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Indium-induced reconstructions of the Si(111) surface studied by scanning tunneling microscopy

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The simple metal indium is known to induce different reconstructions of the silicon (111) surface in the range of metal coverages below one monolayer (1 ML). We have studied both the $\sqrt{3}\times\sqrt{3}$ and the 4×1 reconstructions with scanning tunneling microscopy. Images of the $\sqrt{3}\times\sqrt{3}$ surface are consistent with $\frac{1}{3}$ ML of In adatoms resting in threefold sites. The higher-coverage 4×1 surface consists of large reconstructed terraces often bounded by abrupt, stepped edges. Growth of flat metal islands is also seen around 1 ML.

The simple metal indium is known to induce reconstructions of the silicon (111) surface in the range of metal coverages below one monolayer (1 ML).[1] Much of the previous work done has focused on this fact, with the transitions between the various surface phases being studied both as a function of metal coverage and temperature.[2-5] The changes in atomic structure have also been correlated with changes in electronic properties of the surface.

Of the different reconstructions possible, the $\sqrt{3}\times\sqrt{3}$ phase, which occurs at about 0.3-ML coverage, has been studied to the greatest extent. A very straightforward structure for the surface has been proposed which has already both theoretical and experimental support.[6,7] It is often compared to the analogous surface for Al/Si(111).[5,7] They are expected to have the same structure, and comparing one to another provides some basic understanding of the bonding of the group-III metal adatoms on the Si surface. The fact that these trivalent atoms can entirely satisfy all the dangling bonds on the Si(111) surface in the $\sqrt{3}\times\sqrt{3}$ (denoted $\sqrt{3}$) structure perhaps holds some clues into passivating the surface to further reaction.

The behaviors of In and Al diverge at higher metal coverages. For In on Si(111) at elevated temperatures, as more metal is deposited the surface order changes from $\sqrt{3}$ to $\sqrt{31}\times\sqrt{31}$ and then finally to 4×1 at about 1 ML.[2] Epitaxial growth of ordered In metal islands on the 4×1 surface has been seen at still higher coverages. There appears to be a strong difference in the bonding of the first layer of metal and any subsequent layers. For example, electromigration studies show that In moves relatively easily on an ordered 4×1 surface.[8,9] This is attributed to a total saturation of dangling bonds at the surface. Unfortunately there is very little information on the nature of the 4×1 surface itself.

The In/Si(111) system provides a good opportunity for study with scanning tunneling microscopy (STM). The fact that a variety of ordered surfaces can be prepared simply by varying the initial metal coverage makes this system an ideal subject. We present here STM images of both the $\sqrt{3}$ and the 4×1 surfaces. The results for the $\sqrt{3}$ surface support a $\frac{1}{3}$-ML In adatom model.[6] The images of the 4×1 show a strong periodicity that rules out models consisting of pairs of 2×1 rows.[3] It is hoped that these results will stimulate further work on this system.

The vacuum-STM system had the capability of transferring the sample between the microscope and a standard manipulator, allowing sample cleaning and preparation to be done *in situ*. Surface order was monitored by low-energy electron diffraction (LEED). A detailed description of the STM itself is given elsewhere.[10,11]

The samples were cut from *n*-type doped Si(111) wafers. Clean, well-ordered 7×7 surfaces were prepared by Ne ion sputtering, followed by annealing to 925 °C and a slow cooling. Indium metal evaporations were from a W filament. Deposition rates were calibrated with a quartz crystal microbalance and were held to less than 0.5 ML per minute. Pressures remained below 2×10^{-10} Torr during evaporation, and quickly recovered afterwards to a sub-10^{-10} Torr base pressure.

Ordered In/Si reconstructions were prepared by evaporating In at room temperature and then annealing, or by evaporating onto a hot substrate. The sample was allowed to cool for about 1 h after annealing in order to minimize heating of the STM. LEED was used to check the surface immediately before the sample was transferred to the microscope stage. The surface could be recleaned without sputtering by heating to at least 1000 °C and then cooling slowly. Once In was deposited onto the sample, flashing to only 925 °C did not necessarily produce 7×7 surfaces that were well ordered to the STM, as was the case for sputter-cleaned surfaces.

