Phase Transition of Monolayer Pb/Ge(111): \( \beta-\sqrt{3} \times \sqrt{3} R30^\circ \#1\times1 \) at \#180 °C

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Phase transition of monolayer Pb/Ge(111): $\sqrt{3}\times\sqrt{3}R30^\circ\leftrightarrow1\times1$ at $\sim180^\circ$C

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(Received 26 January 1994; revised manuscript received 15 April 1994)

We study a reversible phase transition of 1 monolayer (ML) of Pb on a Ge(111) surface using a scanning tunneling microscope (STM) over a temperature range from below to above the transition ($\sim175^\circ$C). Below the transition temperature, a periodic array of Pb trimers centered on H$_3$ sites is resolved. The controversial high-temperature phase is actually a simple Pb-terminated 1$\times$1 structure. Just above the transition temperature, we observe a strongly fluctuating structure. Between $\frac{1}{2}$ and 1 ML of Pb coverage, the transition is found to start in the vicinity of the phase boundary with a $\frac{1}{2}$-ML $\sqrt{3}$ phase. At 1 ML we also observe the transition beginning at the step edges on the upper terraces. A sharp increase in the transition temperature occurs near 1 ML. The transition temperature is also found to depend on the domain size. The role of surface-strain fields on the phase transformation is discussed.

I. INTRODUCTION

The study of phase transitions has been an important subject in modern condensed-matter physics. Symmetry and dimensionality play a crucial role, with two-dimensional (2D) phase transitions expected to be more strongly influenced by fluctuations than those in three dimensions. Traditionally, experimental studies of surface phase transitions using diffraction measurements have provided important information for the understanding of 2D phase transitions. However, diffraction studies are affected by interference from the bulk crystal and are not sensitive to the role of inhomogeneities at surfaces. We shall see how a microscopic study can be essential for a complete understanding of these phase transitions.

In this paper, we present a hot tunneling microscope study of a temperature-driven phase transition, $\sqrt{3}\times\sqrt{3}R30^\circ\leftrightarrow1\times1$ of Pb on Ge(111) at 1-ML coverage. The literature shows that there has been confusion and controversy about the exact coverage and atomic structures of both phases. We resolved both structures, revealing that this is an order-order transition. Atomic spatial and temporal fluctuations just above the transition temperature are also observed. In addition, the influence of strain, phase boundaries, step edges, and finite-size domains is identified.

II. HISTORICAL BACKGROUND

Pb/Ge(111) has been studied for years. Bulk Pb and Ge do not intermix$^1$ and Pb atoms do not evaporate from the surface at temperatures below 350°C.$^2$ Thus, Pb atoms remain at the surface after the deposition. The first studies of chemisorbed Pb on Ge(111) were done independently by Metois and Le Lay$^3$ and by Ichikawa.$^4$

Metois and Le Lay identified two room temperature $\sqrt{3}\times\sqrt{3}R30^\circ$ (in short $\sqrt{3}$ hereafter) phases occurring at $\frac{1}{4}$ and 1 ML, respectively, using low-energy electron diffraction (LEED) and Auger electron spectroscopy. At very high Pb coverages ($\sim500$ ML), Pb was found to form 3D crystalline islands (Stranski-Krastanov growth mode), with orientation (111)$_{Pb}||$(111)$_{Ge}$ and (011)$_{Pb}||$(011)$_{Ge}$ (|| means parallel to). Ichikawa used reflection high-energy electron diffraction (RHEED) to determine the phase diagram.$^3$ He found two $\sqrt{3}$ phases (labeled as the $\alpha$ and the $\beta$ phases for the low and high Pb coverage structures, respectively) but they occur at $\frac{1}{2}$ and $\frac{3}{4}$ ML, as measured by a quartz oscillator. He proposed a 30° rotated close-packed model for the $\beta$ phase.

