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High-temperature scanning-tunneling-microscopy observation of phase transitions and reconstruction on a vicinal Si(111) surface

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The step structure of a vicinal Si(111) surface misoriented 10° to [11$\bar{2}$] is studied using high-temperature scanning tunneling microscopy (STM). Phase transitions on the vicinal Si(111) surface are observed in real time on an atomic scale. During cooling from above the (1×1)-to-(7×7) transition temperature, slender (111) facets with a 7×7 structure appear, and these facets widen as the temperature decreases. At the initial stage of step bunching, no surface reconstruction is observed on the step bunch. Below 700 °C, however, nucleation of reconstructed (331) facets starts on the step bunch. These STM results are compared with our previous reflection high-energy electron-diffraction results [Jpn. J. Appl. Phys. **30**, 1337 (1991)].

Understanding the step configuration of vicinal semiconductor surfaces is very important because vicinal surfaces have been used for basic studies on epitaxial growth[1] and fabrication of sophisticated structures, such as fractional order superlattices.[2] We may expect that vicinal surfaces consist of terraces of low-index orientation and steps. In reality, however, vicinal surfaces have various structural phases depending on the temperature and misorientation angle. Reconstruction, which usually occurs at a low-index semiconductor surface, plays an important role in determining the structural phases. In some cases, reconstruction induces the formation of low-index facets,[3] because reconstruction stabilizes the low-index surface. In other cases, reconstruction induces changes in the average step height,[4,5] because reconstruction changes the relative free energy of steps of different heights.

Extensive low-energy electron-diffraction (LEED) studies[3,6] have shown that above the (1×1)-to-(7×7) transition temperature, a vicinal Si(111) surface misoriented to [1$\bar{1}$0] and [11$\bar{2}$] is uniformly covered with single steps, but below the transition, 7×7-reconstructed (111) facets are formed due to the free-energy gain for forming the 7×7 structure. As the temperature is lowered, the (111) facets spread, and the inclination angles of the step bunches increase. Surfaces misoriented to [1$\bar{1}$0] and [11$\bar{2}$] behave similarly down to 700 °C, but make different types of transitions below 700 °C. On the [1$\bar{1}$0]-misoriented surface, the step bunches change into two types of stepped surfaces: one with an ordered array of kinks, misoriented slightly away from [1$\bar{1}$0], and the other with poor step order, misoriented to [12$\bar{1}$].[6] On the [11$\bar{2}$]-misoriented surface, as recently shown by reflection high-energy electron diffraction (RHEED),[7] after the inclination of the step bunch reaches about 15° at a temperature below 700 °C,[8] the step bunch is transformed into a reconstructed (331) facet inclined 22°. The (331) facets are therefore caused by this reconstruction. In this paper, we present scanning-tunneling-microscope (STM) images of the phase transitions of the vicinal Si(111) surface misoriented to [11$\bar{2}$]. These STM observations are compared with previous LEED and RHEED results.

We used an STM (Ref. 9) which can produce images at sample temperatures as high as 900 °C.[10] A sample was cut from a vicinal Si(111) wafer (B-doped, 1–10 Ω cm) misoriented 10° toward [11$\bar{2}$]. After rinsing in acetone, the sample was introduced into a UHV chamber through a load lock. The sample was heated by passing a dc electric current through it, and cleaned by flashing at 1250 °C below 1×10^{-10} Torr. In order to avoid the step bunching induced by a dc current,[11,12] the current flow was in the step-up direction. In order to reduce thermal drift, the sample was kept at the desired temperature for a few hours before STM observation.

We measured the sample temperature with an infrared pyrometer. Temperature measured in scanning position was lower than that measured when the tip was retracted (739 °C and 777 °C, respectively). This is due to the presence of the tip in view of the pyrometer. We compensated for this decrease by simply adding 38 K to the measured temperatures during scanning. Under these experimental conditions, the (1×1)-to-(7×7) phase transition temperature was determined to be 868 °C, at which 7×7 structures just appeared on the (1×1) terraces on a nominally flat Si(111) surface.[13]

During heating, a heating voltage V_h was applied be-

tween the sample ends. When we applied an additional voltage V_b to one end of the sample, the potential of the sample at the tip position, which is the sample bias voltage of the STM measurement, became $V_h/2+V_b$ when the potential gradient in the sample was uniform and the tip was approached at the center of the sample. The typical sample bias voltage was +2 V and the typical tunneling current was 0.02 nA. Because fast scanning is required to observe dynamical processes, STM images at elevated temperatures [all the following STM images except Fig. 4(a)] were taken in constant height mode with slow feedback to avoid touching the tip to the sample.

