Arsenic-Terminated Ge(111): An Ideal 1 × 1 Surface

R. D. Bringans, R. I. G. Uhrberg, R. Z. Bachrach, and John E. Northrup
Xerox Palo Alto Research Center, Palo Alto, California 94304

(Received 20 May 1985)

Arsenic interaction with the Ge(111) surface results in the replacement of the outer Ge layer with an As layer. This system has a 1 × 1 symmetry and the calculated positions of the As atoms are very close to the positions expected from bulk bond lengths Ge(111):As is thus a model ideal surface and a comparison is made of an experimental and a theoretical determination of its fully occupied surface band.

PACS numbers: 73.20.Cw, 68.20.+t, 79.60.Eq

The nature of the driving forces which produce the complicated reconstructions on the surfaces of the covalent semiconductors is a subject of long-standing interest. It is generally believed that dangling-bond reduction is the dominant mechanism which drives the reconstruction for the (111) surfaces of Si and Ge. In this Letter we present results for As-terminated Ge(111), a system in which the dangling bonds have been completely removed, leaving us with an ideal surface. This was achieved by replacement of 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. Although a great deal of theoretical work has been carried out on unreconstructed Si(111) and Ge(111) (see Appelbaum and Hamann,[1] Pandey and Phillips,[2] and Chelikowsky,[3] for example), this is the first time an "ideal" (111) surface has been realized and should provide a great deal of insight into the behavior of semiconductor surfaces.

On the Ge(111) surface, the ideal termination of the bulk leaves the last layer of Ge atoms threefold coordinated with a half-filled band of nonbonding surface states.[1-3] This situation is energetically unstable, and the surface reconstructs to a lower symmetry: 2×1 after cleavage and then $c(2\times8)$ after annealing. By replacing the outer layer of Ge atoms on the ideal Ge(111) surface with As atoms, one obtains a system in which every atom can achieve its optimal bonding configuration. Every Ge atom is fourfold coordinated, every As atom is threefold coordinated, as in bulk As, and the lone-pair electrons on the As atoms form a fully occupied band. 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. It should be pointed out that because the number of bonds between atomic layers alternates between one and three 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.

In the remainder of the Letter, we will present experimental and theoretical determinations of the dispersion of the surface state of 1×1 Ge(111):As. The experimental dispersion was obtained by the carrying out of an angle-resolved photoemission investigation of both the clean and As-terminated surfaces. Clean surfaces of Ge(111) were formed by sputtering and annealing and showed a sharp $c(2\times8)$ low-energy electron-diffraction (LEED) pattern. Arsenic was added *in situ* to the surface as As_4 molecules, by use of a molecular-beam-epitaxy effusion cell. 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, a sharp 1×1 pattern was seen with LEED. Annealing experiments were carried out in 50 °C steps and produced no change in the photoemission spectra until a temperature of 690 °C was reached. This is well above the temperature of 250 °C we use for evaporating bulk As in our effusion cell and provides solid evidence for the absence of any excess As adlayer. The Ge(111) $c(2\times8)$ LEED pattern and photoemission spectra were fully developed after a 2-min anneal at 740 °C. The sharpness of the transition shows that all As atoms were bonded in one site on the surface. Evaporation of As from an analogous system, GaAs(100), also occurs at lower temperatures. The transition from an excess As surface to the GaAs(100) $c(4\times4)$ reconstruction occurs below 350 °C and to the GaAs(100) $c(2\times8)$ surface with $\leqslant 1.0$ monolayer of As occurs at 450 °C, with the same calibration as in the present work.

