Surface phase transitions of Ge(100) from temperature-dependent valence-band photoemission

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Valence-band photoemission at a photon energy of 32 eV has been carried out on Ge(100) from below room temperature to 1173 K. The $c(4\times2)\rightarrow2\times1$ phase transition is accompanied by a shifting of a back-bond-derived surface state. The high-temperature $2\times1\rightarrow1\times1$ transition is apparent in the discontinuity in the measured emission intensity of both a bulk and a surface electronic state. A further discontinuity occurs in both of these features and of the Fermi level intensity at higher temperature, approximately 1075 K, indicating the presence of a further reversible phase transition whose nature is discussed. [S0163-1829(98)02404-7]

Evidence of surface phase transitions as a function of temperature can be obtained from both core-level and valence-band photoemission. Surface core-level shifts are widely used to deduce the number of distinct geometrical identities of an atomic species and their relative populations on a reconstructed surface. Appropriately selected experimental geometries and photon energies can be used to enhance the surface sensitivity of the measurements. Examples of this methodology applied to elemental semiconductor surfaces include studies of Si(111),¹⁻⁴ Ge(111),⁵⁻¹⁴ Si(100),^{15–17} and Ge(100).^{18–21} Complementary information can be extracted from valence-band spectra collected at highsymmetry points in the surface Brillouin zone. Dispersion or its absence as a function of photon energy and angle of electron emission and sensitivity to contamination may be used to distinguish between surface- and bulk-derived states, although this is often far from straightforward. Theoretical input is essential. Indicators of surface phase transitions in valence-band spectra include shifts and changes in intensity as a function of temperature.

In the case of Ge(100), both the core levels^{18–21} and valence bands^{22–29} have already attracted both experimental and theoretical attention. One,¹⁸ two,^{19,20} and latterly three²¹ surfaces components have been used in the interpretation of the 3*d* core-level spectra. Bulk and surface contributions to the valence-band spectra have been distinguished and their dispersions measured.^{23,24,28,29} One photoemission study concentrated on the angular and temperature dependence of a surface state in the range 77–500 K.^{25,26} A state overlapping the Fermi level at room temperature moved 0.15 eV to higher binding energy at the metal-to-insulator transition at 220 K accompanied by a change of surface symmetry from 2×1 to $c(4 \times 2)$. A further study¹⁹ of the temperature evolution of the core and valence states provided some evidence of changes in the 3*d* line shape on going from liquid nitrogen temperature to room temperature. Additionally, at higher temperature, a rigid shift in the center of mass of the 3*d* levels was observed, but not commented on.¹⁹

The basic building block of the Ge(100) surface is the asymmetric dimer.³⁰ A reversible $2 \times 1 \rightarrow 1 \times 1$ transition at 955 K was discovered using surface x-ray diffraction, while on the basis of the same diffraction data, a further irreversible transition was supposed to occur at 1023 K.³¹ It was suggested that dimer breakup and adatom and vacancy proliferation accounted for these transitions, but core-level photoemission measurements at high temperature seem to demonstrate that dimers are conserved up to 1143 K at least, contradicting this hypothesis.¹⁹ Furthermore, a He atom scattering study failed to find these transitions.³² Dimer dynamics, the flip-flop and twist motion of dimers, has been used to explain many observations of the geometrically and electronically similar Si(100) surface as the temperature is

14 654



FIG. 1. Normal-emission photoelectron spectra of Ge(100) taken with a photon energy of 32 eV taken at room temperature (a) and 200 K (b). The low-temperature spectrum has been shifted by 0.1 eV so that the bulk-derived peaks coincide.

increased.³³ In this picture, the $c(4 \times 2)$ structure has a small amount of flip-flop and twist motion, the 2×1 structure is characterized by dimer disorder, and the 1×1 phase is characterized by a large fraction of "instantaneously symmetric" dimers, giving rise to an altered optical response. At higher temperatures, further transitions can include dimer breakup as previously suggested and or surface melting, as occurs on Ge(111) (Refs. 13, 14, and 34–36) and which is believed to occur on Si(100).³⁷

