Phase transitions on the Ge(111) and Si(111) surfaces from core-level studies

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Detailed studies of clean Ge(111) and Si(111) surfaces in a large interval of temperatures around the $c(2\times8)\leftrightarrow(1\times1)$ and $(7\times7)\leftrightarrow(1\times1)$ transition points have been made by means of core-level photoemission spectroscopy. Through the decomposition of the Ge $3d$ and Si $2p$ core levels we bring the evidence that with increasing temperature a part of the surface reconstruction of both semiconductors progressively changes to a nonadatom structure. This new atom configuration seems to be the (2×1) reconstruction and it appears far below the transition-point temperature.

Within the last few years a consensus has been reached concerning the stable reconstruction of Si(111) and Ge(111) surfaces at room temperature (RT). For Si(111) the surface native reconstruction, the 7×7, is best described by a model proposed by Takayanagi et al.[1] consisting of dimers, adatoms, and partial subsurface stacking fault (the DAS model). The annealed Ge(111) surface possesses a reconstruction described by a $c(2\times8)$ unit cell which remained somewhat mysterious for a long time. As settled by recent experiments using x-ray diffraction,[2] medium-energy ion scattering,[3] and scanning tunneling microscopy[4] (STM), the Ge(111)-$c(2\times8)$ surface is built up with adatoms occupying threefold on-top ($T4$) sites arranged in (2×2) and $c(2\times4)$ configurations on a (1×1) substrate. For both reconstructions the building block is the adatom cluster consisting of a top atom bonding to three underlying atoms which lie in the first surface layer. The total energy of the surface is then reduced by lowering the dangling bond density. This is quite different from cleaved surfaces where no adatom structure has been observed.

The high-temperature reconstructions are still not well understood. It is known that the initial superstructure transforms reversibly into an apparent (1×1) structure at 300 and 870 °C for Ge and Si, respectively. Detailed experimental investigations of these phase transitions have been rather scarce up to now.[5-8] The low-energy electron diffraction spectroscopy (LEED) studies of the high-temperature phases show a (1×1) structure, but also an enhanced amount of diffuse scattering near positions of half-order spots.[5,6] In the case of Ge(111) the new structure can be interpreted either by a (2×1) or a (2×2) reconstruction[5] while for the Si(111) surface no evidence for a (2×1) reconstruction was found[6] by LEED studies. Photoemission from the $3d$ core levels of Ge(111) shows no discontinuous change in binding energy of the two surface contributions, nor any significant change in the relative amounts of surface atoms.[7]

More effort has been devoted to laser-stabilized surfaces[4,6,9-11] for several reasons. Indeed, there is a technical simplicity in studying the samples at RT. From the point of view of physics, the interest in these surfaces consists of possible similarities with the surfaces at high temperatures. At first it was believed that the laser-stabilized surfaces are just a truncated bulk, i.e., without reconstruc-

tion. Various experiments failed to agree on the nature of the observed 1×1 LEED pattern with models ranging from the graphitelike (1×1) Si structure to a somewhat disordered (7×7) structure.[12] Photoemission and intensity LEED experiments suggested[9] that a buckled (2×1) reconstruction takes place upon laser quenching, but another photoemission work[10] found that both laser-stabilized and (7×7) reconstructed Si(111) surfaces are very similar. Recent STM studies[4] of Si(111) and Ge(111) surfaces prepared by various procedures bring evidence that the adatom structure is conserved even after the laser annealing. Laser-stabilized surfaces appear to have loosely packed (2×2) arrays on a (1×1) substrate with adatoms occupying $T4$ sites.

