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Electronic structure of the annealed Ge(111) and Si(111) surfaces: Similarities in local bonding

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We have studied the valence-band and surface-core-level states for thermally annealed Ge(111)-(2 × 8) and Si(111)-(7 × 7) and laser-annealed Ge(111)-(1 × 1) and Si(111)-(1 × 1) surfaces with high-resolution photoelectron spectroscopy using synchrotron radiation. We find two surface states near the top of the valence band which exhibit characteristic emission patterns within the hexagonal 1 × 1 surface Brillouin zone as well as characteristic surface-core-level spectra which indicate the existence of a common local bonding geometry for all these surfaces.

The annealed (111) surfaces of Ge and Si are observed to reconstruct in different ways: a (1 × 1) LEED (low-energy-electron-diffraction) pattern is obtained from the laser-annealed Ge(111) and Si(111) surfaces, a (2 × 8)-type pattern from thermally annealed Ge(111) and a (7 × 7) reconstruction from thermally annealed Si(111). Despite these differences, similar types of geometries have been proposed for all thermally annealed surfaces, e.g., buckling models,[1,2] island-type microdomains,[3] or (2 × 2) building blocks centered around vacancies.[4] Each of these models has a characteristic short-range order, or local bonding, and can accomodate different long-range order for different surfaces as seen in LEED observations. Photoelectron spectroscopy (PES) directly yields information about the local bonding but is less sensitive to the long-range order than LEED. Therefore, we have used PES to determine the electronic surface states and surface core levels associated with different Ge(111) and Si(111) surfaces (laser annealed and thermally annealed) and have looked for common features.

Previously, photoemission measurements have been reported for Ge(111)-(2 × 8) (Refs. 5 and 6), Si(111)-(7 × 7) (Refs. 2 and 7–12), and Si(111)-(1 × 1) (Refs. 13–15). In this paper, we report new measurements for Ge(111)-(1 × 1) and Ge(111)-(2 × 8) and find for all four annealed Ge(111) and Si(111) surfaces that surface-state emission near the top of the valence band is dominated by two surface states which have distributions in $\vec{k}$ space characteristic of a 1 × 1 unit cell. We observe a semiconducting surface for Ge(111)-(2 × 8), Ge(111)-(1 × 1), and Si(111)-(1 × 1) and a weakly metallic surface for Si(111)-(7 × 7). Also, there is a surface-core-level feature common to all four surfaces which corresponds to about $\frac{1}{4}$ monolayer of surface atoms with a large shift of 0.6–0.8 eV towards lower binding energy. These findings suggest a common local bonding geometry not only for laser-annealed and thermally annealed Si(111) surfaces, as shown in Ref. 15, but also for both annealed Si(111) and annealed Ge(111) surfaces, even though thermally annealed Si(111)-(7 × 7) and Ge(111)-(2 × 8) surfaces have different long-range order.

It has been previously suggested that Si(111)-(7 × 7) and Ge(111)-(2 × 8) have a similar short-range order [e.g., Lander and Morrison's (2 × 2) vacancy model[4]]. Our measurements appear to be the first to demonstrate this similarity conclusively. Within a band picture, either a suitably distorted (2 × 2) vacancy model or buckled surface models which have both sufficient distortions so as to have strong backbonds, as well as weaker long-range order [(2 × 8) and (7 × 7)] could be consistent with our findings. Photoemission spectra for thermally annealed Ge(111)-(2 × 8) are "sharper" versions of laser-annealed Ge(111)-(1 × 1) and suggest that the (1 × 1) surface might simply be mainly a disordered (2 × 8) surface; a similar conclusion has been reached for Si.[15]

We have used a display-type spectrometer[16] at the synchrotron radiation source Tantalus I to determine the extent of the surface states in $\vec{k}$ space, their symmetries and binding energies, and to obtain the number of special surface atoms which exhibit shifted core levels. All samples were nearly intrinsic (~5 Ω cm). For laser annealing, radiation from a *Q*-switched pulsed ruby laser (15×10^{-9}-sec pulse width) was used to irradiate crystals in the UHV ($\leq 1 \times 10^{-10}$ Torr) environment of the spectrometer system. Energy densities of 1.7 and 2.0 J/cm^2 were used for Ge and Si crystals, respectively. Typically, five pulses were used to prepare the surfaces for photoemission measurements. Previous work has shown that these conditions lead to "atomically clean" surfaces from which sharp (1 × 1) LEED patterns are obtained.[17]

Figure 1 shows angle-integrated (1.8 sr) photoelectron spectra for clean (laser-annealed and thermally annealed) and hydrogen-covered Ge(111) and Si(111) surfaces. Note that all four clean surfaces have a doublet of states near the top of the valence band (E_v) which are quenched by hydrogen exposure (about one monolayer of H). Relative to E_v, these states lie at −0.4 and −1.3 eV for the two Si(111) surfaces and at −0.7 and −1.3 eV for the two Ge(111) surfaces. For referencing our spectra to E_v, we have used the following values for the position of the Fermi level E_F with respect to the top of the valence band E_v: $E_F - E_v = 0.17$ eV for Ge(111)-(2 × 8) (Ref. 6), 0.10 eV for Ge(111)-(1 × 1) [this work, determined relative to Ge(111)-(2 × 8)], 0.51 eV for Si(111)-(7 × 7) (Ref. 12), 0.51 eV for Si(111)-(1 × 1) (Ref. 15). The width of these surfaces states is ~0.5 eV (full width at half maximum). No dispersion is observed when $\vec{k}_\parallel$ is changed (detection limit ~0.1 eV).

