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Photoemission study of Si(111)-Ge(5×5) surfaces

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Photoemission spectroscopy was used to study Si(111)-Ge(5×5) surfaces prepared by annealing Ge films deposited onto Si(111)-(7×7) substrates. The Si $2p$ core-level line shape was modified in going from (7×7) to (5×5) systems. By decomposing the spectra into bulk- and surface-shifted components the changes in line shape were identified as due to selective replacement of Si by Ge in different layers of the substrate, without any drastic change in the surface structure. The Ge $3d$ core-level line shape for the Si(111)-Ge(5×5) surface was also measured and compared with that for the Ge(111)-$c(2\times8)$ surface. These results are discussed in terms of models for the Si(111)-(7×7) structure. A surface state was observed on the Si(111)-Ge(5×5) surface, which gave rise to a metalliclike Fermi edge in the angle-integrated spectra; a similar surface state was observed on the Si(111)-(7×7) surface but not on the Ge(111)-$c(2\times8)$ surface.

I. INTRODUCTION

The structure of the annealed Si(111)-(7×7) surface represents a system which is still not well understood, despite a large amount of experimental and theoretical work.[1-6] It is interesting, then, that the surface can be converted to one displaying a (5×5) reconstruction by dissolving small amounts of Ge into the surface. The electron diffraction patterns from this (5×5) surface show intensity distributions which are similar to those of the clean Si(111)-(7×7) surface, suggesting that the two reconstructions are closely related.[7] Thus, study of the (5×5) reconstruction may provide insight into the (7×7) case.

Previous studies involving electron diffraction and Auger spectroscopy have shown that, at room temperature, Ge grows on Si(111) smoothly, without clustering or interdiffusion, but forms disordered films.[8] The (5×5) reconstruction can be produced by (1) annealing a Si(111) sample upon which Ge has been deposited at room temperature, (2) depositing Ge with the Si substrate held at elevated temperatures, or (3) codepositing Si and Ge onto a Si(111)-(7×7) surface, again at elevated temperatures.[8,9] In any case, the (5×5) reconstruction is thought to be driven by strain present in mixed Si-Ge, due to the 4% lattice mismatch between the elemental constituents.

In many solids, core-level binding energies for atoms at the surface are shifted relative to those of the bulk.[10] These shifts have been observed to depend on the particular surface studied and also on differences in surface reconstruction; in some cases, the core-level shifts have been related to surface atomic arrangements.[2,10-13] High-resolution photoemission spectroscopy, with its adjustable surface sensitivity, provides a convenient way to isolate and study surface-shifted core levels. In this paper, we report results of such spectroscopy carried out on the Si $2p$ and Ge $3d$ core levels from Si(111)-Ge(5×5) systems. We find that the surface components of the Si $2p$ core line shape are selectively modified in going from the (7×7) to the (5×5) surface, indicating selective replacement of Si by Ge in different layers of the substrate. In addition, photoemission spectra from the valence bands and surface states of the (5×5) system were obtained. These will be compared to similar spectra for the Si(111)-(7×7) and Ge(111)-$c(2\times8)$ surfaces. The results will be discussed in relation to structural models for the Si(111)-(7×7) surface.

II. EXPERIMENTAL DETAILS

The photoemission experiments were carried out using synchrotron radiation from the Tantalus I storage ring Synchrotron Radiation Center, University of Wisconsin—Madison at Stoughton, Wisconsin. Light from the ring was monochromatized by the Mark-V Grasshopper monochromator which produced usable flux from 20 to over 130 eV. A double-pass cylindrical mirror analyzer detected electrons emitted from the sample. High-resolution measurements of Ge and Si core levels were made with an overall resolution of about 0.2—0.4 eV, giving peak count rates of the order of 1500 counts/sec.

Si(111)-(7×7) substrates were formed from n-type wafers cut into rectangles about 13×5 mm. These were etched with a 0.05% bromine-methanol solution before insertion into the vacuum chamber. Heating was provided by passing current directly through the samples, and temperature was monitored using an infrared pyrometer. The samples were cleaned by flashing to 1250 °C, after which high-energy electron diffraction (HEED) gave a very sharp (7×7) pattern. Sample surface quality was judged by the HEED background and by the sharpness of the well-known surface states near the Fermi edge seen with photoemission.[14-17]

(5×5)-reconstructed surfaces were prepared by first depositing 6 monolayers (ML) of Ge onto the Si substrates at room temperature, and then annealing at 750 °C [a monolayer is defined as 7.83×10^{14} atoms/cm^2; that is, one-half of a double Si(111) layer]. The rate of deposition (and thus the film thickness) was measured using a quartz-crystal film-thickness monitor. At intervals during annealing, the heating current was turned off momentarily and the HEED pattern was examined; after a few minutes the development of three-dimensional islands could be seen followed by a "flattening out," and the (5×5) reconstruction became fully developed after a total annealing time of about 5 min. This is in agreement with previous observations.[9]

The spectra for pure Ge used for reference in these studies were from the (111) surface of a separate bulk Ge sample. The clean $c(2\times8)$ surface was obtained by repeated cycles of sputtering with 2-kV Ar ions and annealing to 800 °C. HEED from this surface displayed sharp $\frac{1}{8}$-order spots and a low background.

