

## Combined $(1 \times 2) \rightarrow (1 \times 1)$ transition and atomic roughening of Ge(001) studied with surface x-ray diffraction

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(Received 14 May 1990; revised manuscript received 26 December 1990)

Surface x-ray-diffraction measurements are presented that show a reversible  $(1 \times 2) \rightarrow (1 \times 1)$  phase transition of the Ge(001) surface. The variation of the  $(1 \times 2)$  superlattice reflection intensity with temperature gives a transition temperature of  $T_c = 955 \pm 7$  K. The data are interpreted as being due to the creation of adatoms and vacancies on the surface with consequent break up of surface dimers. X-ray reflectivity indicates a corresponding loss of height-height correlation across the surface. A simple three-level model is used to describe the reflectivity, and the results are compared with a simple Monte Carlo simulation of the transition.

### INTRODUCTION

The (001) surface of Ge, like that of Si, is characterized by a strong short-range reconstruction, combined with a weaker long-range ordering. The termination of the bulk lattice leaves two dangling bonds per surface atom and it is generally accepted that these are partially satisfied by the formation of rows of buckled, asymmetric dimers.<sup>1,2</sup> A previous low-energy electron diffraction (LEED) and photoemission study<sup>3</sup> has indicated that the Ge(001) surface undergoes a  $c(4 \times 2) \rightarrow (2 \times 1)$  transition at  $T \approx 220$  K, corresponding to a flipping of the dimer buckling. We present here surface x-ray diffraction measurements which show that the Ge(001) surface undergoes a further, reversible,  $(2 \times 1) \rightarrow (1 \times 1)$  transition at  $T_c = 955 \pm 7$  K. We propose that this transition is due to the vertical movement of surface atoms with the creation of adatoms and vacancies, and the accompanying deconstruction of the surface.

Predictions of surface roughening transitions have been known for many years<sup>4</sup> and in recent years several experimental studies have been reported for metallic surfaces.<sup>5,6</sup> The nonreconstructed (001) surface of a diamond-type lattice should be unstable against roughening since this

would involve no change in the total number of dangling bonds. The stability of Ge(001) and Si(001) surfaces can be attributed to the reconstruction in dimers which generates an energy penalty against vertical movement of atoms. The transition described here involves the breaking of dimer bonds which correspondingly undermines the stability of the surface.

### EXPERIMENT

The measurements were made on the wiggler beamline of the Synchrotron Radiation Source at Daresbury laboratory using unfocused radiation of wavelength 1.13 Å. The sample,  $8 \times 10 \times 2$  mm,<sup>3</sup> was mounted in a UHV environmental chamber<sup>7</sup> coupled to a five-circle surface x-ray diffractometer 40 m from the tangent point. The incident beam was defined by slits to be 3 mm (vertical)  $\times$  0.3 mm (horizontal). Scans across the fractional order rods were made by rotating the sample about the surface normal, i.e., by rotating the  $\phi$  axis of the diffractometer. The scattered radiation was collected by a Ge solid-state detector mounted after a set of slits which defined the angular resolution to be  $\pm 0.17^\circ$  in plane (vertical) and  $\pm 0.21^\circ$  out of plane. The vertical slit settings were chosen to accept all of the diffracted intensity in one

reflection. The integrated intensity is then the peak area in a  $\phi$  scan.

The sample was cleaned by heating for 15 min to 750 K, then sputtered with 800-eV  $\text{Ar}^+$  ions at  $1 \mu\text{A}$  for 10 min and finally annealed for 15 min at 980 K followed by a slow cooling of  $< 1 \text{ K sec}^{-1}$ . This procedure was repeated until the width of the  $(1.5, 0)$  and  $(0, 1.5)$  reflections stabilized at a minimum value. A further reduction in the half widths was achieved after one monolayer of Ge was deposited from a Knudsen cell and one cycle of the cleaning procedure repeated. Inspection of the final surface with reflection high-energy electron diffraction (RHEED) showed a sharp pattern with both  $(1 \times 2)$  and  $(2 \times 1)$  superlattice reflections. The angular width of the  $(0, 1.5)$  x-ray diffraction reflection corresponded to a correlation length of 1600 Å and the width of the  $(1.5, 0)$  reflection to a 1200 Å correlation length. The integrated intensities of these reflections indicated equal areas of each domain to within 4%. Sample temperatures between RT and 1050 K were obtained by radiative heating and electron bombardment from a tungsten filament and were measured with an optical pyrometer which was calibrated with a chromel-alumel thermocouple to an accuracy of  $\pm 7 \text{ K}$ .

