Core-level study of the phase transition on the Ge(111)-c (2×8) surface

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Measurements of the Ge 3d core level of the Ge(111) surface have been performed between room temperature, where the surface shows a c(2×8) reconstruction, and 400 °C, where the reconstruction has disappeared. Analysis of the data shows that no significant changes occur in either the binding energies or the relative intensities of the two different surface contributions. This shows that the phase transition is of the order-disorder type. A simple model for the occurrence of disorder is proposed.

I. INTRODUCTION

At room temperature the stable reconstruction of the Ge(111) surface is now believed to be $c(2\times8)$. Usually, low-energy electron diffraction (LEED) patterns taken from this surface do not fully comply with the $c(2\times8)$ designation, since the expected quarter-order spots are mostly missing.[1] However, it was shown by Yang and Jona[2] that the missing spots are still best explained by assuming a $c(2\times8)$ instead of a simple (2×8) reconstruction. Later on, the missing spots were found by Phaneuf and Webb,[3] who showed that their typical intensity is 2 orders of magnitude lower than the intensity of the integer order spots. The quarter-order spots were also seen by reflection high-energy electron diffraction[4,5] (RHEED). Finally, experiments with a scanning tunneling microscope (STM) showed the presence of surface areas which can be described with a $c(2\times8)$ unit cell.[6]

The atomic structure of the reconstruction is not yet completely known, but it is virtually certain that it involves adatoms on top of the first complete layer. In the STM measurements[6] protrusions were found on the surface which could be interpreted as adatoms. The arrangement of adatoms, which number about 25% of a monolayer, is such that this would lead directly to a $c(2\times8)$ unit cell as seen with electron diffraction.[2,3] The STM measurements also showed parts of the surface where such adatoms were organized in (2×2) and $c(4\times2)$ entities. These entities might be used as building blocks for the full reconstruction, as proposed by Chadi for the case of Si(111)-(7×7) and Si(111)/Ge-(5×5).[7] Also, the surface valence-band structure can be partly explained by adatom geometries.[8] Photoemission measurements of the Ge 3d core level on the Ge(111)-c (2×8) surface show the presence of two different surface components,[9,10] suggesting the presence of two different types of surface atoms. The estimated ratio of these types is about 4:1 and this fact has been used to suggest that the component with smaller intensity is due to the adatoms.[3,10] The same argument has been put forward in the case of Si(111).[11] This interpretation is not so straightforward as it appears, as will be shown in the discussion. This notwithstanding, the simplest model for the $c(2\times8)$ reconstruction appears to be an ordered

structure of adatoms. A rather more complex model was recently proposed by Takayanagi and Tanishiro[12] and includes both adatoms and dimers in a manner similar to the dimer-adatom-stacking-fault model for Si(111)-(7×7).[13] As recent medium-energy ion scattering measurements do not support this model,[14] we shall not discuss it further.

Between 200 and 300 °C the reconstruction transforms reversibly to a different structure. The electron diffraction pattern of the high temperature phase shows a (1×1) structure, but also an enhanced amount of diffuse scattering near positions of half-order spots.[3,4] The transformation was therefore interpreted as taking place from an ordered state into a disordered state, which consists of quasiperiodic (2×1) or (2×2) structures.[4] In this paper we present results of temperature-dependent studies of the Ge 3d core level on the Ge(111) surface. We find that going through the transition no discontinuous change in binding energies of the two surface components takes place; nor do we find any significant changes in the relative amounts of surface atoms. Specifically, this implies that the ordered adatom structure becomes disordered without an appreciable change in the number of adatoms present, or in their position. We shall propose a simple possibility for the occurrence of such disorder.

II. EXPERIMENT

The experiments were carried out in a vacuum chamber equipped with an electron energy analyzer, a Knudsen cell for MBE growth of Ge and a facility for surface characterization by reflection high-energy electron diffraction. The base pressure of the cryo- and ion-pumped system was about 2×10^{-10} torr. This system was attached to the toroidal grating monochromator of the A61 beam line at the ACO storage ring (LURE, Orsay).[15] In all experiments the angle of incidence θ_i of the incident radiation with respect to the surface normal was 45°. The data were taken in normal emission. Electron energies were analyzed using a HAC-50 hemispherical analyzer of the Vacuum Science Workshop (Manchester, U.K.), equipped with a four-element lens and at the exit plane a position-sensitive detection system, consisting of two channel plates for amplification and a resistive anode

for detection.[16] The decoding of the positional information from the resistive anode was performed by Canberra electronics in a configuration as described in Ref. 17. The experiments were mainly performed at a photon energy of 55 eV, which was, in our experiments, the best compromise between intensity from the monochromator and surface sensitivity (the electron escape depth at this energy is about 6 Å).