Figure 1 shows the transformations of the step configuration of the vicinal Si(111) surface during cooling from a temperature higher than the (1×1)-to-(7×7) transition temperature. To achieve an equilibrium step structure, the sample was cooled very slowly, for about two hours, from 780 °C to 600 °C. Figures 1(a)–1(c) are sequential STM images obtained 16.7 s apart, after the sample was cooled from 778 °C to 777 °C. Just after cooling, no features, not even steps, were observed in the STM images, as seen in Fig. 1(a). However, this surface

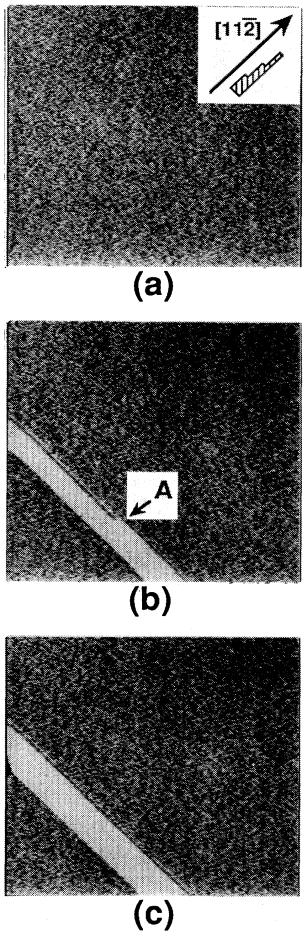

FIG. 1. 1100×1100-Å^2 STM images of vicinal Si(111) surfaces misoriented 10° to [11$\bar{2}$]. These STM images were taken at 777 °C during cooling. White bands in the images are the (111) terraces with 7×7 structures.

should be uniformly covered with single steps.[3,6,7] The reason that steps were not observed may be because steps fluctuate much faster than the tip scanning speed. In the STM image 16.7 s later, a slender (111) facet with a 7×7 structure suddenly appears, as seen in Fig. 1(b). Although Fig. 1(b) cannot resolve the 7×7 structure due to the limited number of pixel points, the white band in the image is a (111) facet with the 7×7 structure.[14] Phaneuf *et al.* have already reported such linear (111) facets using a low-energy electron microscope (LEEM).[15] Our observations using STM, which have higher spatial resolution than LEEM, first revealed that the facet width increase is quantized by a 7×7 unit cell. Figure 1(b) shows that an increase in the (111) facet width from four to five 7×7 unit cells was observed when the STM tip reached *A*. In Fig. 1(c), the (111) facet width has been widened by an additional 7×7 unit cell. Moreover, our STM results indicated that there is a critical size for the nucleation of the 7×7 structure, since we did not observe (111) facets one to two 7×7 unit cells wide at the initial stage of the faceting. The temperature at which the 7×7 structure appears, 777 °C, is about 90 °C lower than the phase transition temperature of the 7×7 structure on a nominally flat Si(111) surface.[13] This result is in agreement with previous LEED results by Phaneuf and co-workers.[3,6]

The (111) facet grew more as the temperature decreased, which is consistent with the increase in the inclination of the step bunch observed by diffraction experiments. As described previously, however, reported RHEED results show that after a continuous increase in the inclination, the step bunch (inclined about 15°) is transformed into a (331) facet (inclined 22°) over a very wide temperature range, 700–620 °C. In this temperature range, the 15°-inclined step bunch and the reconstructed (331) facet coexist in the RHEED patterns. Figure 2(a) confirms this coexistence in real space. In Fig. 2(a), regions *S*1 and *S*3 are identified as the (331) facets, because the periodicity agrees with the RHEED pattern from the reconstructed (331) facet, and region *S*2, which has no atomic images, is the step bunch inclined about 15°. In this experiment, we could not observe nonreconstructed step bunches below 639 °C, as shown in Fig. 2(b).

RHEED results[7] have also reported that narrow 5×5 structures are created with the appearance of the (331) facets. Three reconstructions, the 7×7 and 5×5 structures on the (111) facets and the reconstruction on the (331) facet, coexist on the same surface. In Figs. 2(a) and 2(b), these three reconstructions are clearly shown. The wide (111) facets formed by faceting on (111) are always covered with a 7×7 structure, because this faceting is induced by the (1×1)-to-(7×7) transition. The 5×5 structure is observed only on the narrow (111) facets adjacent to the (331) facets. The widest 5×5 reconstructed (111) facet we observed was four unit cells wide. These STM images confirm the RHEED results.