The sample surface normal was aligned with a laser beam to an accuracy of  $\pm 0.01^\circ$  after which the crystallographic axes were oriented by determining the position of three in-plane and one out-of-plane x-ray reflections. The sample miscut was thus found to be  $0.044^\circ$  along the  $[110]$  bulk azimuth. At each subsequent measurement temperature, the laser alignment was repeated to correct for small movements of the sample mount. The scattered radiation can be assigned to a point  $(hkl)$  in reciprocal space. We employ a tetragonal surface unit cell which is related in reciprocal space to the conventional cubic unit cell of the bulk lattice by  $(100)_{\text{tet}} = \frac{1}{2}(2\bar{2}0)_{\text{cub}}$ ,  $(010)_{\text{tet}} = \frac{1}{2}(220)_{\text{cub}}$ , and  $(001)_{\text{tet}} = (004)_{\text{cub}}$ .

## RESULTS AND DISCUSSION

Figure 1 shows a representative set of transverse  $\phi$  scans, parallel to the  $h$  axis, through the  $(0, 1.5)$  fractional order rod at a perpendicular momentum transfer of  $l=0.03$ . The scans were obtained with the incident and exit grazing angles set at  $0.68^\circ$  which is more than a factor of 2 greater than the critical angle for total external reflection for Ge:  $0.24^\circ$  at wavelength  $1.13 \text{ \AA}$ . For each temperature the position of the detector arm corresponding to the (vertical) in-plane scattering angle was corrected to allow for changes in the lattice constant. Thermal expansion of the Ge lattice is responsible for the shift in the center of each peak in Fig. 1. The sample was allowed  $\sim 25$  min at each temperature to reach equilibrium before measurements were made, and checks were made to ensure that the data collected were not time dependent.

The fractional order reflection is due to the dimer-row surface reconstruction. It is evident from the figure that the peak height drops rapidly over a narrow temperature range, and above 980 K the reflection cannot be separated from the background. The same behavior was ob-

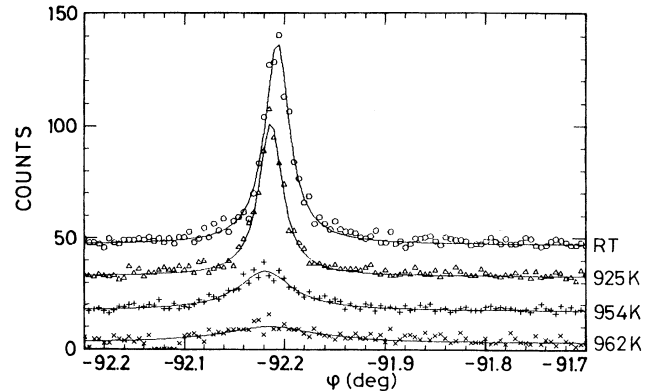


FIG. 1. Transverse  $\phi$  scans of the  $(0, 1.5, 0.03)$  superlattice reflection at various sample temperatures between room temperature and 962 K. The small shift in the center of the peak is due to expansion of the Ge lattice.

served for the  $(1.5, 0, 0.03)$  reflection due to the orthogonal domain. The RHEED pattern obtained *in situ* confirmed that above this temperature only a  $(1 \times 1)$  symmetry corresponding to the unreconstructed bulk remained. This is consistent with earlier RHEED measurements of Kajima *et al.*<sup>8</sup> who observed a  $(2 \times 1)$  to  $(1 \times 1)$  transition above 900 K.