III. RESULTS AND DISCUSSION

A. Core-level intensities

In preliminary experiments, photoemission scans of both the Ge 3d and the Si 2p core levels were made for a Si(111)-Ge(5×5) system as annealing progressed. In both cases, the photon energy used yielded a short electron escape depth (about 5 Å) to emphasize changes in the surface composition. Figure 1 shows the integrated intensity of the Ge 3d signal as a function of annealing time at a temperature of 750 °C for a Si(111) sample initially covered by 6 ML of Ge. The intensity has been normalized to the intensity expected for a single monolayer of Ge on the surface. This normalization was obtained from the intensity of the Ge 3d peak from submonolayer Ge deposited on the Si substrate at room temperature and not annealed; smooth growth with no clustering or diffusion is expected under these conditions.[8] The Ge signal decreased with time of annealing for the duration of the experiments, indicating gradual diffusion of Ge into the substrate. All of the data points in Fig. 1 represent (5×5) surfaces except the last one at 94.5 min; this one showed mainly a (7×7) pattern, with a small admixture of a (5×5) pattern.

B. Si 2p core levels for Si(111)-(7×7)

Figure 2 shows high-resolution scans of the Si 2p core levels at two different photon energies, 108 and 130 eV. Because of the dependence of the electron mean free path on energy, the 108-eV spectrum shows mainly features characteristic of the bulk sample, whereas the 130-eV spectrum emphasizes surface-related features.[2] Ignoring the backgrounds, most of the apparent differences be-

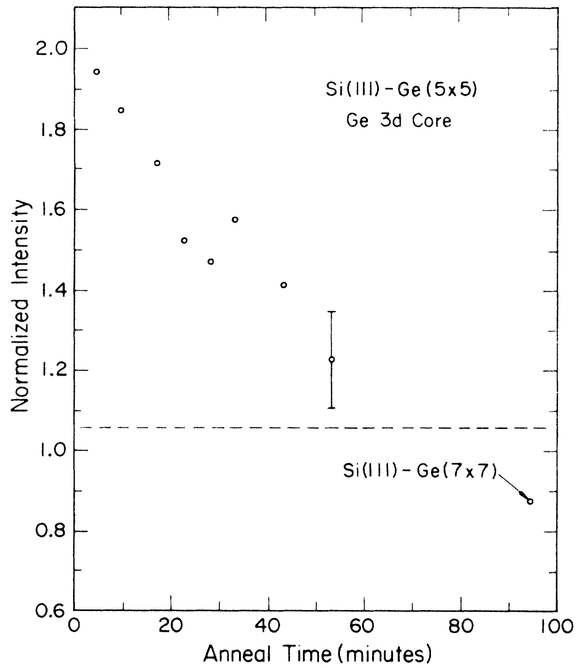

FIG. 1. Integrated Ge 3d core intensity as a function of annealing time for a Si(111) sample, initially covered by 6 ML of Ge. A photon energy of 90 eV was used to emphasize changes in surface composition. All data points shown here corresponded to (5×5), except for the last one, which was largely (7×7) with a small admixture of (5×5). The dashed horizontal line separates the data points corresponding to pure (5×5) from that corresponding to mixed (7×7) and (5×5). The intensity has been normalized to the intensity expected for a single monolayer of Ge deposited on the Si substrate. The uncertainty in intensity is about ±10%. The first data point (not shown here because it is outside the scale), corresponding to 6 ML of Ge on Si without annealing, has a normalized intensity of 4±0.4.

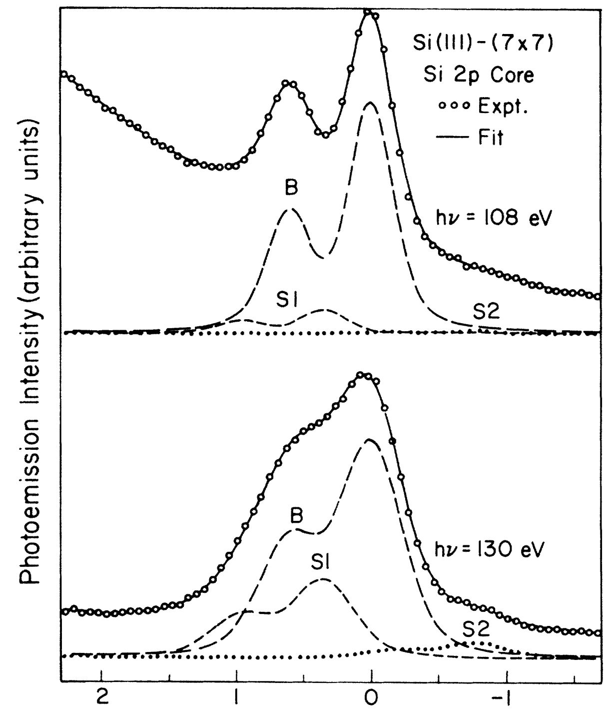

FIG. 2. Si 2p core-level spectra for clean Si(111)-(7×7). The upper spectrum, taken with a photon energy of 108 eV, includes mainly emission from the bulk; the lower spectrum, taken at 130 eV, emphasizes surface features. Circles are data points; the solid curves are a fit to the data. The long-dashed curves represent the bulk (B) component of the spectra. The short-dashed and dotted curves are surface components, referred to as *S*1 and *S*2, respectively, in the text. The binding-energy scale is relative to the bulk Si $2p_{3/2}$ line.

