Formation of Facet Structures by Au Adsorption on Vicinal Si(111) Surfaces

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Scanning tunneling microscopy (STM) and reflection-high-energy electron diffraction (RHEED) were used to observe changes in facet structures induced by depositing Au atoms on vicinal Si surfaces misoriented from (111) toward [112] and [112] directions. The facets structures were found to be quite different from each other for the two misorientations. Several kinds of one-dimensional stripes were observed on different facets, and the Au coverage for each facet structure was determined. The surface was almost uniformly covered by (775) facets for [112] vicinal by 0.25 monolayer coverage of Au, while by (557) facets for [112] one at 0.2 ML. High-resolution STM images are also presented and discussed in relation to the previously proposed models of atomic structures.

Keywords: Vicinal surfaces; Facets; Si; Au; Scanning Tunneling Microscopy; Reflection-High-Energy Electron Diffraction; One-dimensional structures

I. INTRODUCTION

Nanostructures and low-dimensional structures generated by metal adsorptions on semiconductor surfaces have attracted a considerable interest from technological as well as academic points of views. Among them, facet surface structures induced by Au adsorptions on vicinal Si(111) surfaces are known to introduce one-dimensional (1D) metallic structures, such as Au/Si(557)[1–4], Au/Si(335)[5] and Au/Si(553)[6] surfaces. Due to their electronic instability of the low dimensionality, the systems have been playgrounds to study non-Fermi liquid behaviors of electrons and low-dimensional phase transitions [1–8].

The surfaces are prepared on Si(111) wafers with a miscut angle toward [112] or [112] direction. Due to the symmetry of bulk Si crystal structure, the surfaces misoriented towards these directions have inherently different structures from each other. Figure 1 shows the ideally truncated surfaces of misoriented Si(111) crystal toward [112] (left) and [112] (right) directions, respectively. These two surfaces have different chemical bond configurations at step edges; only one dangling bond (DB) at a step-edge Si atom for the [112]-directed miscut, while two DB's for the [112] case.

Gold adsorption on these two surfaces also show a distinction between them. The previous electron diffraction studies have provided detailed phase diagrams of long-range orders in surface structures with various Au coverages on Si(111) crystals with miscut angles of 4.3° toward [112] direction and 10.5° toward [112] direction.[9, 10]. Local structures on these vicinal surfaces, on one hand, have investigated only with limited Au-coverage ranges with different preparation procedures. In order to understand formation processes of Au-induced 1D nanostructures on vicinal Si surfaces, it is essential to pursue changes of local structures with Au adsorption on the surfaces in systematic ways. Especially, the structure of Au/Si(111) with miscut angles of 9° to 10° is very interesting and important because they provide 1D electronic systems that have recently attracted a considerable attention due to the exotic low dimensionality [1–4]. A group insists a character of Tomonaga-Luttinger liquid in the surface states of a Au-induced Si(557) facet [1], while the other groups present a Fermi-liquid picture for seemingly the same facet [2–4].

In the present work, we have performed systematic measurements by scanning tunneling microscopy (STM) and reflection-high-energy-electron diffraction (RHEED) on the initial growth of Au on Si(111) wafers misoriented by 9.45° toward [112] and [112] directions. Morphological transformations of facet structures upon Au adsorption at 600 ~ 700°C were observed in high-resolution STM images. Changes in the overall features were basically consistent with the previous electron-diffraction results [9, 10], but several new local structures were found which might be a key to the debate on the electronic structure.

II. EXPERIMENTAL

The experiments were performed using a commercial ultrahigh vacuum STM (UNISOKU USM-802 type) equipped with a RHEED system and evaporation sources. The base pressure of the chamber was less than 6 × 10−11 Torr. All STM images shown here were taken with elec-

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trochemically etched tungsten tips in the constant-current mode at room temperature (RT).

