

## Intrarow diffusion of Au atoms in the Si(111)-(5×2)Au structure

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Intra-row diffusion of Au atoms in the Si(111)-(5×2)Au reconstructed structure has been observed by using high-temperature scanning tunneling microscopy. Loosely bonded Au atoms, which are arranged with  $2(n+1)a$  spacings at room temperature, diffuse in the twofold direction at higher temperatures among adsorbed sites arranged at  $2a$  intervals. These diffusing Au atoms seem to be the reason there is a nonintegral number of Au atoms in the (5×2) unit cell. [S0163-1829(96)09639-7]

The analysis of surface structures is a major part of surface science, but despite extensive studies, many surfaces are still under investigation. For example, the atomic arrangement of the Si(111)-(5×2)Au reconstructed structure is still unclear, though a large amount of information on the structure has been collected through a variety of analytical methods since its discovery by Bishop and Reviere in 1969.<sup>1</sup>

The (5×2) structure appears in the initial stage of Au adsorption on a Si(111)-(7×7) surface at substrate temperatures from 350 to 800 °C.<sup>2</sup> The saturation coverage of Au has been estimated to be 0.443 ML,<sup>3</sup> which indicates a nonintegral number (4.43) of Au atoms may exist in a (5×2) unit cell on average. The saturation coverage suggests that the (5×2) structure is disordered with partial occupancies of some Au adsorption sites; e.g., four Au atoms in some (5×2) unit cells and five in the other unit cells. These partial occupancies were assumed to explain the result of an x-ray-diffraction study.<sup>4</sup> Also, scanning tunneling microscopy (STM) images of the (5×2) structure show rows of bright protrusions running in the  $\langle 1\bar{1}0 \rangle$  direction with  $5a$  spacings.<sup>5-7</sup> In each row, the bright protrusions are irregularly arranged at  $2(n+1)a$  intervals. The irregularity seems to be related to the partial occupancies of Au adsorption sites. However, the x-ray standing-wave method<sup>8</sup> and transmission-electron-diffraction patterns<sup>9</sup> do not show such disorder except for phase slippage in the  $\langle 1\bar{1}0 \rangle$  direction. Recently, a transmission-electron-microscopy/-diffraction (TEM/TED) study has suggested that two Au atomic rows running in the  $\langle 1\bar{1}0 \rangle$  direction may exist,<sup>10</sup> which distribute only four Au atoms in a (5×2) unit cell. Thus, the problem of the nonintegral number of Au atoms in a (5×2) unit cell is still unsolved.

The growth process of the (5×2) structure has also been revealed by using real-space methods.<sup>3,11-13</sup> For instance, a (5×2) structure usually starts growing at a step edge of a (7×7) structure that runs in the  $\langle 1\bar{1}0 \rangle$  direction, and the twofold direction of the (5×2) structure is always parallel to that step edge. A domain of a (5×2) structure grows much faster in the twofold direction than in the fivefold direction. However, the origin of these characteristics is also still unclear.

STM has been used to study the surface dynamics, such as atomic level step fluctuations, on metal surfaces.<sup>14-16</sup> In this paper, we report on the intrarow diffusion of Au atoms, which is confirmed by the movement of bright protrusions in

STM observations at higher temperatures. The diffusing Au atoms seem to be the cause of the nonintegral number of Au atoms in a (5×2) unit cell.

The experiments were done using a high-temperature STM.<sup>17</sup> Gold was deposited onto a Si(111)-(7×7) surface whose temperature was kept at 500 °C by direct joule heating of the sample in an ultrahigh vacuum ( $1.3 \times 10^{-8}$  Pa). Observations were taken from the same sample at different substrate temperatures (room temperature up to 500 °C) after growth of the (5×2) structure. The direct joule heating was also used to hold the substrate temperature at the higher temperatures during the observations. The STM images were taken in a series at 40-sec intervals.

Figure 1 shows the Si(111)-(5×2)Au surface imaged at different temperatures. Figures 1(a)–(d) were taken at room temperature, 200, 250, and 500 °C, respectively. The sample position differs in each image due to thermal drift caused by the change in the substrate temperature.