tween the two spectra are attributable to surface-atom emission, which is shifted in energy with respect to the bulk. Two features, in particular, the small bump on the low-binding-energy side of the doublet and the filling-in of the valley between the two spin-orbit-split peaks, are obvious in the surface-sensitive spectrum but not in the bulk-sensitive one. The separation of the small bump from the main peak is larger than the spin-orbit splitting which can be clearly seen in the bulk-sensitive spectrum. This observation suggests that there are at least three spin-orbit-split doublets comprising the total spectrum; one from the bulk and at least two from the surface region.

Previously, we have decomposed similar spectra from the clean (100) surface of Ge into bulk and surface components, and related these features to details of the Ge(100)-(2×1) reconstruction.[11] A similar procedure was adopted here. A nonlinear least-squares method was employed to fit both bulk- and surface-sensitive scans simultaneously to a model function described below. Each spectrum was assumed to consist of three spin-orbit-split doublets on top of a secondary-electron background, approximated by a cubic polynomial. All doublets had the same spin-orbit splitting and natural (Lorentzian) linewidth. The three doublets for each scan all had the same branching ratio (the intensity ratio of the $p_{1/2}$ to the $p_{3/2}$ component), but this was allowed to be different for bulk- and surface-sensitive cases to allow for energy-dependent final-state effects. The relative positions of the three components (the surface shifts) were constrained to be the same for both scans. Finally, Gaussians were convoluted with the resulting functions to simulate experimental and phonon broadening. The results of the fit are shown in Fig. 2 and are tabulated in Table I. The spin-orbit splitting from the fit is 0.611 eV; the branching ratios of 0.525 (130 eV) and 0.509 (108 eV) are both close to the statistical ratio of 1/2. Comparison of the bulk- and surface-sensitive cases leads to the interpretation of the middle component (labeled B) as due to the bulk, whereas the other two (labeled $S1$ and $S2$) are from the surface.

Scanning tunneling microscopy (STM) of the clean Si(111)-(7×7) surface reveals 12 bumps in each surface unit cell, raised 0.7 Å from the mean surface level.[3] Structural models consistent with this include $\frac{12}{49}$ ML of atoms in special sites, such as adatoms[3,5] or rebonded trimer atoms.[6] We can interpret the $S2$ peak as originating from this $\frac{12}{49}$ ML on top. Assuming these "adatoms" do not attenuate the signal from below, and adding up contributions to the peak intensity by double layers, we obtain

$$R=\tfrac{12}{98}[1-\exp(-d/\lambda)]\ ,$$

where R is the ratio of the $S2$ intensity to the combined B and $S1$ intensity, d is the spacing between double layers (3.14 Å for Si), and λ is the escape depth. From our fit for the 130-eV spectrum, $R=0.054$, giving an escape depth of 5.3 Å. This is in agreement with earlier measurements of the escape depth in Si.[6,18] Himpsel *et al.*,[2] using similar data but different analysis, identified a peak shifted −0.7 eV from the bulk component, which would correspond to our $S2$. The intensity of this peak was found to correspond to $\frac{1}{6}\pm\frac{1}{12}$ ML,[6] in agreement with the present results.

Peak $S1$ on the higher-binding-energy side is 4.9 times as intense as $S2$ in the 130-eV spectrum. Assuming no attenuation of this peak and that $S2$ corresponds to 12 adatoms per surface unit cell, this intensity corresponds to emission from 1.2 ML.[19] The simplest interpretation of

TABLE I. Fitting parameters for the core-level spectra shown in Figs. 2–4. All energies are in eV. SS and BS refer to the surface- and bulk-sensitive spectra, respectively. The branching ratio, in the case of Si, is the $2p_{1/2}$-to-$2p_{3/2}$ intensity ratio, and in the case of Ge, is the $3d_{3/2}$-to-$3d_{5/2}$ intensity ratio. The Lorentzian width refers to the full width at half maximum. The Gaussian sigma multiplied by 2.35 equals the Gaussian full width at half maximum. The binding energy shifts of the two surface components ($S1$ and $S2$) are referred to the bulk component in each case. The weights (relative intensities) of the bulk, $S1$, and $S2$ components add up to one.

