Surface and bulk electronic structure of Ge(111) $c(2 \times 8)$ and Ge(111):As 1×1

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The surface band dispersion of the annealed (111) surface of germanium has been determined experimentally using angle-resolved photoemission. The $c(2 \times 8)$ symmetry seen in low-energy electron diffraction is not seen in the surface-state dispersion, which exhibits a 2×2 periodicity. This result is interpreted as indicating that the Ge(111) $c(2 \times 8)$ surface unit cell contains 2×2 subunits. The surface-state dispersion and bandwidth are consistent with a 2×2 adatom model for the surface. An examination is made of the effect of the surface on the near-surface electronic structure. Results for the heavily reconstructed Ge(111) $c(2 \times 8)$ surface are compared with those for the Ge(111):As 1×1 surface. This latter surface was chosen for comparison because the arsenic termination removes the reconstruction and leads to an extremely stable surface with a geometry close to that of an ideal (111) surface. Spectral features corresponding to bulk initial states were compared with calculated values and found to agree throughout most of the surface Brillouin zone. Discrepancies were found near $\overline{K}$ and attributed to the effect of back-bond formation. At finite values of $k_{||}$, a free-electron parabola with its zero at 9.70 eV below the top of the bulk valence band is the final state which best explains the bulk data. At normal emission, on the other hand, a Bloch conduction-band state was found to be more appropriate. The effect of secondary cone emission on the photoemission is discussed.

I. INTRODUCTION

The apparent simplicity of the ideal (111) surfaces of Si and Ge would seem to make them attractive for studying the electronic properties of semiconductor surfaces. In reality these surfaces strongly reconstruct and exhibit a 2×1 periodicity after cleavage and 7×7 and $c(2 \times 8)$ periodicities after annealing for Si(111) and Ge(111), respectively. These reconstructions affect at least the first two atomic layers and represent major reorganizations from the ideally terminated bulk. For Si(111) 2×1 and Ge(111) 2×1, a π-bonded chain model[1] in which rebonding of second-layer atoms occurs, is now generally accepted. Several experiments, notably scanning tunneling microscopy,[2] have shown that Si(111) 7×7 has several atomic layers significantly altered from bulk Si.

In this paper we present results for the annealed $c(2 \times 8)$ Ge(111) surface, which is less well characterized than its counterpart, the (7×7) reconstruction of Si(111). Two aspects have been studied with angle-resolved photoelectron spectroscopy (ARPES). The first concerns the surface states themselves and the second considers how bulklike is the environment near the surface. Because ARPES probes the first few atomic layers near the surface, we can compare the bulklike contributions from the second and third atomic layers with calculations of the bulk band-structure. In order to make this comparison, we will consider the bulk-derived photoemission process in detail for both Ge(111) $c(2 \times 8)$ and Ge(111):As 1×1. The As-terminated surface has been shown to approximate closely an unreconstructed (111) surface and to provide a valuable model system.[3] The surface states of the Ge(111):As 1×1 system will only be discussed briefly as a detailed comparison with calculated surface dispersions has been published elsewhere.[3]

A. Surface states on Ge(111) $c(2 \times 8)$

The surface band structure of Ge(111) $c(2 \times 8)$ has not been calculated because of its large unit cell. In addition, it has only recently been accepted that the observed LEED pattern corresponds to a three-domain $c(2 \times 8)$ (Ref. 4) rather than an 8×8 or a three-domain 2×8 symmetry. Experimentally, there have been several determinations of the surface-state dispersion using angle-resolved photoemission. The first study[5] showed two bands centered at 0.85 and 1.4 eV below the top of the valence band, each with a bandwidth of 0.2 eV. By comparison with a bulk band-structure calculation, the remaining peaks observed in the photoemission spectra were identified as direct bulk transitions. A later experimental dispersion determination[6] with $h\nu = 21.22$ eV showed similar results except for evidence of a third surface state at 1.1 eV seen in two spectra. Recently, data has been taken with lower photon energies and appears to reveal additional structure.[7]

In this paper we present the experimental surface-state dispersion of Ge(111) $c(2 \times 8)$ obtained with two different photon energies to avoid confusion with bulk features. Polarized photons have been used to determine the symmetry of the surface states. We find two strong states which exhibit p_z character near the zone edge leading us to identify them as being dangling-bond derived.

B. Back bonds

In order to make a comparison between the bulklike states for the reconstructed Ge(111) $c(2 \times 8)$ surface and pure bulk states, we have carried out measurements on the Ge(111):As 1×1 surface. This system has a 1×1 periodi-
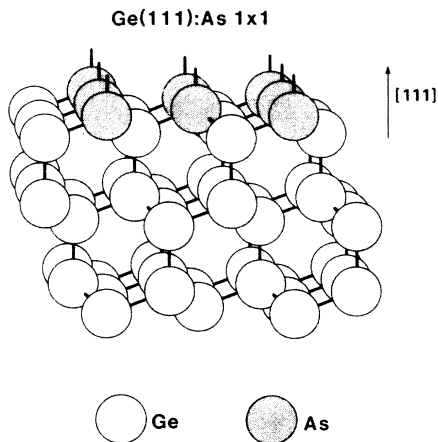
Ge(111):As 1x1

FIG. 1. Model of the structure of Ge(111):As 1×1.

city, no dangling bonds, and all atoms are in positions close to bulk lattice sites.[3] Ge(111):As 1×1 is thus an experimentaly obtainable ideal surface. The surface is formed by replacing the Ge atoms in the outer half of the topmost double layer by As atoms which, in turn, replaces Ge dangling-bond states with As lone-pair states. This structure is shown in Fig. 1 where it can be seen that every Ge atom is now fourfold coordinated, and every As atom is threefold coordinated, as in bulk As. This full coordination, and also the similarity in size of As and Ge atoms, allows the surface to form without any reconstruction and with all atoms lying close to the positions for an exact termination of the bulk. Because the number of bonds between atomic layers alternates between 1 and 3 per atom pair in the [111] direction, it is much less favorable energetically for the As atoms to adsorb as adatoms onto the ideal Ge(111) surface. Such an adatom system would require much larger strains of the bonds and bond angles. The surface-state dispersion and a comparison with a total-energy calculation of Ge(111):As have been presented elsewhere.[3] A very good agreement was obtained giving us confidence in the model shown in Fig. 1.

