

## Step Edges as Reservoirs of Ag Adatom Gas on a Si(111) Surface

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The Si(111) $\sqrt{3} \times \sqrt{3}$ -Ag surface, prepared under various annealing conditions, was systematically investigated by scanning tunneling microscopy (STM) and reflection-high-energy electron diffraction (RHEED). Although the RHEED patterns were seemingly the same for all cases, the STM images showed a clear difference in surface morphology; step edges were roundish and decorated by random adatom adsorption when annealed below 600°C, while steps were straight with periodic protrusions along them by higher-temperature and prolonged annealing. Such distinctions may be the origin for different results in core-level photoemission spectroscopy (CLPES); the step edges may act as a reservoir of on-terrace adatom gas of Ag that makes the CLPES spectra broaden for samples with insufficient annealing, while the sufficient annealing removes the reservoir and adatom gas, resulting in very sharp CLPES spectra. [DOI: 10.1143/JJAP.42.4894]

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### 1. Introduction

Surface superstructures induced by metal adsorption on semiconductor surfaces have now become important platforms for exploring low-dimensional physics as well as application to nanotechnology. With various combinations of metal adsorbates and semiconductor substrates, an abundance of surface ordered phases has been reported to exhibit new intriguing physical properties. This is due, on one hand, to great advances in experimental techniques such as very high-resolution electron spectroscopies and microscopies. However, in spite of very precise measurements on an atomic scale, there still remain many controversial issues regarding surface structures that are partially due to ambiguous sample preparation procedures. A typical example is Si 2*p* core-level photoemission spectroscopy (CLPES) results of the Si(111) $\sqrt{3} \times \sqrt{3}$ -Ag surface. The CLPES is one of the most powerful techniques to determine local atomic arrangements around specific chemical species. Although, however, the local structure should be the same, recent CLPES results of this surface from four groups have shown quite different features in the spectra.<sup>1–4</sup> The surface-core-level shifted components were clearly resolved in one of the reports, while not in the others. Since this is not due to the difference in energy resolution of electron analyzers, we speculate that the sample preparation conditions are a clue to the difference. We believe that it is essentially important to clarify this problem and learn what is the important factor that has not yet been recognized for CLPES measurements, because the  $\sqrt{3} \times \sqrt{3}$ -Ag surface has been one of the most important prototype systems hence, it has been a testing ground for various experimental and theoretical techniques.<sup>5–7</sup>

In this study, we performed systematic observations of scanning tunneling microscopy (STM) and reflection-high-energy electron diffraction (RHEED) by changing the annealing conditions in preparing this surface superstructure. It was found that the surface morphology, especially shapes as well as local structures of step edges, showed significant changes with annealing temperature (540–600°C) and duration (15–120 s). By insufficient annealing, step edges were roundish and decorated by random protrusions, while they were straight with periodic protrusions and aligned

along  $\langle 10\bar{1} \rangle$  directions by sufficient annealing. Step density and domain size did not change so much depending on the annealing conditions. Therefore, we do not speculate if the step edges and domain boundaries themselves directly affect the CLPES results. The step edges and domains boundaries with random adsorbates along them, when annealed insufficiently, may act as reservoirs of Ag adatom gas on terraces. The dilute adatom gas phase is known to exist on this surface and to donate electrons to the surface-state band, which changes the band bending in the substrate.<sup>5,8,9</sup> Since the density of the gas may be different from domain to domain, CLPES spectra are broadened due to inhomogeneous band bending over the sample surface. When the sample is sufficiently annealed to remove the reservoirs and gas phase itself, the band bending in the substrate becomes homogeneous, resulting in sharp CLPES spectra.

