New surface states on the annealed Ge(111) surface

J. M. Nicholls,* G. V. Hansson, and R. I. G. Uhrberg†
Department of Physics and Measurement Technology, Linköping Institute of Technology, 581 83 Linköping, Sweden

S. A. Flodström
MAX-Laboratory, 220 07 Lund, Sweden
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From angle-resolved photoemission measurements on the annealed Ge(111)c-(2×8) surface, detailed dispersions are presented for two previously reported surface-state bands. Additional surface states dispersing between these bands are observed. The resulting surface-state dispersions show similarities with recently observed surface-state bands on the annealed Si(111)7×7 surface and with metal-adatom-induced surface states on Si(111). It is suggested that a similar adatom bonding mechanism may be present on these surfaces.

The geometric and electronic properties of the annealed Ge(111) surface have been the object of numerous experimental and theoretical studies.[1] In low-energy electron diffraction (LEED) a complex pattern with $\frac{1}{2}$-order and $\frac{1}{8}$-order spots has been observed from this surface,[2] but a definite determination of the corresponding unit cell has so far not been possible. Among different reconstructions suggested are the (2×8) (Ref. 2), (8×8) (Ref. 3), and c-(2×8) (Ref. 4). None of these, however, can be directly related to the LEED patterns actually observed. Structure-factor cancellations must be assumed to explain the absence of several superstructure spots for all of the reconstructions suggested.

In a recent study Yang and Jona[5] presented a method for gaining structural information from missing spots in LEED patterns that favored the c-(2×8) reconstruction, while the (2×8) reconstruction was ruled out. It can be argued that since the number of missing spots in the LEED patterns will be larger for the (8×8) than for the c-(2×8) reconstruction, the latter is the most probable. The c-(2×8) reconstruction is also supported by reflection high-energy electron diffraction measurements[6] in which extra spots consistent with this reconstruction are present. Although a definite choice between the alternatives cannot be made, the actual surface reconstruction will be referred to as the c-(2×8) reconstruction.

In the first angle-integrated photoemission study on annealed Ge(111) surfaces by Murotani *et al.*,[7] the existence of surface-state bands close to the valence-band edge was suggested. In later angle-resolved work,[8–11] two surface-state bands at ≈ -0.8 and ≈ -1.4 eV below the top of the valence-band edge were observed. In none of these studies has surface-state distributions been observed to show the periodicity of the small superstructure Brillouin zone. Rather, the observed surface-state bands have been found to correspond to (1×1) (Ref. 8) or (2×2) (Ref. 10) surface cells, indicating that photoemission is sensitive to the short-range order of the surface.

In the present study, surface-state distributions not previously observed for the annealed Ge(111) surface are presented. Not merely are two almost flat bands present, but dispersing states are found in between them. Similarities with recent measurements on the Si(111)7×7, Si(111)$\sqrt{3}\times\sqrt{3}$-Al (Ref. 12), and Si(111)$\sqrt{3}\times\sqrt{3}$-In (Ref. 13) surfaces are discussed, suggesting similar local adatom geometries on these surfaces.

The experimental apparatus has been described elsewhere.[14] For the photon energy range 7.8–11.0 eV, a total-energy resolution $\Delta E \leq 0.2$ eV was obtained (for 10.2 eV, $\Delta E = 0.05$ eV), while the angle resolution of the analyzer was ±2°. A clean and well-ordered c-(2×8) surface was produced by argon-sputtering and annealing a nominally undoped Ge(111) wafer ($\approx$50 Ω cm) to $\approx$750 °C. The base pressure in the ultrahigh-vacuum chamber was $\approx 1\times10^{-10}$ Torr during the experiments.