After an outline of the methods used to create the surfaces and carry out the measurements, results will be given for the low-binding energy surface bands of Ge(111) $c(2 \times 8)$ and Ge(111):As 1×1 followed by a discussion of the information that can be obtained about the bulk band-structure of Ge from these measurements.

II. EXPERIMENTAL DETAILS

The germanium used in these experiments was sliced from a 0.1-Ω cm, p-type single crystal. (111) surfaces were cut to an accuracy of $\pm 0.5°$ and polished with successively finer grades of alumina followed by a chemical/mechanical polish with a suspension of silica.[8] After introduction into the vacuum chamber, clean surfaces of Ge(111) were formed by sputtering with 500-eV Ar$^+$ ions followed by annealing to 790 °C. The annealing step was carried out by passing dc current through the 0.3-mm thick slices, a method which kept the sample holder at a

low temperature. The resulting surface showed a sharp $c(2 \times 8)$ low-energy electron diffraction (LEED) pattern. Arsenic was added *in situ* to the surface as As$_4$ molecules using a molecular-beam epitaxy effusion cell. To stimulate the cracking of the As$_4$ molecules, to enable the As to diffuse along the surface, and to prevent the adsorption of additional monolayers, the sample temperature was held at 400 °C in the As$_4$ flux. After the As exposure of $\sim 10^4$ L, a sharp 1×1 pattern was seen with LEED. [1 langmuir (L) $\equiv 10^{-6}$ Torr sec.] Angle-integrated photoemission measurements of the Ge $3d$ and As $3d$ levels were consistent with the formation of a single monolayer of As on the surface.[9] The surface component of the Ge $3d$ was replaced by an As-shifted component and the As $3d$ core level showed only a single component. It was also found that the Ge(111):As 1×1 surface was extremely resistant to further As adsorption, much more resistant than the analogous GaAs(111) surface. After a total As$_4$ exposure of $\sim 10^5$ L with the sample at room temperature, only a 5% increase was found in the As $3d$ core-level intensity.

Annealing the Ge(111):As sample produced no change in the photoemission spectra until a temperature of 690 °C was reached. This is well above the temperature of 250 °C at which solid As reaches a vapor pressure of 10^{-4} Torr and provides additional evidence for the absence of any excess As adlayer. The Ge(111) $c(2 \times 8)$ LEED pattern and photoemission spectra were fully developed after a 2-min anneal at 740 °C.

Angle-resolved photoemission measurements were carried out using an unpolarized He I discharge lamp ($h\nu = 21.22$ eV) and with linearly polarized radiation at the Stanford Synchrotron Radiation Laboratory. Photon incidence angles Θ_i and electron emission angles Θ_e were measured relative to the sample normal. Unless specifically noted, the radiation was linearly polarized in the plane of the emission angle and the sample normal. The combined resolution of the photons and the electron analyzer was less than 0.3 eV full width at half maximum (FWHM), determined by measuring the Fermi edge of the Mo sample holder. Energies were measured relative to this Fermi energy E_F and the positions of the top of the bulk valence band E_{VB} were found by measuring the energy of the centroid of the bulk Ge $3d$ peak with $h\nu = 37$-eV photons. The value of 29.57 eV for E(Ge $3d$) $- E_{VB}$ given by Kraut *et al.*[10] was used and yielded a $E_F - E_{VB}$ separation of 0.1 ± 0.1 eV, consistent with the value of 0.17 eV given by Guichar *et al.*[11] The valence band was found to shift away from E_F by a further 0.05 eV after As adsorption.

III. RESULTS AND DISCUSSION
A. Surface states on Ge(111) $c(2 \times 8)$

Surface-related features dominate the angle-resolved photoemission spectra for Ge(111) $c(2 \times 8)$. This is revealed by the dramatic changes which occur in the spectra after the addition of arsenic to the surface. The surface states associated with the clean surface disappear and a new surface state appears in the region near the top of the bulk valence band. An example of this change is shown in Fig. 2 for electron emission angles corresponding to the
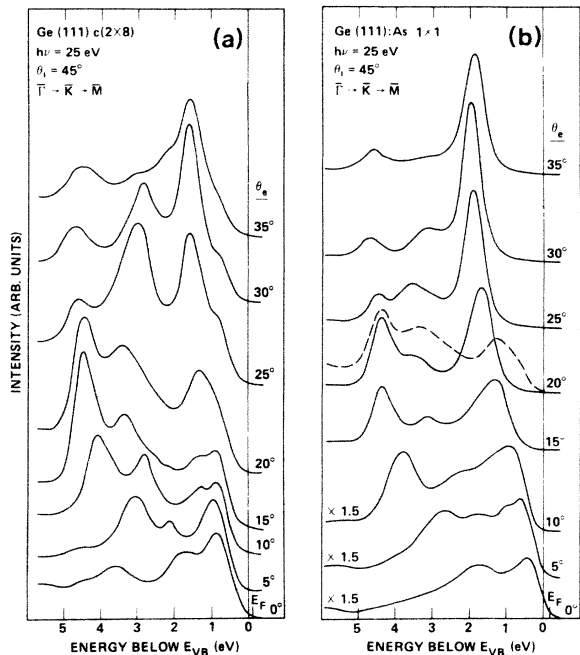
FIG. 2. Angle-resolved photoemission spectra as a function of electron emission angle Θ_e for (a) Ge(111) $c(2\times8)$ and (b) Ge(111):As 1×1. The spectra correspond to the direction $\bar{\Gamma}\to\bar{K}$ in the surface Brillouin zone and were taken with a photon energy of 25 eV. Spectra are normalized to photon flux with those in (a) being multiplied by 2 compared to the $\Theta_e > 10°$ spectra in (b). The $\Theta_e = 20°$ spectrum for Ge(111) $c(2\times8)$ is plotted as the dashed curve in (b).

