Soft incommensurate reconstruction on Pb/Si(111): Structure, stress modulation, and phase transition

Citation

Hwang, Ing-Shouh, R. E. Martinez, Chien Liu, and J. A. Golovchenko. 1995. Soft Incommensurate Reconstruction on Pb/Si(111): Structure, Stress Modulation, and Phase Transition. *Physical Review B* 51, no. 15: 10193–10196. doi:10.1103/physrevb.51.10193.

Published Version

doi:10.1103/PhysRevB.51.10193

Permanent link

<http://nrs.harvard.edu/urn-3:HUL.InstRepos:29406269>

Terms of Use

This article was downloaded from Harvard University's DASH repository, and is made available under the terms and conditions applicable to Other Posted Material, as set forth at <http://nrs.harvard.edu/urn-3:HUL.InstRepos:dash.current.terms-of-use#LAA>

Share Your Story

The Harvard community has made this article openly available.
Please share how this access benefits you. [Submit a story](#).

[Accessibility](#)

Soft incommensurate reconstruction on Pb/Si(111): Structure, stress modulation, and phase transition

Ing-Shouh Hwang

*Division of Applied Sciences, Harvard University, Cambridge, Massachusetts 02138
and Institute of Physics, Academia Sinica, Taipei, Taiwan, Republic of China*

R. E. Martinez

*Department of Physics, Harvard University, Cambridge, Massachusetts 02138
and Department of Physics, University of Texas at Austin, Austin, Texas 78712*

Chien Liu

Division of Applied Sciences, Harvard University, Cambridge, Massachusetts 02138

J. A. Golovchenko

*Division of Applied Sciences, Harvard University, Cambridge, Massachusetts 02138;
Department of Physics, Harvard University, Cambridge, Massachusetts 02138;
and Rowland Institute for Science, Cambridge, Massachusetts 02238*

(Received 6 December 1994)

We resolve the atomic structure of the one-monolayer incommensurate (IC) reconstruction of Pb on Si(111) using a tunneling microscope. The local structure of this surface consists of two types of Pb trimers and a quasi- 1×1 region, while on larger ($> 10 \text{ \AA}$) scales the trimers are assembled into alternating domains discommensurate with the substrate. One feature of this surface is the sensitivity of the domain morphology to surface-stress inhomogeneities. This sensitivity dramatically alters the temperature at which the IC phase transforms locally to a 1×1 phase.

Because of the development of experimental techniques to investigate surface structures, there has been significant progress in the understanding of two-dimensional (2D) reconstructions.¹ However, very few studies have been conducted on incommensurate (IC) systems, especially on semiconductor surfaces,² where bonding is relatively strong. Current understanding and theoretical studies of the IC phase and IC-C transitions are mainly based on rare gases on graphite. We found that Pb/Si(111) is a unique system for studying IC reconstructions. First, it is a displacive IC phase,⁴ which involves lateral displacement in atomic positions. To the best of our knowledge, no other 2D example has been reported so far. Second, it does not have a close-packed structure, as found in other IC systems.^{2,3} Third, the lateral displacement of Pb atoms and domain morphology are very sensitive to stress fields originating from nearby reconstructions or imperfections, so that the structure has no long-range periodicity. Fourth, the stress fields are observed to induce the IC-C transition and to affect the transition temperature. The study of this IC structure may advance our understanding of the origin of surface reconstructions and IC-C transitions.

The Pb/Si(111) system has been considered as a model system for the study of abrupt Schottky barriers because Pb and Si have negligible mutual bulk solubility.⁵ It has been studied extensively using x-ray diffraction, low-energy electron diffraction (LEED), reflection high-energy electron diffraction (RHEED), photoemission, Auger electron spectroscopy, ellipsometry, etc.⁶⁻¹⁶ However, previous results have been very confusing because of the complicated phase diagram of Pb/Si(111). In

an x-ray diffraction study, Grey *et al.*¹¹ proposed a 30° rotated close-packed model for the IC phase. Recently, using scanning tunneling microscopy (STM) and Rutherford backscattering (RBS), Ganz *et al.*^{17,18} identified the distinct phases and their saturation coverages, and characterized most of the atomic structures. However, they did not resolve individual atoms in either the unannealed or annealed high-coverage phases.