In this work, we present normal-emission valence-band spectra of Ge(100) taken at a photon energy of 32 eV as a function of temperature from below room temperature to 1173 K. The shift of a back-bond-derived surface state on going from below room temperature to room temperature is associated with the $c(4\times2)\rightarrow2\times1$ phase transition. A discontinuity in the attenuation of a surface and a bulk state near to 955 K is associated with the high-temperature 2 $\times 1\rightarrow1\times1$ transition. A further discontinuity of these features and of the spectral intensity at the Fermi level provides evidence of another phase transition taking place at high temperature (≈ 1075 K). All this behavior is reversible with temperature.

Measurements were carried out at the undulator beam line SU6 of the Super-ACO storage ring at the Laboratoire pour l'Utilisation du Rayonnement Electromagnétique (LURE), Orsay, France. Samples were cut from an *n*-type, Sb-doped Ge(100) wafer (ρ =0.1 Ω cm). Sample preparation and experimental procedure are as described elsewhere.¹⁴ All measurements were carried out at a photon energy of 32 eV and angle of incidence of 45°, and normally emitted electrons were analyzed by a VSW HA 50 angle-resolving hemispherical analyzer with an acceptance angle of 1°. The overall resolution as determined by measurement of the Fermi level (E_F) of a piece of copper was 0.16 eV. In the following binding energies are referenced to the Fermi level E_F .

Low-temperature, approximately 200 K, and roomtemperature normal-emission valence-band spectra taken at a photon energy of 32 eV are shown in Fig. 1. Four features are present in the valence-band spectra. At the Fermi level there is a narrow feature due to emission from dimer up atom dangling bond states,²⁹ which is unresolved in our spectra from the emission centred at ≈ 0.4 eV, which is due to direct



FIG. 2. Normal-emission photoelectron spectra of Ge(100) taken with a photon energy of 32 eV taken between 513 and 1173 K at the temperatures indicated. The data have been normalized to the beam flux, and there is a constant offset between the spectra.

transitions which have a high probability at this photon energy.²⁹ The peak at 1.4 eV is due to back bond emission and is confined to the second and third surface layers.²⁸ Finally, at 3.25 eV, there is emission from bands of the bulk electronic structure.²⁴ With these assignments in mind, we shall discuss the data as a function of temperature. The 200 K spectrum has been shifted by 0.1 eV to lower binding energy so that the bulk-derived peaks coincide. At low temperature, there are peaks at 0.4, 1.2, and 3.25 eV, and at room temperature, their positions are 0.4, 1.4, and 3.25 eV, respectively, the back-bond-derived surface peak having increased its binding energy by 0.2 eV.

Figure 2 shows a series of spectra taken at temperatures from room temperature to 1173 K; the presented data are normalized to the beam flux. Each of the three features is broadened with temperature, and the one at 0.4 eV above 650 K is visible as a shoulder up to 1000 K. The temperature dependence of the emission intensities at 1.4 ± 0.3 and 3.25 ± 0.3 eV and of the Fermi level (0 ± 0.06 eV) are plotted in Fig. 3(a), where the data have been normalized to the emission intensity at 0.7 ± 0.3 eV, and in Fig. 3(b), where the data have been normalized to the beam flux. In Fig. 3(a), the peaks are seen to lose intensity until 979 K, to remain approximately constant until 1075 K, and to lose intensity again thereafter. The same trends are observed if, instead of comparing areas, point intensities at 1.4 and 3.25 eV are compared to the point intensity at 0.7 eV (indicating that thermal broadening does not effect the measured ratios) or if the background window used in the normalization procedure is located either between the back bond and the 3.25 eV state or beyond the 3.25 eV peak. The actual window used was chosen so as to minimize the effects of small changes in background with temperature which are smallest at low binding energy. This is important in our case, as only a constant background, equal to the emission intensity above the Fermi level, has been subtracted from the data. The emission at the Fermi level rises with temperature without showing the



