X-ray diffraction study of the Si(111)-$\sqrt{3}\times\sqrt{3}$-Ag surface structure

H. Tajiri,* K. Sumitani, S. Nakatani, A. Nojima, and T. Takahashi†
Institute for Solid State Physics, University of Tokyo, 5-1-5 Kashiwanoha, Kashiwa-shi, Chiba 277-8581, Japan

K. Akimoto
Department of Quantum Engineering, Nagoya University, Furo-cho, Chikusa, Nagoya 464-8603, Japan

H. Sugiyama, X. Zhang, and H. Kawata
Photon Factory, High Energy Accelerator Research Organization, Tsukuba 305-0801, Japan
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In-plane structures of a Si(111)-$\sqrt{3}\times\sqrt{3}$-Ag surface at both room temperature (RT) and 50 K are determined by x-ray diffraction. The honeycomb-chained triangle model with strongly anisotropic thermal vibrations of Ag atoms is preferred over the inequivalent triangle (IET) model at RT. On the other hand, at 50 K, the IET model better explains the experimental results. The phase transition temperature of $T_C = 150 \pm 4$ K is obtained from the temperature dependence of the fractional-order reflection intensity. The critical exponent β is also found to be 0.27 ± 0.03.

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I. INTRODUCTION

It is widely accepted that the structure of a Si(111)-$\sqrt{3}\times\sqrt{3}$-Ag surface at room temperature (RT) is explained by a honeycomb-chained triangle (HCT) model[1,2] supported by a number of experimental and theoretical results.[2] The HCT model belongs to the $p31m$ plane group with a mirror line along the $[11\bar{2}]$ direction. In the model, top-layer Ag atoms are located on the mirror lines and form large triangles as indicated by dashed lines in Fig. 1(a). Si trimers on the second layer are arranged in the same manner. Therefore, two small Ag triangles of the same size are found in the unit cell as indicated by solid lines in Fig. 1(a).

Recently, however, it is suggested that the most stable structure of the Si(111)-$\sqrt{3}\times\sqrt{3}$-Ag surface is not the HCT structure but an inequivalent triangle (IET) structure by first-principles calculations and scanning tunneling microscopy (STM) studies at low temperatures.[3–5] The IET model is characterized by slight rotations of Ag triangles and Si trimers from the symmetric positions in the HCT model. As a result, the mirror lines vanish and two Ag triangles of different sizes appear as drawn by solid lines in Fig. 1(b). The rotation angle is estimated to be about 6° from the calculations,[3] which correspond to atomic displacements of 0.3 Å. The structure of the surface at low temperatures is still controversial,[6] and is not yet determined experimentally. Another question also arises whether the structure at RT is explained by the symmetric HCT model or by thermal fluctuations between two structures in which Ag triangles rotate in opposite directions in the IET model.

In this work, we make a structural investigation of the Si(111)-$\sqrt{3}\times\sqrt{3}$-Ag surface both at RT and at low temperatures by x-ray diffraction. The grazing incidence x-ray diffraction (GIXD) method is just suitable to distinguish between these two models because the GIXD method is sensitive to a lateral structure. We first show that atomic arrangements of the surface observed at 50 K are consistent with the IET model and then reinvestigate the structure at RT by using anisotropic thermal vibrations. Furthermore, we investigate a phase transition of the surface by measuring the temperature dependences of the x-ray diffraction intensities. This reveals a transition temperature T_C and a critical exponent β.