	Si 2p Si(111)-(7×7)	Si 2p Si(111)-Ge(5×5)	Ge 3d Ge(111)-c(2×8)
Spin-orbit splitting	0.611	0.611	0.585
Branching ratio (SS)	0.525	0.525	0.626
Branching ratio (BS)	0.509	0.509	0.489
Lorentzian width	0.182	0.182	0.148
Gaussian sigma (SS)	0.186	0.170	0.151
Gaussian sigma (BS)	0.114	0.117	0.147
Surface component $S1$			
Shift	−0.355	−0.365	0.268
Weight (SS)	0.252	0.063	0.473
Weight (BS)	0.093	0.0059	0.209
Surface component $S2$			
Shift	0.769		0.770
Weight (SS)	0.052	0.0	0.092
Weight (BS)	0.011	0.0	0.040

*S*1 is that it originates from the first full monolayer (referred to as the surface layer or the first layer in the following). The ratio of intensity of the *S*1 peak to the *B* (bulk) peak, again using the layer-attenuation model, is consistent with this. This fits well with adatom models[3,5] in which a full monolayer exists below the twelve "special" sites. We adopt this interpretation for the remainder of this paper. It should be noted that STM images show more complex corrugation than only adatom sites on top of a smooth layer.[3] Also, in adatom models the atoms in the first complete layer are not all bonded identically. Therefore, one might expect different core-level shifts for atoms within this layer. Our fitting assumption of three components is based largely on visual inspection of the composite spectrum. We simply cannot directly see clear evidence of another component. In addition, the Gaussian broadening parameter for the fit is reasonable in terms of our experimental conditions. So, while the possible existence of additional components, shifted by relatively small amounts, is not ruled out, we do not determine any here.

C. Si 2*p* core levels for Si(111)-Ge(5×5)

After deposition of Ge and annealing to obtain the (5×5) surface, the Si 2*p* spectra shown in Fig. 3 were obtained. This sample was annealed for 10 min; other annealing times produced qualitatively similar spectra (not shown here to conserve space). The bulk- and surface-sensitive scans now resemble each other much more closely than in the clean (7×7) case. Comparing the surface-sensitive spectrum in Fig. 3 to that in Fig. 2 shows that the *S*2 feature is absent. Also, the valley between the spin-orbit-split peaks is more pronounced; evidently, the *S*1 component of the Si(111)-(7×7) spectrum has been modified. We fit these spectra using the method and assumptions used for the Si(111)-(7×7) case discussed above. The Lorentzian width, spin-orbit splitting, and branching ratios were fixed from the fit for Si(111)-(7×7). The results are plotted in Fig. 3 and the corresponding final parameter values are listed in Table I. As can be seen in Fig. 3, the result of this fit consists of a large bulk component (*B*) and a small surface component (*S*1) on the higher-binding-energy side. The *S*2 peak has zero intensity from the fit, and is therefore not shown in Fig. 3. The position of the small peak (*S*1), relative to the bulk peak, is very close to that of the *S*1 component of the Si(111)-(7×7) spectrum; the shifts differ by only 10 meV. The Gaussian broadening parameters obtained from the fit are also quite close to those for Si(111)-(7×7).

As previously mentioned, the distribution of intensity among low-energy electron diffraction spots for the Si(111)-(7×7) and the Si(111)-Ge(5×5) surfaces are similar, indicating that the two reconstructions are probably similar except for the difference in the size of the surface unit cell.[7] In view of this, we can interpret the surface component *S*1 in the Si(111)-Ge(5×5) spectrum as a remnant of the *S*1 component of the Si(111)-(7×7) spectrum; the large reduction in its relative intensity in going from (7×7) to (5×5) indicates that most of the Si atoms in the first layer of Si(111)-(7×7) are now replaced by Ge atoms. Sets of spectra obtained for other annealing times were subjected to the same analysis and produced results similar to those in Fig. 3. For the data analyzed, the intensity of the *S*1 peak varied; however, in no case was any intensity corresponding to the *S*2 peak observed for the (5×5) surface.

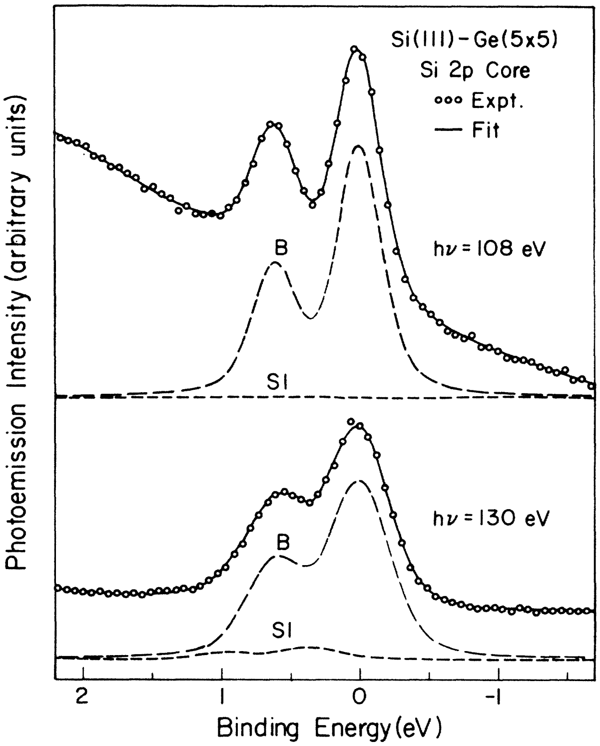

FIG. 3. Si 2*p* core-level spectra for Si(111)-Ge(5×5). The fit is similar to that of Fig. 2, except that the *S*2 component is not present.

