

Photoemission measurements of surface states for cleaved and annealed Ge(111) surfaces

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(Received 16 December 1974)

The electronic surface states of cleaved and the annealed Ge(111) surfaces have been investigated by photoemission measurements using ultraviolet light. From the energy distribution curves of photoelectrons, the surface states of cleaved Ge are found to form a single band centered at 0.7 eV below the valence-band maximum, $E_{V_{\max}}$, with half-width of 0.7 eV. By annealing at 100°C, two bands centered at 0.7 and 0.3 eV below $E_{V_{\max}}$ have been observed, and by annealing at 300°C, only the latter has been observed.

From low-energy-electron-diffraction (LEED) studies, it was found that a cleaved Ge surface has a 2×1 superstructure, which is converted to a 2×8 superstructure by annealing at above 300°C.¹ The changes observed, from energy-distribution curves (EDC) of photoelectrons in the distribution of surface states, the work function, and the electron affinity of annealed and cleaved surfaces are reported in this paper, to understand the correlation between the atomic structure and the electronic properties of the surface.

A hydrogen discharge tube is used as the light source with the light incidence at 45° from the normal. The energies of the photoelectrons are analyzed with a spherical analyzer which has a resolution of better than 0.3 eV for electrons of 5 eV. The pulse signals from an electron multiplier are counted using a multichannel analyzer. The vacuum system consists of a 110-liter/sec sputter-ion pump and a Ti sublimation pump, and the base pressure is $\sim 4 \times 10^{-10}$ Torr.

The samples are cleaved in a *L* shape in cross section using a tungsten-carbide blade exposing the (111) surfaces. The crystals are 0.8- Ω cm ($N_D = 5 \times 10^{15}$ cm⁻³) *n*-type Ge. For the heat treatment of the samples, electron bombardment is used. Five cleaves have been made, all of which follow the same run.

Figure 1 shows EDC from the cleaved surface, the cleaved and annealed surface, and the gas-adsorbed surface at the photon energy of $h\nu = 10.2$ eV. On the ordinate is plotted the count rate of photoelectrons. On the abscissa of the figure is plotted the initial-state energy of the emitted electrons with respect to the Fermi level E_F . The position of E_F is determined from the upper edge of the EDC for clean molybdenum. Curve A of Fig. 1 shows the EDC from a freshly cleaved surface in a vacuum of $\sim 4 \times 10^{-10}$ Torr, and curve B shows the EDC 2 h later. The dotted curve of A is the difference between curves A and B multiplied by a factor of 3, and this is interpreted to indicate the optical density of states for the transition from

the filled dangling-bond states to the higher states, as the emission from the surface states is diminished in curve B. The portion which remain unchanged after the residual gas exposure is attributed to bulk emission.

The surface states of the cleaved 2×1 surface form a single band centered at 0.7 eV below E_F with a half-width of 0.7 eV, and this is in agreement with the result of Eastman and Grobman.² The ratio of surface to bulk emission is $\frac{1}{13}$ and the electrons are emitted from a 5.3-eV-wide part of the 12.5-eV-wide valence band, by light of $h\nu = 10.2$ eV. The density of the bulk atoms is

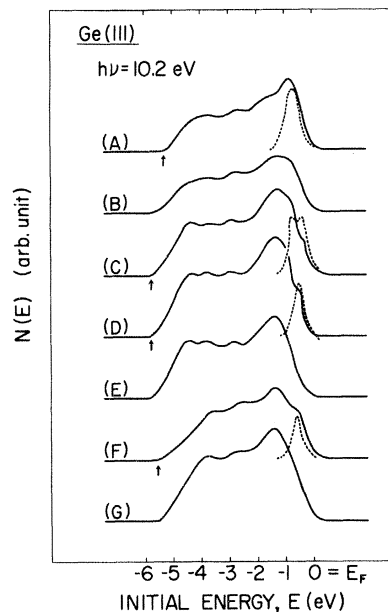


FIG. 1. Photoemission EDC from cleaved and annealed Ge(111): (A) freshly cleaved; (B) 2 h after cleavage in a vacuum of $\sim 4 \times 10^{-10}$ Torr; (C) annealed at 100°C; (D) annealed at 200°C; (E) exposed to H₂ gas; (F) annealed at 300°C; (G) exposed to H₂ gas. The dotted curves indicate the surface sensitive portions multiplied by a factor of 3.