The angle-resolved photoemission spectra changed dramatically after the addition of As to the Ge(111) $c(2\times8)$ surface. The surface states associated with the clean surface disappeared and a new surface state appeared in the region near the top of the bulk valence band. An example of this change is shown in Fig. 1 for an electron emission angle corresponding approximately to the $\bar{K}$ point of the (1×1) Brillouin zone. For Ge(111) $c(2\times8)$, two relatively flat surface-state bands, centered around 0.8 and 1.4 eV, have been identified,[4,5] The two states can be seen in the uppermost curve of Fig. 1. The remaining features in that spectrum are bulk related. After As adsorption, a very strong peak is seen at 2.0 eV below the top of the

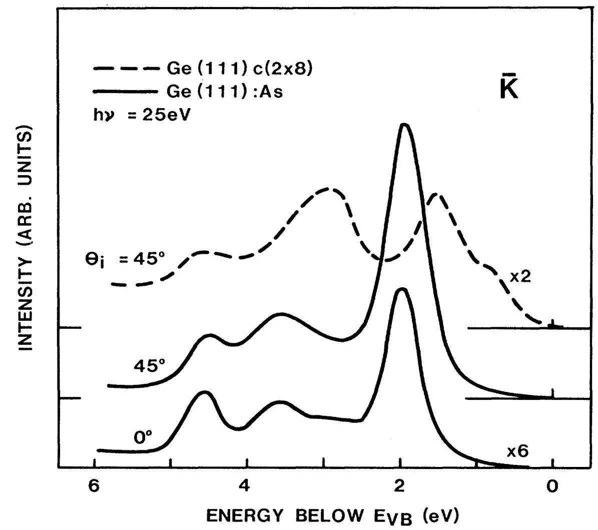

FIG. 1. Angle-resolved photoemission spectra for Ge(111) $c(2\times8)$ (dashed curve) and Ge(111):As (solid curves). The spectra were taken at an emission angle of 25°, which corresponds approximately to the $\bar{K}_{1\times1}$ point in the surface Brillouin zone. The peaks within 2.5 eV of E_{VB} represent surface states and θ_i is the angle between the photon beam and the surface normal.

valence band, which we identify as the occupied lone-pair band on the As atoms. The weak dependence of the intensity of this peak on the z component of the incident radiation suggests that the surface state does not have purely p_z character at $\bar{K}$. All of the data presented here utilized synchrotron radiation as the photon source, with the polarization vector of the light being kept in the same plane as the surface normal and the electron emission direction. The spectra are plotted relative to the top of the bulk-Ge valence band, E_{VB}, which was located by measurement of the binding energy of the Ge $3d$ core levels. Using the value of 29.57 eV determined for the bulk separation by Kraut *et al.*,[6] we obtained a value for Ge(111) $c(2\times8)$ of 0.1 ±0.1 eV for $E_{\mathrm{F}}-E_{\mathrm{VB}}$, which is consistent with the value of 0.17 eV given by Guichar, Garry, and Sebenne.[7] After As adsorption, E_{F} shifted away from E_{VB} by a further 0.05 ±0.01 eV.

Spectra such as those shown in Fig. 1 were taken for a variety of emission angles and photon energies in order to map out the surface-state dispersion for Ge(111):As. Positions of spectral features were located in energy and $k_{\parallel}$ (the wave-vector component in the surface) and results for 25-eV photons are shown in Fig. 2 for the direction $\bar{\Gamma}\rightarrow\bar{K}\rightarrow\bar{M}$. The surface state is seen at low binding energies and shows a downward dispersion of 1.7 eV. The features in the spectra associated with the bulk are compared with those for Ge(111) $c(2\times8)$ and with the $E(k_{\parallel})$ locations calculated for transitions from pure bulk initial states to a free-electron final state with its zero of energy 9.70 eV below E_{VB}. Bulk initial states were calculated with an empirical local pseudopotential method and scaled to match the nonlocal pseudopotential bands of Chelikowsky and Cohen.[8] Details of this comparison for Ge(111) $c(2\times8)$ and Ge(111):As will be presented elsewhere, but the data shown in Fig. 2 reveal that the lower band is very close to the bulk dispersion for both surfaces. The uppermost "bulk"