Later, Feidenhans'l et al.$^5$ proposed models for the $\alpha$ and $\beta$ phases based on surface x-ray diffraction measurements.$^3$ The saturation coverages were $\frac{1}{4}$ and $\frac{3}{4}$ ML for the $\alpha$ and $\beta$ phases, respectively. In the $\alpha$ phase, Pb atoms occupy the $T_4$ site. For the $\beta$ phase, they proposed that one Pb atom occupies an $H_3$ site and three Pb atoms occupy the bridge sites between $T_4$ and $T_1$ sites, with a small displacement towards the latter sites. This structure is essentially a 1% compressed, Pb(111) close-packed layer rotated by 30° with respect to the underlying Ge(111) plane, similar to the model proposed by Ichikawa except for a translation of the Pb overlayer. The model for the $\alpha$ phase was later confirmed by other studies,$^6$ but that for the $\beta$ phase remained under debate. One fundamental issue is the saturation coverage of the $\beta$ phase. Both 1 and $\frac{3}{4}$ ML have been reported. Another controversial issue was the 3D Pb island growth on the $\beta$ phase. Tonner$^7$ et al. argued that the model of the $\beta$ structure proposed by Feidenhans'l et al.$^5$ would require a thick film of Pb to grow with [011]$_{Pb}||[211]_{Ge}$, 30° rotated relative to Ge(111) basis vectors, which does not agree.
with experimental observations.9

Recently, Seehofer, Falkenberg, and Johnson using scanning-tunneling microscope (STM), proposed a model for the β phase similar to that proposed by Feidenhans’l et al. except that the Pb atoms on the bridge sites have a small displacement toward the T₂ site rather than the T₁ site.10 Another quite different model was also proposed by Ancilotto, Selloni, and Car based on ab initio molecular-dynamics calculations.11 Both models have a saturation coverage of 3/4 ML. As we will show, the β phase is actually composed of Pb trimers and the saturation coverage is 1 ML.

The β phase undergoes a reversible phase transition to a 1×1 phase at ~180°C. The nature of the high-temperature 1×1 phase has also been controversial. Ichikawa claimed that the 1×1 phase was a 2D isotropic liquid layer unperturbed by the Ge substrate because of the observed weak isotropic halos of diffuse scattering in reflection high-energy electron diffraction (RHEED).3,4 However, Metois and Le Lay argued that it was an ordered Pb layer because the 1×1 LEED pattern remained sharp above the transition temperature.2 In 1988, Dev et al. conducted an x-ray standing-wave study of the phase transition.12 Their measurements suggested that the high-temperature 1×1 phase is composed of small islands of the original β overlayer, rather than an isotropic 2D liquid. Dev et al. adopted the model of the β phase proposed by Feidenhans’l et al., but they did not have a detailed model for this high-temperature phase. However, a surface x-ray diffraction study by Grey and coworkers also showed a ring of diffuse scattering in the 1×1 phase, and they concluded that the 1×1 phase was a 2D liquid weakly modulated by the underlying Ge substrate.13–15 As we will see in our high-temperature tunneling microscope study, this is an order-order phase transition.

III. EXPERIMENTAL PROCEDURES

Our experiments were performed in an ultrahigh vacuum chamber with a base pressure of 6×10⁻¹¹ torr. Clean reconstructed Ge(111)-c(2×8) surfaces are produced by successive Ne ion sputtering and annealing until very sharp and bright c(2×8) LEED spots are observed from the entire sample. Pb is then deposited from an effusion cell onto a clean Ge(111)-c(2×8) surface. After checking the surface structure and conditions for the phase transition with LEED, the sample was transferred to the STM stage for imaging. At very low coverage, most Pb atoms substitute for Ge atoms in the adatom sites. Our STM images show that further Pb deposition leads to the nucleation of a √3 phase with adatoms occupying T₂ sites, agreeing with the STM observations by Seehofer, Falkenberg, and Johnson.10 Above 3/4 ML, domains of the high-coverage β phase were found, and most of them nucleate at step edges on the lower terraces. To observe the phase transition of the β phase, we image the surfaces at sample temperatures from 24°C to 200°C. The temperature was calibrated by gluing a thermocouple directly to the sample after the last STM run. Its accuracy was estimated to be ±5°C and its precision to be ~0.2°C.

