

Order-disorder phase transition of Si(111)- $\sqrt{3} \times \sqrt{3}$ -Ag surface studied by reflection high-energy positron diffraction

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Phase transition of Si(111)- $\sqrt{3} \times \sqrt{3}$ -Ag surface has been investigated in the temperature range from 103 K to 293 K using reflection high-energy positron diffraction. Temperature dependences of the diffraction spot intensities below the critical temperature ($T_c=116$ K) are well explained in terms of the disordering of the inequivalent triangle (IET) structure. From the structure analyses of the rocking curves obtained above and below T_c based on the dynamical diffraction theory, it is concluded that the order-disorder phase transition takes place.
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I. INTRODUCTION

Since the discovery of the $\sqrt{3} \times \sqrt{3}$ periodicity associated with Si(111)-Ag surface [1, 2], its structure has been extensively studied because of the importance as a template to fabricate the self-assembled nanoparticles [3–5]. In 1988, from the x-ray diffraction (XRD) study, the honeycomb-chained triangle (HCT) model shown in Fig. 1(a) was proposed as the room temperature phase [6]. In 1999, the inequivalent triangle (IET) model shown in Figs. 1(b) and 1(c) was proposed as the low temperature phase from the first principles calculations and scanning tunneling microscopy (STM) observation at 62 K [7]. In this structure, the positions of the topmost Ag atoms are slightly shifted from those in the HCT model and hence the mirror symmetry with respect to the $[11\bar{2}]$ azimuth vanishes. The STM image changes from the IET structure to the mirror symmetric one, which seems to be consistent with the HCT model, at room temperature [7, 8]. The above phenomenon was explained as a displacive phase transition [9, 10].

However, the theoretical studies based on the Monte Carlo simulations implied that the order-disorder phase transition may occur rather than the displacive phase transition [11–13]. That is, the high temperature phase corresponds to the thermally fluctuated state between two topologically different IET structures denoted as IET(+) and IET(-) in Figs. 1(b) and 1(c). The potential barrier between IET(+) and IET(-) was estimated to be approximately 100 meV [11]. The angle-resolved photoemission spectroscopy (ARPES) demonstrated no degeneration of the related energy band at both low and room temperatures suggesting that the IET structure is maintained at room temperature [14]. Thus, it is still in debates whether the phase transition of the Si(111)- $\sqrt{3} \times \sqrt{3}$ -Ag surface is displacive or order-disorder and hence whether the HCT model is responsible for the high temperature phase or not.

We studied the Si(111)- $\sqrt{3} \times \sqrt{3}$ -Ag surface using reflection high-energy positron diffraction (RHEPD) [15, 16]. One great advantage of RHEPD is the occurrence of the

total reflection because of the positive charge of positron. In the total reflection condition, positrons hardly penetrate the bulk region. One can therefore accurately determine the topmost surface structures and thermal vibrations [17, 18]. In this paper, we measured the temperature dependences of the RHEPD intensity below room temperature. We will show an evidence of the order-disorder phase transition.

II. EXPERIMENTAL

Samples ($10 \times 5 \times 0.5 \text{ mm}^3$) were cut from a mirror-polished *n*-type Si(111) wafer with the resistivity of 1-10 Ωcm . To form a 7×7 reconstructed surface, the sample was heated at 700 K in several hours and subsequently flashed at 1500 K in 10 seconds a few times in an UHV chamber equipped with a positron beam apparatus. One monolayer Ag atoms were deposited on the Si(111)- 7×7 surface at 773 K using an electron beam evaporator. Sub-