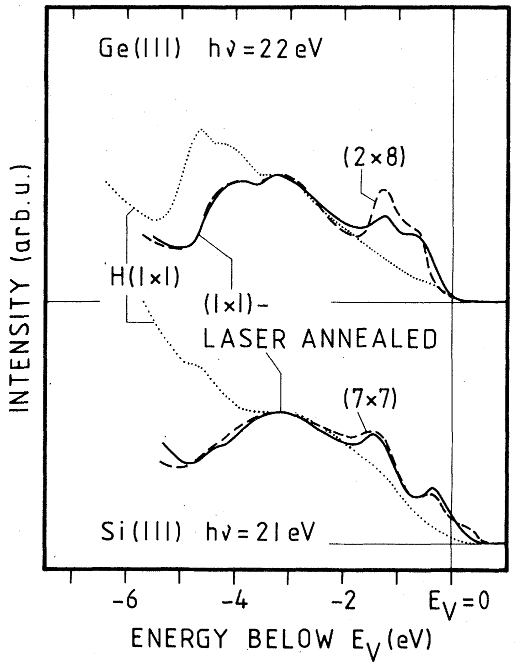

FIG. 1. Angle-integrated photoelectron spectra for the annealed Ge(111) and Si(111) surfaces showing emission from two surface states near the top of the valence band which is quenched by hydrogen exposure (dotted lines).

Using angle-resolved polarization-dependent photoelectron spectroscopy, we find that the surface states have distributions in momentum ($\vec{k}_\parallel$) space and symmetries which are similar for all four surfaces. These results are summarized in Fig. 2. Relative to the hexagonal 1 × 1 surface Brillouin zone, the lower-lying states appear near the zone boundary and in a small region around the zone center. The upper states have a distribution which peaks near the zone center but falls off much more slowly than the distribution of the lower states. At the zone center, the upper and lower states have opposite symmetries (symmetric s,p_z-like and antisymmetric $p_{x,y}$-like, respectively). We obtain these symmetries by applying dipole selectron rules to the observation that for $\vec{k}_\parallel = 0$ (normal emission), the upper (lower) state is only excited by the component of the electric field vector perpendicular (parallel) to the surface.[9,11] For other points in $\vec{k}_\parallel$ space, the symmetry is too low to make a clear-cut classification in terms of $s,p_{x,y,z}$-orbital character.

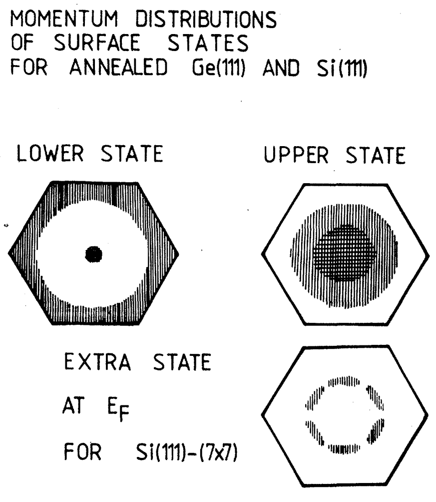

FIG. 2. Characteristic locations (dashed areas) of different surface states in the (1 × 1) surface Brillouin zone (hexagon) for the annealed Ge(111) and Si(111) surfaces. At the zone center, the lower surface state has $\Lambda_3(p_{x,y})$ character and the upper state has $\Lambda_1(s,p_z)$ character.

The distributions in $\vec{k}_{\parallel}$ space for the annealed Si(111) surfaces are quite different from the cleaved Si(111)-(2 × 1) surface where the highest-lying surface state (at $E_v - 0.15$ eV) resides near the zone boundary and the lower state (at $E_v - 0.7$ eV) fills the whole zone.[18] At best, the lower state on Si(111)-(2 × 1), which is symmetric s,p_z-like can be compared with the upper state on Si(111)-(7 × 7) and Si(111)-(1 × 1) (see Ref. 2).

It is remarkable that the predominant surface states for the thermally annealed Ge(111) and Si(111) surfaces match the (1 × 1) surface Brillouin zone and show no indication of the small reciprocal (2 × 8) or (7 × 7) unit cells. This may be taken as a confirmation that we indeed sense the short-range order (given by the larger 1 × 1 unit cell in $\vec{k}_{\parallel}$ space). There is one exception for the Si(111)-(7 × 7) surface: We find a weak third surface state near the Fermi level (see Fig. 1) which makes Si(111)-(7 × 7) metallic, in contrast to the other three surfaces. This state is sensitive to the long-range (7 × 7) order.[19] This is consistent with a band picture wherein the Si(111)-(7 × 7) surface has to be metallic because there is an odd number of electrons in the (7 × 7) unit cell. Each band holds two electrons, which leaves us with a partially filled band. The extra surface state for Si(111)-(7 × 7) is concentrated near the middle of the edges of a (2 × 2) surface Brillouin zone (see Fig. 2).