IV. RESULTS

A. The β phase

Figure 1 shows a room-temperature tunneling image of the α and β phases at a sample bias of +2.0 V. The β phase appears higher at this bias and shows much fewer defects than the α phase. Dark atoms in the α phase are Ge adatoms, but no dark atoms are seen in the β phase. Phase boundaries usually run along the substrate directions, i.e., (01T) directions, but defects are often seen there. Each bright spot of the β phase is centered on an H₃ site, which can be determined by triangulating from the well-understood α phase. At ~0.57-V sample bias, a periodic array of trimers was resolved in the β phase (Fig. 2), with a trimer corresponding to a bright spot in the previous figure. The same trimer structure is also seen at the opposite tunneling polarity with sample bias less than +1 V. Therefore, we believe the trimer seen in Fig. 2 represent the real atomic structure. A simple model for the β phase is drawn in Fig. 3. Each Pb atom is displaced from the T₁ site above a first-layer Ge atom, to which it is bonded, towards the threefold hollow H₃ site. The resulting trimers are centered on H₃ sites, and the displacement of each Pb atom from its ideal T₁ site is ~0.3 Å. Trimmers centered on T₄ sites would be rotated 60°, and none are observed in our room-temperature images. The spacing between Pb atoms in the trimer is 3.5(±0.3) Å; in contrast, the spacing between two neighboring T₁ sites is 4.0 Å. Therefore, the formation of Pb trimers in the β phase is due to the attractive interaction between neighboring Pb atoms. Note that the β phase is just a slight

![FIG. 1. 130×125 Å² room-temperature tunneling image of the α and β phases, taken at a sample bias of +2 V and a tunneling current of 50 pA.](image-url)
deformation of the Pb terminated 1×1 structure. The coverage of the β phase determined from our tunneling images is 1 ML. We confirmed the coverage measurement by Rutherford backscattering.\textsuperscript{16}

We note that very high resolution is required to resolve the fine structure of the trimers, and any imperfection in the tunneling tip can affect the image. The trimer structure is the one we can consistently get at both tunneling polarities when the tip is sharp. The threefold symmetry of the β phase in our model is inferred from the diffraction pattern. However, small deviations from the threefold symmetry are sometimes seen and vary from tip to tip, presumably due to the atomic structure of the tip. Low tunneling biases (\(< 1\) V in both polarities) are usually required to clearly resolve the atomic structure of the β phase. We do not observe any structure similar to the one observed by Seelhofer, Falkenberg, and Johnson for the β phase.\textsuperscript{10} The trimer structure is not purely electronic, as described by Ancilotto, Selloni, and Car,\textsuperscript{11} because the trimers can be consistently imaged at both tunneling polarities.

We close this section with the following observation, which may be of great practical utility. We found that the β phase is very inert to contamination from the vacuum because the Pb overlayer passivates the Ge(111) surface. The β phase can stay in vacuum for over a week with little degradation, as seen in STM images. We also prepared a sample covered with about 1 ML of Pb. It was then exposed to air for several seconds and transferred back into the vacuum again. Very nice c(2×8) appears immediately after removing the Pb overlayer by annealing to about 600°C. This suggest that Pb can be used to passivate Ge(111) surfaces and Pb may be a good candidate for surfactant growth.

### B. The high-temperature 1×1 phase

Figure 4 shows a tunneling image of the high-temperature 1×1 structure taken at 200°C. As we shall show, each bright spot corresponds to a Pb atom on the T\textsubscript{4} site. The transition is not homogeneous near the transition temperature. Figure 5 shows the high-coverage phase taken at 168°C with a sample bias of -0.8 V (the transition temperature is \(\sim 172°C\)). The upper part of the image is the β phase. Near the bottom of the image, a 1×1 structure appears in the vicinity of the phase boundary with the α phase. This indicates that the transformation starts from the boundary with the α phase.

Above the transition temperature, the long-range \(\sqrt{3}\) order of the β phase is destroyed by thermal fluctuations. Figure 6 shows a tunneling image obtained at 173°C (just

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**FIG. 3.** Simple atomic model of the β phase on the Ge(111) surface. Each Pb atom is bonded to the Ge atom underneath, and is displaced by about 0.3 Å (not to the scale in the figure) from the T\textsubscript{1} site toward an H\textsubscript{3} site to form a trimer with two other neighboring Pb atoms. A unit cell and crystal directions are indicated.