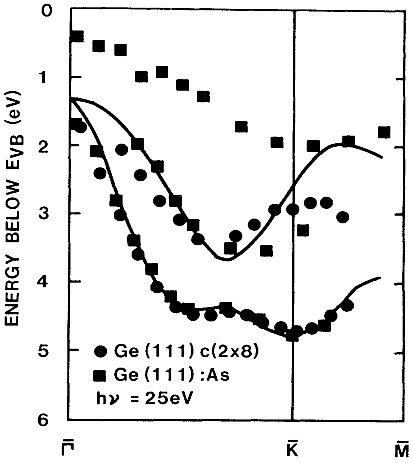

FIG. 2. Positions in energy and $k_{\parallel}$ of bulk-related features for Ge(111) $c(2\times8)$ and Ge(111):As and of the dangling-bond surface state for Ge(111):As. Surface states for Ge(111) $c(2\times8)$ were omitted for clarity. The data are for a photon energy of 25 eV and positions expected for bulk related features are shown by the curves.

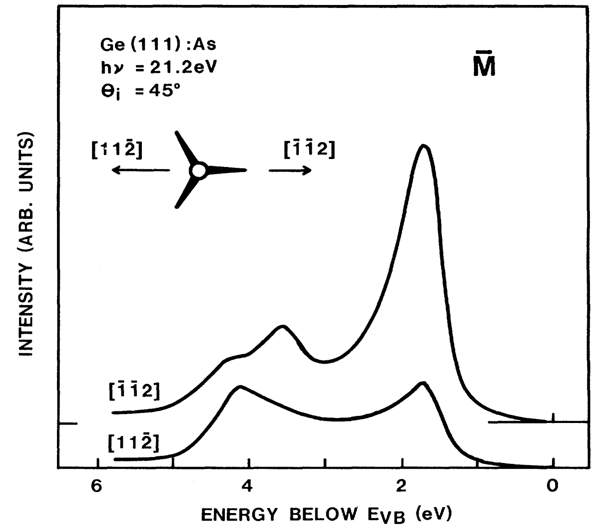

FIG. 3. Spectra taken at an emission angle of 27.5°, corresponding approximately to the two $\bar{M}$ points. The inset shows a top view of a surface atom on the ideal (111) surface and the directions of its three back bonds.

feature appears to contain contributions from backbond states. This shows up near the $\bar{K}$ point as (i) a deviation from the calculated dispersion, and (ii) a difference between the clean and As-covered surface, as can be seen clearly in the spectra in Fig. 1. In particular, the Ge(111):As dispersion moves towards a gap centered around $\bar{K}$ in the projected bulk band structure.

The intensity of the surface state exhibited a threefold symmetry as illustrated in Fig. 3 for the $[\bar{1}\bar{1}2]$ and $[11\bar{2}]$ directions. These spectra correspond to the $\bar{M}$ point in the surface Brillouin zone and the difference between them shows that the surface state is not purely p_z but has a significant component in the direction towards the back bond.

One of the main results seen in Fig. 2 is that a clear separation between the surface and bulk features is possible. This becomes more obvious when other photon energies are used. Data for the surface are collected in the surface-band structure of Fig. 4 and compared with a calculation of the Ge(111):As surface band. The calculations were carried out for an energy-minimized geometry with use of the first-principles pseudopotential method and the local-density approximation. The calculated band is closely related to that for the ideal Ge(111) surface, which also has a downward dispersion. Replacement of the surface Ge atoms by As atoms introduces an extra proton, which lowers the energy of the surface band, and an extra electron, which doubly occupies it. There is a good qualitative agreement between the experiment and the calculation. The band width and the binding energy are underestimated in the calculation, the latter appearing to be a systematic failing of the density-functional approximation used in the calculation. An underestimate of similar magnitude occurs for the Ge(111)2×1[9] and C(111)2×1[10] surfaces.