Next, we discuss why the 5×5 structure is formed on the narrow (111) facet. It has been reported that a 5×5 structure is energetically more stable than a 7×7 structure under compressive stress.[16] So the narrow (111) facet may be compressively stressed due to the rebonding at the step edge and/or reconstruction on the adjacent

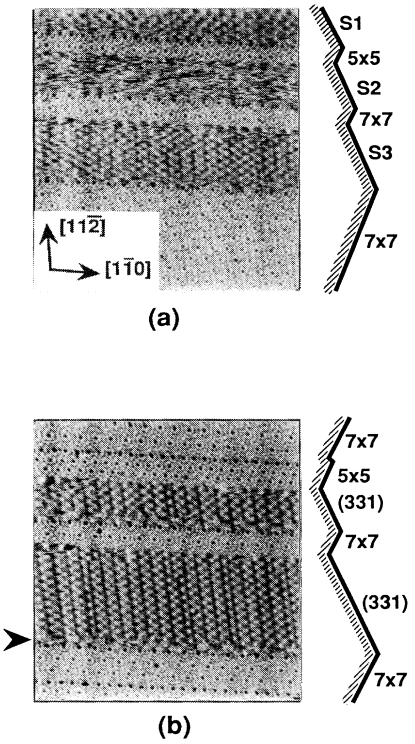

FIG. 2. 500×600-Å^2 STM images of vicinal Si(111) surfaces misoriented 10° to [11$\bar{2}$] at temperatures of (a) 658 °C and (b) 620 °C. These images are slightly distorted due to thermal drift.

facets. The STM images show, however, that the 7×7 structure is also present on the narrow (111) facet created with the (331) facets. This result suggests that the 5×5 structure is not due to the stress. It has been also shown that kinetics causes a metastable 5×5 structure on a Si(111) surface grown by molecular-beam epitaxy (MBE).[17,18] At the (331) faceting temperatures, the 7×7 and 5×5 structures coexist on Si(111) grown by MBE. We therefore think that the 5×5 structure is due to kinetics rather than stress.

In the STM images, the (331) facets and the step bunches inclined about 15° are often connected across the narrow (111) facets, as shown in Fig. 2. Because RHEED results show that the narrow facets are formed during (331) facet formation, it is suggested that the step bunches are broken up into (331) facets and narrow (111) facets during (331) facet formation. For a clear demonstration of this (331) faceting transformation, we estimated the large-scale surface morphology from the facet widths assuming that the local misorientation is close to 10° everywhere. Schematic views of the surface morphologies before and after the transition are shown in Figs. 3(a) and 3(b). Comparing 3(a) and 3(b), it is clear that the step bunches break up into (331) and (111) facets during transition. Because the transition from the step bunch into the (331) facet requires a large mass transfer, the kinetics causes the break up of the step bunch. Figure 3(b) shows that the narrow (111) facets are also located at the inside corner between the wide (111) facet caused by the (1×1)-to-(7×7) transition and the (331) facet. A typical

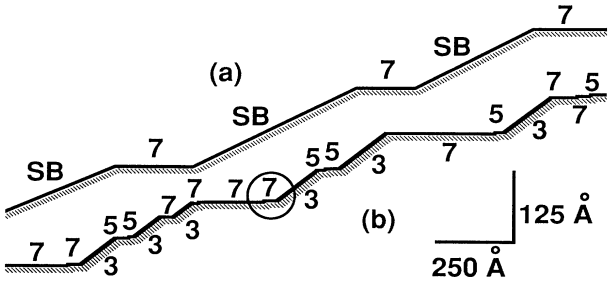

FIG. 3. Schematic views of the macroscopic shape of the surface. (a) 750–720 °C, (b) 630–610 °C. Regions indicated by *SB*, 7, 5, and 3 are respectively the step bunch, the 7×7 and 5×5 structure on the (111) facet, and the (331) facet.

case is marked by a circle in Fig. 3(b). We do not understand, however, why a narrow (111) facet is formed at this position.