II. X-RAY SCATTERING FROM DOMAINS

The IET model has x-ray scattering properties different from the HCT model. The IET model can form two types of domains in the relation of twins with each other by losing the mirror symmetry existing in the HCT model. In the two domains, Ag triangles rotate in opposite directions. Such a domain structure is observed as the inversion of protrusions through twin domain boundaries in STM studies at low temperatures.[3–5] We define two structure factors of the IET model, F_{cw} and F_{ccw}, for atomic structures of the two domains. Assuming that the two domains are equally distributed, we can express the x-ray diffraction intensity at fractional-order peak as follows:[7,8]

$$I(\mathbf{q}) = I_M(\mathbf{q})S(\Delta\mathbf{q}, L_o) + I_D(\mathbf{q})S(\Delta\mathbf{q}, L_t'), \quad (1)$$

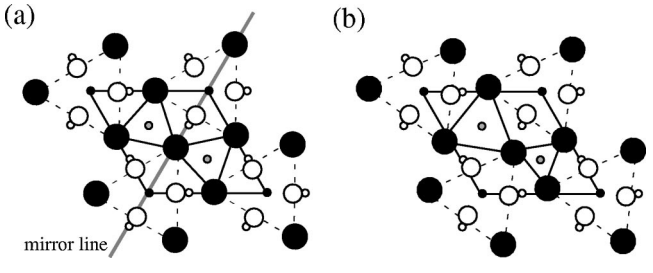

FIG. 1. Top views of proposed structure models for the Si(111)-$\sqrt{3}\times\sqrt{3}$-Ag surface. (a) The honeycomb-chained triangle model belongs to the $p31m$ plane group which has mirror lines. (b) The inequivalent triangle model whose space group is $p3$. Large solid circles indicate Ag atoms, and the others show Si atoms.

$$I_{\mathrm{M}}(\mathbf{q}) \propto |F_{\mathrm{cw}}(\mathbf{q}) + F_{\mathrm{ccw}}(\mathbf{q})|^2, \tag{2}$$

$$I_{\mathrm{D}}(\mathbf{q}) \propto |F_{\mathrm{cw}}(\mathbf{q}) - F_{\mathrm{ccw}}(\mathbf{q})|^2. \tag{3}$$

In addition to the first term representing the conventional narrow peak, the second term appears in Eq. (1).[9] Here $\Delta\mathbf{q} = \mathbf{q} - \mathbf{q}_0$; $\mathbf{q}$ is a momentum transfer, and $\mathbf{q}_0$'s indicate diffraction spots. $I_{\mathrm{M}}(\mathbf{q})$ is concerned with a mean surface structure, and $I_{\mathrm{D}}(\mathbf{q})$ reflects structural deviations from the mean structure. $S(\Delta\mathbf{q}, L)$ is a shaping function of a Lorentzian characterized by a correlation length L. The correlation length L_o of the out-of-phase domain is longer than that of the twin domain, L_t, which is included in $L_t' = (1/L_o + 1/L_t)^{-1}$. The formation of the twin domain brings broad reflection components in addition to conventional narrow reflections. Therefore, we can easily distinguish the IET model from the HCT model by observation of the broad scattering peak. The differences between these models can be found also in conventional reflections.

III. EXPERIMENT

The experiments were conducted by using a six-circle surface x-ray diffractometer with a ultrahigh-vacuum chamber[10] installed in the beamline $15B_2$ of the Photon Factory (KEK-PF) in Tsukuba, Japan. The substrate was an *n*-type Si(111) wafer with dimensions of $16.5 \times 16.5 \times 0.4$ mm^3. After a clean Si(111)7×7 surface was fabricated by flashing several times with indirect heating, the Si(111)-$\sqrt{3}\times\sqrt{3}$-Ag surface was formed by depositing one monolayer of Ag with a Knudsen cell at a substrate temperature of 500 °C. Sharp patterns in reflection high-energy electron diffraction showed the excellent qualities of both surfaces. The base pressure was kept below 1.5×10^{-10} Torr during x-ray measurements. The GIXD measurements were performed at RT and 50 K for structure analysis. We also measured the temperature dependences of the GIXD intensities, focusing on some fractional-order reflections. The substrate was cooled down from RT to 50 K with a closed-cycle helium refrigerator with an accuracy of less than 1 K. A photon energy of 14.4 keV was used. The incident and exit angles were kept at 0.5° which corresponds to a vertical momentum transfer of $l \sim 0.2$.