FIG. 3. (a) The temperature dependence of the surface state emission at 1.4 eV (triangles) and the bulk state emission at 3.25 eV (circles), measured by plotting the ratio of the peak intensities up to 0.3 eV either side of their respective maxima and the integrated intensity between 0.4 and 1.0 eV. (b) The temperature dependence of the surface state emission at 1.4 eV (triangles) and the bulk state emission at 3.25 eV (circles), measured by plotting the ratio of the peak areas of (a) to the beam flux. Also shown is the behavior of the Fermi level (0 \pm 0.06 eV) to the beam flux (solid squares).

900

Temperature (K)

1000

1100

1200

700

800

marked discontinuities of the other data. In Fig. 3(b), the emission intensities as normalized to the beam flux are seen to diminish gradually up to about 950 K, to lose intensity more quickly until 1075 K, and then to increase thereafter. The emission at the Fermi level exhibits the same general behavior except for a gradual increase up to 950 K. Again, only a constant background was subtracted from the data. Normalization with respect to the secondary electron background above the Fermi level due to transitions induced by higher-order radiation yields the same behavior as seen in Fig. 3(b).

At a temperature of 220 K, the Ge(100) surface undergoes a change of surface reconstruction from $c(4 \times 2)$ (below 220) K) to 2×1 (above 220 K).^{25,26} If the surface dimers are regarded as spins,³⁰ this can be thought of as an antiferromagnetic (below 220 K) to ferromagnetic transition. As shown in Fig. 1, there were shifts of both bulk and surface derived states, but only the latter could be expected in a surface phase transition. This may be due to the surface photovoltage (SPV) effect as has been observed for Si(111) (Ref. 38) and Si(113) (Ref. 39) surfaces at low temperature. Both the size and direction of the shift are consistent with this hypothesis. A shift of the opposite sign but the same magnitude was seen in the core-level spectra of p-type Ge(100) on going from room to liquid-nitrogen temperature, but not commented on,¹⁹ again consistent with the earlier work on Si. In our spectra, therefore, the shifts of 0.1 eV of the bulkderived states (0.4 and 3.5 eV) are attributed to the SPV effect, while the shift of the back-bond-derived surface state is attributed to a combination of the SPV effect acting in one direction and a larger shift due to the phase transition acting in the opposite direction. There is thus a phase-transition-induced shift in the position of the back-bond-derived surface state of 0.2 eV towards lower binding energy on lowering the temperature. A weakening and a shift of 0.15 eV towards higher binding energy of the dimer dangling bond surface state on lowering the temperature was observed by Kevan and Stoffel;²⁵ in our data, it is masked by the presence of overlapping bulk transitions. Narrowing of a surface state at the center of the surface Brillouin zone and a reduction in the surface state bandwidth has been observed for Si(100),⁴⁰ which undergoes the same type of phase transition.

A second phase transition is evident in the discontinuity of the attenuation of both the surface state at 1.4 eV and the bulk one at 3.25 eV, as can be seen in Fig. 3(a) and 3(b). The attenuation of the bulk-derived feature is not necessarily indicative of changes in the bulk, but of changes in the surface which affect electron transport through the surface layer and thus the way in which the bulk is perceived. It is known from surface x-ray diffraction that a phase transition $2 \times 1 \rightarrow 1$ $\times 1$ takes place at a temperature of 955 \pm 7 K.³¹ The explanation of this was dimer breakup, which, until 1023 K, is reversible. This is inconsistent with the core-level results of LeLay et al.¹⁹ who saw dimer numbers conserved beyond this temperature. This inconsistency may be resolved by resorting to dimer dynamics wherein dimer numbers are conserved although they adopt an instantaneously symmetric character, leading to the 1×1 symmetry observed.³³ Again, the previous study¹⁹ followed the attenuation of both bulk and surface states at the J' point in the surface Brillouin zone (a point which is equivalent for both domains in the two domain 2×1 surface), but they did not have enough data points to be able to follow it closely and so observe this phase transition.