Bright protrusions arranged in rows along the  $[1\bar{1}0]$  direction are clearly seen in the image taken at room temperature [Fig. 1(a)]. The rows are arranged with a spacing of  $5a$ . The direction in which the rows run corresponds to the twofold direction of the (5×2) structure.<sup>18</sup> The bright protrusions are

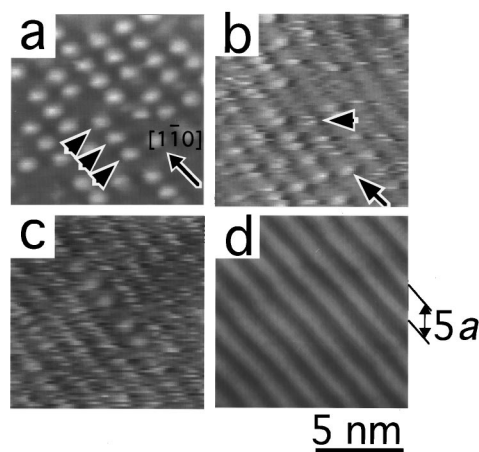


FIG. 1. A series of STM images of the (5×2) structure taken at different temperatures: (a) room temperature, (b) 200 °C, (c) 250 °C, and (d) 500 °C. The movement of the Au atoms, which appear as bright protrusions at room temperature, is clearly shown.

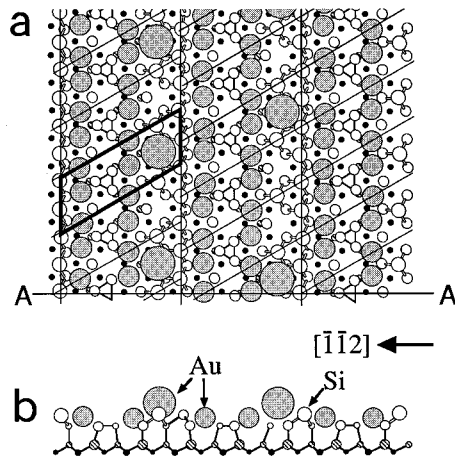


FIG. 2. Our structural model for the  $(5 \times 2)$  structure: (a) top view, and (b) side view. Gray circles represent Au atoms, and open circles represent Si atoms on top of the double-layer Si substrate.

irregularly arranged with  $2(n+1)a$  spacings in each row.<sup>5-7</sup> The arrowheads indicate protrusions arranged with the minimum spacing of  $4a$  within a row. Due to the nonuniformity of the arrangement, the density of the bright protrusions is less than 0.5 per  $(5 \times 2)$  unit cell. This density seems to coincide with the decimal part of the nonintegral number of Au atoms in a  $(5 \times 2)$  unit cell (i.e., 0.43). Accordingly, we attributed each bright protrusion to a single Au atom, and proposed a structural model of the  $(5 \times 2)$  structure which is shown in Fig. 2.<sup>19</sup> The Au atoms represented by large gray circles in Fig. 2 correspond to the bright protrusions in the STM image. The Au atoms represented by small gray circles form the two Au atomic rows suggested by the TEM/TED study<sup>10</sup> that distribute the integral part of the nonintegral number of Au atoms in a  $(5 \times 2)$  unit cell (i.e., 4).

In the image taken at 200 °C [Fig. 1(b)], short lines that look like *scratches* are observed within each row, as indicated by the arrowhead. These scratches were caused by movement of the Au atoms, which appear as bright protrusions at room temperature, during image acquisition. A scratch indicates that a Au atom was there when the STM tip scanned the line that included the scratch, but the Au atom was not there when the adjacent lines were scanned. Therefore, the scratches are parallel to the direction of the tip scanning. Gold atoms that did not move during the tip scanning at 200 °C continued to appear as bright protrusions, as indicated by the arrow.

In the observation at 250 °C [Fig. 1(c)], the scratches filled the rows almost completely, and few bright protrusions could be seen. At 500 °C [Fig. 1(d)], even the scratches became blurred due to the extensive movements of the Au atoms. As a result, only bright rows were observed.

This series of STM images clearly shows the diffusion of Au atoms along the rows at higher temperatures. The movement became more frequent as the temperature was raised. Since the movement has never been observed at room temperature, the influence of the proximity of the STM tip on the movement is likely to be negligible or nonexistent. The diffusing Au atoms are probably the loosely bonded Au atoms,