### 2. Experimental

The STM experiments were performed with a commercial ultrahigh vacuum STM (UNISOKU USM-802 type) equipped with a RHEED system. The base pressure in the chamber was in the range of  $5.5 \times 10^{-11}$  Torr. An *n*-type (P-doped) Si(111) wafer with nominal resistivity of 2–15 Ωcm at room temperature (RT) and  $2 \times 15 \times 0.5$  mm<sup>3</sup> in size was used. The surface was cleaned to obtain a clear  $7 \times 7$  RHEED pattern and STM image, by several repetitions of flash heating up to 1250°C with a direct current through it. The substrate temperature was measured using an optical pyrometer (CHINO pyrostar model IR-U). Deposition of Ag was carried out using an alumina-coated tungsten basket. The deposited amount of Ag was estimated by deposition duration with a constant deposition rate under an assumption of one monolayer (ML) of Ag required for a complete conversion from the  $7 \times 7$  pattern to the  $\sqrt{3} \times \sqrt{3}$  pattern in *in situ* RHEED and STM observations. The Ag deposition rate was  $\sim 1$  ML/min.

In the present work, the  $\sqrt{3} \times \sqrt{3}$ -Ag structure was prepared based on the recent Si 2*p* CLPES study.<sup>3</sup> The surface preparation and post-annealing procedures are shown in Fig. 1. First, Ag of 1.2 ML was deposited on a clean  $7 \times 7$  surface at 520°C (Process 1) to convert the RHEED pattern from  $7 \times 7$  into  $\sqrt{3} \times \sqrt{3}$  completely. Next, the sample was subsequently annealed at 540°C for 2 min

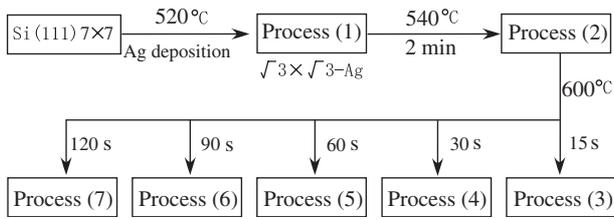


Fig. 1. Sample preparation procedures.

(Process 2), followed by 600°C annealing for 15 s (Process 3), 30 s (Process 4), 60 s (Process 5), 90 s (Process 6), and 120 s (Process 7). At each step, STM observations were performed after the sample was cooled to RT.

### 3. Results and Discussions

Figure 2 shows typical STM images at each process indicated in Fig. 1. The images of large and small areas are given in the left and right columns, respectively. The width of a terrace on the sample surface is typically  $\sim 3000$  Å. At Process 1, as shown in Fig. 2(a), the whole surface is covered with the  $\sqrt{3} \times \sqrt{3}$ -Ag superstructure, showing a clear  $\sqrt{3} \times \sqrt{3}$  RHEED pattern. The surface contains numerous  $\sqrt{3} \times \sqrt{3}$ -Ag islands of various shapes and sizes

on terraces. Step edges of the islands as well as terraces are roundish. Figure 2(a) has a close resemblance with the previously reported STM images of this surface prepared by 1 ML-Ag deposition at 450°C.<sup>10)</sup> At Process 2, the islands roughly obtain a hexagonal shape with dull apexes, and the step edges show a tendency to run along  $\langle 10\bar{1} \rangle$  directions. This trend is more enhanced at Process 3 in Fig. 2(b), where the step edges are straight lines along  $\langle 10\bar{1} \rangle$  directions, and the islands are hexagonal with sharp apexes. These features do not change much at Process 5, as shown in Fig. 2(c). However, one can recognize that there appear darker narrow domains near step edges and also on terraces in (c). According to the previous reports,<sup>11–13)</sup> the domains are attributed to the Si(111) $6 \times 1$ -Ag superstructure with a Ag saturation coverage of 1/3 ML. This is due to partial desorption of Ag atoms during annealing.<sup>14)</sup> With further prolonged annealing (Process 6), the  $6 \times 1$ -Ag domains grew as shown in Fig. 2(d), and weak  $6 \times 1$  spots came to coexist with the  $\sqrt{3} \times \sqrt{3}$  spots in the RHEED pattern. Finally, at Process 7, the  $6 \times 1$ -Ag domains occupy about a half of the whole surface, as shown in Fig. 2(e), with clear spots of both  $\sqrt{3} \times \sqrt{3}$  and  $6 \times 1$  in the RHEED pattern. The previous STM observations of the  $6 \times 1$ -Ag structure,<sup>10,11)</sup> prepared by annealing the  $\sqrt{3} \times \sqrt{3}$ -Ag surface at 600°C–650°C, showed large  $\sqrt{3} \times \sqrt{3}$ -Ag domains with straight edges, surrounded by the  $6 \times 1$ -Ag domains. Our results are in agreement with them.