From Fig. 2(a), the coexistence of the step bunch inclined about 15° and the (331) facet results from the partial nucleation of (331) facets in a large step bunch. An important factor in explaining this coexistence is that the (111) facet width is quantized by a 7×7 or 5×5 unit cell. In Fig. 2, the corner holes of the 7×7 and 5×5 structures are arranged at the boundary of the (111) facets. This arrangement of the corner holes at the boundary of the (111) facet would be energetically favorable. In this situation, a step bunch with a given number of steps and a given width is not always transformed into a combination of the (111) and (331) facets without discrepancy due to the discreteness of the (111) facet width. We observed a narrow, nonreconstructed step bunch remaining after the partial transformation of the step bunch, *S*2 in Fig. 2(a). It is particularly unlikely that such a narrow step bunch would match the sum of the (111) and (331) facets. There is therefore mismatch, which leads to production of an energetically unfavorable rough region between the (111) and (331) facets. A typical example is marked by an arrowhead in Fig. 2(b). Transition is impossible until the energy gained by reconstructing the (111) and (331) facets overcomes the energy lost in the rough region. Nonreconstructed step bunches and (331) facets therefore coexist over a wide temperature range.

In order to investigate the atomic structure of the reconstructed (331) facet, we obtained a constant-current STM image of the (331) facet at room temperature, Fig. 4(a). In this figure, the unit cell of the reconstructed (331) facet is overlaid. Figure 4(b) illustrates the periodicity of the bright spots in the STM images and the unit cell of the reconstruction. Except for a $c(13\times1)$ structure,[19] which is thought to be caused by impurities,[20] two kinds of reconstructions, 6×2 (Refs. 21 and 22) and 12×1 structures,[20,23] have been reported on the flat (331) surface and the (331) facet on a vicinal Si(111) surface. Between the two reconstructions, the STM image is consistent with the 12×1 structure reported on the flat (331) surface by Wei, Williams, and Park,[20] as well as with the reconstruction observed on a vicinal Si(111) surface using RHEED.[7,24] As shown in Fig. 4(b), the 12×1 structure is understood as a structure in which a periodicity of 6*a* along [1$\bar{1}$0], where *a* is the length of a basic unit cell,

shifts by $R+$ and $R-$ in turn. The 12×1 unit cell consists of two bright spots; one is at the corner and the other is near the center. On the other hand, in the 6×2 structure, the $6a$ periodicity always shifts only by $R+$ (or $R-$). The 6×2 unit cell has a same area as the 12×1 structure and also contains two bright spots. This unit cell, however, includes a bright spot exactly at the center. Therefore, whether the unit cell of the STM image contains a bright spot at the center or not is an easy criterion discriminating between the 12×1 and 6×2 structures. In Fig. 4(a), the unit cell has a bright spot shifted from the center. This clearly demonstrates that the reconstruction in Fig. 4(a) is the 12×1 structure. However, the $6a$ periodicity common to the 12×1 and 6×2 structures suggests that the local atomic structures are similar and the energy difference is small. These two structures may coexist on a same surface. The atomic structure of the 12×1 structure has not been determined by the STM images. The (331) surface is a repetition of the narrow (111) and $(11\bar{1})$ terraces and an adatom arrangement is the simplest way to reduce dangling bonds on the (111) surface. Therefore the atomic structure may be simply explained by adatoms. Full determination of the atomic arrangement however requires further studies.

In conclusion, we studied the surface structure of a vicinal Si(111) surface misoriented to $[11\bar{2}]$ using high-temperature STM. During cooling from above the (1×1)-to-(7×7) transition temperature, narrow (111) facets with three to four 7×7 unit cells nucleated and widened as the temperature decreased. Reconstructed

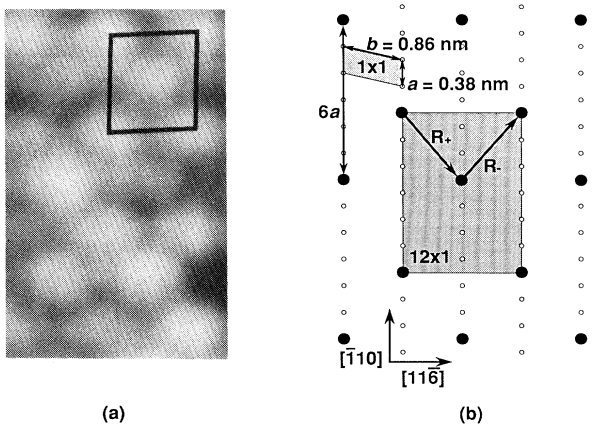

FIG. 4. (a) A constant-current STM image of a reconstructed (331) facet. The area shown is 80×50 Å^2 and data were recorded at a sample bias of 2 V and a tunneling current of 0.3 nA. (b) Periodicity of the 12×1 structure.

(331) facets appeared with narrow (111) facets below 700 °C and 5×5 and 7×7 structures were observed on the narrow (111) facets. The 12×1 reconstruction on the (331) facet is in agreement with the periodicity obtained from previous RHEED observations.