In the previous study by Bringans and Höchst,[9] two pronounced surface-state bands at ≈ -0.8 and ≈ -1.4 eV below the valence-band edge were found for the Ge(111)c-(2×8) surface. These surface states showed almost no dispersion. One additional very weak surface-state structure just below the valence-band edge was also observed. Yokotsuka *et al.*[10] later repeated this experiment at the same photon energy, $\hbar\omega = 21.2$ eV, but with better energy resolution, $\Delta E = 0.1$ eV, as compared with $\Delta E = 0.3$ eV in the measurement of Bringans and Höchst. Two surface-state bands were again present in the later study but more details of the dispersions were observed. In one spectrum a "triplet structure" sensitive to contamination was present, and this state was also associated with the surface.

In the present work the two surface-state bands from the earlier studies are observed, but additional surface structures dispersing between the previously observed surface-state bands are also present. Some parts of the previously observed dispersions were not observed in the present work, indicating that the visibility of the surface states on the Ge(111)c-(2×8) surface is strongly dependent on the photon energy.

In the analysis of measured spectra the interpretation of observed structures as surface states is complicated by in-

terference from direct transitions present due to the low photon energies used. In previous studies of the cleaved Ge(111)2×1 surface[14,15] for polarized as well as unpolarized light of photon energy 10.2 eV, these bulk transitions have been investigated in detail. The position and intensity of the direct transitions are therefore known and possible misinterpretations can be avoided. The surface was also exposed to various amounts of oxygen and hydrogen to sort out further the structures originating from the surface. Spectra were also recorded for different angles of light incidence to determine the polarization dependence of the features observed. The structures that have been assigned to surface states are all more stable in energy (for changes in photon energy) than the calculated direct transitions. The energy positions of the structures can, however, have small shifts due to the finite width of direct-transition features that are close to the surface states. Finally, the identified surface states are unique for the c-(2×8) reconstructed surface since structures with the same energy dispersion have not been seen in our studies of the (2×1) reconstructed surface.

In Fig. 1, spectra recorded along the [1$\bar{1}$0] direction at a photon energy of 10.2 eV are shown. The geometry of the (1×1) and c-(2×8) surface Brillouin zones (SBZ's) and the various directions probed in the experiment are shown in Fig. 2. In Fig. 1 four surface-state structures in the spectra are marked A—D and in Fig. 3 initial-state dispersions $E_i(\mathbf{k}_{\|})$ for these states are plotted. (Strictly speaking, these states should be referred to as surface resonances when they are within the projected bulk bands.) For comparison, the dispersions obtained by Yokotsuka *et al.* using 21.2-eV photon energy[10] are also included. States A and B can be seen to coincide with those observed by Yokotsuka *et al.* The lower part of state C and the weak structure D are also in agreement with the dispersions previously observed. One important difference, however, is the upper part of dispersion C which was not observed in the earlier measurements, except as a weak triplet structure in the $\theta_e = 10°$ spectra in Ref. 10.

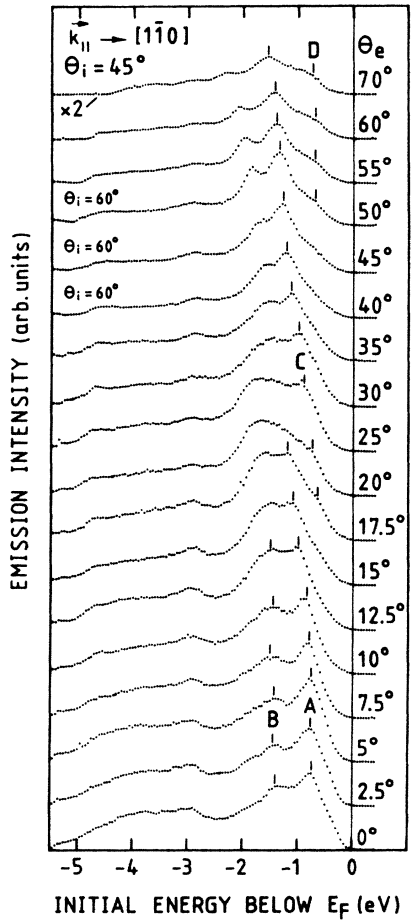

FIG. 1. Photoemission spectra recorded at a photon energy of 10.2 eV for various angles of emission (θ_e) along the [1$\bar{1}$0] direction. Structures A—D correspond to surface states. $\mathbf{k}_{\|}$ is the component of the wave vector parallel to the surface plane and is directed along the [1$\bar{1}$0] direction.