Clean surfaces were prepared by growing a buffer layer of Ge on a Ge(111) surface. The surface normal of the substrates used was oriented along the (111) direction to within a misorientation of 0.05°. The growth temperature of the buffer layer was about 550 °C. After cooling the substrate to 20 °C a sharp RHEED pattern was always found, showing the three domains of the $c(2\times8)$ structure and including the $\frac{1}{4}$-order spots. It was found, however, that valence-band spectra taken directly after growth were not yet of high quality. The sharpness and intensity of the features could be increased considerably by annealing the sample for several hours at 500 °C, which we ascribe to the increase of local atomic order on the surface.[8]

III. DATA ANALYSIS AND RESULTS

A. Line-shape analysis

Before analyzing the spectra, which were measured over a range of 8 eV, the data were corrected for a background which turned out to consist of secondary electrons and of a small contribution of the Auger MVV transition. In our experiments this transition lies around a kinetic energy of 19.5 eV, which is 1.5 eV below the kinetic energy of electrons emitted from the Ge $3d$ state when they are measured with photons of 55 eV (the bulk binding energy of the $3d$ electrons in about 29.5 eV, the photoelectric threshold is about 4.5 eV). Due to the unusual shape of the background it was not possible to make a line-shape analysis by including a single background in the fitting function, although this is commonly thought to give better results.[18] Instead the background was emulated by fitting one parabola to the measured background on each side (low and high binding energy side) of the spectrum and joining these in the middle of the fitted interval with the constraint of continuous values for the functions and their first derivatives in that point. This procedure turned out to work well as was found by comparing its results with results of measurements at a photon energy of 60 eV, and with results from the literature. However, small discrepancies between the measured line shape and results of the fitting procedure, which were often found at the high binding energy side of the spectrum, may be due to the background subtraction. After subtraction, the spectra were analyzed with a curve-fitting program based on minimizing the sum of the squares of the differences between data points and fitted curve. This sum of residues was further used as a criterion for the goodness of the fit.

As stated in the introduction, the full line shape is a sum of contributions from bulk atoms and differently bound surface atoms. This leads to two parameters for each contribution, namely the binding energy and the intensity. In the case of Ge, photoemission from the $3d^{10}$ level results in a splitting of the line due to spin-orbit coupling in the $3d^9$ final state. This splitting is characterized by two parameters, the energy difference $\Delta_{s.o.}$ and the intensity ratio ("branching ratio") R between the components. These were assumed to be the same for all contributions to the measured line. Every line is further broadened by the finite lifetime of the final (hole) state. For semiconductors the broadening can be taken as simple Lorentzian [with a full width at half maximum (FWHM) called W_L] and the same width was assumed for each contribution. The Lorentzian was convoluted with a Gaussian distribution (FWHM called W_G) representing the instrumental uncertainties. For several measurements on clean surfaces, values for the spin-orbit splitting and branching ratio were optimized and the values for these parameters were then used in analyzing the measurements at higher temperatures. Three contributions were taken to describe the full line, which means that six free parameters were used for the fits.

B. Results

Figure 1 shows a core-level spectrum measured on a clean Ge(111) surface. In this figure the zero of energy is taken at the bulk binding energy of the $3d_{5/2}$ line. The result of the best fit to this line shape using three different contributions is also shown. The values used for $\Delta_{s.o.}$, R, W_L, and W_G are given in Table I. Some remarks on these values can be made. Analysis showed that good fits could be obtained by using a branching ratio of 0.58. This is somewhat lower than the expected ratio of 0.67,
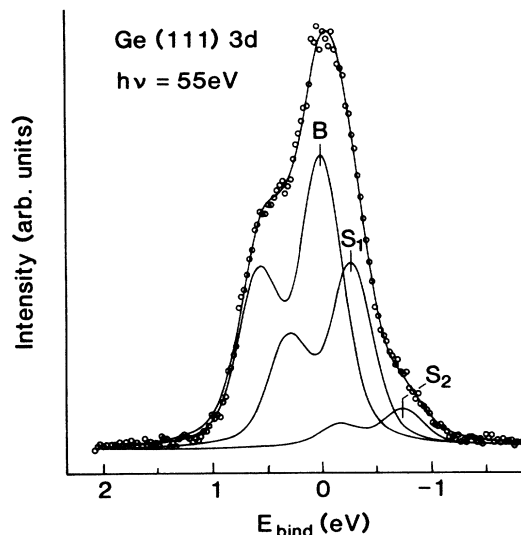