From the sequence of the STM images above, it is clear that the subsequent annealing of the Si(111) $\sqrt{3} \times \sqrt{3}$ -Ag surface induces marked changes in the shape of step edges. By prolonged annealing, the step edges change from roundish to straight, which is related to the formation of very narrow domains of  $6 \times 1$ -Ag structure at the step edges. The step edge density and domain size did not change much by annealing.

The previous Si  $2p$  CLPES studies of the  $\sqrt{3} \times \sqrt{3}$ -Ag surface have reported that, with the same processes for sample preparation as in Fig. 1, the spectra become very sharp by post annealing at 600°C to lead a clear deconvolution of the surface-shifted core-level components, while the spectra remain broad if without the post annealing.<sup>3)</sup> We have confirmed their CLPES results at synchrotron radiation facilities at Tsukuba, Japan and Trieste, Italy, which will be published elsewhere. Since, according to our present atomic-resolution STM investigation, the local atomic structure of the  $\sqrt{3} \times \sqrt{3}$ -Ag surface on terraces and the step density do not alter by the 600°C annealing processes, the difference in CLPES spectra is most likely related in an indirect way to the changes in the structure of step edges as observed in Fig. 2.

Figure 3 shows high-resolution STM images near step edges on the surfaces prepared at (a) Process 1 and (b) Process 3, corresponding to Figs. 2(a) and 2(b), respectively. The local structures at step edges are quite different between them. In Fig. 3(a), without 600°C post-annealing, the step edges are decorated by random protrusions of various sizes (15–30 Å). On the other hand, the step edges in Fig. 3(b) clearly show the growing  $6 \times 1$ -Ag domains of  $\sim 20$  Å width. The boundaries between the  $\sqrt{3} \times \sqrt{3}$ -Ag domain and  $6 \times 1$ -Ag domain are well-ordered without random protrusions on the left side, but rather disordered on the right