A precise quantification of the core-level shifts in photoemission experiments provides details concerning the local chemical environment of surface sites,[7,11,13,14] and is of paramount interest for an elucidation of the interplay between specific features of the reconstruction and surface electronic properties in general. In the literature there is a consensus about the decomposition of the Si $2p$ and Ge $3d$ core-level spectra, respectively, in the (7×7) and $c(2\times8)$ reconstructions: in addition to the bulk contribution there are two surface peaks[15,16] [an example for Ge is shown in Fig. 1(b)]. However, the attribution of the surface peaks to specific features on the surfaces is somewhat contradictory. At first it was believed that in both semiconductors, Si and Ge, the surface peaks with the lowest binding energy (BE) represent the adatoms,[15-19] and the second one the atoms of the first layer, just under the adatoms. Reevaluation of the surface-peak intensities for the Si(111)-(7×7) surface, together with the analysis of the charge transfers between surface atoms based on first-principles calculations,[20] reversed the picture. Now the low BE peak is assigned to the so-called rest atoms in the DAS model[1] and the other one to adatoms with possible contribution of the first layer of atoms.[14] Recently, the same assignment of the surface peaks was also discussed for Ge(111)-$c(2\times8)$.[7] In the following we adopt the same interpretation of these surface-shifted core-level components.

In this paper we present a new thorough investigation of the core-level measurements using synchrotron radiation on clean Si(111) and Ge(111) surfaces between 20 °C and above the temperature where the respective transi-
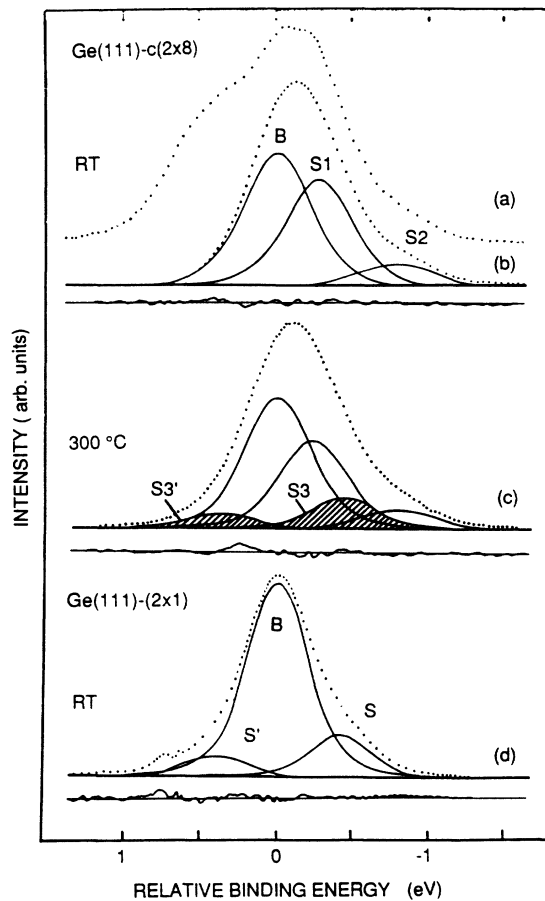
FIG. 1. (a) Ge $3d$ core-level spectrum for clean Ge(111)-$c(2\times8)$ taken at room temperature ($h\nu = 60$ eV). (b) The same spectrum after a subtraction of the $3d_{3/2}$ part. The solid line represents the three spectral components; B is bulk origin and $S1$ and $S2$ are surface derived. (c) Ge $3d_{5/2}$ spectrum recorded at 300 °C. The new surface components ($S3$ and $S3'$) are shown by the shaded area. (d) Ge $3d_{5/2}$ core-level spectrum for the cleaved Ge(111) surface. The binding energy is referred to as component B of the Ge $3d_{5/2}$ line. Under each spectrum we plot the residual of the subtraction of the measured and calculated curves.

tions occur.

The photoemission experiments have been performed at the SUPERACO storage ring (LURE, Orsay). The base pressure in the experimental chamber was about 2×10^{-10} mbar. This system was attached to the toroidal grating monochromator of the undulator SU6 line. The data were taken at normal emission while the incident angle of the light was 45°. Photoelectrons were collected by a hemispherical analyzer with 2° acceptance angle. Clean surfaces of Ge(111) (undoped) were prepared by ion sputtering with 600-eV Ar ions during 1 h and simultaneously heating to 600 °C. The sample was subsequently annealed at 800 °C for several minutes and cooled down to room temperature.