Although it is possible to vary both the metal coverage and the annealing temperature in order to prepare different reconstructions, the best results were obtained by evaporating at room temperature and then annealing to a fixed temperature of 450 °C. The sequence of reconstructions with coverage as seen by LEED was consistent with previous studies observing In metal growth on the 7×7 surface at or below this temperature.[2-4] Specifically, $\sqrt{3}\times\sqrt{3}$ was seen between 0.3 and 0.5 ML, the $\sqrt{31}\times\sqrt{31}$ at or just above 0.5 ML, and the 4×1 between 0.7 and 1.1 ML. We have imaged the $\sqrt{3}\times\sqrt{3}$ and the 4×1 surfaces with the STM.

Figure 1 shows a STM image of an area of $\sqrt{3}\times\sqrt{3}$ surface, taken at positive tip bias. The hexagonal array of bright dots is consistent in both lateral geometry and spacing with $\frac{1}{3}$ ML of raised adatoms above threefold sites on an otherwise unreconstructed Si(111) surface. Recent

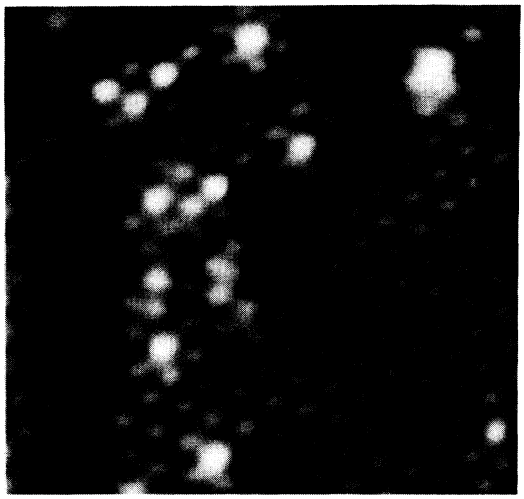

FIG. 1. A greyscale image of the In/Si(111)$\sqrt{3}\times\sqrt{3}$ surface. Bright dots represent areas of greater height. The tip was biased at +2 V, and the tunneling current was held constant at 0.5 nA. This image is approximately 100 Å square.

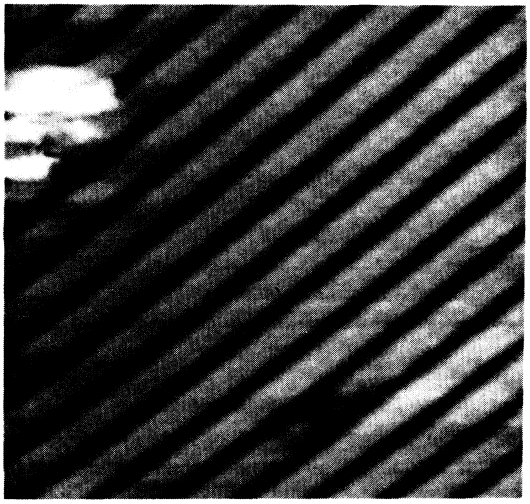

FIG. 2. An image of the 4×1 surface. The dark furrows define the long axis of the unit cell; they are spaced 15.4 Å apart, along the [$\bar{1}$01] direction.

theoretical calculations and angle-resolved photoemission measurements of the band structure both support a model where the raised adatoms would be In.[6,7] Band-structure considerations alone cannot differentiate between In adsorption on a threefold-hollow site (H_3) as opposed to a threefold site above a second-layer Si atom (T_4), although energy minimization calculations favor the latter choice by 0.2 eV/atom. The bright dots in the STM images are always in registry with a grid of triangles, even in cases where the periodicity is interrupted by disordered areas. There is no evidence of coadsorption on H_3 and T_4 sites on different areas of any single image that has been obtained.

There are also isolated defects visible. These have the appearance of single adatoms that have been raised from the surrounding atoms, while remaining more or less in lateral registry with their neighbors. The apparent height of these defects is about 0.6 Å in comparison to an average corrugation of 0.2 Å, measured at a tip-to-sample bias of +2 V. The origin of these defects is unknown.

Figure 2 shows an image of the higher coverage 4×1 reconstruction, taken at positive tip bias. The principal features are ridges running in the [$\bar{1}$10] direction separated by deep furrows. The spacing of the furrows defines the long axis of the 4×1 unit cell. The ridges themselves have a much smaller depression running down the middle, as well as structure along the rows that has a periodicity of the unit cell (define u = 3.84 Å = size of 1×1 unit cell). This particular image has not been corrected for thermal drift and so the structure along the rows is not at the correct angle to the row direction.