Following our interpretation of the clean Si 2*p* line shape, the absence of the *S*2 component indicates that the "special" Si atoms (i.e., adatoms) are completely replaced by Ge for the (5×5) surface. The intensities of the *S*1 and *B* components for the Si(111)-Ge(5×5) sample correspond to 12% and 64%, respectively, of those for Si(111)-(7×7). Thus, the Ge concentration in the first layer of this Si(111)-Ge(5×5) sample is about 88 at. %. If we assume that there exists a uniformly mixed Si-Ge region below the first layer, extending throughout the photoemission probe depth, we obtain a Ge concentration of about 36% in this region. It is likely that the "uniform region" actually has a concentration gradient characteristic of the diffusion of Ge into the Si substrate. Since we cannot, from our analysis, distinguish signals from different subsurface layers, the concentration gradient cannot be determined. Different Ge distributions in the subsurface region can be assumed, with the Si and Ge core-level intensities estimated from the layer-attenuation model consistent with the measured values (see Fig. 1) within experimental accuracies. For example, one possible Ge concentration profile corresponds to 100%, 88%, 36%, 36%, etc., respectively, for the adatom layer, the first (surface) layer, the second layer, etc., as noted above; another possible profile corresponds to 100%, 88%, 57%, 0%, 0%, etc., respectively, for these layers. In any case, the first layer has a much higher Ge concentration than the subsurface region.

D. Ge 3*d* core levels for Ge(111)-*c*(2×8)

Spectra analogous to those for the Si 2*p* levels in Si(111)-(7×7), discussed above, were measured for the Ge 3*d* core levels in clean Ge(111)-*c*(2×8). The upper and lower spectra in Fig. 4, taken with photon energies of 40 and 90 eV are bulk- and surface-sensitive, respectively. The analysis procedure was the same as for Si. The spectra and fitting results are qualitatively similar except that now the bulk component has the highest binding energy. The results shown in Fig. 4 and Table I correspond well with those of DiCenzo *et al.*[20] Note that our surface-sensitive spectrum shows an *S*1 surface component slightly more intense than the bulk component; this is different than the intensity order of the components reported in Ref. 20.[21] This difference is caused by different experimental conditions [our 90-eV spectrum should correspond to a shorter electron escape depth than the 68-eV spectrum of Ref. 20; our sample normal pointed nearly directly into the cylindrical mirror analyzer axis, as opposed to 45° (Ref. 22)].

The different binding-energy order of the bulk and the two surface core-level components observed in Ge(111)-*c*(2×8), relative to Si(111)-(7×7), indicates possible significant differences in the surface atomic structure in these two systems, other than just the difference in surface unit-cell size [as in the case of (5×5) versus (7×7)]. Indeed, STM images of these surfaces showed that the surface corrugations in these two systems exhibit qualitative differences.[23] The surface structure of Ge(111)-*c*(2×8), as in the case of Si(111)-(7×7), remains undetermined.

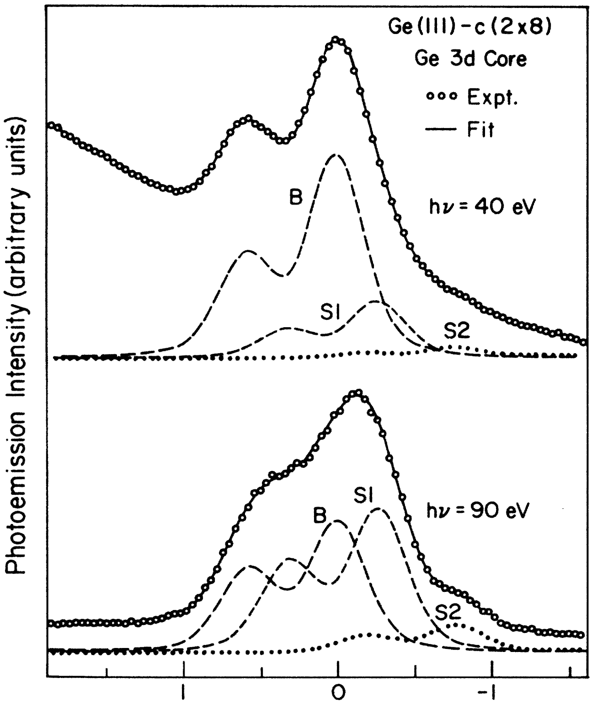

FIG. 4. Bulk- and surface-sensitive Ge 3*d* core-level spectra for clean Ge(111)-*c*(2×8), using photon energies of 40 and 90 eV, respectively. Symbols used are the same as for Fig. 2. The binding-energy scale is referenced to the bulk Ge $3d_{5/2}$ line.