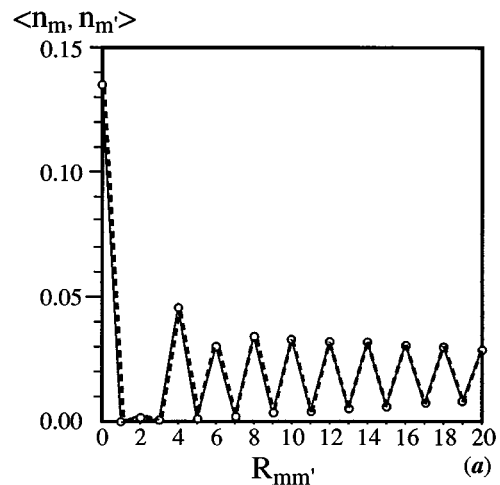


FIG. 3. Correlation functions,  $\langle n_m, n_{m'} \rangle$ , along the twofold direction obtained from experimental images (solid line) and a simulation (dashed line) (Ref. 21). Here,  $n_m$  ( $n_m = 0, 1$ ) is the occupation number of the  $m$ th site along the row.

as has been suggested based on a reflection high-energy electron diffraction study.<sup>20</sup> We will refer to these Au atoms as *diffusing* Au atoms. The Au atoms represented by the small gray circles in Fig. 2 are considered strongly bonded Au atoms.

The nonuniform arrangement of the diffusing Au atoms has been well explained theoretically by assuming a repulsive force exists between the diffusing Au atoms which causes the minimum spacing of  $4a$ . Figure 3 shows the positional correlation functions of the diffusing Au atoms along the rows obtained by Yagi *et al.*<sup>21</sup> The experimental correlation function obtained from our STM images taken at room temperature almost coincides with the simulated one with fitting parameters of repulsive force and chemical potential. The diffusion is also expected to be dominated by the repulsive force and chemical potential.

The movement of the diffusing Au atoms in a row is clearly shown in Fig. 4. Figures 4(a)–(e) are magnified images of a series taken at 40-sec intervals (160 ms/line).

In addition to the scratches in each image, the changes in the position of the bright protrusions between the images clearly show that the diffusing Au atoms moved among adsorption sites arranged at  $2a$  intervals. For instance, the left-end Au atom in the row moved among the sites, as indicated

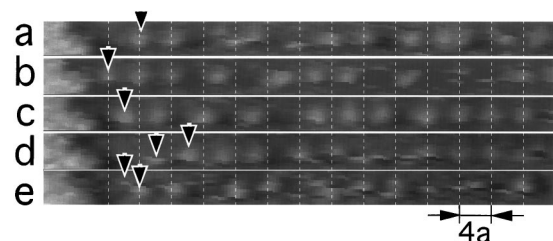


FIG. 4. A series of STM images showing intrarow diffusion of the Au atoms at 200 °C. White dashed lines are drawn at  $4a$  intervals. The edge of a  $(7 \times 7)$  terrace is seen at the left end of the row.

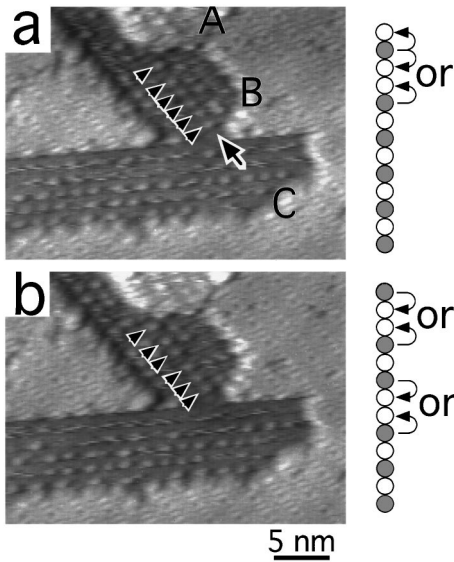


FIG. 5. A pair of STM images taken at 200 °C. The arrangements of the Au atoms indicated by the arrowheads are shown besides each image. Open and hatched circles indicate unoccupied and occupied sites of  $2a$  intervals, respectively.

by the arrowheads. It is also clearly shown that the minimum spacing of  $4a$  between the diffusing Au atoms was also maintained during the movements. This result suggests that the repulsive force between the diffusing Au atoms is also effective during the movement.

Figure 5 is a pair of STM images taken at 200 °C, in which three domains of the  $(5\times 2)$  structure can be seen, as indicated by A, B, and C.

In the five rows of domain C, scratches are most common in the upper two rows, while bright protrusions are most common in the lower three rows of both images. This indicates that the diffusing Au atoms in the upper two rows were moving more frequently than those in the lower three rows. Therefore, in addition to the substrate temperature, there appears to be another factor which affects the movement. This factor is most likely the density of diffusing Au atoms in a row, which differed among the rows even within the same domain.