IV. RESULTS AND DISCUSSION

A. In-plane structure

In this section, we determine the surface structures both at RT and at 50 K. Figures 2(a) and 2(b) represent reciprocal-space maps of the conventional reflection intensities at RT and 50 K, respectively. We obtained the intensities of the fractional-order reflections at each temperature by averaging over measured reflections with $p31m$ plane group symmetry, in which 26 reflections were irreducible. The uncertainties were about 13%. All reflections are indexed with respect to the $\sqrt{3}\times\sqrt{3}$ unit cell given by $\mathbf{a}_1 = \frac{1}{2}[11\bar{2}]_{\mathrm{cubic}}$ and $\mathbf{a}_2 = \frac{1}{2}[\bar{2}11]_{\mathrm{cubic}}$ in the surface plane and $\mathbf{a}_3 = [111]_{\mathrm{cubic}}$ which is normal to the surface. We can see differences between the intensities at RT and at 50 K for reflections with rather large lateral momentum transfers.

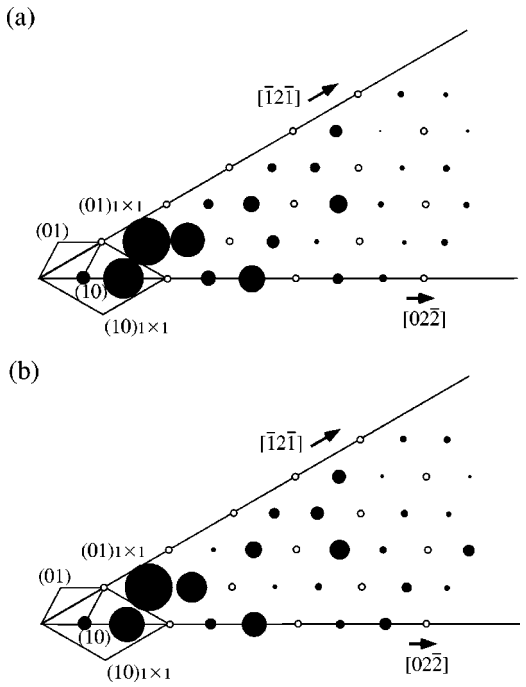

FIG. 2. Irreducible in-plane reciprocal intensity maps at (a) room temperature and at (b) 50 K. Solid circles show measured fractional-order reflections whose radii are proportional to the structure factors. Integer-order reflections indicated by open circles are not measured. For the data observed at 50 K, only narrow reflection components as shown in Fig. 3 are plotted.

Figure 3 shows a rocking curve of (3 2) reflection obtained by rotating the sample around the surface normal direction at 50 K. The profile with broad tails is well decomposed into narrow and broad components by double Lorentzian fitting. The appearance of the broad components clearly indicates that the IET structure is formed at 50 K.

Figures 4(a) and 4(b) show the Patterson maps and the corresponding interatomic vectors of the structure models at RT and 50 K, respectively. Only positive peaks are drawn and brightness increases toward intensity in the map. The overall integrated intensities including the two reflection

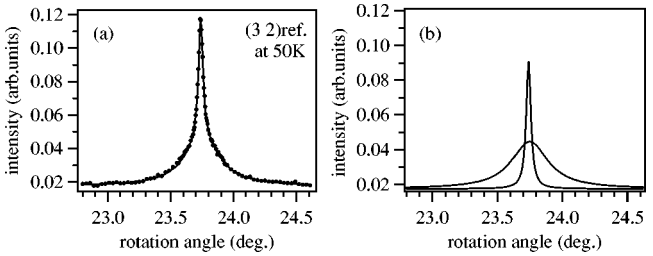

FIG. 3. A rocking curve of (3 2) reflection observed at 50 K. (a) Solid circles are experimental results. The solid line shows the fitted results by a double Lorentzian. (b) Decomposed intensities for narrow and broad reflection components.

TABLE I. Structure parameters determined by χ^2 fitting for both anisotropic HCT model at RT and anisotropic IET model at 50 K.