At first glance, the behavior of the emission intensity at the Fermi level appears to be very peculiar; for a semiconductor, a monotonic increase in metallicity with temperature and thus in emission intensity at the Fermi level is to be expected and has been observed for Ge(111) and Si(100). This apparent contradiction can be explained by examining the details of the electronic structure of symmetric and asymmetric dimers, particularly near the Γ point of the surface Brillouin zone. As there is a lack of relevant calculations for Ge(100), we use calculations performed for the electronically similar Si(100) surface.^{27,41} For asymmetric dimers, there is a finite dimer up atom dangling bond density of states at Γ , which gives rise to a finite intensity at the Fermi level at room temperature and this emission increases until the 2 $\times 1 \rightarrow 1 \times 1$ phase transition. The 1×1 phase, however, is characterized by an increasing fraction of symmetric dimers, but the symmetric dimer bonding band, despite being occupied over much of the surface Brillouin zone, is unoccupied at and near Γ . As the temperature is increased beyond 955 K, the number of symmetric dimers increases and, therefore, the emission intensity at the Fermi level falls.

Besides the aspect of working in normal emission, polarization effects may also contribute to the unexpected weakness of the intensity at the Fermi level. In our experimental geometry, transitions from states with p_z symmetry are suppressed. The dangling bond emission of both the symmetric dimers and of the same atoms of the unreconstructed surface is not expected to be visible in our data. Due to the distortion of the asymmetric dimer configuration, though, some dimer up atom emission is expected. This provides a second reason for the fall in emission intensity across the $2 \times 1 \rightarrow 1 \times 1$ transition.

A second discontinuity in the data of Figs. 3(a) and 3(b) is evidence of a further reversible phase transition having taken place close to 1075 K. Dimers having been conserved up until 955 K and beyond, further phase transitions involve the possibility of dimer breakup and adatom and vacancy proliferation, as originally proposed for the 955 K transition,³¹ and/or surface melting which occurs on Ge(111) at close to the same temperature as we observe our final phase transition^{13,14,34–36} and which is believed to occur on the structurally similar Si(100) surface.³⁷

Johnson *et al.*³¹ in their x-ray-diffraction study saw a final phase transition at 1023 K, while LeLay *et al.*¹⁹ failed to find evidence of transitions up to a reported temperature of 1143 K.

Surface melting of a semiconductor is accompanied by an increase in the density of states at the Fermi level as liquid germanium is a conductor [even though Ge(100) is already metallic at room temperature], and we see just such an increase in Fermi level intensity in Fig. 3(b). For the same reasons as outlined previously, this intensity increases only

slowly with temperature. The second possibility, dimer breakup with adatom and vacancy proliferation, cannot be discounted, however, because the persistence of both the bulk state and the surface back bond state is also compatible with this model. Valence-band photoemission at this final state energy probes too many atomic layers to be able to distinguish between the possible mechanisms.

Comparing other elemental semiconductors, though, favors the surface-melting hypothesis, as Ge(111) is known to undergo surface melting close to the same temperature^{13,14,34–36} and the comparable Si(100) surface is also believed to undergo surface melting.³⁷ Complementary measurements, however, are required to properly distinguish between the two.

Valence-band photoemission at a photon energy of 32 eV has been carried out on the Ge(100) surface across the $c(4\times2)\rightarrow2\times1$ low-temperature and the $2\times1\rightarrow1\times1$ hightemperature surface phase transitions. Clear evidence is seen for both of these transitions and of a further reversible transition at a temperature close to 1075 K whose nature is not certain, although for systematic reasons, surface melting is favored.

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