Two types of vicinal Si crystals (P-doped, 1 \sim 10^2 \text{cm at RT}) were used; one with a miscut of 9.45° toward [112] direction and the other toward [112] direction from (111) surface. The samples were resistively heated with direct current parallel to the surface steps ([110] direction) in ultrahigh vacuum. After enough outgassing of the samples at 650°C, a clean surface was prepared in a procedure, following the previous report[11]. After cleaning by 1250°C flashing for 10 seconds, the sample was quenched to 800°C and annealed at this temperature for 7 minutes, and then the heating current was slowly reduced to 0 A for 5 minutes. Gold was evaporated from a hot alumina basket in the pressure kept below 5 \times 10^{-10} \text{Torr during deposition. By following the phase diagrams in the previous reports [12, 13], the Au coverage was separately calibrated by STM images and RHEED patterns by depositing Au on a flat Si(111) surface. In brief, the Au coverages of 0.44 and 0.67 ML were referred by completions of 5 \times 2 and \sqrt{3} \times \sqrt{3} phases, respectively. One ML corresponds to the atom density of the topmost layer on Si(111) surface, 7.8 \times 10^{14} \text{atoms/cm}^2. All RHEED patterns which are shown in this paper were taken at 12keV.

### III. RESULTS AND DISCUSSIONS

#### A. Samples misoriented toward [112] direction

Figure 2 shows typical changes in the surface (facet) structures during Au deposition on a [112]-miscut Si(111) crystal at 600°C. At each stage of deposition, the long-range order was checked by RHEED (shown in the left column in Fig. 2) before STM observations. Before the Au deposition, the surface, as shown in Fig.2(a), consists of wide 7\times7 terraces and step bunching regions (upper-left in the STM image of Fig. 2(a)), as schematically shown in the right column. The steps run parallel to [110] direction. This surface clearly shows the 1/7th-order RHEED spots which come from the wide 7\times7 terraces.

After Au deposition of 0.25 ML, the surface shows a regular step structure or a facet structure (Fig.2(b)), in which white rows are located at step edges. The terrace width is 2.10 nm which equals to 6_{1 \frac{1}{4}}{a_1} (a_1 is a half distance to the second nearest neighbor in the ideally truncated Si(111) \times 1 surface, corresponding to 0.332 nm, as shown in Fig. 1(a) [14]). Since the facet angle is 8.48° as calibrated from the height of a single monatomic step (0.313nm) and the width of terraces in the image, the observed surface is a (775) facet. The RHEED pattern shows sharp fractional spots corresponding to the regular step arrays, as well as a half-order ring indicating a double-periodicity modulation along the narrow terraces.

Further Au deposition up to 0.4 ML resulted in a surface consisting of a mixture of (111) flat surface areas with a 5 \times 2-Au structure and a small fraction of (553) facets, as shown in Fig. 2(c). The STM image of a Si(111)-5 \times 2-Au structure is seen at the upper-left part in Fig.2(c), together with a step structure of a (553) facet at the center in this image. The RHEED shows sharp 1/5th fractional spots coming from both of the (553) facets and (111) terraces, and also a half-order ring. As the Au coverage increases to 0.55 ML, a RHEED pattern of Si(111)\sqrt{3} \times \sqrt{3}-Au reconstruction appears and coexists with that of (553) facets. Figure 2(d) is a STM image of the (553) facet after 0.55ML Au deposition, which is the same as those of the (553) facets taken at 0.4 ML coverage. In the image, white lines and black lines along [110] direction are terraces and steps, respectively, as indicated by a white thin line in the middle of the image. The terrace width is 1.44 nm (=4_{1 \frac{1}{4}}{a_1}) and the facet angle is 12.3°. Since the present Si wafer has a misorientation angle of 9.45°, this large facet angle results in a formation of so-called "hill and valley structure"[10] at 0.4 and 0.55 ML coverages.

The present results are basically consistent with a phase diagram reported by the previous Spot-Profile-Analysis-Low-Energy-Electron Diffraction study of Au on Si(111) with a miscut of 4.3°[9]. However, while their phase diagram shows a mixture of flat surfaces and facet phases at each Au coverage, the present STM results provide a formation of almost a single phase of Au/Si(775) at \sim 0.25 ML coverage. This is because the miscut angle of (775) facet, 8.48°, is close to the miscut angle, 9.45°, of our crystal.

