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Abstract

In contrast to our earlier measurements as well as the band calculated from the π-bonded chain model, a very narrow dangling bond band has been reported from a recent photoemission experiment on the Ge(111)2x1 surface ($35 \leq \hbar\omega \leq 50$ eV). We present new photoemission measurements for a broad range of photon energies ($8.6 \leq \hbar\omega \leq 35$ eV) in which a highly dispersive dangling bond band is found, in good agreement with the π-bonded chain model.

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During the last few years, there has been much activity in the study of semiconductor surfaces, both experimentally[1-6] and theoretically[7-10]. In particular, the broken bonds of the cleaved surface of Si(111)2x1 have been the subject of many studies.

An angle resolved photoemission experiment, using low photon energies (8.6, 10.2 and 11.0 eV), has also been performed for the Ge(111)2x1 surface[6], to investigate the nature of the surface state bands. Several main directions in the (2x1) surface Brillouin zone (SBZ) were probed and, especially in the $\bar{\Gamma}$-$\bar{J}$ and $\bar{\Gamma}$-$\bar{K}$ directions, a sharp highly-dispersive structure near the Fermi level was identified as the dangling bond surface state. It is generally believed that the geometric and electronic structures of Si and Ge are similar, hence the π-bonded chain model proposed for Si has also been applied to the Ge(111)2x1 surface. The results from the photoemission experiment [6] on Ge were later compared with a calculation using the π-bonded chain model, but with a slightly modified[10] top layer of the surface. A tilt of the π-bonded chain was found to be energetically favourable. For this optimum geometry, the dispersion of the theoretical band is in good agreement with the experimental band.

Recently, Solal et. al.[11] have presented new photoemission measurements on Ge(111)2x1 performed at 20 K with photon energies between 35 and 50 eV. The measured dispersion of the dangling bond differs considerably from the previously-published dispersion[6], a bandwidth of only 0.25 eV being obtained, as opposed to the earlier reported value, 0.75 eV[12]. In the paper by Solal et. al., the application of the π-bonded chain model to the Ge(111)2x1 surface was questioned as were the earlier proposed buckling models, and

they therefore consider the structure of the cleaved surface of germanium to be still an open question.

The disagreement in the dangling bond dispersion found in the two experiments - using different photon energies - is a serious discrepancy, since the dispersion of a true surface state should be independent of the photon energy. It is, therefore, important to determine whether the dispersion of this state is dependent on the photon energy or if the observed anomaly is an effect of different experimental conditions.

In this paper, our results from three different photoemission experiments on the Ge(111)2x1 surface at room temperature are presented. The dispersion of the dangling bond band is found to be practically invariant for a broad range of photon energies: 8.6-35 eV.

The photoemission experiments have been performed with three different experimental set-ups: (1) Low photon energy (8.6, 10.2 and 11.0 eV) measurements[6] with unpolarized light from a hydrogen discharge lamp. (2) Higher photon energy (16.8, 21.2 eV) measurements using unpolarized light from a resonance lamp, in a different vacuum system[13]. A total energy resolution of 0.14 eV (for 21.2 eV) and an angular resolution of $\pm 2^{0}$ were used in this experiment. (3) Synchrotron radiation measurements at the storage ring Doris II at HASYLAB DESY[14], with photon energies in the range 10-35 eV. In the measurements of the dangling bond dispersion at 21.2, 32 and 35 eV, energy resolutions (monochromator + analyzer) of 0.21, 0.31, and 0.39 eV respectively were used and the angular resolution was $\pm 2^{0}$. The pressure in the UHV chambers was $\leq 2 \cdot 10^{-10}$ Torr in all experiments.

In the first two experiments, the cleave samples were of n type, $\rho \sim 60$ Ωcm, cut into bars with a square cross-section of 5x5 mm^2 and, for the third experiment, bars of cross-section 8x8 mm^2 were cut from a nominally undoped crystal, $\rho \sim 50$ Ωcm.