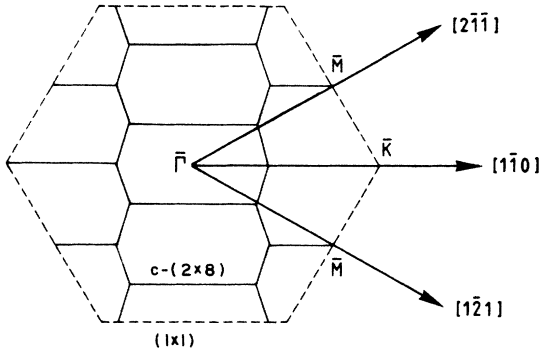

FIG. 2. Various directions investigated in the photoemission experiment relative to the (1×1) and c-(2×8) surface Brillouin zones. The figure shows a single domain of the c-(2×8) reconstruction, whereas in the experiment, three (or six, Ref. 4) domains rotated 120° relative to each other are always present. Possible reconstruction models other than c-(2×8) exist, see main text.

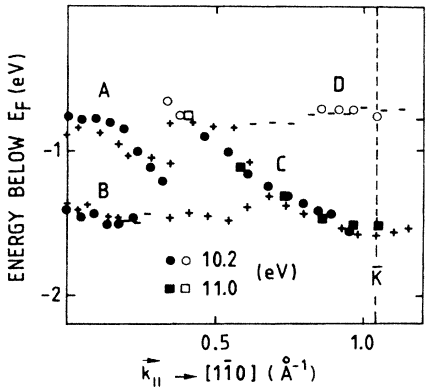

FIG. 3. Initial-state energy dispersions for the surface structures in Fig. 1. Also indicated are the surface-state dispersions from Ref. 10 ($\hbar\omega = 21.2$ eV), where strong and weak features are indicated by (+) and (−). Strong and weak structures in the present study are indicated with solid and open symbols, respectively. $\mathbf{k}_{\|}$ is directed along the [1$\bar{1}$0] direction.

The appearance of structure C is reminiscent of the "S_3 surface state" observed on the Si(111)7×7 surface.[12] Similar to the S_3 state, state C has a strong dependence on the incident angle of the light. It is strongly reduced at normal incidence, when the component of the electric field vector perpendicular to the surface is reduced, indicating that it is mainly of p_z character. The dispersion of state C is also reproduced at a photon energy of 11.0 eV (marked with squares in Fig. 3).

Among the different structures observed in the present study, structure B at an initial energy ≈ -1.4 eV below the Fermi level is the one for which the nature is the most difficult to determine. In a previous study[15] of the Ge(111)2×1 surface, some emission is observed for many photon energies at about this binding energy. This emission is probably due to transitions from a high density of states close to the L_3' point.[15] For photon energies close to 10.2 eV, a structure corresponding to direct transitions is also observed near this energy. For increasing angles of the emission, that structure can be seen to disperse downwards in energy,[14,15] unlike structure B on the Ge(111)c-(2×8) surface that has a flat dispersion. Calculated transitions[15] for the energy region of structure B are allowed for photon energies around 10.2 eV. However, none of the calculated transitions has the flat-type dispersion observed for structure B, but disperses rapidly towards higher binding energies for increasing $k_{\parallel}$ values.

The dispersion of peak B is not marked for emission angles larger than 12.5° (in the [1$\bar{1}$0] direction), since a bulk structure observed for the same bulk directions on the Ge(111)2×1 surface has a dispersion with the same initial energies for emission angles 15°–20°. Also, a calculated initial-state dispersion for transitions from the uppermost valence band to a primary free-electron-like band is predicted in this region.