$\bar{\Gamma}$ to $\bar{K}$ direction of the (1×1) surface Brillouin zone. For Ge(111) $c(2\times8)$, the two relatively flat surface-state bands centered around 0.85 and 1.4 eV below E_{VB} disappear after As adsorption and are replaced by a single strong feature which disperses from 0.45–2.0 eV below the top of the valence band, and which we identify as the occupied lone-pair band on the As atoms.[3] For comparison, the $\Theta_e = 20°$ spectrum for the clean surface is shown by the dashed curve in Fig. 2(b) where it is normalized with respect to the photon flux. It can be seen that the intensity of the As-related state is significantly stronger than the surface states on the clean surface. The remaining features have a similar dispersion to the bulk-related features seen in the Ge(111) $c(2\times8)$ data. The low-binding energy surface states for Ge(111):As 1×1 have been discussed in detail elsewhere.[3]

Data such as that shown in Fig. 2 were taken for the three symmetry directions in the surface and for a range of photon energies. Bulk-derived features in the spectra were identified by comparison with a bulk band-structure calculation as described in Sec. III C, allowing us to concentrate on the remaining surface features. This identification was reinforced by the observation that the states identified as surface related disappeared after exposure to hydrogen[5] and arsenic and the fact that the states had the same binding energy for all photon energies.

The dispersion of the Ge(111) $c(2\times8)$ surface features

with $k_{||}$, the wave-vector component parallel to the surface, was derived from the data and is shown in Fig. 3. Data is presented for mixed polarization 21.2-eV photons and for linearly polarized 25-eV photons. The accuracy to which the features can be located in energy and $k_{||}$ is given by the size of the symbols in the figure. It can be seen that the two photon energies give the same dispersion, consistent with the assignment to surface states. It was found that the dispersions for the $[11\bar{2}]$ and $[\bar{1}2\bar{1}]$ directions were identical and these are plotted together in Fig. 3(b). The sixfold symmetry seen for the dispersion of the two uppermost surface states implies that they are not strongly coupled to the bulk which has threefold symmetry about the [111] direction. The $[11\bar{2}]$ and $[\bar{1}2\bar{1}]$ directions exhibit distinctly different bulk-derived spectral features as will be discussed in Sec. III C.

The surface-state dispersion is similar to that reported earlier by Bringans and Höchst,[5] and Yokotsuka et al.[6] In both the $\bar{\Gamma}\to\bar{K}$ and $\bar{\Gamma}\to\bar{M}$ directions, two surface
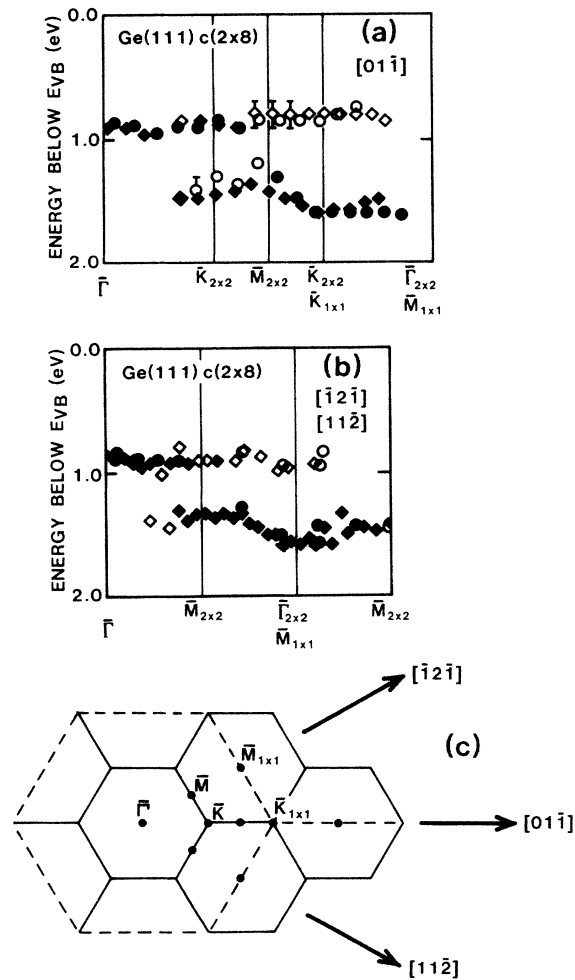

FIG. 3. Experimental Ge(111) $c(2\times8)$ surface-state dispersion for (a) the $[01\bar{1}]$ direction and (b) the $[11\bar{2}]$ and $[\bar{1}2\bar{1}]$ directions shown plotted together. Data for $h\nu=21.2$ eV (unpolarized) and 25 eV are shown by ♦ and ● symbols, respectively. Closed (open) symbols represent stronger (weaker) spectral features. The 1×1 (dashed lines) and 2×2 (solid lines) surface Brillouin zone are shown in (c).

bands can be seen. The uppermost band is strongest near $\bar{\Gamma}$ and decreases in intensity near the zone boundary. The lower band has a larger bandwidth and has its maximum intensity near the zone edge. This lower band cannot be identified reliably near $\bar{\Gamma}$ because direct transitions from bulk initial states occur in this region for $h\nu=21.2$ and 25 eV. In the $\bar{\Gamma}\rightarrow\bar{K}$ direction [Fig. 3(a)] there is a hint of a third feature near $\bar{M}_{2\times2}$, which coincides with a third peak seen at this value of $k_{||}$ by Yokotsuka et al.[6] This feature lies very close to the edge of the projected bulk bands, however, and may not represent a surface state.