Silicon single crystals (n type, P doped) were cleaned by heating to 1100 °C during 30 s. The surface reconstructions were controlled by LEED. In both cases the heating was obtained by passing a dc current directly through the samples.

The raw data were first background subtracted (second-degree polynomial). Second, we decomposed the spectra into same-shaped $3d_{5/2}$, $3d_{3/2}$ (Ge) and $2p_{3/2}$, $2p_{1/2}$ (Si) contributions. From this, a spin-orbit splitting of 0.580 and 0.608 eV was determined with a branching ratio of 0.61 and 0.52 for Ge and Si, respectively. The decomposition into individual contributions from bulk and surface atoms was then made on the assumption that all the peaks of a given element are truly of the same shape. The Lorentzian lines with the 0.15 eV (Ge) and 0.18 eV (Si) full width at half maximum (FWHM) were each convoluted with a Gaussian with the same FWHM equal to 0.45 eV, representing all instrumental broadening. An example of the decomposition is shown in Fig. 1(b). The spectra taken at room temperature are in excellent agreement with previous works.[15–18] We note that for Si(111) the values for the bulk core-level line-shape parameters have been confirmed by an independent experiment.[21] After an evaporation of two monolayers of Pb on the Si(111) surface, all its reconstructions are removed and the bulk Si $2p$ core levels can be exactly fitted.

First we discuss the results for Ge(111). To our knowledge the only study of the $c(2\times8)\leftrightarrow(1\times1)$ phase transition by means of core-level spectroscopy was performed by Aarts, Hoeven, and Larsen.[7] These authors did not find any appreciable difference between measurements at 20 and 400 °C where the surface is apparently (1×1), so they concluded that the phase transition from $c(2\times8)$ to (1×1) is due to a disorder occurring in an originally ordered adatom structure. In the decomposition of their high-temperature spectra they had to introduce a small ($+0.05$ eV) shift of the $S1$ peak (see Fig. 1). They attributed the origin of the shift to different binding energies for adatoms between initially assumed hollow ($H3$) sites and on-top ($T4$) positions (beyond the transition temperature) on the surface.

We have recorded the $3d$ spectra between RT and 380 °C. Before doing any mathematical treatment of the spectra we plot the peak FWHM versus temperature (Fig. 2, curve a). This gives us qualitative information about the changes of the structure on the surface. We point out that by means of photoemission the phase transition point is clearly visible as a dip between 260–300 °C, indicating some rearrangement of intensities of the different components contributing to the spectra. In order to obtain more details about the behavior of the surface atoms we next proceed to the decomposition of the spectra. Our starting assumption consists of maintaining the same components with identical parameters (position, shape) as at RT. With this procedure new surface peaks [denoted by $S3$, $S3'$, and the shaded region in Fig. 1(c)] must be introduced to fit the data at higher temperatures. We note that unlike the peak $S3$, the determinations of the position and the intensity of $S3'$ components are not very accurate because at high temperatures electron energy losses contribute to a tail of the high-binding-energy side of the spectra. Our discussion will therefore be based especially on the presence of the peak $S3$. In Fig. 1 under each spectrum we plot the residual of the subtraction of the measured and calculated curves.

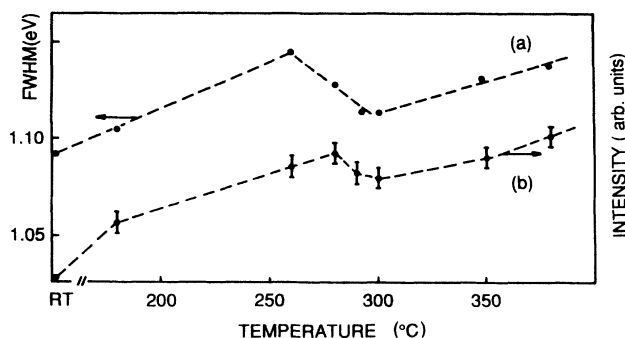In doing this decomposition we are aware, of course,

FIG. 2. Temperature dependence of the FWHM of Ge $3d$ core levels (curve a) and of the intensity of the third surface component ($S3$) (curve b).

that upon adding new lines, it is always possible, from the mathematical point of view, to fit a spectrum of a given form, often without any reasonable physical meaning of the resulting values. However, in the following we raise evidence that the introduction of the new surface peaks gives a more consistent explanation of the core-level evolution.