$4.4 \times 10^{22} \text{ cm}^{-3}$, and the escape depth of the photoelectrons is about 12 \AA . Using these values a rough estimate can be made of the surface-state density N_s following the work of Wagner and Spicer.³ The value thus obtained is $N_s = 7 \times 10^{14} \text{ cm}^{-2}$, which shows that there is one dangling-bond state per surface atom, as in the case of Si(111).³

The bulk-emission peaks arise from the peaks in the joint density of states of the direct transition from the valence band to the conduction band, and the peaks at -0.7 , -1.4 , -2.8 , and -3.6 eV are attributed to the transitions at Γ , L , Δ and Σ , and Σ points in the Brillouin zone, respectively.⁴

A shift of the bulk peaks due to residual gas adsorption has not been observed. This indicates that there are net negative surface charges sufficient to keep the band bending unchanged, which is consistent with the estimate that only $2 \times 10^{11} q \text{ C/cm}^2$ (q is the electronic charge) of surface charges are required to bend the band by 0.5 eV , as it is mentioned in the latter part of this paper. Curves C and D are EDC measured at room temperature after annealing the cleaved surface at 100 and $200 \text{ }^\circ\text{C}$, respectively. In these cases new cleaved surfaces are annealed, and the reproducibility of curve A is checked. Curve E is obtained after the annealed surface is exposed to 10 langmuir of H_2 ($1 \text{ L} = 10^{-6} \text{ Torr sec}$). One notes that the peaks at -0.7 and -0.3 eV of curves C and D disappear in curve E in spite of the very low surface coverage of H_2 .⁵ This might indicate that the surface states are removed by the long-range interaction of the adsorbed particles. The extrinsic surface states of hydrogen have not been observed, probably because the photon energy used was too low for emission from such states.

Curve F is the EDC from the surface annealed at $300 \text{ }^\circ\text{C}$ after the measurement of curve E, and the spectrum is from a clean surface, as hydrogen is removed by annealing at this temperature.⁵ The dotted curves in C, D, and F are the difference spectra between the clean surfaces and the gas-adsorbed surfaces obtained by normalizing the amplitudes at -1.4 eV , and these curves correspond to the optical densities of surface states.

The distributions of surface states for the annealed surfaces show (a) for the surface annealed at $100 \text{ }^\circ\text{C}$, the existence of two bands which are centered at -0.7 and -0.3 eV ; (b) at $200 \text{ }^\circ\text{C}$, the decrease of the former and the growth of the latter; and (c) at $300 \text{ }^\circ\text{C}$, the observation of only a single band centered at -0.4 eV . It is observed that the band width of the surface states for the surface annealed at $300 \text{ }^\circ\text{C}$ is narrower than that for the cleaved surface and that the surface-state density estimated from the ratio of surface to bulk emission decreases to $\sim 2 \times 10^{14} \text{ cm}^{-2}$. Each sur-

face structure has its own characteristic distribution of surface states, and the higher and the lower bands correspond to the surface states of the 2×8 and the 2×1 structure, respectively. The surface obtained by annealing at a moderate temperature of 100 or $200 \text{ }^\circ\text{C}$, is interpreted to be covered with the domains of both the 2×1 and the 2×8 structures.

The data on both the field-effect mobility and the surface conductivity have been analyzed by Henzler⁶ using the two-levels model for surface states. In this analysis, two sets of different distributions of surface states have been proposed to explain the data. The present observation supports the correctness of such a treatment. As for Si(111), the cleaved surface with a 2×1 structure is converted to the surface with a 7×7 structure by annealing at $500 \text{ }^\circ\text{C}$, and it has been reported that the distribution of surface states shifts to high energy in connection with the surface reconstruction.^{7,8} These experimental results suggest a strong correlation between the distribution of surface states and the surface atomic structure.

The work function ϕ_w can be estimated from the position of the lower edge of the EDC. For the cleaved surface, the position indicated by the arrow in curve A of Fig. 1 is the lower edge E_L , therefore, the work function is $\phi_w = h\nu - E_L = 10.2 - 5.3 \text{ eV} = 4.9 \text{ eV}$. For the surfaces annealed at 100 – $200 \text{ }^\circ\text{C}$ and $300 \text{ }^\circ\text{C}$, the work functions are 4.5 and 4.7 eV , respectively. From the measurement of the work function by means of the Kelvin method, Gobeli and Allen⁹ have reported values of 4.8 and 4.6 eV for cleaved and annealed p -type Ge surfaces, respectively, and these values are in agreement with the present estimate, though the bulk doping densities are different in the two experiments.

The upper edge of the EDC in Fig. 1(A) is near the Fermi level, which indicates that the Fermi level is pinned near $E_{V_{\text{max}}}$ at the surface. This is in agreement with the measurement of photoemission yield,⁹ where the threshold of 4.8 eV has been attributed to bulk emission, and the value equals the work function. This interpretation is reasonable as our result (Fig. 1) shows that the contribution of the bulk is three times larger than that of the surface emission near the upper edge of the EDC.