This image clearly rules out models of the 4×1 surface made up of pairs of 2×1 rows with some minor differences between the halves of the unit cell, such as small displacements of atomic positions.[3] It suggests instead a model with strong 4×1 character that is symmetric across the midpoint of the long axis of the unit cell.

Additional information is obtained by examining the difference between topographies seen at opposite bias polarities. Figure 3 shows pairs of traces from an image taken with the feedback voltage alternating between ±2 V on succeeding lateral scans of the surface. In this manner it is possible to take images at opposite polarities in parallel, simultaneously mapping the density of occupied and unoccupied states of the surface.[12] The traces taken at positive tip bias show the same structure as in the grayscale image (Fig. 2); ridges are defined by alternating deep and shallow furrows. At negative tip bias the difference between deep and shallow furrows disappears or even reverses; the amplitude traces look almost sinusoidal with a period of $2u$. There is a small shift of the positive bias traces with respect to the negative bias traces which places the two maxima of the negative traces asymmetrically with respect to the unit cell evident in the positive traces.

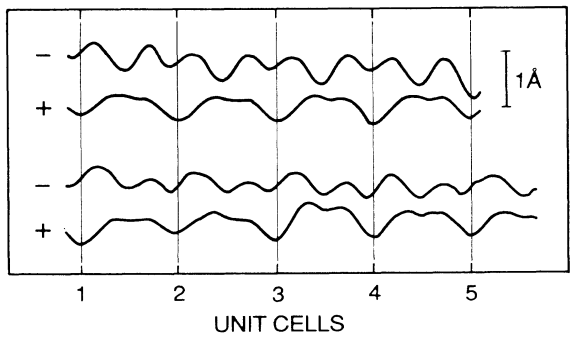

FIG. 3. Several horizontal amplitude traces from scanning the 4×1 surface. Pairs of traces were taken at opposite bias voltage polarities over the same line scan; the traces in each pair were acquired within 0.25 sec of each other. The cross sectional structure seen at positive tip bias corresponds to the appearance of the surface in Fig. 2. Vertical ticks mark the position of the minima in the positive bias traces which correspond to the $4u$ periodicity of the unit cell.

FIG. 4. A 200-Å-square area of the 4×1 surface showing several steps separating reconstructed terraces. The data are presented in a perspective view with simulated illumination. Step edges run preferentially in the ⟨110⟩ directions.

The size of the shift is not strictly reproducible from image to image and so the registration between the positive traces shown may not be accurate. It is reasonable to shift the negative bias traces slightly so that they are symmetric with respect to the unit cell. Positioned in this way, the maxima of the unoccupied states appear to straddle the positions of the maxima of the occupied states. This effect is reminiscent of the symmetric dimer structure of the Si(100)2×1 surface,[13,14] but of course the lateral scale in this case is double.

In addition to flat 4×1 areas, we have also imaged well-ordered steps separating reconstructed terraces. Figure 4 shows an area with many steps. Rows of 4×1 in all three possible directions are visible on different terraces. The orientation of the step edges is preferentially along the ⟨110⟩ directions. There is no correlation between the direction of a step and the orientation of rows on either adjacent terrace, nor is there a fixed relationship between the orientation of the rows on neighboring terraces. The height of single steps corresponds to the Si(111) double-layer step height of 3.1 Å.

Occasionally there are areas with little or no apparent corrugation that are bounded by step heights different from that between two 4×1 terraces. Figure 5(a) shows such a flat area adjacent to a large area of 4×1. These flat areas are probably due to the growth of In metal islands. These images were taken on samples at 1–1.2 ML In coverage. Epitaxial growth of In metal islands on the Si(111) surface has been seen at above 1-ML deposition at room temperature.[5,15] In such cases, LEED shows a 1×1 pattern rotated at 30° with respect to the substrate but otherwise similar to that of the In(111) surface. Growth of In metal on the 4×1 surfaces has also been seen at elevated temperatures, with a clear 1×1 diffraction pattern coming from the metal.[8] Figure 5(b) shows a raised hexagonal area with no apparent corrugation. In this case the boundaries of the island are not aligned with the surrounding reconstruction. The shape and thickness of the island suggest that it is a single close-packed layer of In atoms. The orientation of the island is consistent with the LEED observations.

