Surface Diffusion and Phase Transition on the Ge(111) Surface Studied by Scanning Tunneling Microscopy

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(Received 20 March 1991)

The formation of disordered regions is observed on the Ge(111)$c2\times8$ surface, at temperatures in the range 150–350 °C. The disorder occurs by the diffusion of surface adatoms in the $\langle 01\bar{1}\rangle$ directions. The disordered regions form at domain boundaries, and grow continuously with temperature until the entire surface becomes disordered at 300 °C. We argue that this phase transition is an example of premelting in two dimensions, i.e., "edge melting."

PACS numbers: 61.16.Di, 68.35.Rh

At room temperature, the lowest-energy structure of the (111) surface of germanium is a centered 2×8 reconstruction, consisting of Ge adatoms bonded on top of a bulk-terminated (111) bilayer.[1-3] At a temperature near 300 °C, the surface is known to undergo a reversible phase transition in which the $c2\times8$ structure disorders, forming a structure characterized by an apparent 1×1 diffraction pattern with weak half-order spots. This transition has been studied by a number of techniques,[3-7] with the definitive work arguably being the low-energy electron diffraction (LEED) study of Phaneuf and Webb.[3] Above the transition temperature, they find that the weak half-order spots split and broaden, indicating that the disordered phase is actually incommensurate with the underlying lattice. They also argue that the transition is first order, based on an observed hysteresis in the LEED spot intensity between warming and cooling scans. These conclusions were supported by subsequent Monte Carlo simulations.[8]

In this work, we use the scanning tunneling microscope (STM) to directly observe the 300 °C phase transition of the Ge(111) surface. Since few high-temperature STM measurements have previously been reported,[9-11] it is necessary for us to establish the conditions under which atomic motion can be identified from STM images. To this end, we first study the surface at temperatures of 150–220 °C, where the motion of individual surface adatoms and rows of adatoms can be clearly seen. As the temperature is increased, this activity accelerates, and the rapidly moving atoms form disordered regions on the surface. These disordered regions are found to form at surface domain boundaries or steps. The regions grow continuously in size as the temperature is increased, and above 300 °C the entire surface is disordered. As discussed below, this type of behavior is precisely what is expected for a two-dimensional phase transition which is first order for an infinite-size domain, but is continuous near domain boundaries due to the occurrence of premelting at the boundaries.[12,13]

This work was performed on a newly built STM, incorporating a tube scanner and inchworm[14] approach, with a symmetrical design to minimize thermal drifts. Germanium samples, p-type with resistivity of 0.1 Ω cm, were prepared by cleaving and then annealing at a temperature of about 400 °C. Cooling at a rate of 2 °C/min following the anneal resulted in $c2\times8$ domain sizes of about 2000 Å. Samples were heated by direct-current heating. Imaging could be started several hours after heating up the samples, with residual thermal drifts of <1 Å/s being reduced to <0.1 Å/s by electronic compensation.[11] Temperature was measured with a thermocouple pressed against the cleaved surface, with an absolute accuracy of ±10 °C and relative accuracy of ±2 °C. With the samples hot, the base pressure of the vacuum system was 2×10^{-10} Torr. STM images were acquired at constant tunnel currents in the range 0.1–1 nA, and at positive sample biases in the range 1.5–2.5 V. Typical scanning speed was 1000 Å/s. STM topographic and spectroscopic characterization of our samples at room temperature has previously been reported,[15] and is in good agreement with the results of Becker *et al.* for this surface.[1,2] In the observations reported below, we focus our attention on surface domain boundaries, although similar results have been obtained in the vicinity of surface steps.

In Fig. 1 we display an STM image of the Ge(111) surface, obtained at a temperature of 215 °C. A large ordered region of $c2\times8$ reconstruction can be seen on the right-hand side of the image, separated by a domain boundary from a domain appearing on the left-hand side of the image which is rotated 120° counterclockwise relative to the first. The stacking arrangement of the adatoms which form the $c2\times8$ structure is directly seen in the STM images.[2] In the middle of the domain boundary of Fig. 1, there is a small triangular-shaped "hole," one bilayer (3.27 Å) deep; such holes are occasionally observed on the surface. Above the small hole, the STM image of the domain boundary is somewhat indistinct, with some atomic rows appearing to be fuzzy or glitchy. These features in the image arise from the hopping motion of the atoms during the imaging process, as shown below. One final feature of Fig. 1 which is actually atypical, but nonetheless interesting, can be seen at the part of the surface domain boundary occurring in the