In the short row next to the long rows in domain B (indicated by the arrow), the high density of diffusing Au atoms makes movement difficult. There are no scratches in this row but six bright protrusions can be seen in both Figs. 4(a) and (b), as indicated by the arrowheads. Therefore, there appeared to be six diffusing Au atoms in the row, which did not move frequently. The density of diffusing Au atoms in this row was 0.46 per  $(5\times 2)$  unit cell, which was higher than the average in this experiment ( $\sim 0.35$ ). The nearest-neighbor sites of each occupied site should be unoccupied due to the repulsive force between the diffusing Au atoms. As a result, at most two Au atoms were able to change sites at the same time, as shown in the schematics. Thus, movement is restricted by a higher density of diffusing Au atoms.

Figure 6 is an occupied state image of the  $(5\times 2)$  structure taken at room temperature. Bright protrusions arranged at  $2a$  intervals, which were rarely observed at quenched surfaces,

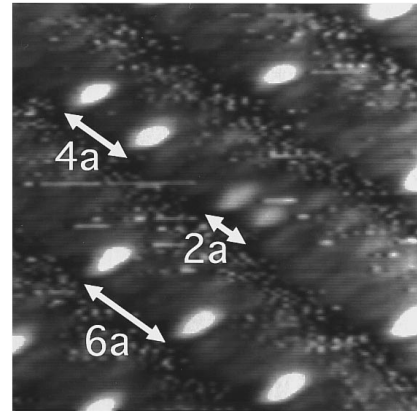


FIG. 6. An occupied state image of the  $(5\times 2)$  structure taken at room temperature ( $Vt=2$  V). The lower brightness of the Au atoms arranged at  $2a$  intervals, compared to those arranged at  $4a$  intervals or longer, suggests a lower charge transfer to the Au atoms.

are less bright than the other bright protrusions arranged at  $4a$  intervals or longer. Gold atoms in the  $(5\times 2)$  structure are thought to be negatively charged based on experimental results concerning electromigration.<sup>22</sup> Therefore, the lower brightness suggests a lower charge transfer to the Au atoms arranged at  $2a$  intervals than to those arranged at  $4a$  intervals or longer. Coulomb repulsion between the denser diffusing Au atoms seems to be the cause of the lower charge transfer, which results in higher surface energy. Therefore, diffusing Au atoms are arranged at  $4a$  intervals or longer. In other words, the contrast indicates that the bright protrusion consists of a negatively charged atom (i.e., a Au atom) since the lower brightness is unlikely to indicate a more positively charged atom.

Since diffusing Au atoms do not arrange uniformly at  $4a$  intervals, deposited Au atoms can be incorporated into a row as diffusing Au atoms without growth of the row. However, the incorporation raises the density of diffusing Au atoms in the row. The higher density of diffusing Au atoms will increase the energy of the row, which will eventually lead to growth of the row to reduce the higher density. By diffusion, Au atoms are easily supplied to the end of the row where the growth occurs. This would be the origin of the anisotropic growth rate of the  $(5\times 2)$  structure. The growth not only increases the number of adsorption sites in a row, but also decreases the number of diffusing Au atoms by incorporating diffusing Au atoms into the underlying two Au atomic rows (see Fig. 2). Thus, the density varies drastically before and after the growth, which causes the differences in density between the rows.

When the whole surface was covered by the  $(5\times 2)$  structure, the higher density could not be reduced by further growth of the row. Therefore, further incorporation of deposited Au atoms into a row makes the  $(5\times 2)$  structure unstable. This instability seems to cause the phase transition to the  $(\sqrt{3}\times\sqrt{3})$  structure before a uniform arrangement of the diffusing Au atoms at  $4a$  intervals occurs. This is consistent with the report that the Au coverage for the phase transition is slightly larger than when the entire surface is covered by the  $(5\times 2)$  structure.<sup>3</sup>

The observations reported in this paper clearly show the intrarow diffusion of loosely bonded Au atoms at higher temperatures. The diffusing Au atoms moved among the sites arranged at  $2a$  intervals in each row. We believe that this diffusing Au atom is the reason there is a nonintegral number of Au atoms in the  $(5\times 2)$  unit cell. This diffusing

Au atom should be taken into account in structural analyses of the  $(5\times 2)$  structure.

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<sup>18</sup>Fine structures showing two-times periodicity are seen in each row in high-resolution STM images (Refs. 5–7), though they are not seen in Fig. 1(a) due to the low resolution of the image.  
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