The first argument is that the peak $S3$ must be introduced already at 180 °C (the first measurements above RT) and its intensity is continuously growing with increasing temperature. This means that the spectrum is already changing at temperatures very far below the transition point. A larger FWHM of the Gaussian, in order to improve the fit with two surface peaks, cannot be introduced here, at least for the bulk component, because in semiconductors the phonon coupling is very low in our range of temperatures.[22] We also let only the Gaussian of the surface components vary, but the fit is worse than for the new peaks $S3$, $S3'$. Another fitting possibility would be to impose a shift to one of the surface peaks, as done in Ref. 7. This cannot be justified at low temperatures because it would imply a disordering on the surface described by jumps of adatoms from initial $T4$ (as proved by several independent studies[2,4]) to $H3$ sites. However, LEED studies showed no change in the intensities of any reflections below 200 °C.[5] In addition, the environment of adatoms in $H3$ and $T4$ sites is very close, so it would not be likely to lead to a measurable shift of the core levels. Moreover, even if the photoemission experiments could reveal the difference in binding energy between the two sites, the shift should stabilize around the transition-point temperature where the disorder on the surface is supposed to be reached. Looking now at our resulting decomposition we see that the fit is very good throughout the whole temperature interval, only upon changing the respective intensities. In Fig. 2, curve b, we plot the intensity of the $S3$ peak versus temperature. The intensity of the peak $S2$ is constant for all temperatures, whereas the uncertainty in the intensity of the peak $S1$ is so high, due to its proximity in energy to the bulk peak, that it is not possible to follow its behavior unambiguously. The discontinuity seen in Fig. 2, curve a is reproduced for $S3$. This indicates that the new $S3$ feature is gradually developing in the temperature range below the transition point, but at

the phase-transition temperature its development is thwarted.

A better picture about the processes occurring at the phase transition could be given by total-energy calculations at different temperatures and possibly by further surface-structure-sensitive experiments.

Silicon $2p$ spectra show comparable behavior to the Ge $3d$ ones. This is not so surprising because of existing similarities in Ge(111) and Si(111) surface structure. Keeping exactly the same binding energies of the peaks, again, we must introduce the third surface component $S3$ at high temperatures. The peak $S3$ even appears at RT for samples prepared by very short annealing when compared with the usual procedure of preparation of the (7×7) reconstruction (Fig. 3).

The intensity of the peak $S3$ at the phase-transition temperature represents 26% (Si) and 13% (Ge) of the total surface peaks signal.

Now the following question arises: To what structure do the peaks $S3$ and $S3'$ correspond? As we stressed in the introduction, the position of the surface peaks for Ge(111)-$c(2 \times 8)$ and Si(111)-(7×7) are well established. The important point is that adatoms and rest atoms, present on both surfaces, show clear signatures in the core-level spectra. As seen in Fig. 1(c), the peaks $S3$ and $S3'$ in our decomposition have quite different positions, so
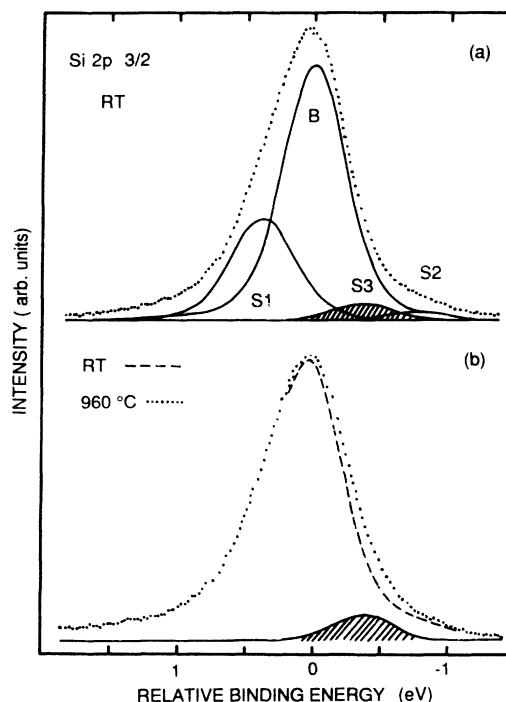