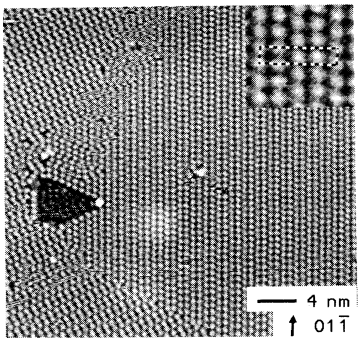

FIG. 1. STM image of the Ge(111)$c2\times8$ surface, obtained at 215 °C. Inset: The surface on a 3× expanded lateral scale, with the dashed lines showing a rectangular 2×8 unit cell. The Ge adatoms have 2× periodicity along the rows running in the [01$\bar{1}$] direction. These rows of adatoms form an 8× stacking arrangement in the [2$\bar{1}\bar{1}$] direction.

lower portion of the image. There, the boundary forms an ordered superstructure, and all atoms can be clearly resolved in the structure, indicating that no atomic motion occurs near this part of the boundary. The absence of vacancies at this ordered boundary (as in the center of a $c2\times8$ domain) apparently suppresses the atomic motion.

Our observations of atomic motion near domain boundaries are shown more clearly in Fig. 2. There we show three images of a domain boundary, obtained consecutively with 85 s used to acquire each image. The domain boundary extends through the center of each image, and the fuzzy or glitchy appearance of atomic features near the boundary is apparent. In Fig. 2(c), the left-hand-side domain extends relatively far into the domain boundary, whereas in 2(b) the boundary is more disordered, and in 2(a) it looks different again. Also, the small black vacancies which appear just to the right of the domain boundary change their location from one image to the next. We have studied such atomic motion in detail, for temperatures in the range 150–220 °C. We find that the adatoms always hop along any of the three equivalent ⟨01$\bar{1}$⟩ surface directions. The 2× spacing between adatoms in a [01$\bar{1}$] row is generally maintained, but the 8× stacking arrangement of the adatom rows is completely broken. The motion is thermally activated, and above about 220 °C we cannot clearly distinguish the individual adatoms on the time scale (10–100 ms) of our measurement.

As the temperature is increased, the disordered regions formed near domain boundaries grow in size, as illustrated in Figs. 3 and 4. Figure 3, obtained at 235 °C, shows a boundary between domains which are rotationally equivalent, but translationally inequivalent. Considerable disorder is visible near the domain boundary, with a few small ordered areas appearing near surface defects. The disordered bands we observe at domain boundaries are in equilibrium with the ordered domains; the average

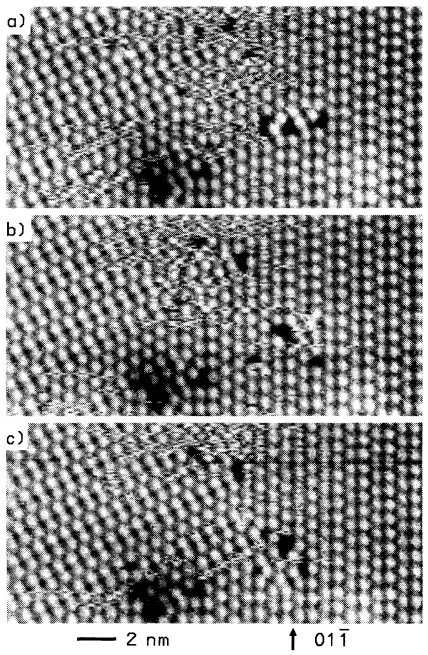

FIG. 2. STM images of the Ge(111)$c2\times8$ surface, obtained at 215 °C. Three consecutive images are shown, separated in time by 85 s each. A domain boundary extends through the center of each image, and motion of the atoms near the boundary is evident.

width of a band is constant over many hours, although fluctuations do occur in the precise shape of a disordered band. Figure 4 shows an image obtained at 280 °C [note that the lateral scale of Fig. 4(a) is twice that of Figs. 1 and 3]. Two ordered domains are visible in Fig. 4(a), one in the lower right-hand corner and the other in the upper left-hand corner. A few small regions of local order can be seen near defects, and the remainder of the image consists of disordered areas formed by the rapidly moving adatoms. Above 300 °C the entire surface becomes disordered, except for small ordered regions appearing near surface defects. A complete set of STM images at all relevant temperatures will be presented elsewhere.

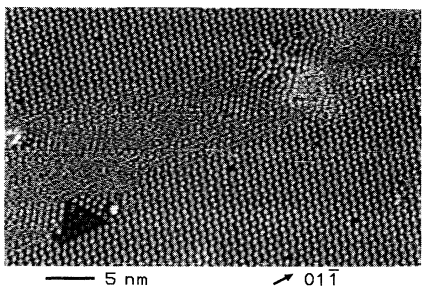

FIG. 3. STM image of the Ge(111)$c2\times8$ surface, obtained at 235 °C. A band of disordered surface area, located at a domain boundary, extends through the center of the image.