FIG. 1. Ge $3d$ core-level spectrum of a clean Ge(111)-$c(2\times8)$ surface at 20 °C. The binding energy is relative to the bulk $3d_{5/2}$ line. The circles are data points. The full lines are the result of the decomposition, using a least-squares fit, as explained in the text.

TABLE I. Analysis parameters and results of deconvolution of the Ge $3d$ core level measured at room temperature and at $h\nu=55$ eV. Left-hand side: Optimized values of the spin-orbit splitting $(\Delta_{s.o.})$, branching ratio (R) and lifetime broadening (W_L). The instrumental width is given by W_G. Right-hand side: Binding energy shifts of the two surface contributions relative to the position of the bulk component $(\Delta E_1, \Delta E_2)$ and intensity ratios (see text).

$\Delta_{s.o.}$ (eV)	0.58	ΔE_1 (eV)	-0.27 ± 0.01
R	0.58	ΔE_2 (eV)	-0.73 ± 0.02
W_L (eV)	0.18	I_S/I_{tot}	0.43
W_G (eV)	0.35	I_{S_2}/I_{S_1}	0.19

FIG. 2. Binding energy shifts ΔE_1 and ΔE_2 of surface components S_1 and S_2 as a function of substrate temperature. $\times$, regular measurements; $\triangle$, prolonged annealing at 300 °C and cooled to 20 °C; $\bigcirc$, prolonged annealing at 400 °C and cooled to 20 °C.

which may be due to the relative nearness of the photon energy to the photoemission threshold.[19] Values lower than the statistical value have been reported before for Ge (Refs. 10 and 20) and measurements we performed on Ge(001) showed a decided dependence of the branching ratio on the photon energy. This may partly explain the different values in use in the literature. For the spin-orbit splitting, values between 0.55 and 0.59 eV proved to give almost the same minimal sum of residues. The corresponding fits did not differ in the value for $\Delta E_{1,2}$ but gave slightly different values for $I_{1,2,3}$. This relative insensitivity of the criterion for goodness of fit to $\Delta_{s.o.}$ is due to the fact that the spin-orbit splitting is rather larger than the energy difference between bulk binding energy and binding energy of the main surface component S_1.

All the above values were used for analysis of measurements at higher temperatures. The spectrum of Fig. 1 was analyzed assuming a bulk contribution (B) and two surface contributions (S_1, S_2) at energies shifted with respect to the bulk component. The result of the analysis is shown in Fig. 1 and in Table I. In Table I the ratio between the surface emission and the total emission, given by $(I_{S_1}+I_{S_2})/(I_B+I_{S_1}+I_{S_2})$ is called I_S/I_{tot}; the ratio between the two surface components is called I_{S_2}/I_{S_1}. All numbers show that our description of the core level is essentially the same as given earlier.[9,10]