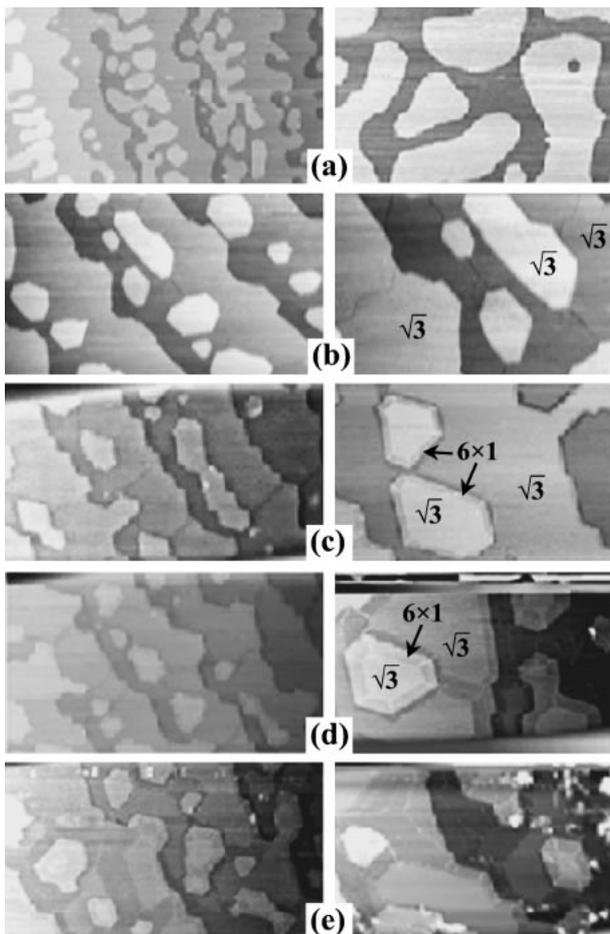


Fig. 2. Filled-state STM images of the  $\sqrt{3} \times \sqrt{3}$ -Ag surface, recorded in constant-current mode with a bias voltage of 1.99 V. The images in the left column are 553 nm  $\times$  1193 nm in size, and the right ones are 378 nm  $\times$  592 nm. (a) at Process 1, (b) at Process 3, (c) at Process 5, (d) at Process 6, and (e) at Process 7.

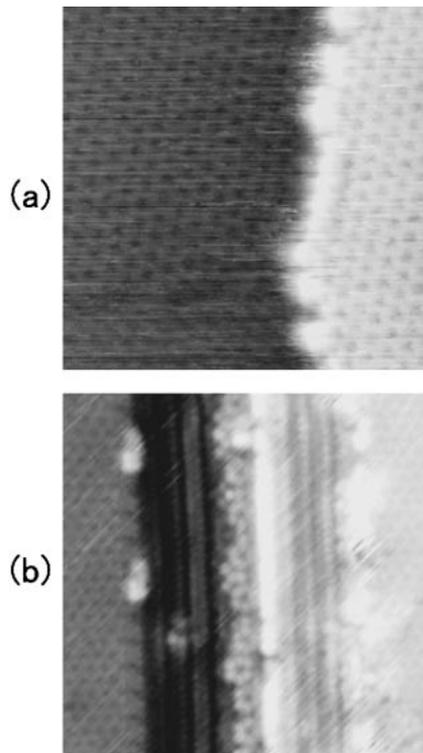


Fig. 3. Filled-state STM images near step edges on the Si(111)- $\sqrt{3} \times \sqrt{3}$ -Ag prepared at (a) Process 1 and (b) Process 3. The images were taken in constant-current mode at (a)  $I = 0.49$  nA,  $V = 1.99$  V and (b)  $I = 0.52$  nA,  $V = 0.99$  V. The images sizes are (a)  $9.1$  nm  $\times$   $9.1$  nm and (b)  $13.1$  nm  $\times$   $13.1$  nm.

side. The width of the  $6 \times 1$ -Ag domains is so narrow that they are hardly observed in large-area images of Fig. 2(b) and in RHEED pattern; they correspond to only  $\sim 1\%$  of the terrace size. The step edges are thus quite different not only in the whole shape as seen in Fig. 2, but also in the local structure (Fig. 3), depending on the annealing conditions.

In Fig. 2(b), one can notice dark and straight narrow lines on terraces, which are  $6 \times 1$ -Ag domains. The  $6 \times 1$ -Ag domains grow near the domain boundaries of the  $\sqrt{3} \times \sqrt{3}$ -Ag superstructure, similar to that at step edges. Figure 4 shows magnified images of such a region on the sample prepared at Process 3. At the both sides of the boundary the  $\sqrt{3} \times \sqrt{3}$ -Ag structure exists on a same-height terrace, while the  $6 \times 1$ -Ag domains at the both sides of the center boundary differ in height by a double-layer height, which is the so-called 'hole-island pairs' due to Si mass transport at the structural change as mentioned below. The center boundary is decorated by random adsorbates, but is straight running parallel to the stripe of the  $6 \times 1$ -Ag structure. The boundary between the right domains of  $\sqrt{3} \times \sqrt{3}$ -Ag and the  $6 \times 1$ -Ag is atomically sharp and very straight with periodic protrusions, while the boundary between the left domains is complicated due to random protrusions. These adsorbates at the boundaries are results of the restructuring of the superstructures. Adopting a honeycomb-chain-channel model for the  $6 \times 1$ -Ag structure,<sup>15)</sup> the Ag and Si coverages in the reconstructed layers are  $1/3$  and  $4/3$  ML, respectively, while the  $\sqrt{3} \times \sqrt{3}$ -Ag surfaces have 1 ML of Ag and Si according to the inequivalent triangle structure model.<sup>16)</sup> This difference in Si concentration in the reconstructed