The line shapes in Fig. 1 were fitted with Lorentzian profiles:

$$I = \frac{A}{1 + q_T^2 L^2} + B, \quad (1)$$

where  $q_T$  is the deviation in momentum transfer from the half-order peak in the transverse direction, that is, along the  $h$  axis, and  $L$  is the associated correlation length.  $B$  is the background level which was found to be constant at all temperatures and  $A$  is a constant fitting parameter. From the fits, the integrated intensity  $I_{\text{int}}$ , given by

$$I_{\text{int}} = \int_{-\infty}^{\infty} (I - B) dq_T, \quad (2)$$

and the correlation length were determined. They are shown as a function of temperature in Figs. 2(a) and 2(b). The data points indicate whether they were obtained during the heating or cooling part of the temperature cycle. The care to achieve stability and the absence of hysteresis confirm that each point corresponds to an equilibrium state of the system.

The change in integrated intensity  $I_{\text{int}}$  implies that the Ge(001) surface undergoes a structural phase transition in which the fraction of the surface area which is coherently reconstructed in dimer rows rapidly falls with temperature. It is well described by the function

$$I_{\text{int}} = I_0 e^{-2MT} (1 - T/T_c)^{2\beta} \quad (3)$$

which applies to a continuous transition with critical temperature  $T_c$ .<sup>9</sup> The curve in Fig. 2(a) is the best fit corresponding to  $\beta = 0.94 \pm 0.05$ ,  $T_c = 955 \pm 7 \text{ K}$ , and  $M = (2.1 \pm 0.1) \times 10^{-4} \text{ K}^{-1}$ . The Debye-Waller param-

ter  $M$  yields<sup>10</sup> a rms atomic displacement at 300 K of  $\langle u^2 \rangle^{1/2} = 0.15 \pm 0.05$  Å. This compares with the value for bulk Ge of 0.07 Å.

The nature of this transition is further revealed by the variation of the angular half width at half maximum (HWHM) and the associated correlation length  $L$ . The HWHM remains constant at a value which corresponds to  $L = 1600$  Å for all temperatures up to and during the sharp fall of the integrated intensity. It only rises significantly when the integrated intensity has dropped to 10% of its value at RT. The Lorentzian profile of the scans indicates an exponential distribution of domain sizes the average dimension of which is smaller than the average terrace width implied by the miscut. For the more stable double steps<sup>11</sup> this would have been 3800 Å in the  $k$  direction and much greater in the  $h$  direction. The instrumental resolution as defined by the coherence

length of the incident beam is 9000 Å and therefore not important.

The constancy of  $L$  during the initial sharp fall means that the loss of  $(2 \times 1)$  reconstructed units occurs in small isolated regions, rather than by the domains shrinking in size. Small defects distribute weak diffuse scattering over a wide region of reciprocal space; measurements far away from a strong reflection could not detect the small increase in the background level. Only after a large number of dimers has been removed, close to the end of the phase transition, does the reconstruction not form a connected network over the surface. Nonpercolating domains remain, the reduced size of which is revealed as an increased width of the fractional-order reflections.

Specular x-ray reflectivity is sensitive to the average roughness of the surface and is frequently used to monitor surface morphology.<sup>12</sup> Figure 2(c) shows the variation of the reflected intensity as a function of temperature. The measurements were made with an incident angle of  $6^\circ$  which is equivalent to  $l = 0.26$ . It was the highest angle which still gave a significant reflected signal above the background of  $0.1 \text{ sec}^{-1}$ . The incident angle is about half the anti-Bragg angle for destructive interference between adjacent planes.