The crystals were cleaved along the $[2\bar{1}\bar{1}]$ crystal direction, producing in most cases large single domain areas. Photoemission was used to determine the distribution of domains on the surface and, after the photoemission experiment was completed, the surface was checked with LEED. All spectra are referenced to the Fermi level, which is determined by photoemission from the sample holder to an accuracy of $\pm$ 0.05 eV. The same geometry has been used throughout the different experiments. For an angle of incidence $\theta_i = 45^{0}$, the emitted electrons were detected in the plane of light incidence. The sample could be rotated 200^{0} azimuthally around its normal.

In Fig. 1 are shown spectra recorded with polarized synchrotron radiation (3), $\hbar\omega$ = 21.2 eV, for various angles of emission along the $\bar{\Gamma}$-$\bar{J}$ line in the (2x1) SBZ (indicated in Fig. 3). For a second measurement at $\hbar\omega$ =21.2 eV (2), unpolarized light was used. The shape of the dangling bond peak is the same in these two measurements, whereas large differences are observed in the emission from the bulk bands. At high angles of emission, the dangling bond appears as a sharp peak (marked A), and disperses down symmetrically on both sides of the $\bar{J}$ point, which is probed for $\theta_e \sim 23^{0}$. For increasing or decreasing emission angles the intensity decreases, and for $\theta_e \lesssim 9^{0}$ it is not possible to separate unambiguously the dangling bond from other structures (the dangling bond state is now a surface resonance within the projection

of the bulk bands). Spectra were also recorded for a photon energy of 35 eV. In Fig. 2, spectra obtained for various angles of emission along $\bar{\Gamma}$-$\bar{J}$ are shown. Once again the intensity of the dangling bond peak increases as the $\bar{J}$ point is approached ($\theta_e \sim 16^0$) from either side, and the peak position moves to lower energies for lower and higher emission angles. Close to normal emission, it is again difficult to trace the dangling bond structure ($\theta_e \lesssim 6^0$). Dangling bond dispersions were also recorded for photon energies of 16.8 and 32 eV, the results being in good agreement with those obtained at the other photon energies. In Figs. 1 and 2 some other structures are present in spectra at higher binding energies. These structures are mainly interpreted as being due to direct transitions in the bulk and will not be discussed further here.

In Fig. 3, the geometry of the (2x1) SBZ is indicated relative to the <$\bar{2}$11> directions. For the $\bar{\Gamma}$-$\bar{J}$ direction, the initial state energy versus momentum vector parallel to the surface ($\bar{k}_{//}$) is plotted for several photon energies from different experiments. (The value E_F-E_V=0.1 eV used is from Ref. 11). The full-drawn curve was obtained in an earlier study[6] at a photon energy of 10.2 eV. The slanting dispersions on both sides of the $\bar{J}$ point overlap for different photon energies. However, for the high photon energies it is not possible to obtain the dispersion from $\bar{\Gamma}$ to the minimum at about half the distance $\bar{\Gamma}$-$\bar{J}$. Comparing the full-drawn curve (10.2 eV) with the points obtained for 21.2 eV and 35 eV photon energy, the corresponding minimum and maximum values of the dispersion are not the same, indicating a narrower bandwidth. This is explained in a natural way by the fact that, as the photon energy is increased, the interval

probed in terms of $\bar{k}_{//}$ is increased. For an angular resolution of $\pm 2^0$ and a photon energy of 35 eV, the width probed at the $\bar{J}$ point ($k_{//} \sim 0.79\,\text{Å}^{-1}$) might be as large as $\Delta k_{//} \leq 0.19\ \text{Å}^{-1}$ (although the collection efficiency is not constant over this whole range). The corresponding value for $\hbar\omega$ = 10.2 eV and angular resolution $\pm 1.5^0$ is $\Delta k_{//} \leq 0.04\ \text{Å}^{-1}$. Consequently while probing, e.g., the sharp maximum at the $\bar{J}$ point, electrons from the surrounding points in the SBZ lower in energy, are also probed, and the resulting peak position will therefore be lowered.

For all the different photon energies used, the value of the full width at half maximum (FWHM) of the dangling bond peak has a minimum at the $\bar{J}$ point, and typically broadens as the dangling bond peak leaves the bandgap and enters the projected bulk band region. The dangling bond peak is also broadened as the photon energy increases due to the increased experimental broadening. For 10.2, 21.2 and 35 eV photon energy, the corresponding FWHM values at the $\bar{J}$ point are 0.25, 0.35 and 0.50 eV.