In this STM study, we resolved the atomic structures of the one-monolayer (ML) IC phases of Pb/Si(111). In contrast to the close-packed model proposed by Grey *et al.*,¹¹ we find that Pb forms two types of trimers as a result of small lateral displacements from a 1×1 mesh. The trimers are arranged in alternating domains, whose sizes and shapes are strongly affected by local stress field and surface irregularities. At high temperature, this IC phase transforms into an ordered 1×1 structure. This transformation can also be induced by local surface stresses.

Our experiments were performed using a homemade STM in an ultrahigh vacuum (UHV) chamber with a base pressure of 6×10^{-11} torr. Si(111) samples with a resistivity of $0.05 \text{ } \Omega \text{ cm}$ were chemically cleaned using the Shiraki procedure¹⁹ before being introduced into the UHV chamber. The samples were cleaned *in situ* by flashing to 1250°C for 10–20 s, and annealing at 920°C for a few minutes before cooling slowly to room temperature. Sample temperatures were measured with an infrared pyrometer. The cleaning procedure consistently yielded high-quality Si(111) 7×7 reconstructions.

Two Pb deposition schemes were used in this study. In the conventional one-stage deposition, 99.999% pure Pb

was evaporated onto a clean room-temperature (RT) Si(111) sample. After a brief anneal at $\sim 300^\circ\text{C}$ and LEED inspection, the sample was transferred onto the STM stage. A mixture of the 1×1 , $\frac{1}{3}$ -ML $\sqrt{3}\times\sqrt{3}$ (in short, $\alpha\sqrt{3}$), and Si(111) 7×7 phases was observed for Pb coverages between 0.3 and 1 ML. Samples having slightly more than 1-ML Pb showed only the IC phase and scattered 3D Pb islands. These phases and their associated Pb coverages have been identified previously.^{17,18} In another deposition scheme, we evaporated additional Pb at RT onto annealed samples that exhibited a mixture of 1×1 , 7×7 , and $\alpha\sqrt{3}$ phases in STM images. This two-stage evaporation procedure produced regions of Pb/Si- 7×7 (the high-coverage phase of RT deposition), together with domains of the IC phase.¹⁸ This coexistence of the two phases cannot be obtained in one-stage deposition. It allows us to determine the registration of Pb atoms in the IC phase, and observe interesting surface-stress effects. All STM images shown in this paper are of RT surfaces prepared using the two-stage deposition.

Figure 1(a) shows a tunneling image of a $60\times 50 \text{ \AA}^2$ region of the IC surface. This sample was prepared by depositing 0.2 ML of Pb at RT onto an annealed surface with originally ~ 0.8 ML of Pb. It exhibits a mixed LEED pattern containing both the IC and Pb/Si- 7×7 diffraction spots.¹⁸ Individual Pb atoms can be seen in this region of the IC phase. Atoms at the periphery of the image are arranged in two types of trimers, differing in orientation by 60° . Alternating domains of trimers having $\sqrt{3}\times\sqrt{3}R30^\circ$ local periodicity can clearly be identified. Atoms near the center of the image are arrayed in a quasi- 1×1 mesh. The trimers and quasi- 1×1 structure are consistently imaged over a large range of sample bias, from $+0.4$ to $+2.2$ V and from -0.45 to -1.3 V. Thus, we believe that they are the real atomic structure of the IC phase rather than merely an electronic artifact. Figure 1(b) is the atomic model for the IC structure in Fig. 1(a). The trimers comprise three Pb atoms displaced laterally from T_1 toward either T_4 or H_3 sites [see Fig. 1(b)]. Note that trimers centered on T_4 sites are 60° rotated relative to those on H_3 sites. The Pb-Pb spacing inside a trimer is $(3.3\pm 0.3) \text{ \AA}$, as measured using STM. Between adjacent trimer domains, we always see a boundary structure comprising a Pb dimer between two trimers, which point toward each other and are aligned along a $[\bar{2}11]$ direction, as marked in Fig. 1. Trimer atoms nearest such a dimer are often slightly displaced toward it. Regions in which boundaries intersect form a quasi- 1×1 structure, with small displacements from T_1 sites that are not shown in Fig. 1(b). Within our observation time (> 10 min), we do not see boundary fluctuations in the IC phase at room temperature.