The plots in Fig. 2 show a close correspondence between the specular intensity and the integrated intensity for the  $(0,1.5,0.03)$  reflection. A sharp fall in the specular intensity can be seen above 900 K suggesting that the phase transition is accompanied by movement of the surface atoms normal to the interface. At high temperatures the specular intensity saturates to a background. The curve was reversible if the maximum temperature was kept below 1020 K. If the sample was taken above this temperature, significantly increased roughening, as indicated by a rapid drop in reflected signal with grazing angle was observed. It did not disappear with a lowering of the temperature; only by repeating the initial cleaning cycle could the surface be recovered. A series of reflectivity curves taken as a function of grazing angle for different sample temperatures is shown in Fig. 3. The solid lines

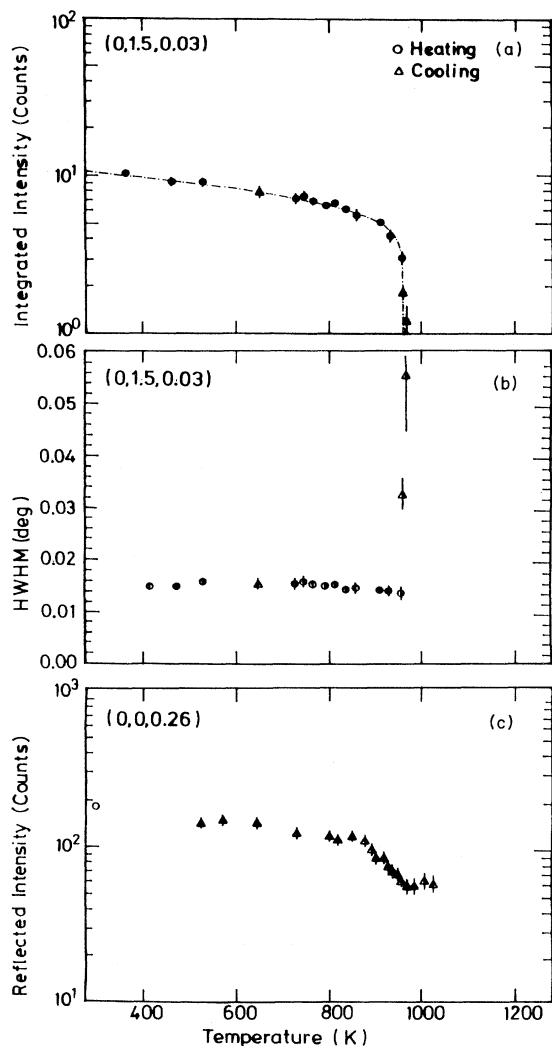


FIG. 2. (a)  $(0,1.5,0.03)$  integrated intensity, (b)  $(0,1.5,0.03)$  HWHM and (c) x-ray reflectivity at  $l = 0.26$ , plotted as a function of sample temperature.

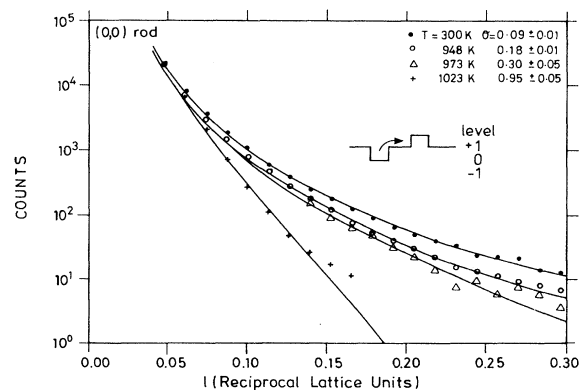


FIG. 3. X-ray reflectivity scans at various sample temperatures between room temperature and 1023 K. The solid lines are fits using the three-level model described in the text. The inset is a schematic diagram showing the three levels resulting from adatom-vacancy creation.

are fits discussed below.

Several modes of disordering can be considered to explain the fall in signal at  $T_c$ . Surface melting has been observed in metals.<sup>13</sup> McRae and Malic<sup>14</sup> observed a new phase transition of Ge(111) at  $T=1058$  K using LEED and discussed the results in terms of a disordering of the outermost Ge double layer. Further LEED results<sup>15</sup> and molecular dynamics simulations<sup>16</sup> have since been used to propose that the transition is due to lateral strain of domains to a depth of one atomic layer, with disordering as a loss of registry between these domains and the substrate.