More recent data by Nicholls et al.[7] at the lower photon energies of 10.2 and 11.0 eV have been interpreted as showing four bands in the $\bar{\Gamma}\rightarrow\bar{K}$ direction. The overall dispersion that they see is similar to that shown in Fig. 3(a) with the addition of two dispersing peaks. These both appear to cross from the upper to the lower surface state, the first near $0.3\times(\bar{\Gamma}\rightarrow\bar{K}_{1\times1})$ and the second near $0.5\times(\bar{\Gamma}\rightarrow\bar{K}_{1\times1})$, close to the edge of the bulk band structure as discussed above. The feature near $0.3\times(\bar{\Gamma}\rightarrow\bar{K}_{1\times1})$ corresponds to a broadening of the spectra in our data and to a weak third feature in the data of Yokotsuka et al.[6] At the photon energies of 10.2 and 11.0 eV, however, the direct transitions from bulk initial states lie very close to the dispersing peak seen by Nicholls et al.[7] near $0.3\times(\bar{\Gamma}\rightarrow\bar{K}_{1\times1})$. It is possible that bulk and surface states both contribute to this feature in their data. It should be pointed out that in all the sets of data, only two peaks can be seen in the region outside the projected bulk band structure.

It can be seen that the surface state dispersion in Fig. 3 has the correct symmetry for a 2×2 unit cell, something which was pointed out by Yokotsuka et al.[6] In the scanning tunneling microscope results of Becker et al.[12] on Ge(111) $c(2\times8)$ films grown epitaxially on Si(111) 7×7, regions with 2×2 as well as regions of $c(2\times8)$ symmetry are seen. It is possible that all Ge(111) $c(2\times8)$ surfaces have regions of both types of symmetry. In any case, the dominant dispersion seen in ARPES appears to be 2×2 like. This type of apparent contradiction has been seen before the GaAs(100) (Refs. 13—15) where LEED shows $c(4\times4)$ and $c(2\times8)$ while ARPES shows 2×1 in both cases. One possible conclusion is that the local bonding is that given by ARPES whereas LEED gives the full symmetry information. This is reasonable for Ge(111) $c(2\times8)$ because Becker et al.[12] point out how the $c(2\times8)$ symmetry that they observe can be decomposed into alternating rows of 2×2 and $c(4\times2)$.

The uppermost surface feature near 0.8 eV was identified in the paper by Bringans and Höchst[5] as a dangling bond and evidence was presented showing that the 1.4-eV peak was also p_z like. Evidence also existed[16] for Si(111) 7×7 that an analogous peak in that system at 1.8 eV was not p_z like at $\bar{\Gamma}$ and so no firm conclusion was made about the 1.4-eV Ge(111) $c(2\times8)$ peak. Later work[17] has shown that the Si(111) 7×7 peak at $\bar{\Gamma}$ corresponded to a bulk-derived feature.

The character of the two surface states near the $\bar{K}_{1\times1}$ point was examined by varying the angle of incidence of the photons. With normal incidence, the intensity of both components dropped significantly indicating strong p_z
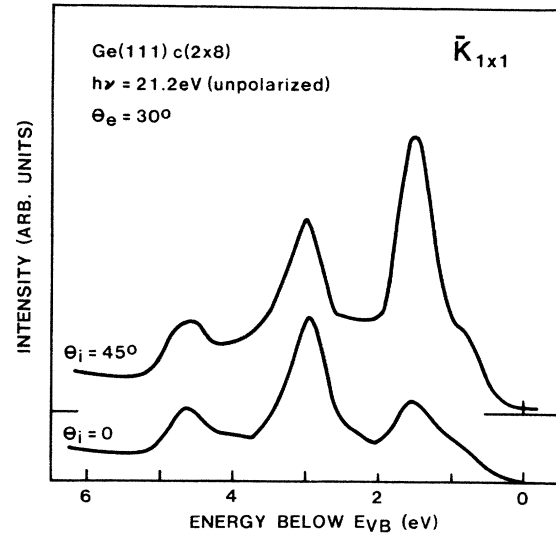

FIG. 4. Spectra at $\Theta_e=30°$ corresponding approximately to the $\bar{K}_{1\times1}$ point in the surface Brillouin zones for two different photon incidence angles.

character in both cases. This is shown for unpolarized 21.2-eV photons in Fig. 4, where the spectra are scaled to keep the higher binding energy peaks at constant intensity. This result provides the first solid evidence that there are two dangling-bond derived peaks on the Ge(111) $c(2\times8)$ surface. This is consistent both with the buckling model of Chadi and Chiang,[18] which contains two inequivalent "up atoms" and two inequivalent "down atoms" and with the surface tunneling microscopy (STM) results[12] which show at least two different types of surface atoms.