Complementary information about the surface geometry is given by the shifts of core levels for specific surface atoms. Figure 3 depicts surface-sensitive angle-integrated photoelectron spectra for Ge 3d and Si 2p core levels [with experimental mean free paths of 5.9 Å (Ref. 20) and 5.4 Å (Ref. 12) for Ge and Si, respectively]. By comparing spectra for the clean surfaces (full lines) with the hydrogen-covered surface spectra (dotted lines), it is clear that there are core levels at lower binding energies which are characteristic of the clean surfaces (marked by arrows in Fig. 3). Other surface core levels are also seen (e.g., at higher binding energies)[12] but will not be discussed here because they are harder to identify owing to contributions from the spin-orbit partners and possible energy-loss features. We have performed least-squares fits to the data using bulk and surface core levels and their spin-orbit partners[21] along the lines of Refs. 12 and 20. The results of our analysis are given in Table I and can be summarized as follows: The annealed Ge(111) and Si(111) surfaces have roughly $\frac{1}{4}$ monolayer of surface atoms with a large core-level shift (0.6–0.8 eV) towards lower binding energy. This differs considerably from the cleaved Ge(111) and Si(111) surfaces for which we find a larger number of surface atoms ($\gtrsim \frac{1}{2}$ monolayer) with core levels shifted by a smaller amount ($\lesssim 0.4$ eV).

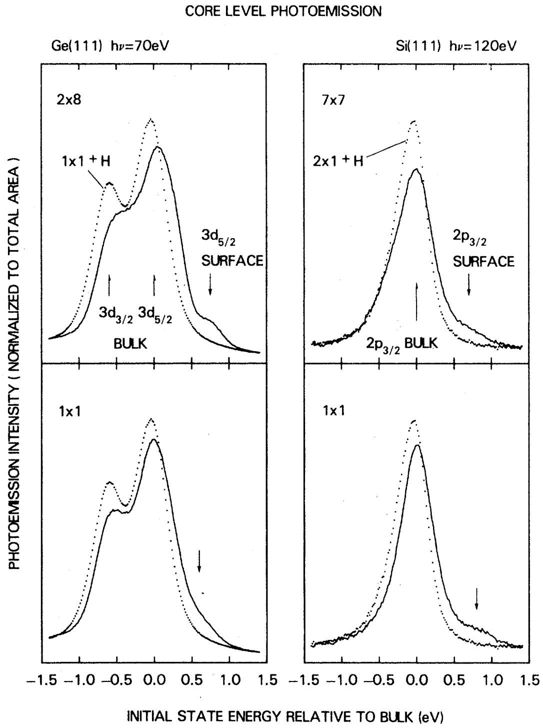

FIG. 3. Surface-sensitive core-level spectra for the annealed Ge(111) and Si(111) surfaces showing shifted core levels for special surface atoms. The Ge data consist of spin-orbit-split $3d_{3/2}$ and $3d_{5/2}$ levels, whereas in the Si data the $2p_{1/2}$ levels have been removed by spin-orbit deconvolution (see Refs. 12, 20, and 21). Dotted lines are for hydrogen-covered surfaces [Ge(111)-(1 × 1) + H and Si(111)-(2 × 1) + H, respectively], wherein the surface core levels at lower binding energies are removed.

TABLE I. Special surface atoms for the annealed Ge(111) and Si(111) surfaces.

	Core-level shift (towards lower binding energy, ±0.1 eV) (eV)	Number of atoms involved (±0.05 layer) (layer)
Ge(111)-(2 × 8)	0.75	0.28
	0.35	≥0.25[a]
Ge(111)-(1 × 1)	0.60	0.37
Si(111)-(7 × 7)	0.70	0.16
Si(111)-(1 × 1)	0.80	0.23

[a] This extra level is seen more clearly at lower photon energies than shown in Fig. 3. The intensity cannot be estimated reliably but seems to be ≥0.25 layer.

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[21] For the Ge $3d$ levels we find an anomalous spin-orbit branching ratio of ~ 0.44 (versus the statistical $\frac{2}{3}$) at threshold, a slight change in the apparent spin-orbit splitting from 0.61 eV near threshold to 0.59 eV at $h\nu = 70$ eV and a different line shape for the two partner lines. This can be explained by a partial bandlike character of Ge $3d$ states similar to the effects observed for the Zn $3d$ states by F. J. Himpsel, D. E. Eastman, E. E. Koch, and A. R. Williams, Phys. Rev. B 22, 4604 (1980). Another cause for these effects could be a splitting induced by the lower symmetry of the crystal potential at the surface [Stark effect, see V. E. Henrich, G. Dresselhaus, and H. J. Zeiger, Phys. Rev. Lett. 36, 158 (1976)]. All these effects are small compared with the core-level shifts discussed in the text (~ 0.03 eV vs 0.7 eV).