**FIG. 4.** 45×40 Å\(^2\) tunneling image of the 1×1 phase at 200°C, taken at a sample bias of -0.4 V and a tunneling current of 50 pA. A 1×1 unit cell is indicated.
above the transition temperature) with a sample bias of $-0.4$ V. The $\alpha$ phase can be seen in the lower left part and the rest of the image is the high-coverage high-temperature phase. Similar to Fig. 5, a $1\times1$ structure appears near the boundary with the $\alpha$ phase. Extrapolating from the $\alpha$ phase, we determine that the bright spots in the $1\times1$ structure are centered on the $T_1$ sites. Thus, the $1\times1$ phase is the Pb-terminated unreconstructed Ge(111) surface and the transition is order-order. Inside the high-converge phase of Fig. 6, a wildly fluctuating structure can be observed. Figures 7(a) and 7(b) show two consecutive tunneling images of the fluctuating region taken at the same conditions. Due to fluctuations of the structure in time, the two images do not repeat except the $1\times1$ structure at the lower left corner. Patches of trimers can be seen inside the domain. Each image is composed of 180 horizontal scan lines, and each scan line takes 0.43 s. In the images, every patch of the trimer structure appears to be elongated in the horizontal direction, which is due to the raster scan of the STM. Therefore, information on both spatial and temporal fluctuations is contained in these two images. A careful examination of the patches of the trimer structure reveals that they are not on the same set of $H_3$ sites, as will be discussed later on.

A study of Fig. 3 shows that there are three possible translationally inequivalent domains of $\beta\sqrt{3}$ on the underlying lattice. Figure 8 shows an atomic model of a snapshot of a possible configuration in the high-temperature phase. It contains small patches of each domain separated by dimers and monomers at the boundaries. Since a Pb atom can be displaced in any one of the three possible directions to form a trimer with neighboring Pb atoms, this system should be closely related to the three-state Potts model. As the temperature increases, the average size of a patch (or the "correlation length") decreases and fluctuations become faster. Each Pb atom, on average, is then centered over the Ge atom underneath. This explains the observation of the ordered $1\times1$ structure in the $200^\circ C$ images shown in Fig. 4.

C. Local effects

As seen in STM images, the transition of the $\beta$ phase to the $1\times1$ phase starts from the boundary with the $\alpha$ phase. This may be due to the fact that the inhomogeneous surface-strain fields originating from the $\alpha$ phase lower the transition temperature. We have also observed that small regions of $\beta\sqrt{3}$ bounded by the $\alpha$ phase transform into $1\times1$ at lower temperatures than significantly larger regions do. However, quantitative measurement and interpretation are difficult because defects and step edges at the boundary of the high-coverage phase can also affect the transition temperature (perhaps due to surface-strain fields and other conditions on the boundaries).

It is known that $\frac{1}{4}$-ML $\sqrt{3}$ reconstructions on semiconductor (111) surfaces (with adatoms on $T_4$ sites) have an intrinsic tensile stress, which would induce elastic relaxation of the first few atomic layers of the substrate. The surface-strain fields induced by the $\beta$ phase (perhaps also tensile stress) may interact with the fields originating from the $\alpha$ phase and raise the total surface free energy. The $1\times1$ structure may provide a relaxation of the surface strain caused by the $\alpha$ phase, so the transition to the $1\times1$ phase would be most favorable near the $\alpha$ phase. Theoretical calculations on this system will be valuable in the understanding of the strain-field effect on the phase transitions.
Strain has also been found to cause the transformation of Si(111)-7×7→1×1 to begin at step edges on the upper terraces.\textsuperscript{24,25} Recently, a transmission electron diffraction study on nanocrystals of CdS showed a large depression in the melting temperature (several hundred degrees) with decreasing size, which was ascribed to surface tension.\textsuperscript{26} The effects of inhomogeneous strain fields originating from surfaces (in 3D cases) or edges (in 2D cases) on phase transformations may be a general phenomena in finite-sized semiconductor crystals, because bonding in semiconductors is strong and directional.