FIG. 3. (a) Si $2p_{3/2}$ core-level spectrum of sputtered, thermally annealed, and then quenched Si(111) surface ($h\nu = 130$ eV). Apart from the bulk (B) and the two conventional surface contributions ($S1$, $S2$) a third surface component ($S3$, shaded area) had to be introduced to fit the measured spectrum. (b) A subtraction of Si $2p_{3/2}$ peaks taken at 960 °C (dotted curve) and at room temperature (dashed curve) gives an evidence of the $S3$ contribution (shaded area). The binding energy is referred to the component B of the Si $2p_{1/2}$ line.

they represent a nonadatom reconstruction. On the one hand there is a possibility that a small part (otherwise it would be seen in the RT spectra) of the intensity of the $S3$ and $S3'$ peaks correspond to structures at boundaries between perfectly reconstructed $c(2\times8)$ and (7×7) areas or to steps on the surface. On the other hand, it is remarkable to notice that without imposing any precise binding energy for the peaks $S3$ and $S3'$, their optimized positions correspond fairly well to the low-binding-energy surface peaks on the cleaved surface of both semiconductors which have the (2×1) reconstruction. In fact, if the decomposition of the Si $2p$ core line for the cleaved Si(111)-(2×1) surface is well established,[14,23] to our knowledge no detailed deconvolution exists for the Ge $3d$ line in the case of the cleaved Ge(111)-(2×1) surface. We have thus performed such an analysis as shown in Fig. 1(d), which gives a result very similar to Si(111)-(2×1). For the Si(111) surface it is impossible to determine the peak $S3'$ because it coincides with the adatoms ($S1$) contribution.

The fact that the positions of $S3$ and $S3'$ agree with the surface components on the (2×1) surface is not so surprising because weak half-order spots have been observed by LEED on both Ge(111) and Si(111) surfaces at high temperatures[5,6] even though these LEED experiments could not decide whether the reconstruction was (2×2) or true (2×1). Our new results bring information about the local atomic configuration and are further fully consistent with recent STM measurements of sputtered, thermally annealed, and then quenched Si(111) surfaces[24,25] on which the (2×1) reconstruction has been effectively observed; indeed we were obliged to introduce

the peak $S3$ even in the spectra recorded at room temperature [Fig. 3(a)]. Becker, Klitsner, and Vickers supposed that the presence at RT of this (2×1) reconstruction on the annealed surface results from a microcleave due to a thermal stress during the rapid cooling of the sample. On the other hand Pashley, Habern, and Friday[25] detected the presence of the (2×1) reconstruction at high temperatures. The appearance of the new surface configuration is not so surprising when one takes into account the energy difference between the (7×7) and (2×1) reconstructions of Si, which is only 0.04 eV according to total-energy calculations.[26]

We have shown that the temperature behavior of the reconstruction on the Ge(111) surface is similar to the case of Si(111). The $c(2\times8)$ reconstruction of Ge is even more fragile[4] in the sense of the energy stability. It is therefore very straightforward to imagine that at higher temperatures a new equilibrium structure configuration is reached by destroying a fraction of the native reconstruction.

In conclusion, by means of core-level photoemission we have observed that, in a large interval of temperatures around the phase transition point, the Ge(111) and Si(111) surfaces still mainly have the adatom local arrangement yet coexisting with a nonadatom configuration which is most probably a (2×1) reconstruction. The proportion of this reconstruction increases with increasing temperature. It is clear that further experiments and calculations are required in order to better understand the nature of the phase transition and the high-temperature structure.

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