Figure 2 shows a tunneling image of a larger $180\times 200 \text{ \AA}^2$ region of this surface, with the trimer domains and 1×1 regions outlined in the lower left. Domain wall atoms are dotted and “+”, “−”, and “0” indicate each of the two types of trimers and quasi- 1×1 regions, respectively. This partitioning can be extended throughout the figure. We refrain from doing so to allow the readers to visualize the raw data themselves. This complicated structure does not have a periodicity commensurate with

the Si(111) substrate,²⁰ but the basic features of alternating trimer domains, the boundary structure, and a quasi- 1×1 region at a boundary intersection are identical to those in Fig. 1. An analysis of many STM images of this surface, containing a total of 451 trimers, showed that $(50\pm 5)\%$ of the trimers were of each orientation. Each domain contains 16 ± 5 trimers. The detailed structure of the IC phase, including the size and morphology of the trimer domains, are strongly influenced by the presence of defects, step edges, or other nearby reconstructions. For example, Pb clusters, such as those indicated by arrows in Fig. 2, are always found to be in a quasi 1×1 region and surrounded by six alternate trimer domains.

Additional evidence for the effect of local inhomogeneities on the reconstruction of the IC phase is seen in Fig. 3, which is an image of another portion of the surface shown in Fig. 1. Pb islands and a small area of Pb/Si- 7×7 divide the image into three regions, labeled A, B, and C. Region A is composed of domains of Pb trimers, as seen in Figs. 1 and 2. Region B, which is bordered by the Pb islands and a remnant of Pb/Si- 7×7 , shows an ordered 1×1 structure with Pb atoms occupying T_1 sites. Note that the Pb atom registration switches smoothly from 1×1 to the trimer domains. In region C, which is part of a $130\times 70 \text{ \AA}^2$ area bounded by the Pb/Si- 7×7 and a sharp step edge (not shown), the surface

FIG. 1. (a) $60\times 50 \text{ \AA}^2$ STM image of Pb/Si(111) IC phase on a surface prepared by two-stage deposition, taken at sample bias $+2.0$ V and tunneling current 50 pA. Parallel lines are drawn to indicate the structure of two domain boundaries. Atomic model for the IC phase in (a) is illustrated in (b).

FIG. 2. $180 \times 100 \text{ Å}^2$ STM image of the same surface as in Fig. 1 taken at $+2.0 \text{ V}$ and 45 pA . Symbols “+,” “-,” and “0” indicate H_3 , T_4 trimer domains, and quasi- 1×1 regions, respectively, with domain-boundary dimers dotted. Two Pb clusters are indicated by arrows. Part of Pb/Si- 7×7 regions can be seen at upper and lower right corners of the image.

is also reconstructed into trimer domains. The Pb-Pb spacing in these trimers is larger than that in region A, making this area look more 1×1 -like than region A. This figure illustrates that the IC phase can be considered soft, in the sense that the lateral positions of IC-phase Pb atoms are easily perturbed, presumably because of their single bond to first-layer Si atoms. We cannot explain the subtle phenomena associated with the IC phase that we have observed based on the 30° rotated close-packed model proposed by Grey *et al.*¹¹

FIG. 3. $100 \times 110 \text{ Å}^2$ STM image taken at the same tunneling condition as in Fig. 1(a).