Figure 3 shows a high resolution STM image and line profiles of a (775) facet at 0.25 ML Au deposition. Bright and dark rows are observed parallel to the steps. The rows evidently show a modulation of a double (2a_0) periodicity along them, indicating a Si(775)1\times 2-Au structure (a_0 is a lattice constant of (111) surface, 0.383nm, as shown in Fig. 1(a)). As shown in a line profile in Fig.3(b), a simple double-periodicity (2a_0) corrugation is observed along the dark rows, while a modulation with the unit periodicity (a_0) is superimposed on the double-periodicity corrugation along the bright rows as shown in Fig. 3(c). Up to now, two models are proposed for the atomic structure of the (775) facet based on their STM images [9, 14]. In both of the models, each bright oval on the (775) facet is assumed to correspond to a single Au atom separated by 2a_0 spacing with each other along the row. This is, however, not in accordance with the present high-resolution STM results, because the arrangement of Si atoms in the dark rows is also modulated with 2a_0 periodicity along the rows, as shown in the line profiles in Fig. 3(b). Comparisons between the present results and proper STM simulations including a reconstruction in the Si substrate are highly required.

Figure 4(a) shows STM images of the (553) facet structure at 0.45 ML Au coverage, taken at a tip bias of 1.79 V. The surface is again composed of chains parallel to the steps with interruption by crevices. The line structures in the chains are imaged at a tip bias of 0.99 V as shown in Fig.4(b). The chains consist of ellipses aligned with 2a_0 periodicity. The size of an ellipse indicates that it is an assembly of several Au and/or Si atoms. A previous report [9] suggests that the assembly is made of two Au atoms. The width of the crevices is 2a_0 or 4a_0, indicating that the crevices are defects of one or two assemblies.

In the case of a low misorientation angle, 4° toward [112] direction from (111) surface, the Au deposition below 650°C produces (111) flat terraces with the 5 \times 2 structure, coexisting with stepped regions [15], though our results for the 9.45° vicinal surface show the formation of the uniform (775) facet structure. Above 650°C, however, Au on the 4°-vicinal surface also produces the (775)
FIG. 2: A series of RHEED patterns (left column) and filled-state STM images (center column) taken at room temperature after the intermittent deposition of Au at a substrate temperature of 600°C, with various Au coverages on a Si(111) surface misoriented by 9.45° toward [112] direction, together with schematic illustrations of stepped structures (right column). Fundamental reciprocal lattice points of the Si(111)1 × 1 unit are presented at the bottom of RHEED patterns. The RHEED electron beam is perpendicular to the steps in (a), and parallel to the steps in (b)-(d). The STM image size is 25nm × 25nm. The total amount of deposited Au is (a) 0, (b) 0.25 ML, (c) 0.40 ML, (d) 0.55 ML, respectively. The tip bias $V_t$ is (a) 0.79 V, (b) 0.99 V, (c) 1.49 V, and (d) 1.49 V, respectively.
The 1/7-th order streaks are clearly observed in both images. White ellipses in (b) are for eye guide. The lozenge by black lines in Fig. 5(a) represents the 7\times7 arrangement of narrow terraces with the 7\times7 structure. Therefore, we can say that the (775) facet structure is the most stable at 0.25 Au coverage. However, upon further Au deposition the (775) facets break into the mixed phase of the (553) facets and the (111)\times2 terraces (Fig. 2(c)), which means that the (775) facet becomes less stable with additional Au adsorption.

**B. Samples misoriented toward [112] direction**

Figure 5 shows changes in RHEED patterns and STM images during Au deposition on a Si sample at 700 ∼ 750°C. Figure 5 (a) is a typical image of the clean surface before the Au adsorption. The surface shows a periodic arrangement of narrow terraces with the 7\times7 structure separated by triple steps running along [110] direction. The lozenge by black lines in Fig.5(a) represents the 7 \times 7 unit cell. The terraces width equals to a single 7 \times 7 unit cell. The 1/7-th order streaks are clearly observed in RHEED.