As the Pb coverage increases from $\frac{1}{2}$ ML, we observe the increase in the transition temperature of $\beta\rightarrow1\times1$ to be very slow (only a few degrees, but it also depends on the domain size of the $\beta$ phase) until the Pb coverage is close to 1 ML, where a sharp increase sets in. Ichikawa\textsuperscript{3} and Grey\textsuperscript{13} also observed this sharp change of the transition temperature around the completion of the first Pb overlayer. As we will see, this is also caused by local strain fields.

For Pb/Ge(111), steps often intercept one another above $\frac{1}{2}$ ML. Near 1 ML, the surface is mainly covered by the $\beta$ phase and the size of each $\beta$ domain is limited by the size of the terrace on which it nucleates. The domain size of the $\beta$ phase near 1 ML varies more than it does at low Pb coverages. Figure 9 shows an STM image of the surface morphology at about 0.95 ML at 187°C. Small regions of the $\alpha$ phase remain in the upper terraces near step edges. High-resolution tunneling images show that the small terrace ($\sim$200 Å) at the left-hand side of the image has transformed into the 1×1 structure as shown in Fig. 4. We also observe fluctuating trimer domains in the terrace at the center of the image, indicating that its transition temperature is about 187°C. The large terraces are still in the $\beta$ phase. On this surface, large terraces ($>1000$ Å) undergo the transformation at about 195°C, but small terraces (100–300 Å) transform at temperatures below 185°C. The transition observed in LEED ap-
pears very sluggish near 1 ML, in contrast, the transition appears to be sharp on surfaces of 0.4–0.6 ML. Similar sluggish behavior was also observed by Grey using surface x-ray diffraction.\textsuperscript{13} Obviously, size effects and conditions at boundaries play important roles in the phase transition.

Step edges also display interesting local effects on the transformation near 1 ML. Figure 10 shows a room-temperature tunneling image of 1-ML Pb/Ge(111), with the surface covered by the $\beta$ phase only. On this surface, LEED shows that the transition temperature is about 210°C, probably because of the absence of the $\alpha$ phase. Figure 11 is 191°C tunneling image of an upper terrace with a step edge at the upper right corner, marked by an arrow. The surface is reconstructed in a periodic array of trimers but near the step edge a $1\times1$ structure is seen, similar to the image in Fig. 5. The boundary between the $\beta$ and $1\times1$ phase was found to move between two consecutive images. Meanwhile, no similar effect on lower terraces of steps are observed. The strain-field interaction between step edges and the $\beta$ phase and its effect on the phase transformation will be an interesting subject for further study. It might prove fruitful to apply external stress to a Pb/Ge(111) sample and study the effects on the phase transformation, such as the change of the transition temperature and the critical behavior.

The step edges observed in Fig. 9 are ragged, and they become smoother in Fig. 10. Pb deposition onto this surface reduces the $\alpha$ regions first and then leads to the smoothing of step edges. Further deposition results in straight and sharp step edges. Figure 12 shows a tunneling image of a higher Pb coverage surface (estimated to be ~1.3 ML) with straight step edges along \langle 01\overline{1}\rangle or \langle 2\overline{1}1 \rangle directions. We also observed that 2D Pb islands start to nucleate at the lower terrace of step edges.

Meanwhile, we observe a sharp increase in the transition temperature. Up to 200°C, only the $\beta$ phase is observed and no $1\times1$ structure appears, even near step edges. The $\beta$ phase on this surface was found to be stable up to 300°C with LEED, consistent with observations by Ichi- kawa\textsuperscript{3} and Grey\textit{ et al.}\textsuperscript{13,14} Pb deposition leads to the

\begin{figure}
\centering
\includegraphics[width=\textwidth]{fig9.png}
\caption{1000×1000 Å\textsuperscript{2} tunneling image of 0.95 ML of Pb/Ge(111), taken at 187°C. Remnant regions of the $\alpha$ phase are indicated by arrows. The crystal directions are the same as those in Fig. 5.}
\end{figure}

\begin{figure}
\centering
\includegraphics[width=\textwidth]{fig10.png}
\caption{1000×1100 Å\textsuperscript{2} tunneling image of 1 ML of Pb/Ge(111), taken at 191°C and a sample bias of +2 V. The crystal directions are the same as those in Fig. 5.}
\end{figure}
disappearing of the \(\alpha\) phase, the modification of step edges, and the formation of Pb islands, and thus, the surface-strain fields change. The sharp increase in the transition temperature most likely results from the change of the strain fields.