Figure 3 shows that the Pb atoms in the center of Pb/Si- 7×7 unit cells are also bonded in a 1×1 array to T_1 sites. Pb atoms in the faulted half of the Si(111) 7×7 remnant (triangular area with vertex pointing to the right) are displaced from registry with those in region B. Previous studies²¹ found that thick Pb overlayers grown on the IC phase and on the Pb/Si- 7×7 phase had different Schottky barrier heights (SBH). Since the local Pb-Si bonding within the Pb/Si- 7×7 unit cell is identical to that in the IC phase, we suggest that the very high defect density in the Pb/Si- 7×7 phase relative to that in the IC phase may be responsible for its lower SBH.

We also studied samples prepared with one-stage deposition. Annealed samples with < 1 -ML Pb coverage contain neighboring 1×1 and $\alpha\sqrt{3}$ phases. The 1×1 phase has the same structure as that shown in region B of Fig. 3. Above 1 ML, where no $\alpha\sqrt{3}$ phase is present, we observed the IC phase, which contains the same trimer domains, boundary structure, and quasi- 1×1 region at a boundary intersection as those shown in Figs. 1 and 2. However, the domains are more irregular than those prepared by two-stage deposition and are often elongated along a $\langle \bar{2}11 \rangle$ direction. The IC phase is never seen bordering the $\alpha\sqrt{3}$ phase at RT. We also imaged surfaces with about 1 ML of Pb, which show only a 1×1 LEED pattern. These surfaces mainly contain the 1×1 structure, but scattered trimer domains are found to nucleate. Clearly, the IC phase evolves gradually from the 1×1 structure with increasing Pb coverage.

Adding between 0.1 and 0.2 ML of Pb to RT samples originally having a mixture of 1×1 and a small portion of $\alpha\sqrt{3}$ transforms these into the IC phase. We also deposited ~ 0.05 ML of Pb onto such a surface and observed that trimers start to nucleate from the 1×1 structure near defects or Pb islands. We observe that adding Pb to the surface in the second, RT deposition alters the IC surface morphology without forming new, higher local-coverage structures. Instead, the additional Pb is adsorbed into clusters, islands, and other defects on the surface that modify the domain structure by adding an extrinsic, long-range perturbation to the surface-stress field. The local coverage of this structure, as well as that of the 1×1 phase, is identically 1 ML. A previous RBS measurement¹⁸ found that the annealed surface exhibits the IC phase above 1-ML Pb, which is consistent with our STM observation.

Since the domain morphology is strongly affected by the local stress field, we find domains with different shapes and relative orientations present in different regions of the surface. The domain structure of the particular region shown in Fig. 2 has its orientation pinned by local defects (the nearby Pb clusters and 7×7 regions) and hence does not reveal itself in the LEED pattern. Most of our tunneling images are either of smaller regions of the surface with high resolution revealing the detailed trimer structure (and not the long-range properties of the domains) or are of large areas of the surface without sufficient resolution to completely resolve the trimers. These are in agreement with the observed LEED pattern. A representative example of such a large area scan (at low resolution) has already been published in Fig.

10(b) of Ref. 18.

The IC and 1×1 phases have the same Pb-Si bonding, and the former can evolve smoothly from the latter as a result of small lateral displacements. Presumably the single Pb-Si bond allows Pb atoms to move laterally and form trimers as a result of an attractive Pb-Pb interaction. It is interesting to note that the IC surface contains T_4 and H_3 trimers with equal populations, in contrast to a similar system, the $\beta\sqrt{3}$ phase of Pb on Ge(111), where only H_3 trimers were seen.²² Perhaps the difference in trimer formation energy between H_3 and T_4 sites is much smaller in the IC phase of Pb/Si(111) than it is in the β phase of Pb/Ge(111). For the former system, the formation of a large domain of commensurate trimers of a given type may induce a significant surface strain, which makes the structure energetically unfavorable. Surprisingly, we never see neighboring domains containing the same type of trimers. Perhaps both the alternating trimer domains and the boundary structure featuring trimers aligned across the domain boundaries lower the total free energy of the surface.