E. Ge 3*d* core levels for Si(111)-Ge(5×5)

Figure 5 shows bulk- and surface-sensitive spectra of the Ge 3*d* cores for the (5×5) sample. Again, in the (5×5) case, the two scans look very much more similar than they do for the Ge(111)-*c*(2×8) sample (see Fig. 4). The broad line shapes indicate the presence of several unresolved components. The spectra could not be uniquely fitted with certainty using our procedure as previously outlined. We have decomposed the spectra by removing one spin-orbit component. We assume that the original spectrum consisted of two identically shaped components separated by the spin-orbit splitting. The splitting and the branching ratio were fixed using the results of the Ge(111)-*c*(2×8) fit. The resulting "peeled" spectra, showing only one spin-orbit component (minus cubic backgrounds), are shown superimposed at the bottom of Fig. 5. For comparison, a Voigt line shape, representing a single component from the *c*(2×8) surface, is also shown. As can be seen, the overall line shape of the peeled spectra

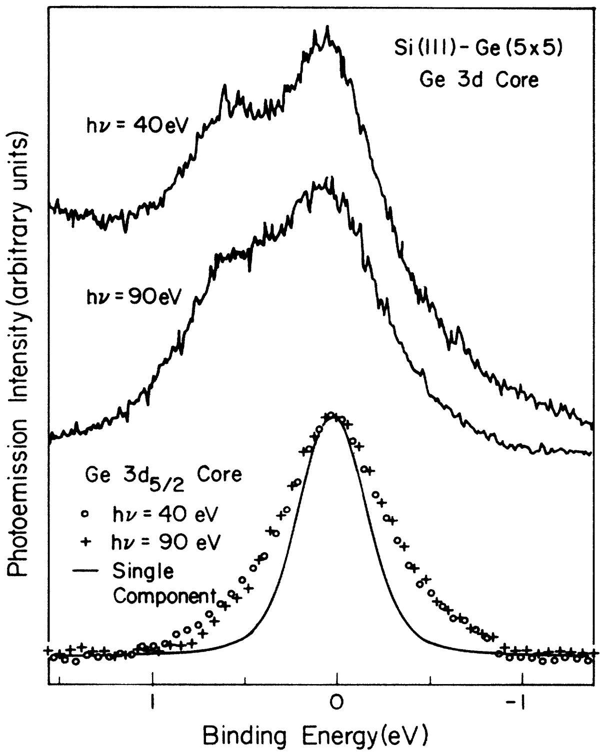

FIG. 5. Bulk- and surface-sensitive Ge 3*d* core-level spectra for Si(111)-Ge(5×5), taken with photon energies of 40 and 90 eV, respectively. The upper two curves are the raw data. The pluses and circles show the $3d_{5/2}$ components of the bulk-sensitive ($h\nu = 40$ eV) and surface-sensitive ($h\nu = 90$ eV) spectra, respectively. The solid curve is a single (deconvoluted) component from the clean *c*(2×8) surface for comparison.

is too wide for a simple, single peak. In addition, the difference between the bulk- and surface-sensitive scans is minor compared to that for Ge(111)-$c(2\times8)$. This is due to the fact that the Ge concentration is much higher at the surface than in the subsurface region for this (5×5) sample as discussed above; therefore, changing the probing depth does not affect the line shape much.

F. Valence bands

Photoemission spectra from the valence bands of Ge(111)-$c(2\times8)$, Si(111)-(7×7), and Si(111)-Ge(5×5) surfaces are shown in Fig. 6. The zero of the energy scale for each is the Fermi level from a gold reference emitter. The spectra for the (7×7) and (5×5) systems were taken using a photon energy of 55 eV; that of the $c(2\times8)$ system was produced using 70-eV photons. Thus all spectra contain significant detail from the region near the surface. Comparing the spectra we see that the Si(111)-Ge(5×5) spectrum and the Si(111)-(7×7) one look similar. The main differences appear near the valence-band maximum. Si(111)-(7×7) shows three surface states at 0.3, 0.9, and 1.8 eV binding energy,[14–17] indicated by arrows in Fig. 6. The 1.8-eV feature is not very pronounced with the photon energy used, but its presence can be verified by its sensitivity to gas adsorption (results not shown here). By comparison, the (5×5) spectrum displays only the 0.3-eV feature clearly. Like the (7×7) surface, the (5×5) surface is metallic with a clearly noticeable Fermi-edge step in the spectrum.