After 0.16ML deposition, narrower stripes emerge along the steps as shown in Fig.5(b). The 7 \times 7 streaks in RHEED almost disappear, instead streaks connecting the fundamental spots in the direction perpendicular to the steps appear. With further deposition up to 0.2 ML, the surface becomes a uniform (557) facet as shown in Fig.5(c). The (557) facet has a terrace width of 1.88nm, corresponding to 5\frac{4}{7}a_1, and posses a facet angle 9.45° that is exactly the same as the sample miscut angle. We could detect the completion of the (557) facet formation by RHEED pattern in which streaks in Fig.5(b) changed into spots as shown in (c). These sharp spots correspond to the regular array of terraces. In the STM image (c), we notice a regular array of small protrusions with double periodicity along the stripe direction. This corresponds to faint half-order streaks in RHEED pattern, as indicated by arrowheads between the fundamental spots in (c). We also notice bigger protrusions along the stripes in the STM image (c), which are not regularly arranged, but the minimum separation between them is 4a_0.

At 0.24 ML coverage, the surface is still mostly covered with the (557) facets, but two different facets, (335) and (556), appear as shown in Fig.5(d). The facet angles of (335) and (556) are 14.4° and 5.05°, and their terrace widths are 1.22nm and 3.54 nm, respectively. At the boundary between the two facets, terraces of intermediate widths are observed. Therefore, many fractional-order spots appear on the Laue zones in RHEED pattern, which shows different terrace widths as shown in (d).

At 0.4 ML coverage, a Si(111)-5\times2-Au surface structure appear on ∼3.3nm wide (111) terraces, as shown at the lower right in the STM image of Fig.5(e). The terrace width corresponds to the two unit cells along the \times5 direction, separated by (556) and (335) facets. The formation of the 5\times2-Au flat terraces require wider regions of (335) facets to achieve the vicinal angle 9.45° as a whole, though the (556) facets are still visible in STM images as shown in Fig.5(f). Difference in (556) facet images between Figs.5(d) and (f) are due to the different tip bias voltages.

These results are summarized as follows. (i) Before the Au adsorption, a regular array of narrow terraces with Si(111)-7\times7 structure, separated by triple steps. (ii) (557) facets at 0.2 ML Au coverage. (iii) (335) and (556) facets coexisting with (557) facets at ∼0.3 ML Au coverage. (iv) (111) terraces with the 5\times2-Au structure and (335)/(556) facets coexisting at > 0.4 ML coverages. The transformation in structure is schematically illustrated in the right column of Fig.5. These results are basically consistent with a phase diagram previously determined by Low-Energy Electron Diffraction with a 10.5° miscut sample[10].

The saturation coverage of Au for the (557) facet formation was determined to be 0.2 ML in the present study, which was equal to that in the previous reports[2, 3, 17]. This coverage corresponds to one Au atom in the unit cell of Si(557)-Au facet structure. Using this coverage as a reference, Au coverages of the (556) and (335) facets are inferred as follows. With an increment of Au coverage from the (557) facet structure, the (556) and (335) facets appear as shown in Fig.5. We have found that the step density does not alter between at 0.2 ML coverage (c) and at 0.24 ML (d). This suggests that the (556) terraces are formed by widening of the (557) ones, while the (335)
FIG. 5: RHEED patterns and STM images at various Au coverages on a Si(111) surface misoriented by 9.45° towards [\bar{1}1\bar{2}] direction, with schematic illustrations of step structure. The incidence direction of RHEED beam is perpendicular to the steps for (a), (b), (c), and (e), and parallel to the steps for (d) and (f). The STM image size is 12.9 nm × 12.9 nm. The amounts of Au are (a) 0, (b) 0.16, (c) 0.20, (d) 0.24, (e) 0.40, (f) 0.40 ML, respectively. The tip bias $V_t$ is (a) 1.99V, (b) 1.49V, (c) -2.00V, (d) -1.50V, (e) 1.49V, (f) 1.49V, respectively.
FIG. 6: (a) A STM image of a (557) facet. The tip bias $V_t$ is 1.99V. (b) A RHEED pattern of the (557) facet. Electrons were irradiated in perpendicular to the step. (c) A high resolution STM image of the (557) facet. $V_t$ = -1.00V. (d) Line profiles along the black lines A-C and D-E in (c). The distance between the two peaks is 0.77nm which is 2$a_0$ in line A-C, while 1.57 nm (4$a_0$) in line D-E. (e) Filled state and empty state STM images of the (557) facet. $V_t$ =0.69V (left) and -1.20V (right), respectively.