Structure B has also been observed at higher photon energies (16.8 and 21.2 eV) in other studies[9,10] of the Ge(111)c-(2×8) surface. When the surface is exposed to gases, this structure decreases in intensity. For the photon energies of 16.8 and 21.2 eV, this effect is very large, whereas in our study (7.8–11.0 eV) the effect is less pronounced, indicating a lower emission from this surface state at the lower photon energies. In the present study, therefore, a strong mixing with emission from a high density of states close to the L_3' point is probably present.

The other surface structures in the present study are more sensitive to gas exposure and the identification of them is less complicated. As for structure B these states have also been compared with measurements on the Ge(111)2×1 surface and with calculated bulk dispersions.

In Fig. 4 are shown spectra recorded along the [1$\bar{2}$1] direction at a photon energy of 10.2 eV. Corresponding initial-state dispersions for this direction are shown in Fig. 5 for several photon energies. In this case also four surface structures (A–D) can be observed that partly overlap the dispersions obtained by Yokotsuka *et al.* Structure C seems to be extended upwards also for this direction, but it is not clear whether or not it is joined with state A. At the photon energies of 7.8 and 8.6 eV, structures A and D are connected by a flat dispersion, in agreement with the higher surface-state band observed in Ref. 10. At a photon energy of 11.0 eV the dispersion of structure C is reproduced. At about −0.4 eV below the Fermi level, a very weak structure E is observed at angles corresponding to $k_{\parallel}$ values close to the SBZ border at the M point. This structure is sensitive to contamination, but, for normal incidence of light, retains the same intensity or even increases slightly, indicating that this state is

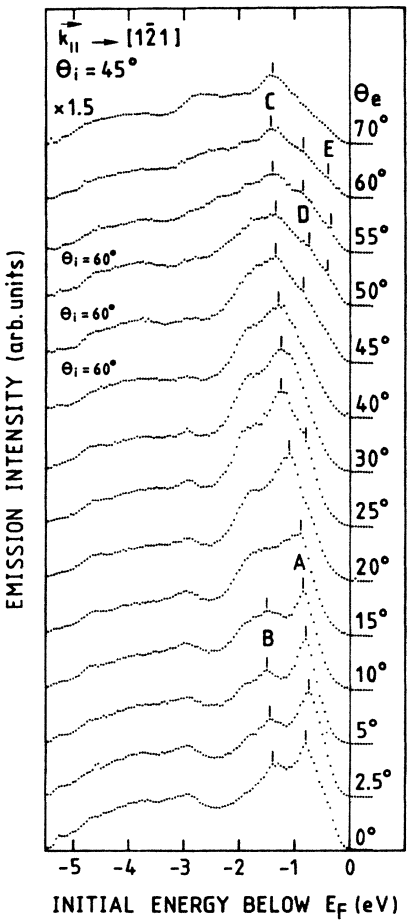

FIG. 4. Photoemission spectra recorded at a photon energy of 10.2 eV for various angles of emission (θ_e) along the [1$\bar{2}$1] direction.

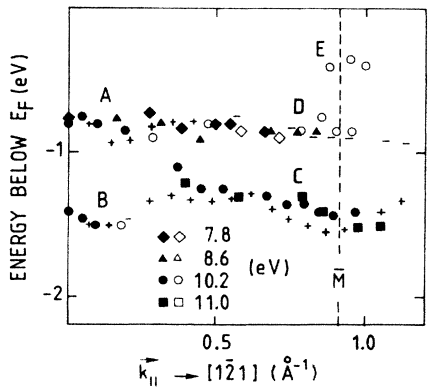

FIG. 5. Initial-state energy dispersions for the surface structures in Fig. 4.

not of the dangling-bond type with p_z character. The very weak peak observed at about this energy by Bringans and Höchst[9] was associated with secondary cone emission from the top of the valence band at Γ. The emission from the $[2\bar{1}\bar{1}]$ direction is very similar to that from the $[1\bar{2}1]$ direction, with the same set of structures (A–E) present (see Figs. 6 and 7). For the three directions probed in the experiment, all structures assigned as surface states are found to be sensitive to contamination with oxygen and hydrogen.