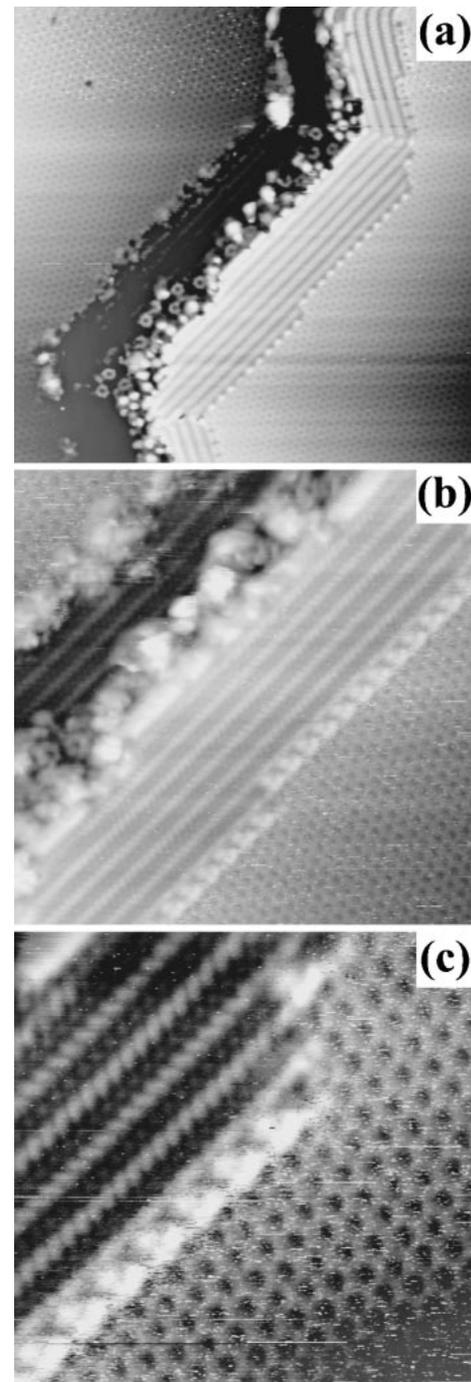


Fig. 4. Filled-state STM images at a out-of phase domain boundary on the Si(111)- $\sqrt{3} \times \sqrt{3}$ -Ag prepared at Process 3, with sizes of (a)  $38.5$  nm  $\times$   $38.5$  nm, (b)  $28.5$  nm  $\times$   $28.5$  nm, and (c)  $11.1$  nm  $\times$   $11.1$  nm, at  $I = 0.52$  nA,  $V = 1.99$  V.

layers leads to mass transport of Si atoms at the structural change. Therefore, the transition from the  $\sqrt{3} \times \sqrt{3}$ -Ag to  $6 \times 1$ -Ag structures induces so-called 'hole-island pair' formations to adjust the Si coverage in the reconstructed layers, similar to that at the transition from the Si(111)- $7 \times 7$  clean structure to the  $\sqrt{3} \times \sqrt{3}$ -Ag one.<sup>10,11,17)</sup> The adsorbates randomly or periodically adsorbed at the boundaries may be Si and Ag atoms which are not incorporated in the ordered structures during the restructuring.

Let us now discuss the relationship between the Si 2*p* CLPES and present STM results. Two possible explanations

can be found as follows.