For the low photon energies 8.6, 10.2 and 11.0 eV, the dangling bond peak is clearly visible in a large part of the SBZ[6], and the resolution in probed momentum is good. For these photon energies, the measured dispersions are in good agreement with one another. In addition, at the photon energy 10.2 eV, spectra were recorded for two different angles of the light incidence, $\theta_i = 45^0$ and $\theta_i = 0^0$. This has a large effect on the emission of the dangling bond electrons, since these are mainly excited with an electric field component normal to the surface. The difference spectra between these two sets of spectra reproduce clearly the whole fulldrawn dispersion (see Fig. 3.)

For all photon energies, the symmetric dispersion around the $\bar{J}$ point is given by a sharp peak in the spectra, especially for the part of the dispersion within the projected bandgap. In the bandgap, the peak is unambiguously interpreted as a surface state, since no

confusion with bulkbands is possible. Within the projection of the bulkbands, the position of the dangling bond peak could possibly change as the photon energy is varied due to variation in the contribution of bulk electrons near the surface resonance. Any such changes are estimated to be less than 0.1 eV in the photon energy range used.

From the three different experiments it is concluded that the dangling bond band on Ge(111)2x1 has a dispersion which is practically invariant for a broad range of photon energies and that the dispersion is well described by the full-drawn curve[6] in Fig. 3.

The dispersion obtained by Solal et. al.[11] indicated in Fig. 3, has a bandwidth of only 0.25 eV, and the agreement between the two measurements at 35 eV photon energy is very poor. This suggests that the conditions of the surfaces must have been essentially different in some way. The spectra in the present study were obtained from freshly-cleaved surfaces at room temperature, and the reproducibility of spectra was very high between different cleavages.

To summarize, the dispersion of the Ge(111)2x1 dangling bond state has been studied for a broad range of photon energies and the results confirm our earlier reported results. We believe that we have found the correct dispersion of the Ge(111)2x1 dangling bond state and, in contrast to a recent publication, we find a highly dispersive dangling bond band, in good agreement with a calculation[10] using the π-bonded chain model.

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FIGURE CAPTIONS

Fig. 1 Photoemission spectra recorded at room temperature for various angles of emission (θ_e) along the $\bar{\Gamma}$-$\bar{J}$ symmetry line in the (2x1)SBZ. The peak marked A corresponds to the dangling bond surface state.

Fig. 2 Photoemission spectra recorded at room temperature for various angles of emission (θ_e) along the $\bar{\Gamma}$-$\bar{J}$ symmetry line in the (2x1)SBZ. The peak marked A corresponds to the dangling bond surface state.

Fig. 3 Initial state energy dispersions for the dangling bond band, along the $\bar{\Gamma}$-$\bar{J}$ symmetry line obtained for various photon energies. For difference spectra see main text. The dispersion from Ref. 11 is shown for comparison. The projected bulk bands are from Ref. 10.