Using the above results, we show in Figs. 2(a), 2(b), and 2(c) the band diagrams near the surface and the distributions of surface states for the cleaved surface and the surfaces annealed at 100 and $300 \text{ }^\circ\text{C}$, respectively. For the cleaved surface [Fig. 2(a)], the band bending of 0.5 eV is inferred from the pinning of E_F near $E_{V_{\text{max}}}$. The region of band bending spreads over $\sim 4000 \text{ \AA}$, and the band

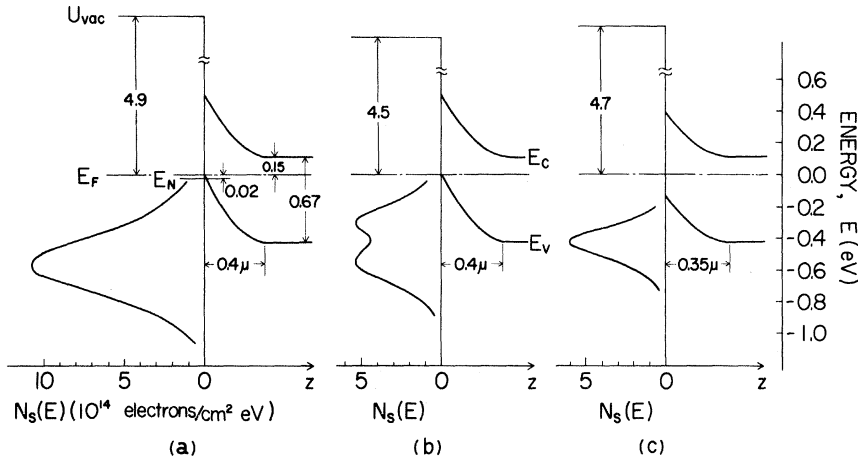


FIG. 2. Energy-band diagrams near the surface and the surface-states distributions: (a) freshly cleaved; (b) annealed at 100 °C; (c) annealed at 300 °C.

bending within the escape depth ($\sim 12 \text{ \AA}$) obtained by solving the Poisson equation is $\sim 0.02 \text{ eV}$, indicating that the effect of band bending on the EDC is negligible. The net negative charges of $2 \times 10^{11} \text{ q C/cm}^2$ bend the band by 0.5 eV, so the position of the neutral level is $\sim 0.02 \text{ eV}$ below E_F . The scale of the distribution of surface states $N_s(E)$ is determined from the total surface-state density of $\sim 7 \times 10^{14} \text{ electrons/cm}^2$.

The band bending of Fig. 2(b) is assumed to be the same as that of Fig. 2(a), because the peak position of the lower band does not change by annealing at 100 °C. On the other hand, for the surface annealed at 300 °C the peak position of the higher band shifts to a lower energy by 0.1 eV, in comparison with the surface annealed at 100 °C, so the band bending decreases by 0.1 eV in Fig. 2(c).

During surface conversion, the work function decreases by 0.4 eV and the electron affinity also changes by the same amount [Fig. 2(b)]. For Si(111), a decrease in electron affinity of 0.55 eV during conversion has been reported.¹⁰ Because of the decrease in electron affinity, the width of

the bulk states from which photoelectrons are emitted increases, and the peak appears at -4.5 eV in curves C, D, and E of Fig. 1. For the surface with 2×8 structure, the work function and the electron affinity decrease by 0.2 and 0.1 eV, respectively, compared to the surface with 2×1 structure [Figs. 2(b) and 2(c)].

In summary, it has been demonstrated from photoemission measurements that the surface-state distribution for Ge(111) changes substantially going from a cleaved 2×1 surface to an annealed 2×8 surface. This result is similar to that obtained for a Si(111) surface and not unexpected, however, several new features are found. These are (i) the existence of only a single surface-state peak in the annealed 2×8 surface, (ii) the coexistence of two different surface-state peaks in the partially annealed surface, and (iii) the changes in electron affinity and band bending in addition to the surface-state redistribution indicate a large change in the total electronic structure during surface reconstruction.

¹J. J. Lander, G. W. Gobeli, and J. Morrison, *J. Appl. Phys.* **34**, 2298 (1963).

²D. E. Eastman and W. D. Grobman, *Phys. Rev. Lett.* **28**, 1378 (1972).

³L. F. Wagner and W. E. Spicer, *Phys. Rev. Lett.* **28**, 1381 (1972).

⁴T. M. Donovan, Ph.D. thesis (Stanford University, 1970) (unpublished).

⁵A. H. Boonstra, *Philips Res. Repts. Suppl. No. 3* (1968).

⁶M. Henzler, *J. Appl. Phys.* **40**, 3758 (1969).

⁷J. E. Rowe, *Phys. Lett. A* **46**, 400 (1974).

⁸T. Murotani, K. Fujiwara, and M. Nishijima, in *Second International Conference on Solid Surfaces*, Kyoto, 1974 (unpublished).

⁹G. W. Gobeli and F. G. Allen, *Surf. Sci.* **2**, 402 (1964).

¹⁰P. P. Auer and W. Monch, in *Ref. 8*.