One is based on an assumption that the observed protrusions at step edges and domain boundaries involve Si atoms, which contribute to the broadened spectra. The  $2p$  core levels of such Si atoms are slightly shifted in energy position from that of Si atoms in the  $\sqrt{3} \times \sqrt{3}$ -Ag domains, because of different chemical environments. This makes the spectra broaden. If the sample is sufficiently annealed to diminish the random adsorbates at step edges and domain boundaries, the Si  $2p$  spectra become sharp.

Another possible explanation assumes that the random protrusions at step edges and domain boundaries involve Ag atoms. It has been reported previously that there exists a dilute Ag adatom gas phase on the  $\sqrt{3} \times \sqrt{3}$  surface,<sup>18)</sup> which induces changes in band bending below the surface by donating electrons into the surface-state band.<sup>8,9)</sup> The adatoms in the gas phase migrate over the surface so briskly that STM cannot image them.<sup>18)</sup> According to the previous results,<sup>8,9,18)</sup> these adatoms seemingly do not exceed a certain concentration on a terrace and extra Ag atoms are accumulated at step edges. So there is a thermodynamical equilibrium between the gas phase and the aggregates at step edges/domain boundaries. Thus, the protrusions at the boundaries act as reservoirs of Ag adatom gas. Since the adatom concentration in the gas phase on terraces may depend on the size of terraces/domains and reservoirs at their peripheries, the concentration is slightly different from domain to domain, and the resulting band bending is inhomogeneous over the sample surface.<sup>3)</sup> Therefore, binding energies of Si  $2p$  bulk components and surface components vary from terraces/domains to terraces/domains, making the Si  $2p$  spectra broaden. If the adatom gas and its reservoirs are removed from the surface by sufficient post-annealing, the band bending should be homogeneous over the sample surface to bring about sharp CLPES spectra.

Since the STM measurements cannot distinguish chemical species of protrusions, we cannot judge based solely on our results which scenario is more reasonable. But we suggest that the latter scenario is more plausible because of two reasons: (1) fractions of areas of protrusions at step edges and domain boundaries seem to be too small to make observable contributions to the CLPES spectra, and the sharpness of CLPES spectra do not seem to depend on the densities of steps and domain boundaries. (2) There is a report<sup>3)</sup> that the Si  $2p$  CLPES spectra become broader by small amounts of additional deposition of Ag onto the sufficiently annealed  $\sqrt{3} \times \sqrt{3}$ -Ag surface. This suggests that excess Ag atoms on top of the surface makes the spectra broader.

Anyway, it is clear from the present study that the sharpest Si  $2p$  spectra are obtained at the very initial stage of the  $6 \times 1$ -Ag formation from the  $\sqrt{3} \times \sqrt{3}$ -Ag domains at step

edges and domain boundaries, corresponding to Figs. 2(b) and 3(b). It is noted that the energy position of the Si  $2p$  peak of the  $6 \times 1$ -Ag phase is significantly different from that of the  $\sqrt{3} \times \sqrt{3}$ -Ag, so that the  $6 \times 1$ -Ag domains on the best sample have to be smaller than the CLPES detection limit.<sup>13)</sup>

#### 4. Conclusions

We have observed marked changes in the surface morphology of Si(111) $\sqrt{3} \times \sqrt{3}$ -Ag superstructure with post-annealing processes by STM. By prolonging the post-annealing at 600°C, the step edges change in shape and local structure from roundish lines with random adatoms adsorption to straight ones with ordered protrusions along  $\langle 101 \rangle$  directions. This change is correlated to the formation of very narrow domains of the Si(111) $6 \times 1$ -Ag superstructure at step edges and domain boundaries. Such changes in steps and boundaries correspond to the changes in Si  $2p$  CLPES from broad spectra to very sharp ones. We have suggested possible mechanisms explaining the relationship between the observed changes in surface morphology and CLPES spectra.

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