Atom	Parameters	HCT at RT	IET at 50 K
Ag	r(Å)	2.85±0.01	2.85±0.01
Si(1)	r	1.41±0.03	1.45±0.02
Si(2)	r	2.15±0.07	2.09±0.03
Ag	θ(deg)	60.0	65.1
Si(1)	θ	0.0	5.1
Si(2)	θ	0.0	0.0
Ag	β_{11} (10^{-2})	1.9±0.2	1.2±0.2
Ag	β_{12}	$\beta_{22}/2$	0.9±0.1
Ag	β_{22}	5.5±0.7	1.3±0.1
Si(1)	β_{11}	0.6±0.3	0.4±0.2 (isotropic)
Si(1)	β_{12}	$\beta_{22}/2$	$\beta_{22}/2$
Si(1)	β_{22}	1.5±0.6	β_{11}
Si(2)	B(Å^2)	2.1±2.6	1.6±0.8
	χ^2	4.9	4.9

components were made into consideration for the data of 50 K. An obvious change was observed in the two Patterson maps. Peak A in Fig. 4(a) corresponds to the Ag-Ag interatomic vector of the Ag triangle in the HCT model at RT. However, peak A splits into two peaks $A1$ and $A2$ at 50 K in Fig. 4(b). In the IET model, the overall integrated intensity of $I(\mathbf{q})$, I^{int}, is represented by the superposition of the intensities from each structure of the twin domains:

$$I^{int} \propto |F_{cw}|^2 + |F_{ccw}|^2. \quad (4)$$

Therefore, the Patterson function calculated from I^{int} is explained as the superposition of the twin IET structure. The split of peak A in Fig. 4(b) just originates from the twin domains formed by emergence of the IET structure in which Ag triangles twist. This is a more clear proof that the IET structure is formed at 50 K.

Based on this result, we performed a χ^2 analysis of the data at RT and 50 K. For the data set of 50 K, both narrow and broad reflection intensities were used in the structure analysis. The fitting parameters are a scale factor, atomic positions in polar coordinates (r, θ), β tensors corresponding to atomic mean-square displacements (m.s.d.) for analysis of anisotropic thermal vibrations,[11] and ordinary Debye-Wallar factors for isotropic atoms. Because of a small vertical momentum transfer in GIXD measurements, only lateral parameters were employed. We assumed that a Si trimer also rotates in the same direction by the same angle as a Ag triangle in the IET model.[3] A total of nine and ten parameters are used for the structures at (Ref. 12) RT and at 50 K, respectively, to take into consideration the top Ag layer, first and second Si layers which have large lateral atomic displacements from bulk positions.[2]

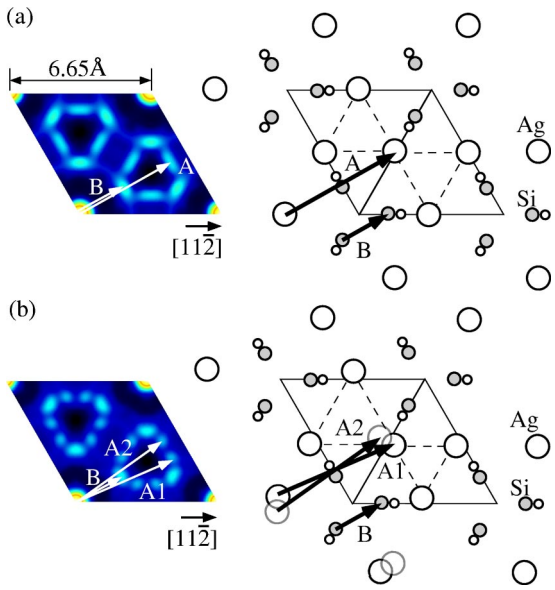

FIG. 4. (Color online) The Patterson maps calculated from the reflection intensities and structural models at (a) RT and at (b) 50 K. A and B correspond to interatomic vectors of a Ag triangle and a Si trimer, respectively. In (b), peak A splits into two peaks $A1$ and $A2$ by the existence of a twin domain structure.