In the next step, experiments were performed at substrate temperatures of 200 °C (below the phase transition), 300 °C (above the phase transition), and 400 °C. The transition was monitored by RHEED. The line shapes were found to change only in a minor fashion. In order to see whether the changes might be due to temperature broadening alone, fits were performed for fixed values of $\Delta E_{1,2}$ (the values obtained for the experiment at 20 °C) at different values of the bulk binding energy (to allow for possible drifts in analyzer electronics) while letting W_L free. In these cases the minimal sums of residues were found to be considerably larger than those obtained for the measurements at 20 °C; the lowest value was obtained for the same bulk binding energy as at 20 °C. Further analysis was performed by fixing W_L at the value found at 20 °C and letting $\Delta E_{1,2}$ free. The best fits now again gave values for the sum of residues of the same magni-
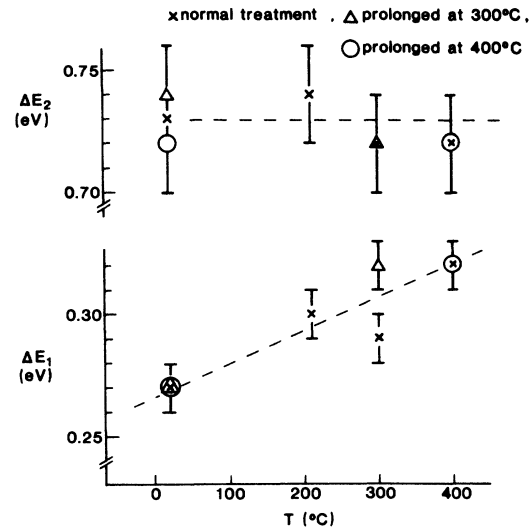
tude as found for fits of the measurements at 20 °C. The ensuing changes in the energy shifts $\Delta E_{1,2}$ as function of temperature are shown in Fig. 2 and Table II. The error bars in Fig. 2 reflect our estimate of the uncertainty in the determination of the energy shifts by the fitting procedure. The contribution S_1 moves continuously to lower binding energies with increasing temperature. At 400 °C, the change with respect to 20 °C is about 50 meV. The binding energy of S_2 remains constant within the accuracy of the experiment. The intensity ratios I_S/I_{tot} and I_{S_2}/I_{S_1} are collected in Table II. They appear to increase somewhat with increasing temperature. In order to make certain that the experiment probed a stationary situation, measurements were also performed after prolonged heating (about 10 h) at 300 °C and at 400 °C. After each of these measurements the sample was cooled to

TABLE II. Results of analysis of the Ge $3d$ core level measured at $h\nu=55$ eV at different temperatures giving energy shifts ΔE_1 and ΔE_2 for the surface components S_1 and S_2 and intensity ratios (see text).

T (°C)	ΔE_1 (eV)	ΔE_2 (eV)	I_S/I_{tot}	I_{S_2}/I_{S_1}
20	-0.27	-0.73	0.43	0.19
210	-0.30	-0.74	0.41	0.21
300	-0.29	-0.72	0.49	0.27
300[a]	-0.32	-0.72	0.44	0.17
400	-0.32	-0.72	0.48	0.23
400[a]	-0.32	-0.72	0.50	0.24
20[b]	-0.27	-0.72	0.42	0.19

[a]After prolonged annealing.
[b]Cooled down after annealing at 400 °C.

20 °C and the line shape was measured again. The sequence 400–20 °C is shown in Fig. 3 and actually gives the best demonstration of the changes in line shape found at higher temperatures. It should be noted that even after the long time taken by the experiment at 400 °C, the line shape at 20 °C is that of a clean surface. The line shapes normalized to the same total area and the difference between the lines are plotted in Fig. 3. At 400 °C there is a clear transfer of weight to lower binding energy which partly obscures the component S_2. The full analysis of the lines is given in Fig. 4 and shows that the weight transfer can be described by a shift of 50 meV of the binding energy of S_1 and some increase in the surface contributions relative to the bulk intensity.

IV. DISCUSSION

As the basis for our discussion of the above results we use the simple model of ordered adatoms for the $c(2\times8)$ reconstructed as shown in Fig. 5. This model is consistent with the results from electron diffraction[2,3] and STM measurements.[6] In the figure the adatoms are drawn in the so-called hollow position, centered above atoms in the fourth layer. With respect to the bonds with the first layer an equivalent site is the "on-top" position, centered above atoms in the second layer, and the same ordered structure can be drawn with "on-top" atoms. In fact, it is not yet clear which site is favored by the adatoms, although experiments on surfaces with a submonolayer coverage of elements such as Sn or Pb indicate a preference of the adsorbed atom for the on-top site. However, the actual configuration is not relevant to the discussion given below.