In a study by Himpsel *et al.*,[8] a similar surface-state emission was found for thermally and laser-annealed surfaces of Ge(111) and Si(111). These surfaces were found to have two prominent surface states close to the top of the valence band. These surface states had distributions in k space consistent with a (1×1) SBZ. In particular, the lower-lying states were found near the zone boundary and at the zone center, while the upper state had a distribution that peaked near the zone center but fell off more slowly in intensity than the lower state when leaving the center. These findings are in agreement with the intensity distributions observed in the present work, where structure B and the lower part of C correspond to the "lower" state and A to the "upper" state.

Further similarities between the annealed surfaces of Ge(111) and Si(111) have been found in temperature-dependent photoemission studies by Yokotsuka *et al.*[11] At elevated temperatures a surface-state structure appears on the Ge(111) surface just above the Fermi level, with an angular dependence similar to that of the "metallic" surface state on Si(111)7×7. In the photoemission studies of the Ge(111)c-(2×8) and Si(111)7×7 surfaces performed so far, the surface states have not shown indications of any of the surface unit cells suggested [(2×8), c-(2×8), (8×8), and (7×7)]. The photoemission experiments, therefore, seem to be more sensitive to the short-range ordering of the surface, in contrast to, e.g., LEED which reveals the long-range periodicity of the surface geometry.

Surface-state dispersions similar to those observed on the Ge(111)c-(2×8) surface have also been observed on the metal-overlayer surfaces Si(111)$\sqrt{3}\times\sqrt{3}$-Al and Si(111)$\sqrt{3}\times\sqrt{3}$-In (Refs. 12 and 13). The metal-adatom-induced states on the (111) surface of Si are derived from p_z orbitals on the Si surface atoms coupling to p_x and p_y orbitals on the adatoms.[13,16] A similar situation is also found for a (2×2) Si-adatom model[17] for the Si(111)7×7 surface. In this model the (2×2) surface lattice has a local environment similar to that in a model of the (7×7) surface suggested by Binnig *et al.* from scanning tunneling microscopy.[18] Comparing the results of Yokosuka *et al.* on the Ge(111)7×7-Sn surface[10] with the present measurements, clear similarities with the Sn-induced surface-state dispersions can be seen. This suggests that a similar adatom geometry may be present on the (111)c-(2×8) and (111)7×7 surfaces as well as on the group-III adatom surfaces on Si(111). Like the adatom-induced states on the Si(111)$\sqrt{3}\times\sqrt{3}$-Al and Si(111)$\sqrt{3}\times\sqrt{3}$-In surfaces, some of the surface states observed on Si(111)7×7 and Ge(111)c-(2×8) may be derived from bonding orbitals between "substrate" and adatoms on the surface. Photoemission studies of differently annealed Ge(111) and Si(111) surfaces indicate that laser-annealed (111)1×1 surfaces have electronic structures very similar to the c-(2×8) and (7×7) surfaces.[8] The surface-state bands may then have the properties of smaller building units of the surface, e.g., (1×1), (2×1), or (2×2).

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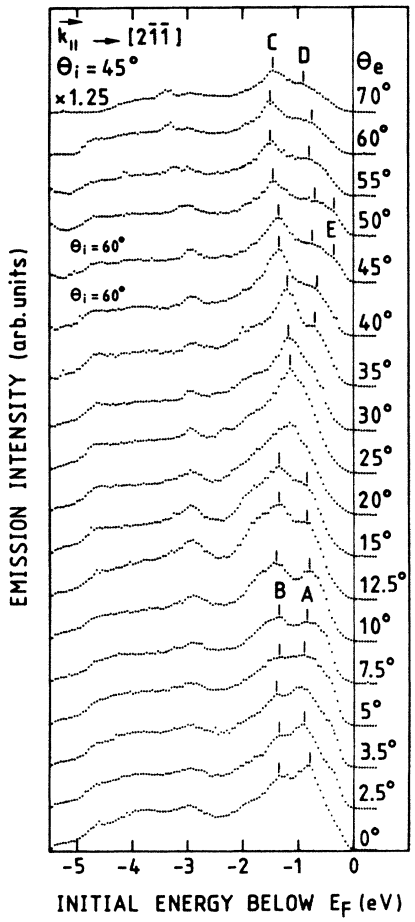

FIG. 6. Photoemission spectra recorded at a photon energy of 10.2 eV for various angles of emission (θ_e) along the $[2\bar{1}\bar{1}]$ direction.