Table I lists the χ^2 fitting results. The most suitable model at RT is found to be the HCT model with $\chi^2=4.9$, in which Ag atoms thermally vibrate with strong anisotropy, rather than the IET model with $\chi^2=6.7$, in which two-state thermal fluctuations are taken into consideration. On the other hand, the IET model with Ag atoms rotating 5.1° is preferred at 50 K, yielding $\chi^2=4.9$. Furthermore, the IET model gives a good χ^2 value of 5.9 with only narrow reflection data at 50 K, while the HCT model yields $\chi^2=9.3$. Although the χ^2 values obtained in the analyses are relatively large by unexpected systematic errors, reliable values for the structure parameters in the HCT model at RT were obtained in comparison with earlier results listed in Table II, which prove the validity of the analyses. One of features of the results is that the lateral size of the Ag triangle is hardly changed with

TABLE II. Parameters of the HCT model at RT obtained by various experimental and theoretical results.

Atom	Parameter	In this work	SXRD [a]	LEED [b]	Theory [c]	Theory [d]
Ag	r(Å)	2.85±0.01	2.851±0.012	2.85±0.12	2.86	2.82
Si(1)	r	1.41±0.03	1.331±0.027	1.44±0.08	1.45	1.49
Si(2)	r	2.15±0.07	2.131±0.044	2.18±0.09		

[a]Reference 2.
[b]Reference 13.
[c]Reference 14.
[d]Reference 3.

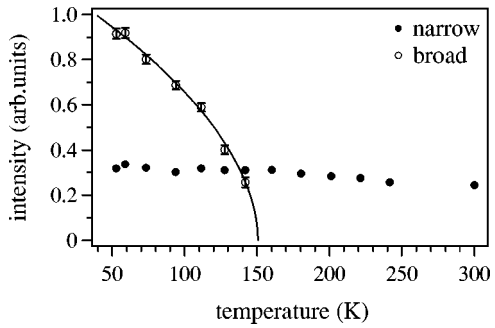

FIG. 5. Temperature dependence of (3 2) reflection intensities. Solid and open circles represent the intensities of narrow and broad components, respectively. The fitted results are shown in solid line. The phase transition temperature T_C and the critical exponent β were found to be 150 ± 4 K and 0.27 ± 0.03, respectively.

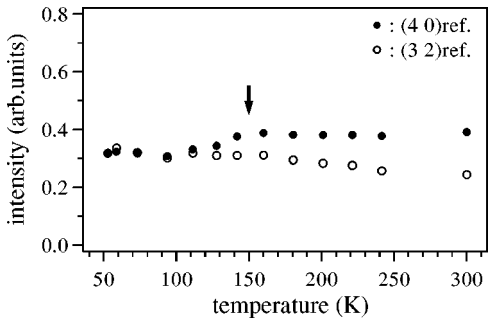

FIG. 6. Temperature dependence of (4 0) and (3 2) reflections represented by solid and open circles, respectively. Obvious changes are observed in the x-ray diffraction intensities around T_C (indicated by the arrow). Error bars are much smaller than the circle's radii.

these two structures. Therefore, the rotation of the Ag triangle makes significant differences between these two structures. The nearest Ag-Ag distance is 3.43 Å for the HCT structure at RT and Ag-Ag distances are 3.01 Å and 3.86 Å in the two Ag inequivalent triangles for the IET structure at 50 K. The Ag-Ag distance of the smaller Ag triangle is close to 2.89 Å of the nearest-neighbor distance in the Ag crystals. These results are well consistent with first-principles calculations.[3]

In the HCT structure at RT, the Ag atom is thermally vibrating with strong anisotropy. The m.s.d. in the rotational direction, $\langle u_\theta^2 \rangle$, has a large value of $(0.30)^2$ Å^2 than that in the radial direction, $\langle u_r^2 \rangle$, of $(0.18)^2$ Å^2. The rather large isotropic values obtained by surface x-ray diffraction in previous works[2,15] would be ascribed to the strong anisotropy. The thermal vibration of the Ag atom in the IET structure at 50 K also shows weak anisotropy.