The Pb-Pb spacing and trimer domain morphology depend sensitively on the stress resulting from inhomogeneities in the surface. The clean Si(111) 7×7 has a greater tensile surface stress than does the IC phase.²³ Although the stress in Pb/Si- 7×7 is now known, this structure retains the dimer, corner hole, and stacking fault of clean Si(111) 7×7 ,¹⁸ which suggests that it may also have a significant tensile stress. The presence of a neighboring Pb/Si- 7×7 region may alter the stress field of the IC phase, driving it to the 1×1 structure over distances of ~ 40 Å, as shown in Fig. 3. The large tensile stress in the $\alpha\sqrt{3}$ reconstruction²⁴ may also suppress the formation of the IC phase.

The Pb/Si(111) IC surface (with > 1 -ML Pb) undergoes a transition to the 1×1 structure above $\sim 300^\circ\text{C}$, as observed using LEED,^{8,9,12} RHEED,¹⁵ and surface x-ray diffraction.²⁵ The transition temperature drops sharply with decreasing coverage (below 1 ML). On surfaces with less than saturation Pb coverage, an x-ray diffraction study showed that the room-temperature 1×1 phase transforms into the IC phase below -20°C .²⁵ Our microscopic observations provide a consistent framework for understanding the phase transition and the coverage dependence of its transition temperature. A coexisting $\alpha\sqrt{3}$ phase drives the IC $\leftrightarrow 1 \times 1$ transition temperature below RT, while the presence of Pb islands and Pb clusters increases the transition temperature and enhances the condensation of the low-temperature trimer structures from the high-temperature 1×1 phase. This behavior is similar to that observed in the $\beta\sqrt{3} \leftrightarrow 1 \times 1$ phase transition of 1-ML Pb/Ge(111).^{22,26,27} It may be interesting to explore the dynamics near the transition temperature using the STM.

To conclude, we observe a displacive IC phase, which is very sensitive to surface stress fields. The special structure in 1-ML Pb/Si(111) uncovered by STM provides an interesting sample for understanding the origin of the formation of the IC phase in chemisorption systems. The temperature for the structural transformation from the IC phase to the 1×1 phase is found to be affected by the presence of surface imperfections. Theoretical study of this IC phase and the phase transformation will prove fruitful.

This work was supported by Joint Services Electronic Program (JSEP) Contract No. (N00014-89-J-1023) and Materials Research Laboratory (MRL) Contract No. (NSF DMR 8920490).

- ¹A. Zangwill, *Physics at Surfaces* (Cambridge University Press, New York, 1988).
- ²K. G. Huang *et al.*, Phys. Rev. Lett. **72**, 2430 (1994).
- ³Y. Hasegawa and Ph. Avouris, Science **258**, 1763 (1992).
- ⁴R. Pynn, Nature **281**, 433 (1979).
- ⁵R. W. Olesinski and G. J. Abbaschian, Bull. Alloy Phase Diagr. **5**, 271 (1984).
- ⁶P. J. Estrup and J. Morrison, Surf. Sci. **2**, 465 (1964).
- ⁷M. Saitoh, K. Oura, K. Asano, F. Shoji, and T. Hanawa, Surf. Sci. **154**, 394 (1985).
- ⁸G. Le Lay, J. Peretti, M. Hanbucken, and W. S. Yang, Surf. Sci. **204**, 57 (1988).
- ⁹G. Le Lay, K. Hricovini, and J. E. Bonnet, Appl. Surf. Sci. **41/42**, 25 (1989).
- ¹⁰G. Quentel, M. Gauch, and A. Degiovanni, Surf. Sci. **193**, 212 (1988).
- ¹¹F. Grey, R. Feidenhans'l, M. Nilsen, and R. L. Johnson, J. Phys. (Paris) Colloq. **50**, C7-181 (1989).
- ¹²G. Le Lay, M. Abraham, K. Hricovini, and J. E. Bonnet, in *Kinetics of Ordering and Growth at Surfaces*, edited by Max G. Lagally (Plenum, New York, 1990), p. 209.
- ¹³R. Feidenhans'l, F. Grey, M. Nielsen, and R. L. Johnson, in *Kinetics of Ordering and Growth at Surfaces* (Ref. 12), p. 189.
- ¹⁴J. A. Carlisle, T. Miller, and T.-C. Chiang, Phys. Rev. B **45**, 3400 (1992).
- ¹⁵H. H. Weitering, D. R. Heslinga, and T. Hibma, Phys. Rev. B **45**, 5991 (1992).