An obvious explanation for the present phase transition would be the proliferation of steps across the surface and the consequent loss of height-height correlation. This would be consistent with the fall in reflectivity measured at  $T_c$  and, since the correlation between reconstructed terraces is lost across a step,<sup>17</sup> would cause an increase in the HWHM of the fractional order peaks. Robinson *et al.*<sup>5</sup> observed an order-disorder transition on W(001). In that case the integrated intensity remained constant and only the peak height decreased in magnitude. The fractional order HWHM changed continuously across the transition indicative of a reduction in domain size caused by the creation of steps or domain wall movement. Such behavior is fundamentally different from that observed here where the integrated intensity is not constant and, significantly, the HWHM increases only near the end of the transition. Thermal desorption of Ge atoms from the surface could be used to describe the change in integrated intensity with constant HWHM and then surface diffusion may be used as a method of restoring the surface to its original state to provide reversibility. However, at the temperatures described here, thermal desorption of Ge is negligible and so cannot be used as a model for the observed transition.

Simple bond breaking at random positions would explain the reduction in the integrated intensity but should not measurably change the vertical height distribution, albeit that the dimer atoms are buckled. Moreover, bond breaking on its own would require a much larger energy expenditure than is available at the temperatures used. There are no reliable estimates of the dimer break-up energy for Ge(001), but for Si typical values are estimated to be between 1 and 2 eV.<sup>18,19</sup> It is therefore concluded that the transition process involves an assisted break-up of dimers together with some vertical atomic movement.

In an attempt to justify this picture we have used a simple model within the limits of kinematic theory. The two-level model of Vlieg *et al.*<sup>20</sup> is extended to three levels (see inset in Fig. 3). It is assumed that the initial surface is flat (level 0) and that no steps occur during the transition. When an adatom is created atoms at a lower level (level -1) are exposed and the adatom is placed at a higher level (level +1). In the absence of vaporization and with low surface mobility the total number of atoms are conserved and we may equate total coverages:

$$\Theta_{\text{adatom}} = \Theta_{\text{vacancy}} = \Theta, \quad (4)$$

where  $\Theta$  is the adatom density. The reflected intensity is thus given by

TABLE I. Values of  $\Theta$  obtained from the fits to specular reflectivity scans using Eq. (5).

Temperature (K)	$\Theta$
300	$0.09 \pm 0.01$
868	$0.08 \pm 0.01$
948	$0.18 \pm 0.01$
973	$0.30 \pm 0.05$
983	$0.37 \pm 0.05$
987	$0.38 \pm 0.05$
1023	$0.95 \pm 0.05$

$$I_{(001)} = C \{ 1 - 2\Theta [ 2 - 3\Theta + 2(2\Theta - 1) \cos 2\pi l - \Theta \cos 4\pi l ] \}. \quad (5)$$

$C$  contains the product  $|F_{001}|^2 |F_{\text{CTR}}|^2$  which is the scattering intensity from a single column of single unit cells and is a function of the momentum transfer.  $F_{001}$  is the structure factor evaluated along the (00) rod and  $F_{\text{CTR}}$  is the crystal truncation rod.<sup>21</sup> The solid lines in Fig. 3 are fitted using Eq. (4), giving the  $\Theta$  values listed in Table I (not all temperatures are included in the figure).

For  $\Theta \geq 0.5$  the result becomes unphysical as there are no atoms left in the original level. The values of  $\Theta$  obtained from the fits show that it remains constant until 868 K, at which point it rises rapidly to  $\sim 0.37$  and then levels at that value. The fit at 1023 K gives a value of  $\Theta$  that is too big to be described by the three-level model, but it was found that after heating the sample to this temperature the surface was irreversibly roughened and the initial cleaning procedure was repeated to restore the surface to its original state. Therefore, between 987 and 1023 K the surface undergoes further roughening, possibly step proliferation, such that the large  $(1 \times 2)$  and  $(2 \times 1)$  domains cannot be restored on cooling.