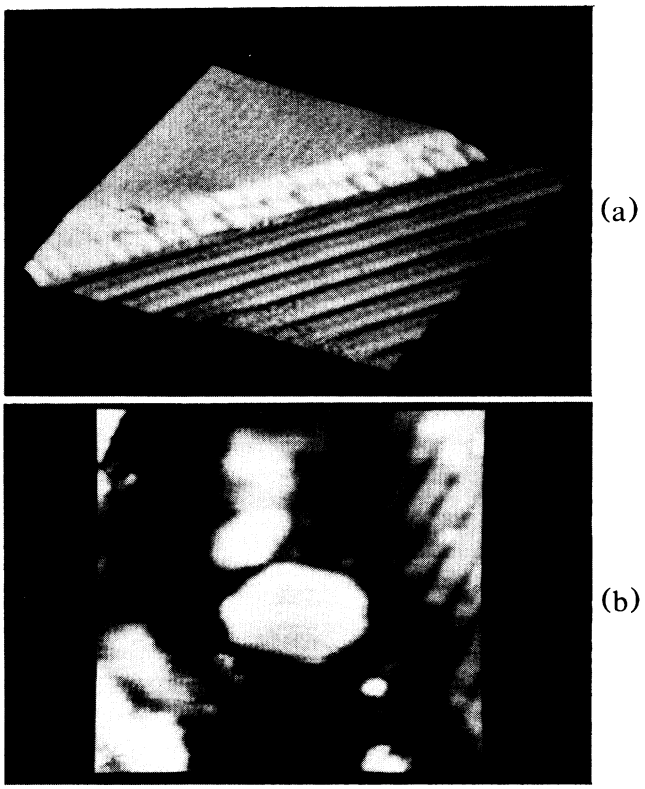

FIG. 5. (a) A flat area of In metal adjacent to a 4×1 reconstructed area. (b) A greyscale image of a hexagonal metal island. The height of the island is about 3 Å.

To summarize, we have presented preliminary results of a STM study on the In/Si(111) system. We have imaged two different ordered reconstructions of the surface. Images of the $\sqrt{3}\times\sqrt{3}$ surface support an existing model. The structure of the 4×1 surface is as yet unclear, although models consisting of paired 2×1 rows can be ruled out. Growth of flat metal islands on the 4×1 is also seen. Both the growth of metal, and the detailed nature of the 4×1 surfaces will be objects of further study.

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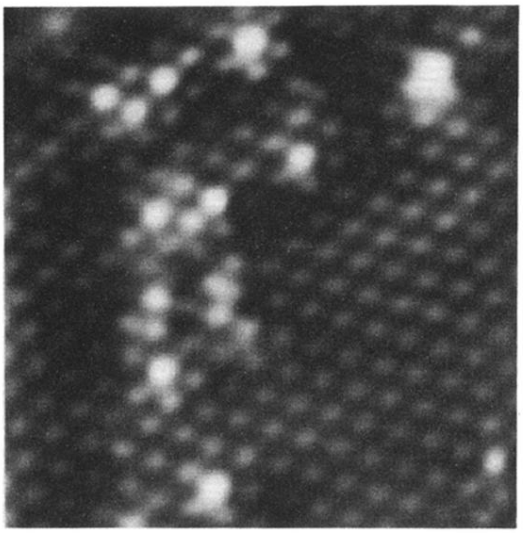
[1]J. J. Lander and J. Morrison, J. Appl. Phys. **36**, 1706 (1965).
[2]M. Kawaji, S. Baba, and A. Kinbara, Appl. Phys. Lett. **34**, 748 (1979).
[3]S. Baba, H. Hirayama, J. M. Zhou, and A. Kinbara, Thin Solid Films **90**, 57 (1982).
[4]H. Hirayama, S. Baba, and A. Kinbara, J. Appl. Phys. **25**, L452 (1986).
[5]M. K. Kelly, G. Margaritondo, J. Anderson, D. J. Frenkel, and G. J. Lapeyre, J. Vac. Sci. Technol. A **4**, 1396 (1986).
[6]J. M. Nicholls, P. Mårtensson, G. V. Hansson, and J. E. Northrup, Phys. Rev. B **32**, 1333 (1985).
[7]G. V. Hansson, J. M. Nicholls, P. Mårtensson, and R. I. G.