V. DISCUSSION

The high-temperature \(1 \times 1\) phase we observe is an ordered phase. The Pb-Ge bonding for the \(1 \times 1\) phase is the same as that in the \(\beta\) phase and the phase transition involves only a displacement of Pb atoms. Therefore, it is reasonable that no clear interface is seen between the \(1 \times 1\) and \(\beta\) phase in our STM image near the transition. If the \(1 \times 1\) phase is a liquid, as claimed by some researchers, a clear phase separation should develop. Fluctuations associated with the phase transformation we have observed also appear in x-ray diffraction,\(^{13}\) which is not consistent with the 2D melting proposed by Ichikawa,\(^{3,4}\) and Grey et al.\(^{14}\)

The diffuse halo observed in the \(1 \times 1\) phase using x-ray diffraction and RHEED may result from the formation of instantaneous trimers and dimers in the \(1 \times 1\) phase due to the attractive Pb-Pb interaction. The position of the diffuse halo suggests the first peak in Pb-Pb pair distribution function to be about 3.5 Å, which is about the Pb-Pb spacing in the trimers. The single Pb-Ge bonding along the [111] direction may allow a lateral displacement of Pb atoms without much cost of energy and thus a large thermal vibration of Pb atoms (0.1–0.2 Å) in the \(\beta\) phase can be expected at room temperature. At the transition temperature, the lateral vibration becomes so large that the long-range order of the \(\sqrt{3} \times \sqrt{3}\) periodicity is destroyed. The Pb-Pb attractive interaction favors the formation of domains of trimers, but the average domain size decreases with the temperature. At high enough temperatures, the formation of Pb trimers becomes very unlikely and instead Pb dimers form instantaneously because of the attractive interaction. Each Pb atom can form a dimer with any one of the six nearest neighbors but the orientation of the dimers may be misoriented from \(\langle 01\overline{1} \rangle\) directions due the large thermal vibration. The diffuse halo observed in x-ray diffraction and RHEED may be the result of these fluctuating dimers.

The observation of fluctuations suggests that the transition of Pb/Ge(111): \(\beta-\sqrt{3} \leftrightarrow 1 \times 1\) is second order. The three-state Potts model can have a second-order transition. However, a small hysteresis (1°C–3°C) is observed both in LEED and in tunneling microscopy. Similar hysteresis was also seen in x-ray diffraction.\(^{13}\) The strain fields, which affect the transition temperature and cause inhomogeneity as described earlier, may drive the system into a weak first-order transition.

Pb/Ge(111) bears as strong resemblance to another system, Pb/Si(111). A monolayer of Pb on Si(111) forms an incommensurate (IC) phase, which also undergoes a reversible phase transition to a \(1 \times 1\) phase. Based on x-ray diffraction, Grey et al. proposed a 30° rotated close-packed model for the IC phase.\(^{27}\) The transition was described as a 2D melting by some researchers because a
diffuse scattering halo was also observed in the $1 \times 1$ phase using RHEED.\textsuperscript{28} However, Le Lay et al. argued that it is an order-order solid transition because of the persistence of a sharp LEED pattern and a pronounced surface state in photoemission measurements above the transition.\textsuperscript{29–31} Almost the same divided arguments occurred for Pb/Ge(111) and Pb/Si(111). Recently, an STM study of the IC phase in Pb/Si(111) also observed formation of Pb trimers in both filled-state and empty-state images.\textsuperscript{32} Two types of trimers were observed in Pb/Si(111): trimers centered on the $H_3$ and on $T_4$ site. The IC phase is composed of small alternating domains of these two types of trimers. This suggests that the formation energies for trimers on the $H_3$ site and on the $T_4$ site are very close for Pb/Si(111), but differ much more for Pb/Ge(111). Also, a $1 \times 1$ structure similar to that for the high-temperature $1 \times 1$ phase of Pb/Ge(111) was observed. The phase transition of the IC phase to the $1 \times 1$ phase is also order-order and the transition temperature also shows a sharp increase near the completion of 1 ML. Similar local strain-field effects on the phase transition also appear in the Pb/Si(111) system.