- ¹⁶Y. Tanishiro, M. Fukuyama, and K. Yagi, in *Atomic-Scale Imaging of Surfaces and Interfaces*, edited by D. K. Biegelson, D. J. Smith, and D. S. Y. Tong, MRS Symposia Proceedings No. 295 (Materials Research Society, Pittsburgh, 1993), p. 261.
- ¹⁷E. Ganz, F. Xiong, I.-S. Hwang, and J. Golovchenko, Phys. Rev. B **43**, 7316 (1991).
- ¹⁸E. Ganz, I.-S. Hwang, F. Xiong, S. K. Theiss, and J. Golovchenko, Surf. Sci. **257**, 259 (1991).
- ¹⁹A. Ishizaka, N. Nakagawa, and Y. Shiraki, in *Proceedings of the Second International Symposium on Molecular Beam Epitaxy*, edited by Y. Mizushima and S. Nomura (Japanese Society of Applied Physics, Tokyo, 1982), p. 182.
- ²⁰This structure belongs to a weakly incommensurate phase, which is composed of commensurate regions separated by domain wells.
- ²¹D. R. Heslinga, H. H. Weitering, D. P. van der Werf, T. M. Klapwijk, and T. Himba, Phys. Rev. Lett. **64**, 1589 (1990).
- ²²I.-S. Hwang and J. Golovchenko, Phys. Rev. Lett. **71**, 255 (1993).
- ²³R. E. Martinez, W. M. Augustyniak, and J. A. Golovchenko, Phys. Rev. Lett. **64**, 1039 (1989).
- ²⁴K. Rao, R. E. Martinez, and J. A. Golovchenko, Surf. Sci. **277**, 323 (1992).
- ²⁵F. Grey (private communication).
- ²⁶T. Ichikawa, Solid State Commun. **46**, 827 (1983).
- ²⁷F. Grey, Ph.D. thesis, Copenhagen University, 1988.

FIG. 1. (a) $60 \times 50 \text{ \AA}^2$ STM image of Pb/Si(11) IC phase on a surface prepared by two-stage deposition, taken at sample bias $+2.0 \text{ V}$ and tunneling current 50 pA . Parallel lines are drawn to indicate the structure of two domain boundaries. Atomic model for the IC phase in (a) is illustrated in (b).

FIG. 2. $180 \times 100 \text{ \AA}^2$ STM image of the same surface as in Fig. 1 taken at $+2.0 \text{ V}$ and 45 pA . Symbols “+,” “-,” and “0” indicate H_3 , T_4 trimer domains, and quasi- 1×1 regions, respectively, with domain-boundary dimers dotted. Two Pb clusters are indicated by arrows. Part of Pb/Si- 7×7 regions can be seen at upper and lower right corners of the image.

FIG. 3. $100 \times 110 \text{ \AA}^2$ STM image taken at the same tunneling condition as in Fig. 1(a).