photothermal displacement spectroscopy,[5] optical reflectivity,[6-8] and photoemission partial-yield measurements,[9] where electrons are excited to the empty surface-state band.

In this Letter we present a direct photoemission study of the surface-state band on Ge(111)2×1 that is empty for a neutral surface, but which for an n-doped crystal is filled to a small fraction to obtain the charging of the surface that is responsible for band bending and Fermi-level pinning. The results of the present experiment are in good agreement with the calculated antibonding band of the π-bonded chain model for the Ge(111)2×1 surface.[10,11] The obtained value for the surface-state band gap is also in good agreement with absorption measurements of the gap,[5-7] implying that excitonic effects are not large in these experiments.

At cleavage, the atoms on the surface of a Ge(111) crystal rearrange themselves into a 2×1 reconstruction. According to the π-bonded chain model[10,11] of this surface, one filled bonding surface-state band is formed as well as an empty antibonding band. The minimum energy of the antibonding band is then positioned lower in the gap then the donor level for an n-doped crystal, and a charge transfer to the surface takes place as some electrons are trapped in the empty surface-state band. The resulting band bending on highly n-doped samples amounts to nearly the full band-gap energy.[12,13] At the doping level used here ($\sim 1\times10^{18}$ cm^{-3}, $\rho \sim 8$ mΩ cm, Sb) the calculated depletion layer is approximately 300 Å wide, and the corresponding occupation level for the antibonding band is $\sim 0.5\%$.[14] In this case only that part of the band close to the minimum energy is occupied. This corresponds to the region around the $\bar{J}$-$\bar{K}$ line at the zone boundary of the 2×1 surface Brillouin zone (SBZ) in the present experiment. In the photoemission spectra it is therefore possible to observe the bonding and antibonding dangling-bond bands in this region simultaneously. This is the first direct observation of the bands that determine the surface-state band gap. With other methods, e.g., optical reflectivity,[6,7] the value of the band gap is measured, but not the absolute energy position, or location in momentum space of the separate bands. The existence of an unoccupied surface state for the cleaved surface of germanium about 0.2 eV above the valence-band maximum has also been inferred from a partial-yield measurement.[9]

In the angle-resolved photoemission experiment, unpolarized radiation in the energy range 8.6–11.1 eV from a hydrogen discharge lamp was used. The cleave samples were cut into bars with a square cross section of 8×8 mm^2. The crystals were cleaved along the $[2\bar{1}\bar{1}]$ crystal direction, and the distributions of the three possible domains on the surfaces were determined with photoemission and were later 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 significantly larger than the light spot were used for the present experiment. The spectra are referenced to the Fermi level, which was determined by photoemission from the metallic sample holder to an accuracy of ±0.025 eV. The pressure in the UHV chamber was $< 1\times10^{-10}$ Torr during cleavage and the photoemission experiment.

Spectra were recorded in two different geometries as shown in Fig. 1. At an angle of incidence $\theta_i = 60°$ of the light, electrons emitted from the $\bar{\Gamma}$-$\bar{J}$ lines were studied, on both sides of the surface normal (θ_e^-, θ_e^+). In Fig. 1 a set of spectra shows the emission from the bonding surface state (A) and the antibonding state (B) at negative angles of emission (θ_e^-).

The emission intensities from the bonding surface state (A) and the antibonding state (B) are markedly different for the two collection geometries (see Fig. 2). For positive angles of emission (Fig. 2, spectrum a), the intensity of emission from the bonding state is

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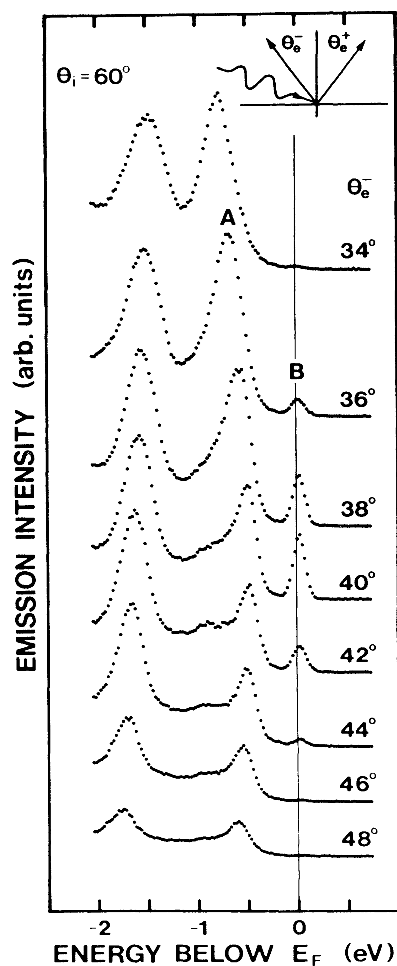

FIG. 1. Photoemission spectra recorded for various angles of emission (θ_e^-) along the $\bar{\Gamma}$-$\bar{J}$ line in the (2×1) SBZ. The peak marked A corresponds to the bonding surface-state band and the peak B to the antibonding surface-state band.