ones are formed by narrowing the (557) terraces. From comparisons in the terrace width and Au coverage, we estimated one Au atom in the (335) facet unit cell and two or three Au atoms in the (556) one. By considering the crystal structure, we can say that seven (557) terraces (the terrace width $W = 5\sqrt{2}a_1$) can change into five (335) terraces ($W = 3\sqrt{2}a_1$) and two (556) terraces ($W = 10\sqrt{2}a_1$) while conserving the step density and the macroscopic miscut angle: $7 \times 5\sqrt{2}a_1 = 5 \times 3\sqrt{2}a_1 + 2 \times 10\sqrt{2}a_1$. If two (three) Au atoms are assumed in the (556) facet unit cell, the coverage should be 0.26 (0.32) ML for complete transformation to the (556)/(335) mixed facet structure from the (557) facet. Since our STM observations revealed that large areas of (557) facet remained at 0.24 ML, three Au atoms are favored in the (556) unit cell. Despite this simple estimation, the result is consistent with the previous STM research [16].

As shown in Fig. 5(c), the (557) facet structure is formed uniformly at 0.2 ML Au deposition at 700°C. This surface has been a center of debates for exotic low-dimensional physics [17, 18]. Contrary to the simple electronic band structure reported, the STM images are quite complicated as shown in Fig. 5(c), especially bright protrusions exist non-periodically. Thus, for proper interpretations of the low-dimensional electronic properties, it may be requested to find natures of these protrusions and control the number density. For this, we increased number of the protrusions by a procedure given below. Figure 6(a) shows a STM image of Au/Si(557) prepared by 0.32 ML Au deposition at 700°C followed by 950°C annealing. The half-order streaks were observed in RHEED just after the deposition, which corresponds to the regular array of small protrusions as seen in Fig. 5(c). But after the annealing at 950°C, the 1/4-th streaks appeared in RHEED as shown in Fig.6(b). The 4$a_0$ periodicity corresponds to the regular array of bigger protrusions along the stripes as seen in Fig. 6(a) and in a magnified image of Fig. 6(c). The protrusions, labeled ‘P’ in Fig. 6(c), are the same as the bigger protrusions in Fig. 5(c). But its number density is clearly different between Fig.6(c) and Fig.5(c). The distance between the bright protrusions is 4$a_0$ as shown in a line profile D-E in Fig.6(d). Thus, the observed 1/4-th streaks in RHEED pattern of Fig.6(b) originate from this 4$a_0$ periodicity of the protrusions along the stripes. Since more protrusions appear after larger amount of Au deposition than the saturation coverage of the (557) facet, the protrusions may be attributed to Au adatoms (in spite of some desorption of excess Au atoms by 950°C annealing). The assignment is consistent with the previous STM work that shows the minimal number of protrusions by 0.2 ML deposition at 700°C followed by 950°C annealing [2, 19]. Beside the 4$a_0$-periodicity protrusions, we find 2$a_0$-periodicity protrusions as shown in a line profile A-C in Fig.6(d). Comparisons between the recent structure model of the (557) facet [17, 19] imply that these small protrusions with 2$a_0$ periodicity are thought to be the Si adatoms in the model. This assignment is consistent with STM simulation [17] in which the empty-state STM image at high bias voltages (above 0.5V) is dominated by the Si adatoms and the filled-state STM image shows the zigzag chain of the Si adatoms and the Si rest atoms. Figure 6(e) shows our filled-state (left) and empty-state (right) STM images. In the filled-state STM image, zigzag chains are observed (highlighted with white line in the figure), while it is hard to observe the zigzag chains in the presence of the bright 4$a_0$-periodicity protrusions. The bright protrusions also affect the Si adatom image in the empty state. The width of the Si adatom image is changed in the presence of the bright protrusion (compare B with C in fig.6(d)).
Facet structures induced by Au adsorption on vicinal Si(111) surfaces misoriented by 9.45° towards [112] and [112] directions were systematically observed by STM and RHEED as a function of Au coverage. Several types of facets were observed: (775) at 0.25 ML, (553) at 0.45 ML for [112] samples, and (557) at 0.30 ML for [112] samples. An interesting thing is that a single-phase facet almost uniformly covers the whole surface around 0.2–0.25 ML coverage. Fine STM images revealed the double-periodicity protrusions along the stripes ([110] direction) in the (557), (556), (775) and (553) facets at room temperature. On the (557) facet, bigger protrusions were also found with the four-fold periodicity. Since this type of protrusions may be a key for the discrepancy on the low-dimensional electronic behavior [1–4], their density should be precisely controlled.