The magnitude of the splitting of the surface states is larger than would be expected for a buckling model. The STM results also seem to indicate a more drastic rearrangement of the atoms at the surface than that obtained by buckling. A more likely structure, in view of the STM results and the large splitting that we see (~0.7 eV at $\bar{K}_{1\times1}$), is a $c(2\times8)$ adatom model composed of $c(4\times2)$ and 2×2 building blocks. This is analagous to the Si(111) $c(4\times2)$ adatom model discussed by Northrup and Cohen.[19] A model such as this can provide a natural explanation for the presence of the two states seen in the gap of the projected bulk band structure and for the energy difference between them. Dangling bonds on the adatoms are unoccupied and so the uppermost state seen in the spectra can arise from dangling-bond orbitals on the rest atoms (the threefold-coordinated surface atoms not bonded to an adatom). The lower state could arise from dangling-bond states which have interacted with adatom p_x and p_y orbitals and are thereby shifted to lower energies. Northrup and Cohen[19] obtained an energy difference of 1.1 eV between the two types of states for Si(111) $c(4\times2)$. It is likely that a similar adatom model for Ge(111) would have a similar band structure.

B. Calculation of bulk initial-state dispersions

ARPES spectra contain contributions from surface states, bulk initial states, and so-called back-bond states. A back bond usually represents a bond between a second-layer atom in a bulklike environment and a surface atom. The separation of spectral features between surface, bulk, and back bond is always rather difficult. The analysis presented here relies on the ability to predict the position in $E(k_{\parallel})$ of bulk-derived features in order to separate out the surface-related features. The prediction is accomplished by calculating the initial-state band structure using an empirical local pseudopotential method. Energies were calculated as a function of $k_{\perp}$ for fixed $k_{\parallel}$. It was assumed that transitions were made into a final state with a free-electron dispersion and with an energy zero at V_0 below the top of the valence band. The rationale for choosing a free-electron final state is not that it provides a good approximation to the Bloch conduction band states, but rather that it selects the only final states with a high probability of reaching the electron detector in the experiment. Outside the crystal the electrons are in a plane-wave state directed towards the detector. The free-electron parabola used as a final state inside the crystal has an identical form but is offset by the potential barrier E_0. In the repeated zone scheme, a single parabola in the $k_{\perp}$ direction is used, or in the reduced zone scheme only G vectors parallel to $k_{\perp}$ are allowed. Other G vectors give rise to so-called "secondary cone" contributions which generally have significantly lower intensity. Given known initial and final states as a function of $k_{\perp}$, possible transitions were found by searching for final and initial states separated by $h\nu$. The dispersion expected for each initial-state band could thus be found as a function of $k_{\parallel}$.

An example of the kind of agreement possible is shown in Fig. 5, where the calculated dispersions $E_i(k_{\parallel}, h\nu)$ are
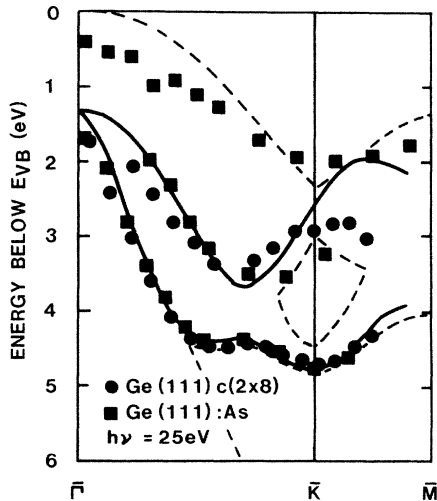

FIG. 5. Positions in energy and $k_{\parallel}$ of bulk-related features for Ge(111) $c(2\times8)$ and Ge(111):As and of the lone-pair surface state for Ge(111):As. Surface states of Ge(111) $c(2\times8)$ were omitted for clarity. The data are for a photon energy of 25 eV and positions expected for bulk-related features at 25 eV are shown by the solid curves. The dashed curves show the edge of the projected bulk band structure.

compared with the measured $E(k_{\parallel}, h\nu)$ data. The zero of the final-state parabola was taken to be $V_0 = 9.70$ eV below E_{VB}. This was the value which was found to give the best overall agreement with the data. Similar calculations carried out earlier[5] for Ge(111) $c(2\times8)$ using a value of V_0 equal to the valence-band width, do not agree as well. The excellent agreement found between experiment and calculation for GaAs(110) by Chiang et al.[20] with $V_0 \approx 8$ eV has shown that the value of V_0 does not have a simple relationship to the valence-band width. The potential barrier at the surface is given by

$$E_0 = 9.70 \text{ eV} + (E_F - E_{VB}) + \varphi ,$$

where φ is the work function of the surface. It is clear, both here and along the $[\bar{1}12]$ and $[\bar{1}2\bar{1}]$ directions discussed below, that there is a very good correspondence between the data and the calculation. This is evidence that (1) ARPES spectra contain information that directly yields bulk initial states. (2) The free-electron final state is the most appropriate final state to use in the $h\nu \geq 20$ eV range. (3) The $c(2\times8)$ surface unit cell does not influence the bulk state dispersion. (4) It is possible to reliably discriminate between bulk and surface-derived spectral features.

A particularly simple situation occurs in the normal emission geometry $(k_{\parallel} = \Theta_e = 0)$. Only states along the line Γ to L in the bulk zone can contribute to the spectra and variation of $h\nu$ allows the bulk initial state dispersion to be measured if the final state is known. Again, a free-electron parabola generally gives good results for semiconductors [see, for example, the early results of Chiang et al.[20] for GaAs and the recent data of Uhrberg et al.[17] for Si(111)]. Wachs et al.[21] have shown that direct transitions determined from a free-electron parabola describe normal emission Ge(111) $c(2\times8)$ data for photon energies above about 45 eV. Results are not so straightforward for Ge(111) for photon energies below about 30 eV as has been pointed out by Nicholls et al.[22] These authors find that they get better agreement with one of the conduction-band states for normal emission. Our data also shows that a conduction band seems to work best for normal emission whereas the free-electron final state provides the best results for off-normal emission. This is shown in Fig. 6 where the final state for the photoemission process is determined by adding the photon energy to the measured initial-state energy for the upper two valence bands and using the calculated initial-state band structure to fix $k_{\perp}$. The final states obtained are compared with both the calculated conduction bands and the primary cone parabola.