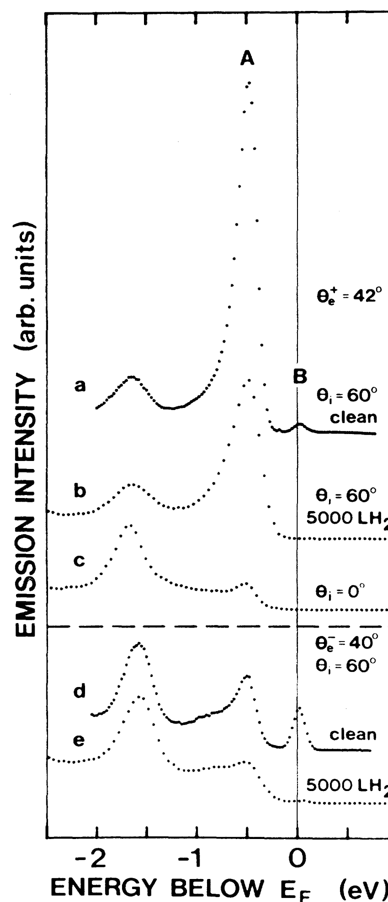

FIG. 2. Photoemission spectra recorded along the $\bar{\Gamma}$-$\bar{J}$ line in the (2×1) SBZ for positive angles (a,b,c) and negative angles (d,e) of the emission. At both geometries spectra were also recorded after the surface was exposed to 5000 L H_2 (1 L=1 langmuir$=10^{-6}$ Torr sec). Spectrum c was obtained for an angle of incidence $\theta_i=0°$.

very high, whereas for negative emission angles (Fig. 2, spectrum d) this state is very much weaker, and instead the antibonding state is somewhat larger. The intensity ratio I_A/I_B changes from 70:1 at positive angles to 1.5:1 at negative angles. This strong matrix-element effect could be a test for the accuracy of the calculated wave functions of the bonding and antibonding bands near $\bar{J}$. The peak at ~ -1.5 eV in the spectra of Figs. 1 and 2 is due to direct transitions in the bulk.

With the experimental setup used in this experiment, a combined theoretical energy resolution, as determined by monochromator slit widths and analyzer voltages, of 0.05 eV is obtained. This small value is due to the narrow linewidth of the 10.2 eV peak in the hydrogen discharge spectrum. The angular resolution of the analyzer was $\pm 2°$. The smallest observed values of the full width at half maximum (FWHM) for the two peaks A and B are 0.20 and 0.14 eV, respectively. The antibonding state is only observed in the vicinity of the $\bar{J}$ point and along the $\bar{J}$-$\bar{K}$ line, where, according to the calculation of the dansion of the filled dangling-bond band (A) is the same state is at its lowest energy. In Fig. 3 the measured initial energy dispersions for the surface states $[E_i(\mathbf{k}_{\parallel})]$ are shown, together with the bands from a calculation by Northrup and Cohen[11] on the π-bonded chain model for Ge(111)2×1. The measured dispersion of the filled dangling-bond band (A) is the same as was found in earlier studies on undoped and lightly n-doped crystals,[3,4] and in the present experiment the obtained dispersions were reproduced for different cleavages.

The antibonding peak (B) has a peak position of 0.025 eV above the Fermi level. However, the density of states of the antibonding band is cut off by the ther-

mally broadened Fermi function. The theoretical step width defined as $E(f=0.9)-E(f=0.1)$ equals 0.11 eV, and the value obtained in photoemission spectra from the metallic sample holder is 0.14 eV. The minimum of the antibonding band could then be slightly higher in energy if its intrinsic peak width is the same as that of the bonding state. The bonding peak (A) has an initial energy of −0.475 eV at the $\bar{J}$ point, and we estimate the value of the band gap to be approximately 0.5 eV. This is in good agreement with the band gap found in absorption experiments with photothermal displacement spectroscopy by Olmstead and Amer[5] (0.5 eV) and optical reflectivity by Nannarone *et al.*[7] (0.5 eV). In our experiment the doping level was much higher than in the absorption measurements; however, it has been shown[15] that the corresponding band-gap narrowing of the bulk bands at the present doping level is quite small (<20 meV). The agreement between the observed gap values thus implies that possible excitonic effects are quite small in the absorption measurements.

From the calculation by Northrup and Cohen[11] on the π-bonded chain model (Fig. 3), the shape of the filled band is found to be in agreement with the experimentally determined surface-state band, although the calculated band needs to be shifted by 0.8 eV to give the best agreement. Consistent with the results of the present experiment, the calculated unoccupied band has a minimum energy at the $\bar{J}$ point, although the predicted band gap is only 0.25 eV.

When exposing the surface to 5000 L of hydrogen in the presence of a hot filament, both surface peaks were reduced, but the antibonding state was found to be proportionally much more reduced in intensity than the bonding state (see Fig. 2, spectra *b* and *e*). After exposure to 5000 L of hydrogen, the surface still exhibited a clear 2×1 pattern in LEED, with a slightly increased background.