Uhrberg, Surf. Sci. **168**, 105 (1986).
[8]Zhou, Jun-Ming, Chin. Phys. **4**, 251 (1984).
[9]H. Yasunaga, Y. Kubo, and N. Okuyama, Jpn. J. Appl. Phys. **25**, L400 (1986).
[10]Sang-il Park and C. F. Quate, Appl. Phys. Lett. **48**, 112 (1986).
[11]Sang-il Park and C. F. Quate, Rev. Sci. Instrum. (to be published).
[12]R. M. Feenstra, W. A. Thompson, and A. P. Fein, Phys. Rev. Lett. **56**, 608 (1986).
[13]R. M. Tromp, R. J. Hamers, and J. E. Demuth, Science **234**, 304 (1986).
[14]R. J. Hamers, R. M. Tromp, and J. E. Demuth, Phys. Rev. B **34**, 5343 (1986).
[15]D. Bolmont, P. Chen, C. A. Sébenne, and F. Proix, Surf. Sci. **137**, 280 (1984).



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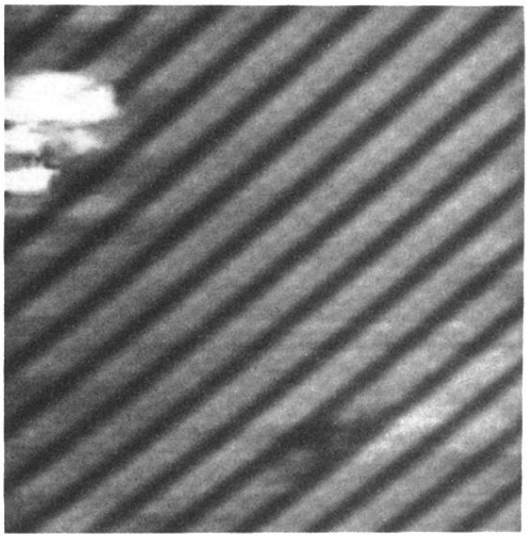

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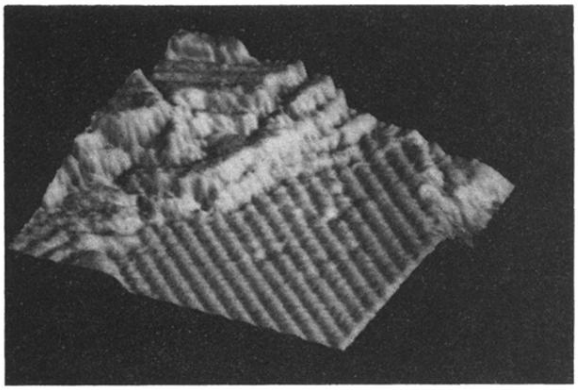

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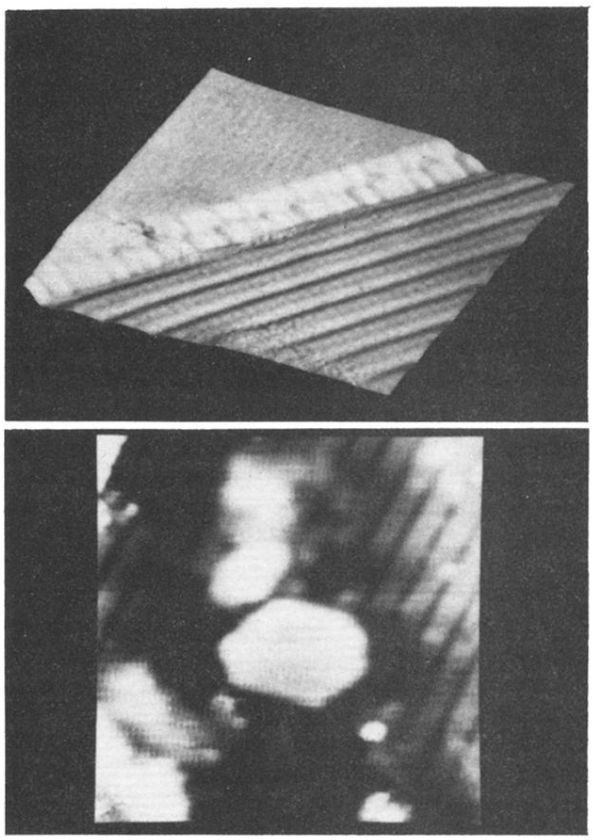

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