The data shown in Fig. 6(a) correspond to the normal emission geometry and come from the Ge(111):As surface which is felt to be closest to a bulklike situation. The initial-state bandwidth was found experimentally by taking the energy at which the uppermost valence band had its turning point in the data. This occurred for $h\nu = 27$ eV at an energy of 1.75 eV below E_F. The initial state was then given the same curvature as the calculation by Chelikowsky and Cohen.[23] It can be seen that the final-state dispersion plotted out does not closely resemble the free-electron parabola. This apparent contradiction with
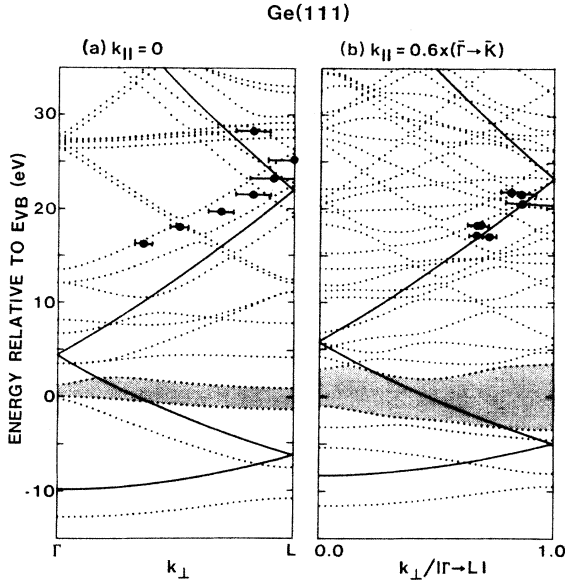
Ge(111)

(a) k∥ = 0   (b) k∥ = 0.6×(Γ̄→K̄)

FIG. 6. Bulk band structure as a function of $k_\perp$ for (a) $k_\parallel = 0$ and (b) $k_\parallel = 0.6 \times (\bar{\Gamma} \rightarrow \bar{K})$. The solid curves show the primary cone free-electron final state with $V_0 = 9.7$ eV. Data points are shown for a number of photon energies in the range 17–30 eV for Ge(111):As 1×1 in (a) and for 21.2 and 25 eV for Ge(111) $c(2\times8)$ and Ge(111):As 1×1 in (b).

the good overall agreement seen in Fig. 5 can be understood by referring to the band-structure calculation shown in Fig. 6. As soon as $k_\parallel$ departs from zero, the experiment begins probing lines in the bulk Brillouin zone which have low symmetry. It can be seen in Fig. 6(b) that at $k_\parallel = 0.6 \times (\bar{\Gamma} \rightarrow \bar{K})$, the final-state bands all separate and tend to fill the whole $E(k_\perp)$ plane. At $k_\parallel = 0$ on the other hand, there are large empty areas. For a direct transition to occur, two conditions must be met:

(1) There must be a conduction-band state to excite into. This state can be considered to be broadened by the finite lifetime of the final state and so there is only a requirement that there is a conduction-band state near $E_i(k) + h\nu$.

(2) The final state must lie near the free-electron parabola because the parabola represents the $E(k)$ relationship of the only electrons that can simply reach the detector in the experiment.

When there are large gaps in the conduction bands, it is difficult for condition (1) to be met and the conduction-band structure dominates as is the case for Ge(111) at normal emission. For either higher photon energies or low-symmetry lines the broadened conduction bands can be considered to fill all of $E(k_\perp)$ and the direct transitions are determined by the free-electron parabola. In the following discussion of the bulk-related spectral features, we will use calculations based only on the free-electron final state with V_0 set to 9.7 eV. The data near $\bar{\Gamma}$ is thus not expected to be as well reproduced by the calculations.

The bulk band-structure calculations were made with a local empirical pseudopotential method using the form factors of Cohen and Bergstresser.[24] The more accurate

nonlocal pseudopotential method of Chelikowsky and Cohen[23] gives bandwidths larger than the results of Cohen and Bergstresser by a factor of ~1.3 for the upper two valence bands. We found that our data fit best when the energies of the upper two valence bands obtained with the local empirical pseudopotential method[24] were multiplied by 1.22. This could be tested for the second valence band at the $\bar{K}$ point in the surface Brillouin zone. The outline of the projected band structure in Fig. 5 shows that the dispersion is required to pass through a narrow band at $\bar{K}$ irrespective of the value of V_0 that is chosen.

C. Back bonds and bulk Ge levels

Now that we have a reliable method for determining the dispersion in the spectra of pure bulk-derived features, we can address the question of how the surface affects bulklike states. The experimentally determined $E(k_\parallel)$ dispersion of the bulk-related features for both Ge(111) $c(2\times8)$ and Ge(111):As 1×1 at $h\nu = 25$ eV are shown in Fig. 5 along with the As-related surface band. The comparison in Fig. 5 shows that the bulk-derived features are relatively unchanged after the surface is transformed from Ge(111) $c(2\times8)$ to Ge(111):As 1×1 and that there is excellent agreement with the calculated dispersion (the solid curve in the figure). A deviation occurs, however, for the uppermost valence band in the vicinity of the gap in the projected bulk-band structure near $\bar{K}$. In this region, differences occur between the two surfaces and both dispersions depart from the bulk calculation. This can be interpreted as showing the effect of back bonds on the data. It should be noted that data taken at $h\nu = 21.2$ eV showed the same behavior.