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[8]A transition from the 15°-inclined step bunch to the (331) facet starts at 620 °C in Fig. 7 of Ref. 7. However, fast cooling used to obtain the data significantly reduced the transition temperature. When the temperature was varied slowly, the transition occurred between 700 °C and 620 °C.

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[23]The reconstruction reported on a flat Si(331) surface in Ref. 20 is the same one as reported on a (331) facet on a vicinal Si(111) surface in Ref. 7. Wei, Willians, and Park have named the reconstruction a 12×1 structure in Ref. 20. However, a matrix notation in Ref. 7 is adequate to precisely describe the reconstruction.

[24]We showed the real space periodicity of the reconstructed (331) facet in Fig. 6 in Ref. 7. We also explained in Ref. 7 the intensity distribution of the diffraction spots using the small difference in the scattering factors between the scattering bodies at the corners and the center of the unit cell. However, the STM images show that the scattering bodies are not at the center of the unit cell. This misunderstanding is caused by not being able to read the diffraction spot intensities in the higher Laue zones from the RHEED pattern. The periodicity obtained from the STM images undoubtedly explains the intensity distribution of the RHEED spots in the lower Laue zones.

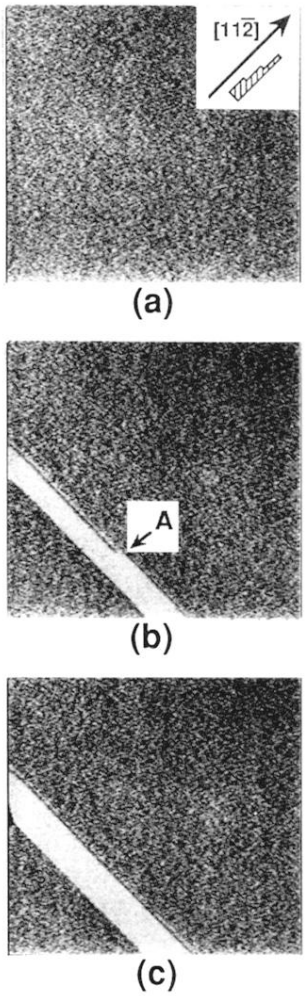
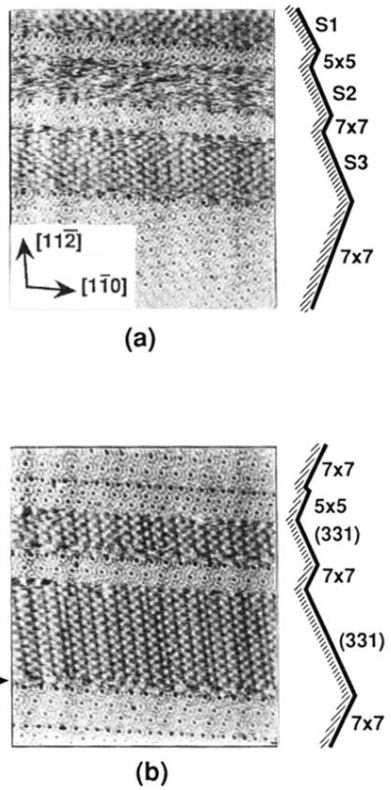


FIG. 1. 1100×1100-Å^2 STM images of vicinal Si(111) surfaces misoriented 10° to [11$\bar{2}$]. These STM images were taken at 777 °C during cooling. White bands in the images are the (111) terraces with 7×7 structures.



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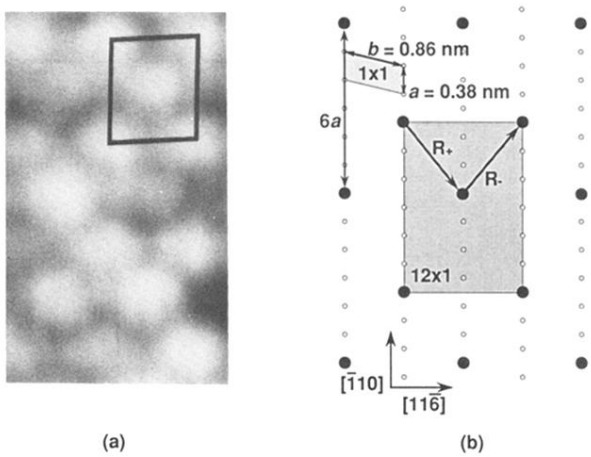

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