B. Phase transition

The χ^2 analyses showed that the surface structures at RT and 50 K are explained by the HCT model and the IET model, respectively. Therefore, a structural phase transition occurs in the temperature range from 50 K to RT. The phase transition can be observed by measuring the temperature dependence of the broad reflections since only the IET structure has the broad reflection term in Eq. (1). Figure 5 shows the temperature dependence of the (3 2) reflection intensities. It clearly shows that the broad components appear below the transition temperature T_C of about 150 K.

While broad peaks, which reflect structural deviations from the mean atomic structure, are affected by the short-range order of the twin domain, we recall that each individual structure factor in Eq. (3) is directly related to long-range order. When the sample temperature T is below T_C, the integrated intensity of $I_D(\mathbf{q})$, I_D^{int}, is represented as follows:

$$I_D^{int} \propto |t|^{2\beta}, \tag{5}$$

with the reduced temperature $t=(T-T_C)/T_C$ and the critical exponent β corresponding to a long-range order parameter $\delta \propto |t|^\beta$ (Ref. 16). The intensities of the broad components were best fitted with $T_C=150\pm4$ K and $\beta=0.27\pm0.03$ as shown in Fig. 5. The range of $|t|$ used in the fitting is 0.06 to 0.6. Compared to the two-dimensional (2D) Ising ($\beta=0.125$) or Potts universality classes,[16] the value of β obtained in this work is considerably large.

Besides, the intensities of narrow (4 0) and (3 2) reflections have changed obviously around T_C as shown in Fig. 6. This suggests that its phase transition type is rather displacive than order-disorder because order-disorder phase transitions of finite states do not exhibit an abrupt change in x-ray diffraction intensity in the vicinity of T_C. This intensity change also ensures the results of the χ^2 analysis that the structure at RT is explained not by the fluctuating IET model but by the HCT model. The large β value and the strong anisotropy in thermal vibrations of Ag atoms at RT also remind us of a displacive phase transition caused by a soft phonon mode connected to anharmonic thermal vibrations. When the displacive phase transition occurs, the order parameter δ is thought to be the rotation angle of the Ag triangle. However, the possibility that the system undergoes an order-disorder phase transition is discussed in Refs. 17 and 18. The critical exponent β would be helpful for further discussion.

It is noticed that we may overestimate the critical exponent β since a finite domain size effect is out of consideration. The average sizes of the out-of-phase domain and the twin domain estimated from the full width at half maximum of the narrow and broad components are 530×530 Å^2 and 70×70 Å^2, respectively. The latter is thought to be small enough in comparison to the former. We could not determine the residual two critical exponents ν and γ because no clear critical scattering is observed in this study. One needs to measure temperature dependences of the x-ray diffraction intensities around T_C in detail.

V. CONCLUSIONS

In conclusion, we determined the in-plane atomic structures of the Si(111)-$\sqrt{3}\times\sqrt{3}$-Ag surface at both RT and 50 K by x-ray diffraction. The Si(111)-$\sqrt{3}\times\sqrt{3}$-Ag surface changes from the HCT structure of the high-temperature phase to the IET structure of the low-temperature phase at

the transition temperature $T_C = 150 \pm 4$ K. The Ag atom thermally vibrates with strong anisotropy in the HCT structure at RT. Not only ordinary narrow reflection peaks but also broad reflection peaks are observed below T_C accompanied by the formation of the twin IET structure. The critical exponent β obtained is 0.27 ± 0.03, which is not explained by simple 2D order-disorder transition models. The temperature dependences of the narrow reflection peaks also support the displacive transition.

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*Present address: Materials Science Division, Japan Synchrotron Radiation Research Institute, SPring-8, 1-1-1 Mikazuki-cho, Sayo, Hyogo 679-5198, Japan.

†Corresponding author. Email address: ttaka@issp.u-tokyo.ac.jp

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[12] The parameter θ is fixed at the symmetry position for the HCT model. The symmetry positions are $\theta = 60.0$ and 0.0 for a Ag atom and a first Si atom, respectively.

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