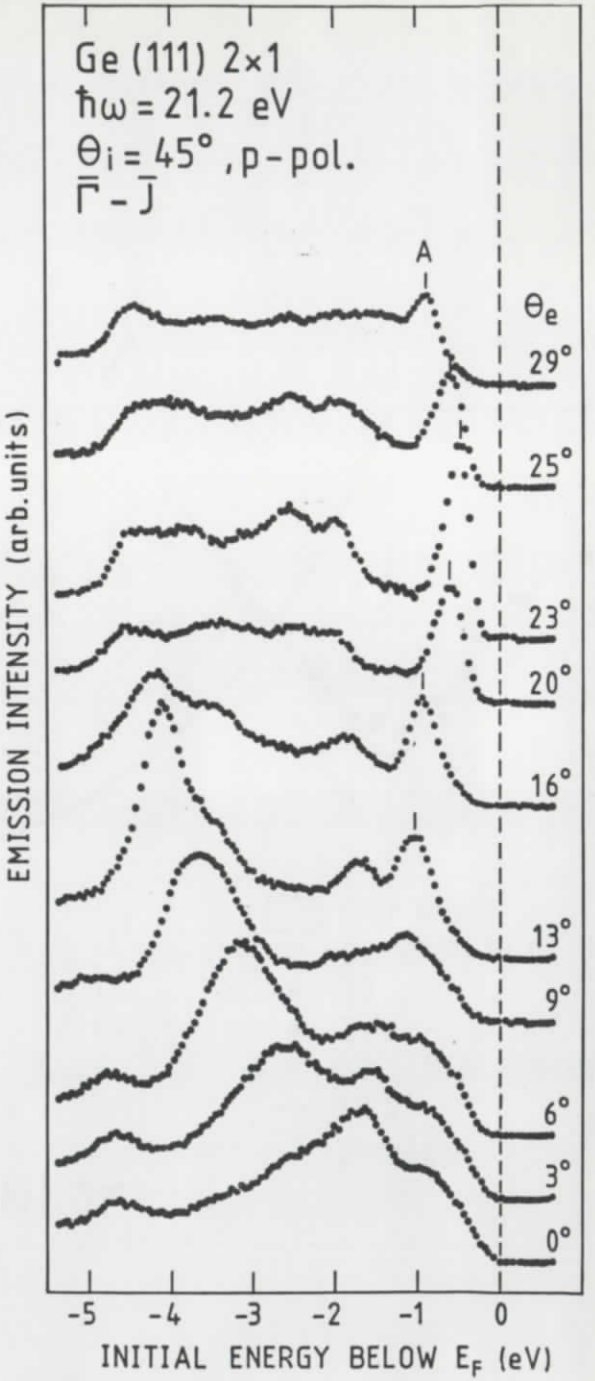

Fig. 1

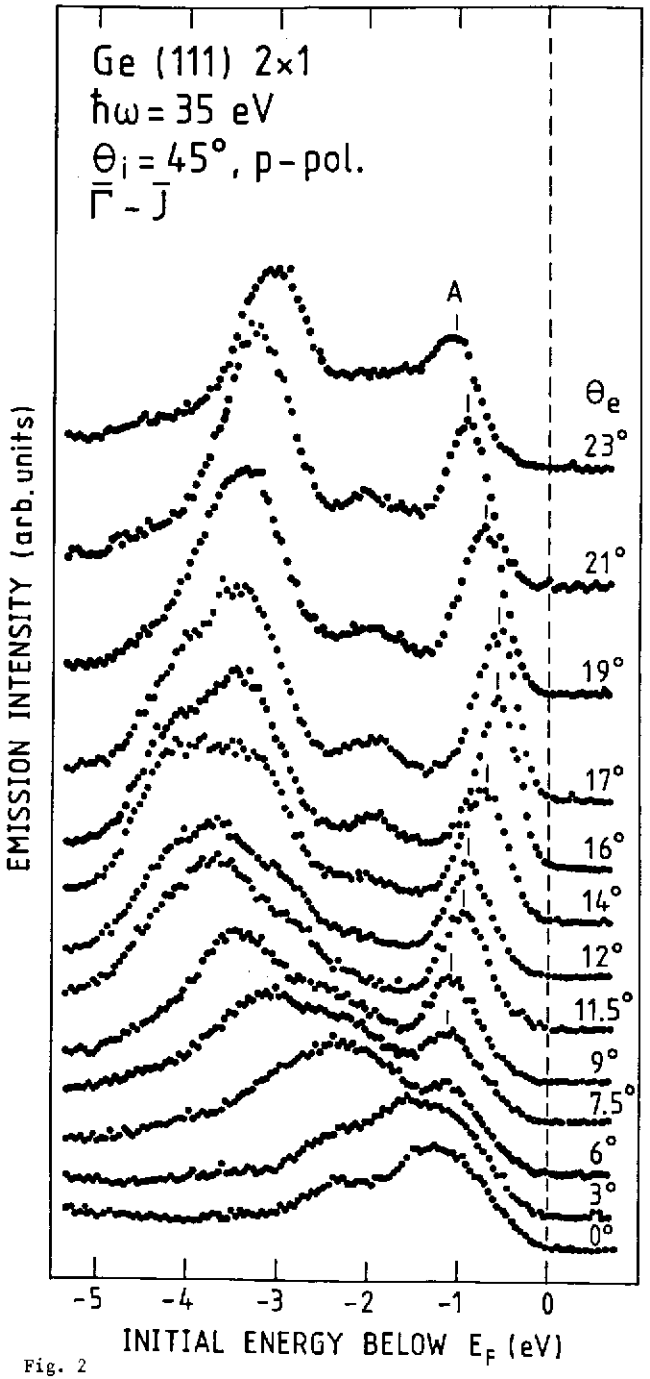
Ge (111) 2×1
ħω = 35 eV
Θi = 45°, p-pol.
Γ̄ - J̄
A
Θe
23°
21°
19°
17°
16°
14°
12°
11.5°
9°
7.5°
6°
3°
0°
EMISSION INTENSITY (arb. units)
-5
-4
-3
-2
-1
0
INITIAL ENERGY BELOW E_F (eV)