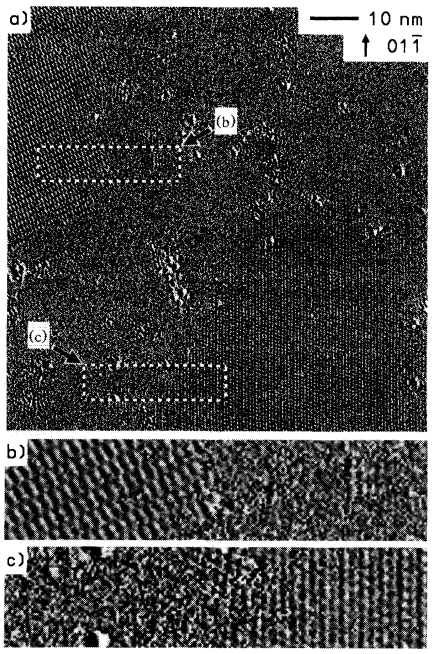

FIG. 4. STM image of the Ge(111)$c2\times8$ surface, obtained at 280 °C. Two ordered domains are present in (a), located in the lower right-hand corner and the upper left-hand corner of the image. The remainder of the surface is disordered. Expanded views of the regions indicated by dashed lines are shown in (b) and (c).

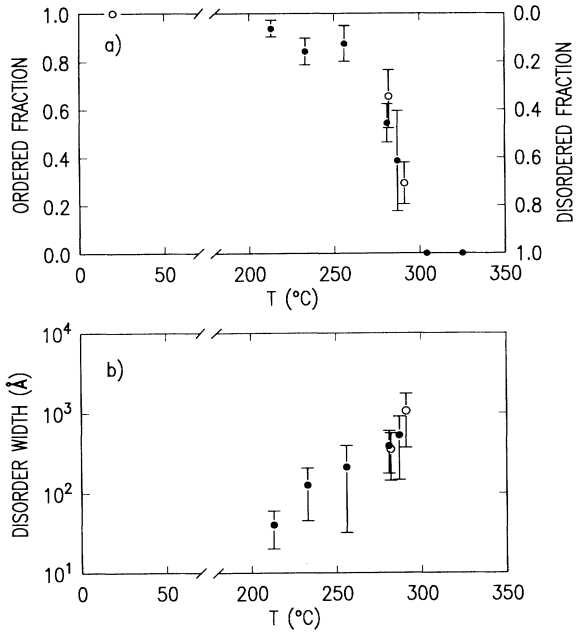

FIG. 5. Temperature dependence of (a) the fraction of the surface with $c2\times8$ order, and (b) the width of the disordered regions. Data acquired with temperature increasing are shown by solid circles, and data acquired with temperature decreasing by open circles. Note the break in the temperature scale between 50 and 200 °C.

Our results for the temperature dependence of the surface order are presented in Fig. 5. In Fig. 5(a), we show the fraction f of surface area which has $c2\times8$ periodicity ($1-f$ is the disordered fraction), as a function of temperature. These data were compiled from an analysis of images the same size as Fig. 4(a), with 5–10 images used at each temperature. We find a transition temperature, where the entire surface is disordered, of 295 $\pm$ 10 °C. Good reversibility of the phase transition is observed, as evidenced by the 20 °C data point on the cooling scan, indicating that residual contamination of the sample during the experiment is not significant. In Fig. 5(b), we plot the width of the disordered regions, as measured directly from the STM images. We find that the apparent width as seen in an image is insensitive to the scanning speed for the image; varying the speed by an order of magnitude has a negligible effect on the images above 220 °C. Essentially, the atoms inside the disordered region are moving rapidly and those outside this region are stationary, and the transition region is relatively narrow in size. At a given temperature, considerable variation over the surface is observed in the width of the disordered regions, as shown by the error bounds ($\pm$ 1 standard deviation) in Fig. 5(b). The uncertainty ranges apparent in Fig. 5 preclude obtaining theoretically predicted critical exponents from fits to the data.[12]

In summary, we observe the coexistence of disordered and ordered regions on the surface at temperatures well below the transition temperature, and we find that these disordered regions grow continuously in size with temperature. We emphasize at this point that the Ge adatom concentration near the domain boundaries is definitely *not* fixed; we observe that the adatoms can move both in and out of the surface plane at temperatures as low as 200 °C.[16] Thus, the existence of the disordered regions does not arise simply from a deficit in the adatom concentration near a domain boundary. The observed presence of the disordered regions at temperatures below the transition temperature is clearly inconsistent with a conventional first-order phase transition. However, if we include the possibility of premelting at the domain boundaries, we then have a scenario which is consistent with the experiment. We cannot strongly exclude the possibility that the phase transition is continuous even in the absence of domain boundaries, but we have never observed the spontaneous formation of a disordered region at any spatial location other than a domain boundary. Thus the identification in terms of a first-order transition (for an infinite domain) which includes premelting at the domain boundaries is the most consistent with experiment. Such an interpretation is also consistent with the LEED observations[3] and Monte Carlo simulations[8] which indicate first-order behavior, and, furthermore, with the mean-field theoretical expec-

tation that this transition must be first order due to the symmetry of the $c2\times8$ unit cell.[17]