The process was simulated with a simple Monte Carlo calculation for an array of  $25 \times 25$  columns of Ge atoms in the diamond structure, starting with a flat surface fully reconstructed in dimer rows. It was assumed that when an adatom sits on top of an existing dimer it breaks this dimer. The energy involved in creating an adatom-vacancy or addimer-vacancy pair was taken as proportional to the change  $N$  in the total number of dimer bonds. Adatom-vacancy creation and annihilation events as well as lateral movements of atoms in all layers were accepted or rejected using the Boltzmann factor  $\exp(-NE_d/k_B T)$ , where  $E_d$  is the energy required to break a single dimer bond and  $k_B$  is Boltzmann's constant. The simulation allowed for dimer creation, in all layers, between neighboring atoms which did not support atoms in higher layers. The additional energy reduction involved in the formation of rows of dimers and rebonding of atoms near defects such as steps, adatoms, and vacancies were not included. In order to calculate the half-order intensity  $I_{\text{int}}$  we counted the average fraction  $D$  of dimer bonds remaining intact at the original surface level, from which we obtained  $I_{\text{int}}/I_0 = D^2$ . The specularly reflected intensity was calculated from the average occupation numbers of all layers using an expression similar

to Eq. (5), but including more than three levels.

The result of the simulation shows that the surface remains stable up to a reduced temperature of  $k_B T/E_d \approx 0.22$ , above which the occupation of the adatom layer and the number of vacancies rises rapidly. Above  $k_B T/E_d \approx 0.25$  the disordering proceeds at a reduced pace. At  $k_B T/E_d = 0.25$  the adatom density  $\Theta$  amounts to  $\sim 20\%$ , the half-order intensity has then been reduced to  $\sim 25\%$ , and the reflectivity at  $l=0.26$  is  $\sim 33\%$  of that for a flat surface. The sharpness of the transition as well as the simulated reductions in diffraction and reflection intensities correspond well with the experimental observations in Fig. 2. From the simulated and experimental transition temperatures we estimate the dimer energy for dimer break-up to be  $E_d = k_B(955\text{K})/0.25 = 0.33$  eV. This compares with the values of 1–2 eV calculated for the dimer-bond energy of Si(001). The low value of  $E_d$  found here may be the effect of the rebonding of atoms which takes place at the surface around defects and which reduces the effective energy involved in the defect creation. We recognize that this is a highly simplified description of the Ge(001) surface; nevertheless we believe the basic model describes the essentials of the real process. This view is supported by a recent, more detailed Monte Carlo simulation of a larger array of Ge columns.<sup>22</sup> It demonstrates that the surface disordering process responsible for the roughening and the behavior of the scattered x-ray intensity is essentially the same as described here.

Since the low-temperature stability of the Ge(001) surface is due to the partial satisfying of dangling bonds by the reconstruction in dimers, it is not surprising that the roughening and the disappearance of the reconstruction go together. This is the starting point of the Monte Carlo calculation. As the surface becomes increasingly more

disordered the average number of dimers destroyed per newly formed adatom-vacancy pair falls. The defects form nuclei for further disordering, since locally the energy penalty for disordering is lowered. Thus the transition accelerates as a function of temperature and the fractional order intensity drops precipitously. In this way it differs from the common roughening transition involving step creation which is of infinite order (within the context of the solid-on-solid model).<sup>23</sup>

It is interesting to compare these results with procedures used to create well-ordered Ge(001) surfaces. Our own experience was that annealing at 980 K (just above  $T_c$ ) for 15 min produced the flattest surfaces at room temperature, whereas Grey *et al.*<sup>24</sup> needed to anneal at 873 K (far below  $T_c$ ) for 2 h in order to produce a good surface. It would appear that the optimum cleaning procedure is an ion bombardment followed by a short anneal just above  $T_c$  and then a slow cool through the transition.

In summary, it has been shown that the Ge(001) surface undergoes a reversible phase transition at  $T = 955 \pm 7$  K, and that the results are consistent with a combined roughening and deconstruction. The surface becomes further roughened between 987 and 1023 K, at which point it is impossible to cool the sample to its original condition, this roughening being attributed to the formation of steps.

#### ACKNOWLEDGMENTS

We would like to thank Dr. G. Baker and staff at Daresbury Laboratory for their assistance during these measurements. A.D.J. gratefully acknowledges financial support from SERC.

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