Fig. 2

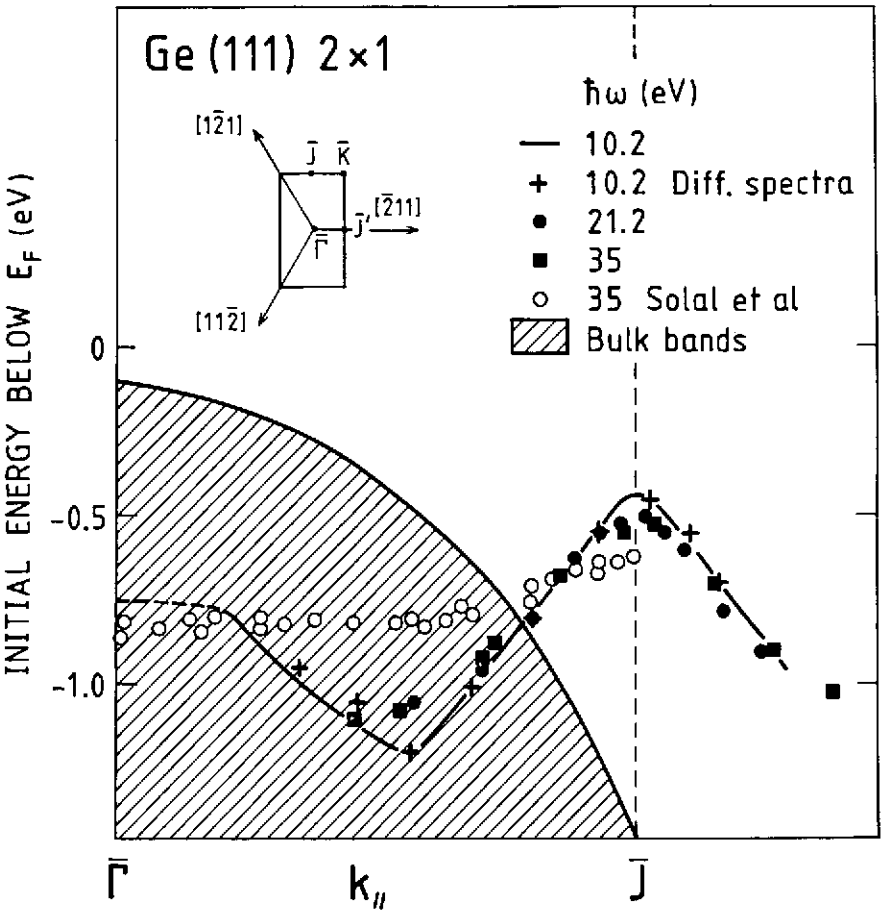
Ge (111) 2×1
ħω (eV)
10.2
10.2 Diff. spectra
21.2
35
35 Solal et al
Bulk bands
[1$\bar{2}$1]
[11$\bar{2}$]
[$\bar{2}$11]
J̄
K̄
Γ̄
J̄'
INITIAL ENERGY BELOW E_F (eV)
0
-0.5
-1.0
Γ̄
k_//
J̄

Fig. 3