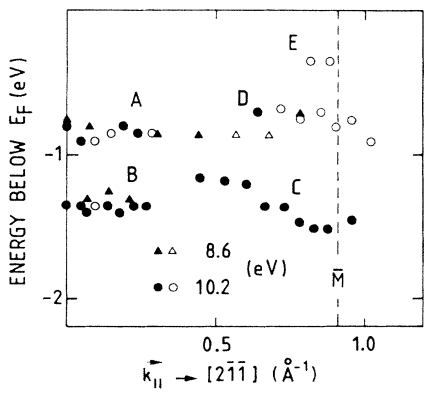

FIG. 7. Initial-state energy dispersions for the surface structures in Fig. 6.

*Present address: IBM Zürich Research Laboratory, CH-8803 Rüschlikon, Switzerland.
†Present address: Xerox Palo Alto Research Center, 3333 Coyote Hill Road, Palo Alto, CA 94304.

[1]For a brief review, see D. Haneman, Adv. Phys. **31**, 165 (1982).
[2]P. W. Palmberg and W. T. Peria, Surf. Sci. **6**, 57 (1967).
[3]M. Taubenblatt, E. So, P. Sih, A. Kahn, and P. Mark, J. Vac. Sci. Technol. **15**, 1143 (1978).
[4]D. J. Chadi and C. Chiang, Phys. Rev. B **23**, 1843 (1981).
[5]W. S. Yang and F. Jona, Phys. Rev. B **29**, 899 (1984).
[6]T. Ichikawa and S. Ino, Surf. Sci. **85**, 221 (1979).
[7]T. Murotani, K. Fujiwara, and M. Nishijima, Phys. Rev. B **12**, 2424 (1975).
[8]F. J. Himpsel, D. E. Eastman, P. Heimann, B. Reihl, C. W. White, and D. M. Zehner, Phys. Rev. B **24**, 1120 (1981).
[9]R. D. Bringans and H. Höchst, Phys. Rev. B **25**, 1081 (1982).
[10]T. Yokotsuka, S. Kono, S. Suzuki, and T. Sagawa, J. Phys. Soc. Jpn. **53**, 696 (1984).
[11]T. Yokotsuka, S. Kono, S. Suzuki, and T. Sagawa, Jpn. J. Appl. Phys. **23**, L69 (1984).
[12]R. I. G. Uhrberg, G. V. Hansson, J. M. Nicholls, P. E. S. Persson, and S. A. Flodström, Phys. Rev. B **31**, 3805 (1985).
[13]J. M. Nicholls, P. Mårtensson, G. V. Hansson, and J. E. Northrup, Phys. Rev. B **32**, 1333 (1985).
[14]J. M. Nicholls, G. V. Hansson, R. I. G. Uhrberg, and S. A. Flodström, Phys. Rev. B **27**, 2594 (1983).
[15]J. M. Nicholls, G. V. Hansson, U. O. Karlsson, P. E. S. Persson, R. I. G. Uhrberg, R. Engelhardt, S. A. Flodström, and E.-E. Koch, Phys. Rev. B **32**, 6663 (1985).
[16]J. E. Northrup, Phys. Rev. Lett. **53**, 683 (1984).
[17]J. E. Northrup and M. L. Cohen, Phys. Rev. B **29**, 1966 (1984).
[18]G. Binning, H. Rohrer, Ch. Gerber, and E. Weibel, Phys. Rev. Lett. **50**, 120 (1983).