When the angle of incidence of the incoming photons was changed to $\theta_i=0°$, the intensities from both surface structures on the clean surface almost completely vanished (see Fig. 2, spectrum *c*), indicating that these states are of p_z type. The essential features of the two surface states observed at 10.2 eV photon energy were also seen at photon energies of 8.6 and 11.1 eV.

At a simultaneous illumination of the crystal with a 40-mW HeNe laser ($\lambda=6328$ Å, $\hbar\omega=1.96$ eV), all structures in the spectra shifted downwards in energy by ~0.1 eV, indicating a reduction in band bending due to the creation of free carriers in the band-bending region. The hole current terminating at the surface will act to decrease the occupation of the surface states. On the other hand, electrons excited to the almost empty surface-state band will act to increase the occupation of this band during illumination. In our experiment the emission from the antibonding band was shifted and slightly broadened, but no change in the intensity was observed. With the use of a laser with photon energy below the bulk band gap, but above the surface band gap, it would be possible to avoid the hole current to the surface. An increase in the occupation of the empty surface-state band would then be expected to be seen if the recombination of the carriers created is a sufficiently slow process.

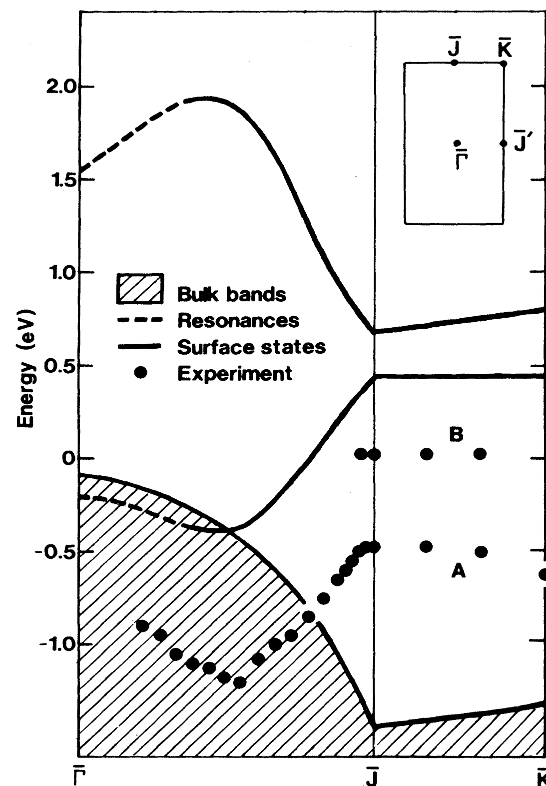

FIG. 3. Initial-state energy dispersions for the bonding (A) and antibonding (B) surface states, along the $\bar{\Gamma}$-$\bar{J}$-$\bar{K}$ lines, and the corresponding calculated bands for the π-bonded chain model (Ref. 11). $E_F - E_V \sim 0.1$ eV.

Surface conductivity, Kelvin, and photoemission yield measurements[12,13] on differently doped Ge crystals have shown that the Fermi level is pinned close to the valence-band edge at the surface independent of the doping. For heavily *p*-doped samples, the bands are flat up to the surface, while for heavily *n*-doped samples, the bands are bent upwards, with the Fermi level for the interior of the crystal positioned close to the conduction-band edge. A schematic drawing of the band bending and the position of the surface-state bands in the present experiment is shown in Fig. 4.

To summarize, a new surface-state structure close to the Fermi level is observed on the cleaved surface of a heavily *n*-doped Ge crystal. This extra structure corre-

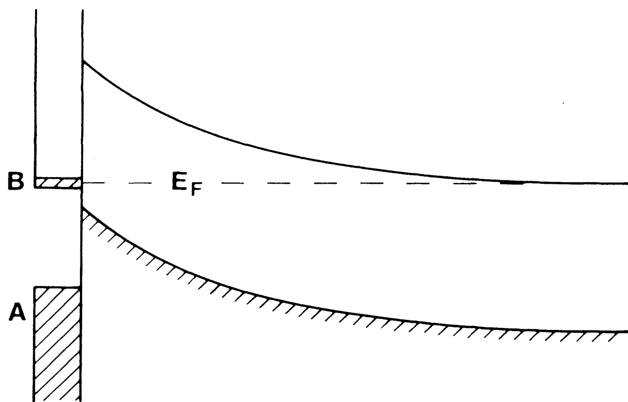

FIG. 4. Schematic drawing of the band bending and the position of the surface-state bands. The partly filled band B is responsible for the negative surface charge and the corresponding band bending.

sponds to the antibonding surface-state band predicted by the π-bonded chain model for the Ge(111)2×1 surface. A minimum surface-state band gap of 0.5 eV between the two dangling-bond bands is obtained in good agreement with absorption measurements.

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