It can be seen in Fig. 5 that both for the adatoms and for the atoms in the first layer the binding geometry is different from the bulk binding geometry, which may lead to shifts in the core level binding energy. This is clear for
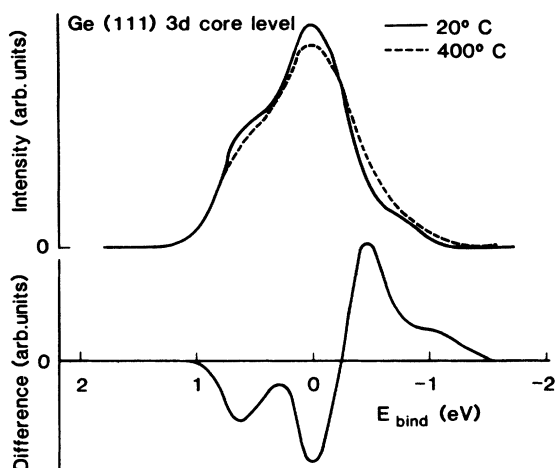
the adatoms, which have three bonds to atoms in the first layer and, in principle, one dangling bond. For the atoms in the first layer two different geometries occur. Per conventional unit cell twelve of the sixteen atoms are bound to the four adatoms. The binding geometry for these atoms differs from the bulk due to the angle of the bond
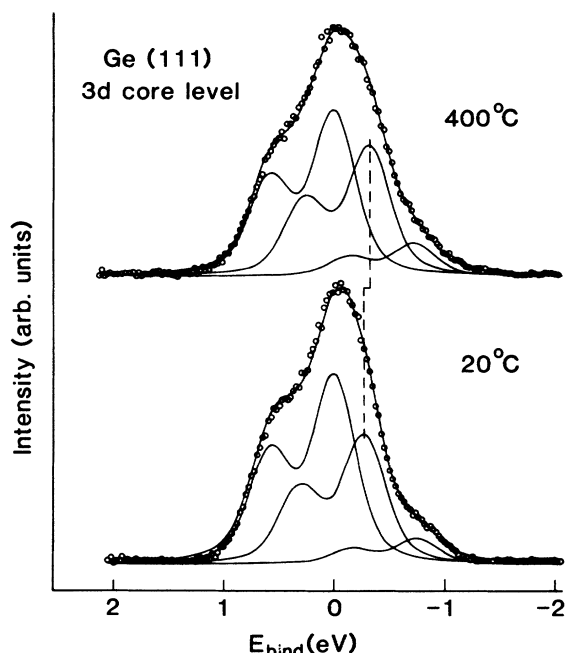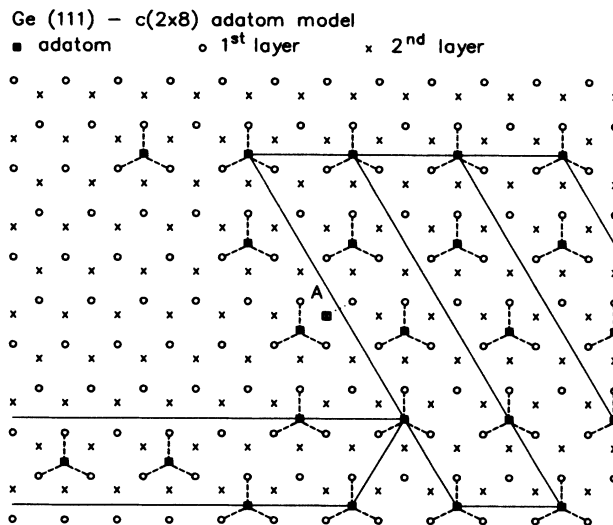

FIG. 4. Data and deconvolution of the Ge 3d core level after prolonged annealing at 400 °C and after cooling to 20 °C. The binding energy is relative to the bulk $3d_{5/2}$ line.

FIG. 3. (a) Ge 3d core level spectra at 20 °C (full line) and 400 °C (dashed line). The lines are smoothed through the data points. The intensities are scaled to equal total areas. The binding energy is relative to the bulk $3d_{5/2}$ line. (b) Difference plot of the core level at 20 °C and the core level at 400 °C.

FIG. 5. Model of the $c(2\times8)$ structure on the Ge(111) surface due to ordered adatoms. Solid lines show (parts of) conventional unit cells. Two differently oriented unit cells out of three equivalent possibilities are indicated. At point A the change in binding geometry of an adatom due to a jump from a hollow site to an on-top site is indicated.

with the adatom. The remaining four atoms, often called the rest atoms, again have a dangling bond. So, if no relaxation of second layer atoms is assumed, three separate surface contributions to the measured spectrum may be expected. As has been shown, two surface components can be analyzed conclusively, which means that two contributions have such a small energy difference that they are not resolved by the experiment. It would of course be possible to fit the spectrum with a total of four lines, adding two variables, but it is doubtful if a physical meaning could be attached to the resulting values. What still can be discussed is to which type of atoms the different shifts belong.