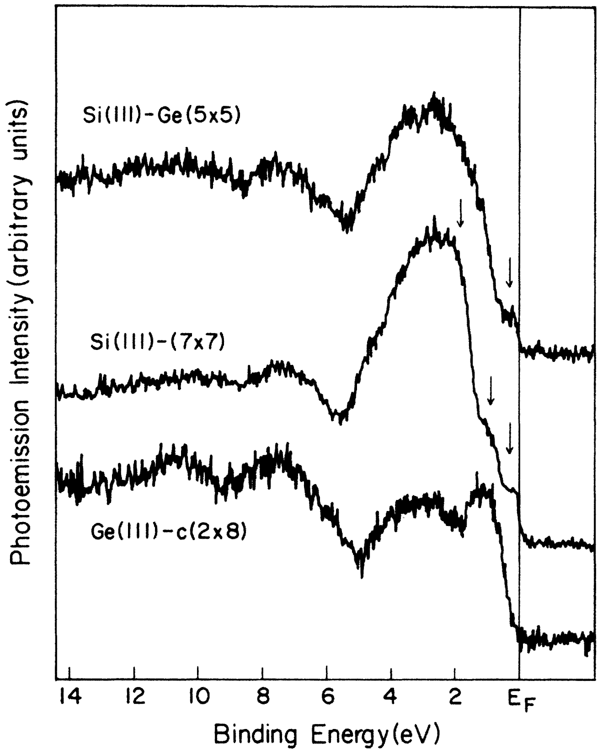

FIG. 6. Angle-integrated photoemission spectra from the valence bands of Si(111)-Ge(5×5), Si(111)-(7×7), and Ge(111)-$c(2\times8)$. The Si(111)-Ge(5×5) and Si(111)-(7×7) spectra were obtained with a photon energy of 55 eV, while the Ge(111)-$c(2\times8)$ spectrum was obtained with a photon energy of 70 eV. The arrows mark positions of surface states for Si(111)-(7×7), and a corresponding peak at 0.3 eV binding energy in the (5×5) spectrum. The zero of the energy scale is the Fermi level. The curves have been shifted and scaled vertically for clarity.

Because of the different photon energy used for the Ge(111)-$c(2\times8)$ spectrum, comparison of it to the (5×5) case is more tentative. The peak around 1.2 eV binding energy is probably derived from surface states, but the angle-integrated photoemission geometry does not allow a clear, unambiguous assignment of the peaks. Three occupied surface-state bands have been observed for Ge(111)-$c(2\times8)$, with angle-resolved photoemission.[17,24–26] It appears that this surface is semiconducting. Notice the absence of a Fermi-edge step in the spectrum for Ge(111)-$c(2\times8)$ shown in Fig. 6. The fact that the Si(111)-(7×7) and Si(111)-Ge(5×5) surfaces are metallic, while the Ge(111)-$c(2\times8)$ surface is semiconducting, indicates again that the (5×5) surface resembles the (7×7) surface more than the $c(2\times8)$ surface.

IV. SUMMARY AND CONCLUSIONS

These results may be summarized as follows. Ge deposited on Si(111)-(7×7) surfaces diffuses slowly into the substrate upon annealing at 750 °C, as shown by the decay of the Ge $3d$ intensity. Conversion of the (5×5) reconstruction back to the (7×7) one occurs while there is still some Ge in the surface region. The Si $2p$ line shape for the Si(111)-(7×7) can be decomposed into two surface components and one bulk component. One of these surface components, at lower binding energy, corresponds well with the bumps seen in STM images and can be identified as adatom emission, while the other, at higher binding energy, corresponds with emission from the first surface layer. This latter feature is still seen in the Si $2p$ spectra of Si(111)-Ge(5×5) surfaces, only with reduced intensity; indicating a similar surface structure and partial replacement of Si by Ge in the first layer. The Si adatoms are completely replaced by Ge atoms in the (5×5) samples. A smaller but detectable concentration of Ge is also present in the subsurface layers.

There is recent theoretical evidence[5] that the (5×5) surface would favor the presence of Ge atoms rather than Si atoms in the adatom sites. Because Ge atoms are 4% larger than Si atoms, the angular strain energy associated with adatom bonds is smaller for Ge adatoms than for Si adatoms. Forcing Ge atoms to fit into the bulk Si lattice will, of course, increase the strain energy. Thus it seems quite natural for Ge to prefer the adatom sites; this is consistent with our observation that the adatom sites are fully occupied by Ge atoms for the (5×5) surface, even though the underlying layers may show significant concentrations of Si. The surface layer shows a Ge concentration much higher than the subsurface region. The concentration gradient of Ge in the subsurface region cannot be determined from the present experiment, but is likely to be governed by the slow diffusion of Ge into the Si lattice; any surface effect (e.g., tendency towards surface segregation) on the concentration gradient is likely to be damped out completely in just a few atomic layers.

Our core-level studies indicate that the Si(111)-Ge(5×5) surface structure, apart from the selective replacement of some Si atoms by Ge atoms in different layers, is very similar to that of Si(111)-(7×7), with the major difference being the surface unit-cell size. The related Ge(111)-$c(2\times 8)$ surface has sometimes been thought to have a structure that is also similar to that of Si(111)-(7×7) in local bonding (that is, the major difference is just the surface unit-cell size). Both Si(111)-(7×7) and Ge(111)-$c(2\times 8)$ show two surface-shifted core-level components in addition to the bulk core. The order in binding energy of the three core-level components is, however, different for these two surfaces. Thus, the differences between the Si(111)-(7×7) and Ge(111)-$c(2\times 8)$ structures may be more significant. STM images from these two surfaces also show qualitative differences in the surface corrugation.