Although a number of previous experimental studies have observed an apparent broad temperature range for the Ge(111)$c2\times8\rightarrow1\times1$ phase transition,[3,5-7] the only explanation offered for this range was that of surface strain.[7] To our knowledge, the only previous observation of premelting in two dimensions in any system was for argon films on graphite, at 14 K.[13] In three dimensions, the occurrence of surface melting has been observed on several systems,[18,19] including the Ge(111) surface at 1050 K.[20] A formalism exists for describing premelting for any dimension, both for a single interface, and, as in the case of our experiment, in the presence of many fluctuating interfaces.[12,21] The present observations, on a much different system from those previously considered, would seem to offer new possibilities for understanding the premelting phenomenon.

We gratefully acknowledge discussions with P. A. Bennett and G. Grinstein.

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[16]Adatom motion both in and out of the surface plane clearly occurs during heating of cleaved samples, for which the 2×1 reconstruction converts into the $c2\times8$ structure at temperatures below 200 °C (see, e.g., Ref. 7).

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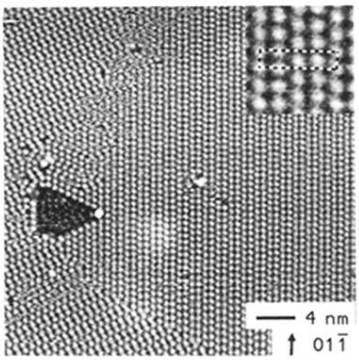
[21]Presumably the ground state of the surface is a single $c2\times8$ domain. Experimentally, however, multiple domains with different orientations are always observed. The transition temperature (the point at which the broadening, disordered domain walls meet) should depend on the distance between these walls in the ordered phase. That is, a surface which at low temperatures consists of many small domains will be completely disordered at a lower temperature than one consisting of fewer, larger domains. The large spatial extent of our domains, taken together with the steep slope of the transition (Fig. 5) strongly suggests that our data closely approximate the thermodynamic, semi-infinite domain-size limit.



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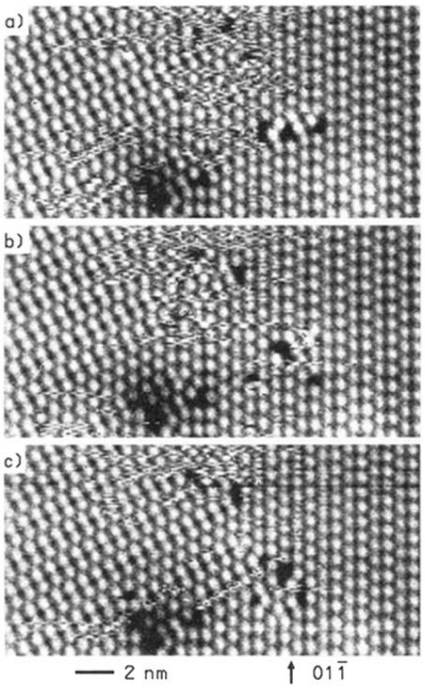

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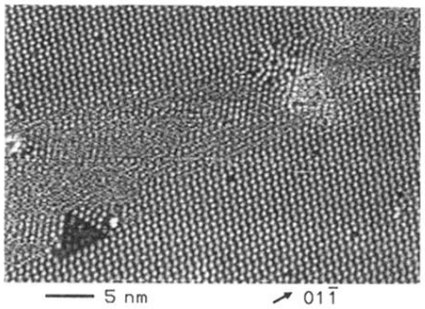

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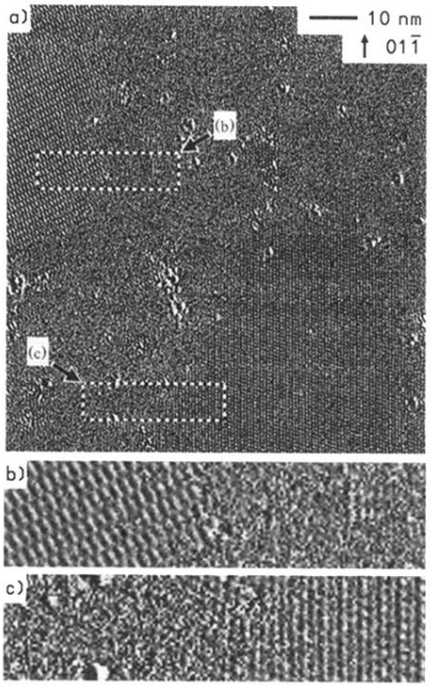

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