A similar set of data corresponding to $h\nu = 21.2$ eV is shown for the [11$\bar{2}$] and [$\bar{1}2\bar{1}$] directions in Fig. 7 for Ge(111) $c(2\times8)$ and Fig. 8 for Ge(111):As 1×1. Turning first to the clean surface, it can be seen that the dangling-bond surface states at low-binding energies are well separated from the calculated bulk dispersions and that the remaining data points closely follow the calculated bulk dispersions. An exception occurs near $\bar{\Gamma}$ where an extra band can be seen at ~3.6 eV. This band does not correspond to a secondary cone feature but is possibly a reflection of the high three-dimensional density of states at this energy[5] or arises from some other higher order effect.[25] It can also be seen that the threefold symmetry of the bulk is reflected in the bulk data. The departures from the calculation are not significant except for the absence of features corresponding to the uppermost band in the [11$\bar{2}$] direction. With the unpolarized photons used, both bands should be seen.

The data for Ge(111):As 1×1 were taken with photons polarized in the plane of the surface normal and the emission angle. Because this is a mirror plane for which the uppermost band represents odd states and the second band even states, the uppermost band should not be seen in the spectra. This can be seen to be the case in Fig. 8. As was true for the clean surface, the surface state (the lone-pair band here) is well separated from the bulk-derived dispersion. Again, there is good overall agreement between the data and the experiment. Deviations do occur, however, in the region near the gap at $\bar{M}$. In the [$\bar{1}2\bar{1}$] azimuth an
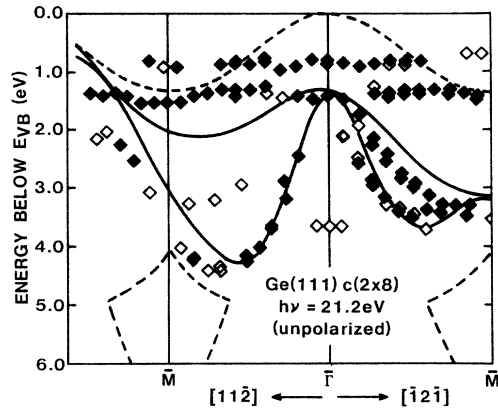
FIG. 7. Positions in energy and $k_{||}$ of spectral features along the $[11\bar{2}]$ and $[\bar{1}2\bar{1}]$ azimuths for Ge(111) $c(2\times8)$. Closed (open) symbols represent stronger (weaker) spectral features. For each azimuth, data were taken for emission angles on the same and opposite sides of the surface normal as the photon direction and results and superimposed in the figure. Data were taken with unpolarized 21.2-eV photons and positions calculated for bulk-related features at 21.2 eV are shown by the solid curves. The dashed curves show the edge of the projected bulk band structure.

extra band is seen which comes very close to the gap at $\bar{M}$ and there is a departure from the calculation with a similar result in the $[11\bar{2}]$ direction. The fact that these deviations lead to a band with sixfold symmetry suggests that a surface-related state is involved, especially as it is close to the edge of the projected bulk-band structure.

Before making an interpretation involving a deep-lying surface or back-bond state, it is necessary to rule out the alternative interpretation that these features arise from a bulk initial state via secondary cone emission. If this were
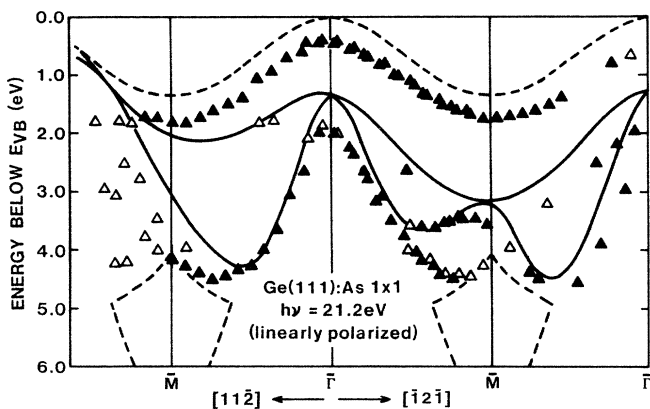

FIG. 8. Positions in energy and $k_{||}$ of spectral features along the $[11\bar{2}]$ and $[\bar{1}2\bar{1}]$ azimuths for Ge(111):As 1×1. Closed (open) symbols represent stronger (weaker) spectral features. Conditions were the same as for Fig. 7, except the data were taken with linearly polarized 21.2-eV photons. Positions calculated for bulk-related features at 21.2 eV are shown by the solid curves and the dashed curves show the edge of the projected bulk band structure.
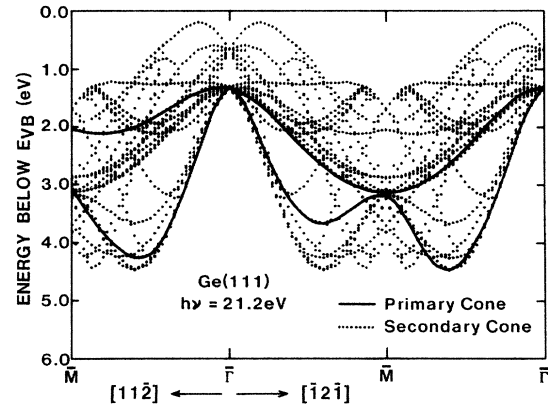