Valence-band photoemission results from Si(111)-Ge(5×5) show a surface feature near the Fermi level similar to the one observed in Si(111)-(7×7). Both surfaces are metallic, while Ge(111)-$c(2\times 8)$ is semiconducting. Lacking a realistic calculation of the electronic properties of these surfaces, we cannot explain with certainty why only one of the three surface states observed in Si(111)-(7×7) is clearly observed in Si(111)-Ge(5×5).

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[1] See, for example, J. J. Lander and J. Morrison, J. Appl. Phys. **34**, 1403 (1963); R. J. Culbertson, L. C. Feldman, and P. J. Silverman, Phys. Rev. Lett. **45**, 2043 (1980); Mark J. Cardillo, Phys. Rev. B **23**, 4279 (1981).

[2] F. J. Himpsel, P. Heimann, T.-C. Chiang, and D. E. Eastman, Phys. Rev. Lett. **45**, 1112 (1980).

[3] G. Binnig, H. Rohrer, H. C. Gerber, and E. Weibel, Phys. Rev. Lett. **50**, 120 (1983).

[4] See, for example, L. C. Snyder, Z. Wasserman, and J. W. Moskowitz, J. Vac. Sci. Technol. **16**, 1266 (1979); J. C. Phillips, Phys. Rev. Lett. **45**, 905 (1980); D. J. Miller and D. Haneman, J. Vac. Sci. Technol. **16**, 1270 (1979); E. G. McRae, Phys. Rev. B **28**, 2305 (1983).

[5] D. J. Chadi, Phys. Rev. B **30**, 4470 (1985).

[6] F. J. Himpsel, Phys. Rev. B **27**, 7782 (1983).

[7] E. G. McRae, H.-J. Gossmann, and L. C. Feldman, Surf. Sci. **146**, L540 (1984).

[8] H.-J. Gossmann, J. C. Bean, L. C. Feldman, and W. M. Gibson, Surf. Sci. Lett. **138**, L175 (1984).

[9] Toshihiro Ichikawa and Shizo Ino, Surf. Sci. **136**, 267 (1984).

[10] See, for example, P. H. Citrin and G. K. Wertheim, Phys. Rev. B **27**, 3176 (1983).

[11] T. Miller, E. Rosenwinkel, and T.-C. Chiang, Solid State Commun. **47**, 935 (1983).

[12] S. Brennan, J. Stohr, R. Jaeger, and J. E. Rowe, Phys. Rev. Lett. **45**, 1414 (1980).

[13] J. F. van der Veen, F. J. Himpsel, and D. E. Eastman, Phys. Rev. Lett. **44**, 189 (1980); P. Heimann, J. F. van der Veen, and D. E. Eastman, Solid State Commun. **38**, 595 (1981).

[14] F. J. Himpsel *et al.*, Phys. Rev. B **24**, 1120 (1981); F. J. Himpsel, Physica **117&118B**, 767 (1983).

[15] H. Neddermeyer, U. Misse, and P. Rupieper, Surf. Sci. **117**, 405 (1982); G. V. Hansson and S. A. Flodstrom, J. Vac. Sci. Technol. **16**, 1287 (1979).

[16] J. E. Demuth, B. N. J. Persson, and A. J. Schell-Sorokin, Phys. Rev. **51**, 2214 (1983).

[17] A. L. Wachs, T. Miller, T.-C. Hsieh, A. P. Shapiro, and T.-C. Chiang, Phys. Rev. B **32**, 2326 (1985).

[18] C. M. Garner, I. Lindau, C. Y. Su, P. Pianetta, and W. E. Spicer, Phys. Rev. B **19**, 3944 (1979).

[19] For this calculation, we did not use the results from the fit to the 108-eV spectrum. For this energy, the $S2$ intensity is very small and difficult to determine accurately, especially with the presence of the large and rapidly varying secondary-emission background. The 130-eV spectrum does not share these problems.

[20] S. B. DiCenzo, P. A. Bennett, D. Tribula, P. Thiry, G. K. Wertheim, and J. E. Rowe, Phys. Rev. B **31**, 2330 (1985).

[21] We analyzed the Ge 3d 61-eV core spectrum as published in Ref. 20, using the same procedure and computer program as used in the present study; the fit of Ref. 20 was closely reproduced. This rules out fitting artifacts and points to an actual difference in the spectra themselves.

[22] T. Miller, A. P. Shapiro, and T.-C. Chiang, Phys. Rev. B **31**, 7195 (1985).

[23] R. S. Becker, J. A. Golovchenko, and B. S. Swartzentruber, Phys. Rev. Lett. 54, 2678 (1985).

[24] R. D. Bringans and H. Hochst, Phys. Rev. B **25**, 1081 (1982).

[25] T. Tokotsuka, S. Kono, S. Suzuki, and T. Sagawa, J. Phys. Soc. Jpn. **53**, 693 (1984).

[26] T. Miller, T. C. Hsieh, and T.-C. Chiang (unpublished).