\section{VI. CONCLUSION}

We have presented a microscopic study of the phase transition $\beta - \sqrt{3} \times \sqrt{3} R 30^\circ \rightarrow 1 \times 1$ of 1-ML Pb/Ge(111). The atomic structures below and above the transition temperature are resolved. Local surface-strain fields are found to affect the phase transition. The presence of the $\frac{1}{2}$-ML $\alpha - \sqrt{3}$ phase reduces the transition temperature, but the formation of Pb island and modification of step edges above 1 ML cause a sharp increase in the transition temperature. The effects of the inhomogeneous strain fields observed on the surface suggest that great care should be taken in the interpretation of structural phase transitions using nonmicroscopic techniques.

\section{ACKNOWLEDGMENTS}

We would like to thank Silva K. Theiss, Dr. Robert Martinez, Professor Frans Spaepen, and Professor Efthimios Kaxiras for fruitful discussions and criticism of this manuscript. This research was supported by the Materials Research Laboratory at Harvard University (Contract No. NSF-DMR-8920490) and the Joint Services Electronics Program (Contract No. N00014-89-J-1023).

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\end{thebibliography}
FIG. 10. 1000×1100 Å² tunneling image of 1 ML of Pb/Ge(111), taken at 191°C and a sample bias of +2 V. The crystal directions are the same as those in Fig. 5.
FIG. 1. 130×125 Å² room-temperature tunneling image of the α and β phases, taken at a sample bias of +2 V and a tunneling current of 50 pA.
FIG. 11. 100×115 Å² tunneling image of the high-coverage phase near a step edge, which lies at the upper right corner of the image and is marked with an arrow. The image was taken at a sample bias of −0.3 V and a tunneling current of 90 pA. The crystal directions are the same as those in Fig. 5.
FIG. 12. 1400×1300 Å$^2$ tunneling image of Pb/Ge(111) at a coverage $\sim$1.3 ML, taken at 193°C and a sample bias of +1.7 V. The crystal directions are the same as those in Fig. 5.
FIG. 2. 55×50 Å² tunneling image of the β phase at room temperature. Tunneling current is 30 pA.
FIG. 3. Simple atomic model of the β phase on the Ge(111) surface. Each Pb atom is bonded to the Ge atom underneath, and is displaced by about 0.3 Å (not to the scale in the figure) from the $T_1$ site toward an $H_3$ site to form a trimer with two other neighboring Pb atoms. A unit cell and crystal directions are indicated.
FIG. 4. 45×40 Å² tunneling image of the 1×1 phase at 200°C, taken at a sample bias of −0.4 V and a tunneling current of 50 pA. A 1×1 unit cell is indicated.
FIG. 5. 55×75 Å² tunneling image of the high-coverage phase taken at 168°C. The β phase is seen in the upper part of the image and the high-temperature phase 1×1 phase is present in the lower part. The α phase lies just below the boundary of the image. The corrugation in the image is ~0.2 Å. A unit cell of the β phase and crystal directions are indicated.
FIG. 6. $85 \times 75 \text{Å}^2$ tunneling image taken at 173°C. Unit cells of the $\alpha$ and $1 \times 1$ phases are indicated. The crystal directions are the same as those in Fig. 5.
FIG. 7. (a) and (b) are $110 \times 125 \, \text{Å}^2$ tunneling images of the high-coverage phase taken at 173 °C, just above the transition temperature. Short-range order with patches of trimers centered on different sets of $H_3$ sites can be seen. At the lower left corner is a boundary with the $\alpha$ phase (indicated by an arrow), and a $1 \times 1$ structure (with a unit cell indicated) can be seen close to it. The image in (b) is taken 100 s after that in (a).
FIG. 8. Model of a snapshot of one possible atomic configuration in the fluctuating high-temperature phase. Different gray scales are used to indicate domains of trimers centered on different sets of $H_3$ sites.
FIG. 9. 1000×1000 Å² tunneling image of 0.95 ML of Pb/Ge(111), taken at 187°C. Remnant regions of the α phase are indicated by arrows. The crystal directions are the same as those in Fig. 5.