From the intensity ratio of S_1 and S_2 it is obvious that S_2 belongs to either the adatoms or the rest atoms so that S_1 comprises the remaining two types. From the comparison of surface band structure measurements on Ge(111) (Ref. 8) with surface band-structure measurements on Si(111) (Ref. 21) and with calculations on Si (111) (Ref. 22), it was inferred that a charge transfer takes place from the adatoms to the rest atoms. This is actually again in accordance with the STM measurements[6] since the adatom bumps on the surface were found by tunneling into empty states. The effect of such a charge transfer on the core level binding energy can be estimated by following Brennan et al.[23] in assuming that this is the same as the effect of core-electron charge transfer on valence-band electrons. This last transfer can be mimicked by adding protons to the nuclear charge; the binding energy changes are then reflected in changes in the sp^3 hybridization energy. Using the data of Harrison[24] for the series Ga (nuclear charge $Z-1$), Ge(Z), As($Z+1$), a value of 1.9 eV per transferred electron can be estimated.

On the basis of this argument a higher binding energy and a positive shift is expected for the adatom, and a smaller binding energy, resulting in a negative shift for the rest atom. The charge transfer argument therefore does not give a complete picture since no positive shifts are found. One further contribution to the energy shift is certainly a surface Madelung-type potential due to the same charge transfer. Unfortunately, without more data on the actual charge distribution it is not possible to estimate this effect. There is, however, a further argument for assigning the shift S_2 to the rest atoms and not to the adatoms. Core-level measurements performed by DiCenzo et al.[9] on Ge(111) covered with submonolayer amounts of Sn show that the intensity of compoment S_2 remains constant upon increasing Sn coverage, while the intensity of S_1 decreases by about 25%. Recent surface x-ray diffraction measurements by Pedersen et al.[25] on this system show that the Sn mainly occupies adatom positions (substituting Ge atoms) while the Ge rest atoms remaining present. Contrary to what is currently believed, we argue therefore that the large shift of S_2 is due to the rest atoms. The shift produced by the adatoms and the remaining first-layer atoms is contained in the contribution S_1.

Turning now to the temperature-dependence measurement it is straightforward to conclude that there is no appreciable rearrangement of atoms above the transition temperature: both the amount of adatoms and the amount of rest atoms remain roughly the same. The transition found in the electron diffraction experiments appears to be due to the onset of disorder in the adatom structure, but the adatoms do not move to widely differing binding positions. The simplest possibility to account for such disorder is that the adatom moves from the hollow to the on-top position (or vice versa, depending on the starting position). As is shown in Fig. 5 at point A, only one bond needs to be switched for such a jump, while a dangling bond is always free to build the new configuration. The small changes in intensity and energy shift witnessed for S_1 are then possibly due to small differences in binding energy for the adatoms at the two sites and to changes in the attenuation of the signal from atoms below the adatom layer. Disorder by the above mechanism does not lead to structures as proposed by Phaneuf and Webb[3] to exist just above the phase transition. On the other hand, any jump of an atom will leave behind different kinds of (2×2) entities, especially so since there are three different $c(2\times8)$ domains. The diffraction pattern of such a random set of (2×2) entities, which is not the same as a single (2×2) reconstruction with antiphase walls (see Ref. 3), may still approach the observations. As a final remark, note that if an adatom neighboring the one at point A also makes a jump, the adatom at A can jump to a new hollow position. In other words, the phase transition signifies the opening of possible paths for diffusion. It is therefore probably no coincidence that around 250 °C the growth of Ge by molecular beam epitaxy starts to take place in bilayer fashion, as shown recently by RHEED experiments.[5]

V. SUMMARY

We have performed Ge $3d$ core-level measurements on clean surfaces of Ge(111) between 20 °C, where the surface shows a $c(2\times8)$ reconstruction, and 400 °C, where the surface is apparent 1×1. Deconvolution of the measured lines into a bulk component and two surface components shows that the surface components do not change appreciably either in intensity or in binding energy shift. It is concluded that the phase transition from $c(2\times8)$ to apparent (1×1) is due to disorder occurring in an originally ordered adatom structure. Using a simple model for the reconstructed surface, a mechanism producing such disorder is discussed.

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