Pseudopotential total-energy calculations[11] were carried out to determine the positions of the As atoms. The resulting minimum-energy geometry corresponds to a Ge-As bond length of 2.52 Å. This is close to the "optimal" value, which is estimated by averaging of the Ge-Ge and As-As bulk bond lengths of 2.45 and 2.51 Å, respectively. The calculated value, which incorporates the geometrical constraint of a 1×1 symmetry, is only 0.04 Å larger than the optimal value and suggests that the 1×1 symmetry need not be broken to achieve a stable reconstruction. In this regard, we report that analagous calculations for Si(111):P give a Si-P bond length of 2.38 Å, whereas the optimal value is 2.23 Å. Thus, the 1×1 constraint is more severe for Si(111):P and suggests a reason why a 1×1 surface does not appear to exist for that system. Evidently, the 1×1 symmetry must be broken to relieve surface stress.[12]

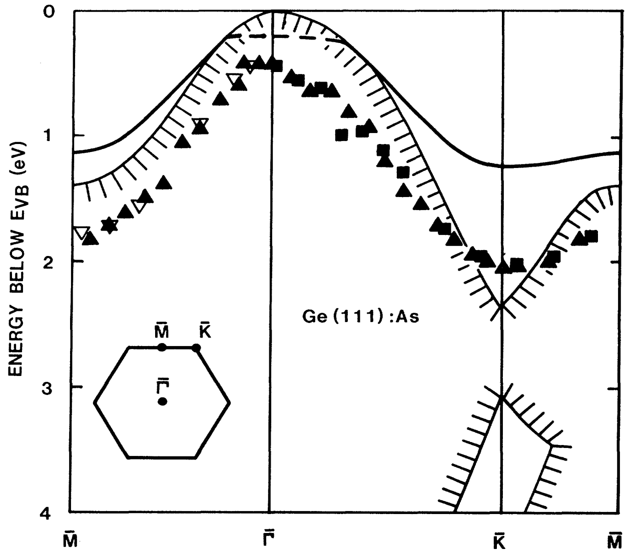

FIG. 4. A comparison between the calculated (solid and dashed lines) and the experimentally determined surface-state dispersion for Ge(111):As. The experimental data are shown by the symbols inverted triangle, triangle, and square for photon energies of 17.0, 21.2, and 25 eV, respectively. The shaded regions show the edge of the projected bulk band structure.

In conclusion, our results indicate that Ge(111):As is an ideal-topology surface. The lone-pair orbitals on the As atoms form a band of surface states with a dispersion characteristic of dangling-bond states on an ideal 1×1 surface. The structural simplicity and chemical stability of the surface make it an optimal system to study with a variety of surface-sensitive probes.

We are grateful for the skillful assistance of L. E. Swartz. Part of this work was performed at Stanford Synchrotron Radiation Laboratory, which is supported by the Department of Energy, Office of Basic Energy Sciences, and by the National Science Foundation, Division of Materials Research. One of us (J.E.N.) was supported in part by the U. S. Office of Naval Research through Contract No. N00014-82-C-0244.

---

[1] J. A. Appelbaum and D. R. Hamann, in *Physics of Semiconductors,* edited by M. Pilkuhn (Teubner, Stuttgart, 1974), p. 675.

[2] K. C. Pandey and J. C. Phillips, Phys. Rev. Lett. **32**, 1433 (1974).

[3] J. R. Chelikowsky, Phys. Rev. B **15**, 3236 (1977).

[4] R. D. Bringans and H. Höchst, Phys. Rev. B **25**, 1081 (1981).

[5] T. Yokotsuka, S. Kono, S. Suzuki, and T. Sagawa, J. Phys. Soc. Jpn. **53**, 696 (1984).

[6] E. A. Kraut, R. W. Grant, J. R. Waldrop, and S. P.

Kowalczyk, Phys. Rev. B **28**, 1965 (1983).

[7] G. M. Guichar, G. A. Garry, and C. A. Sebenne, Surf. Sci. **85**, 326 (1979).

[8] J. R. Chelikowsky and M. L. Cohen, Phys. Rev. B **14**, 556 (1976).

[9] J. E. Northrup and M. L. Cohen, Phys. Rev. B **27**, 6553 (1983).

[10] J. E. Northrup, to be published.

[11] D. Vanderbilt and S. G. Louie, Phys. Rev. B **29**, 7099 (1984).

[12] J. J. Lander and J. Morrison, J. Chem. Phys. **37**, 729 (1962).