FIG. 9. Calculated secondary cone dispersions corresponding to transitions from the upper two bulk valence bands of Ge. The data are for photoemission along the $[11\bar{2}]$ and $[\bar{1}2\bar{1}]$ azimuths from the (111) surface at a photon energy of 21.2 eV. The primary cone dispersion is shown by the solid curve.

the case then one would expect to see the same result for Ge(111) $c(2\times8)$ as for Ge(111):As 1×1 [although it could be argued that the large number of superlattice G vectors from the $c(2\times8)$ reconstruction smears out secondary cone effects]. The secondary cone emission process can be represented by expanding the possible final states to include $(k+G)^2$ for all G vectors. The problem with this interpretation is that there are a large number of possible transitions. Calculations for all of the accessible G vectors are shown in Fig. 9 by the dotted curves for the upper two valence bands, with the primary cone dispersion indicated by the full line. Dispersions do occur near the extra band which was seen in the data, but there seems to be no real reason to expect that only these particular transitions should show up in the data but not all of the others. The weight of the evidence thus seems to favor a surface-related origin for these states.

In summary, the overall results for the bulklike states show good agreement between the calculated and measured dispersions for both Ge(111) $c(2\times8)$ and Ge(111):As 1×1. This implies that the atomic environment of the atoms close to the surface is very similar to that in the bulk. The differences which do occur, and are discussed above, are the exception rather than the rule for these surfaces.

IV. CONCLUSIONS AND SUMMARY

Experimental determinations of surface-state dispersions obtained using angle-resolved photoemission can be used in two different ways to reveal information about surface atomic structure and surface electronic structure. The use of a model system such as Ge(111):As 1×1 allows a direct and quantitative comparison with theory. The Ge(111) $c(2\times8)$ surface, on the other hand, has a large unit cell and a direct comparison is difficult. We have shown that 2×2 subunits of the $c(2\times8)$ structure can be identified by examining the symmetry of the surface-state dispersion and then comparison with theoretical models can be made. The electronic structure

in the gap of the projected bulk band structure consists of two strong surface states split by about 0.7 eV. This suggests that the subunits may consist of an adatom model such as that discussed by Northrup and Cohen[19] for Si(111). The polarization dependence of the surface states, which can reveal their atomic character, is also consistent with an adatom model.

The Ge(111):As 1×1 system shows a strong surface state corresponding to the lone-pair orbitals on the As atoms. The total bandwidth is ~1.7 eV and the dispersion of the state is qualitatively similar to that for the ideal 1×1 Ge(111) surface.

The photoemission experiment also probes bulk initial states. The data can be considered to represent a transition from a bulk initial state to a free-electron final state in the vacuum. Use of an intermediate state makes it simpler to predict the dispersion of bulk-derived features in photoemission data. An intermediate state, consisting of a free-electron parabola with its energy offset by a potential barrier with respect to the final state, was found to give excellent agreement with the experiment. Near $\overline{\Gamma}$, however, the agreement was found to be better if a conduction band is used as the intermediate state. Quantitative agreement such as that obtained here makes it possible to examine surface-related features at large binding energies. In the case of Ge(111):As 1×1, evidence is given for a surface-related feature occurring near $\overline{M}$ at a binding energy of about 4 eV.

ACKNOWLEDGMENTS

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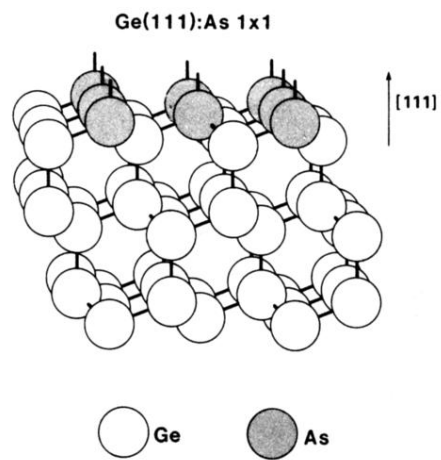
Ge(111):As 1x1

FIG. 1. Model of the structure of Ge(111):As 1×1.
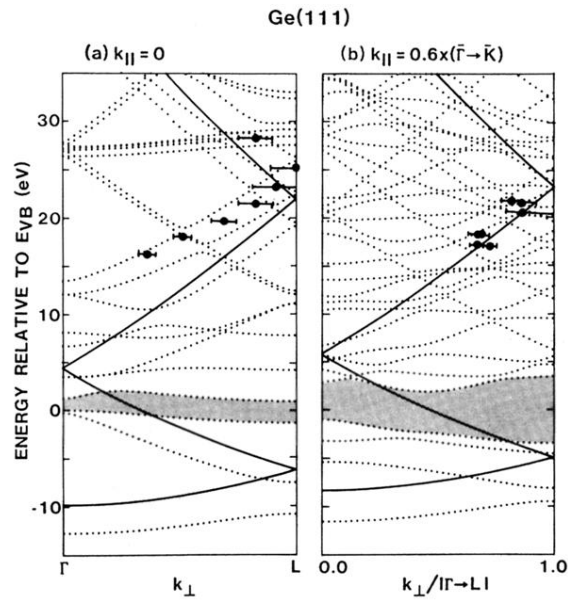
FIG. 6. Bulk band structure as a function of $k_\perp$ for (a) $k_{||}=0$ and (b) $k_{||}=0.6\times(\bar{\Gamma}\to\bar{K})$. The solid curves show the primary cone free-electron final state with $V_0=9.7$ eV. Data points are shown for a number of photon energies in the range 17–30 eV for Ge(111):As 1×1 in (a) and for 21.2 and 25 eV for Ge(111) $c(2\times8)$ and Ge(111):As 1×1 in (b).