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[1] P. Segovia, D. Purdie, M. Hengsberger and Y. Baer, Nature (London) 402, 504 (1999).
[2] R. Losio, K.N. Altmann, A. Kirakosian, J.-L. Lin, D.Y. Petrovykh and F.J. Himpsel, Phys. Rev. Lett. 86, 4632 (2001).
[3] K.N. Altmann, J.N. Crain, A. Kirakosian, J.-L. Lin, D.Y. Petrovykh, F.J. Himpsel and R. Losio, Phys. Rev. B 64, 035406 (2001).
[4] J. R. Ahn, H. W. Yeom, H. S. Yoon, and I.-W. Lyo, Phys. Rev. Lett., in press (2003).
[5] P. Starowitz, O. Gallus, Th. Pillo and Y. Baer, Phys. Rev. Lett. 89, 256402 (2002).
[6] J.N. Crain, A. Kirakosian, K.N. Altmann, C. Bromberger, S.C. Erwin, J.L. McChesney, J.-L. Lin and F.J. Himpsel, Phys. Rev. Lett. 90, 176805 (2003).
[7] George Grüner, Density Waves in Solids (Addison-Wesley, Massachusetts, 1994).
[8] J. Voit, Phys. Rev. B 47, 6740 (1993).
[9] R. Hild, C. Seifert, M. Kammler, F.-J. Meyer zu Heringsdorf, M. Horn-von-Hoegen, R.A. Zhachuk and B.Z. Olsahanetsky, Surf. Sci. 512, 117 (2002).
[10] H. Minoda, T. Shimakura, K. Yagi, F.-J. Meyer zu Heringsdorf and M. Horn von Hoegen, Surf. Sci. 432, 69 (1999).
[11] A. Kirakosian, R. Bennewitz, J.N. Crain, Th. Fauster, J.-L. Lin, D.Y. Petrovykh and F.J. Himpsel, Appl. Phys. Lett. 79, 1608 (2001).
[12] R. Plass and L.D. Marks, Surf. Sci. 380, 497 (1997).
[13] T. Nagao, S. Hasegawa, K. Tsuchie, S. Ino, C. Voges, G. Klos, H. Pfnür and M. Henzler, Phys. Rev. B 57, 10100 (1998).
[14] M. Shibata, I. Sumita and M. Nakajima, Phys. Rev. B 53, 3856 (1996).
[15] M. Shibata, I. Sumita and M. Nakajima, Phys. Rev. B 57, 2310 (1998).
[16] M. Shibata, I. Sumita and M. Nakajima, Phys. Rev. B 57, 1626 (1998).
[17] D. Sánchez-Portal and R.M. Martin, Surf. Sci. 532-535, 655 (2003).
[18] M. Schöck, C. Sürgers and H.v. Löhneysen, thin solid films 428, 11 (2003).
[19] I.K. Robinson, P.A. Bennett and F.J. Himpsel, Phys. Rev. Lett. 88, 096104 (2002).