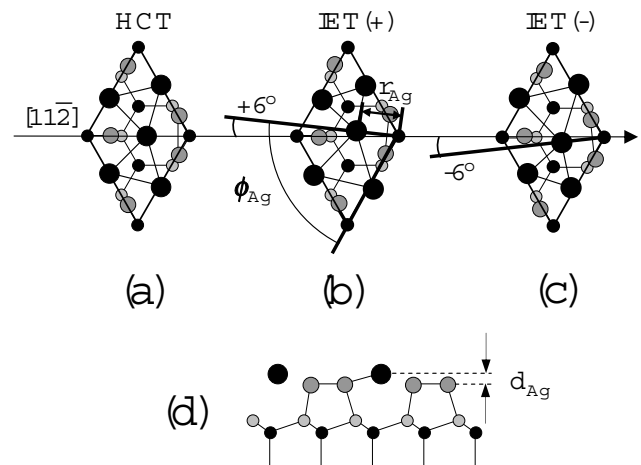


FIG. 1: Schematic drawing of (a) the honeycomb chained triangle (HCT) model, (b) and (c) the inequivalent triangle model with two rotation angles ($\pm 6^\circ$ from the $[11\bar{2}]$ axis) denoted by IET(+) and IET(-), respectively, and (d) the cross sectional structure, for the Si(111)- $\sqrt{3} \times \sqrt{3}$ -Ag surface. The large black circles indicate the topmost Ag atoms and the others are the inner Si atoms. d_{Ag} , r_{Ag} and ϕ_{Ag} , which characterize the position of the topmost Ag atoms, are also defined.

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sequently, the sample was annealed at 793 K for 2 minutes. One monolayer corresponds to the number density of $7.8 \times 10^{14} \text{cm}^{-2}$ for the Si(111) plane. The formation of the Si(111)- $\sqrt{3} \times \sqrt{3}$ -Ag periodicity was confirmed by reflection high-energy electron diffraction (RHEED).

RHEPD experiments were carried out in the temperature range from 103 K to 293 K using a highly parallel and monochromatic positron beam with an energy of 10 keV. The incident azimuthal angle (φ) was varied from 0° to 7.5° relative to the $[11\bar{2}]$ direction. The case of $\varphi = 7.5^\circ$ is the so-called one-beam condition, in which the reflection intensity is dominated by the normal component of the atomic positions to the surface [19]. The glancing angle (θ) was changed from 0.5° to 6.0° at a step of 0.1° by rotating the sample mounted on the manipulator using a stepping motor. The details of the apparatus were described elsewhere [20].

III. RESULTS AND DISCUSSION

Figures 2(a) to 2(f) show the rocking curves obtained at $\varphi = 0^\circ$, $\varphi = 1.5^\circ$ and $\varphi = 7.5^\circ$ and at 110 K and 293 K. In the rocking curves of the (00) spots, broad peaks up to $\theta = 3^\circ$ including the total reflection [21] and the (111) Bragg reflection are commonly observed. The (333) and (444) Bragg peaks are also separately seen in all the conditions. The (222) Bragg reflections are seen at $\varphi = 1.5^\circ$ and $\varphi = 7.5^\circ$, while very weak at $\varphi = 0^\circ$. The curve shapes for the (00) and (2/3 2/3) spots do not change significantly upon cooling, although the intensities in the total reflection region decrease slightly at low temperatures. The rocking curve for the (1/3 1/3) spot changes significantly upon cooling. That is, the intensity increases and the curve shape also changes. Thus, the above results imply that a certain phase transition occurs between 110 K and 293 K.

Figure 3 shows the detailed temperature dependences of the (00), (1/3 1/3) and (2/3 2/3) intensities at $\theta = 2.0^\circ$ and $\varphi = 1.5^\circ$ below room temperature. This glancing angle satisfies the total reflection condition. The slope for the (1/3 1/3) spot intensity abruptly changes at 116 K. The intensities of the (00) and (2/3 2/3) spots slightly decrease below 116 K. These abrupt changes of the spot intensities clearly indicate the occurrence of the phase transition with the critical temperature (T_c) of 116 K. Similar phenomena were reported in the XRD [9] and RHEED [10] studies.

From the change of rocking curves for the (1/3 1/3) spots upon cooling shown in Fig. 2 and the temperature dependences of the spot intensities shown in Fig. 3, it is clear that a certain phase transition takes place at $T_c = 116$ K. The problem here is whether the displacive phase transition from IET to HCT or order-disorder phase transition within IET structure is responsible for it. XRD and RHEED studies proposed the former possibility [9, 10]. Indeed, we tried to calculate the intensities based on the dynamical diffraction theory considering the shifts of the positions of Ag atoms from the IET to the HCT. However, we could not reproduce the observed temperature dependences in terms of displacive phase transition. Thus, the observed temperature effects should be interpreted based on the order-disorder phase transition of the IET struc-

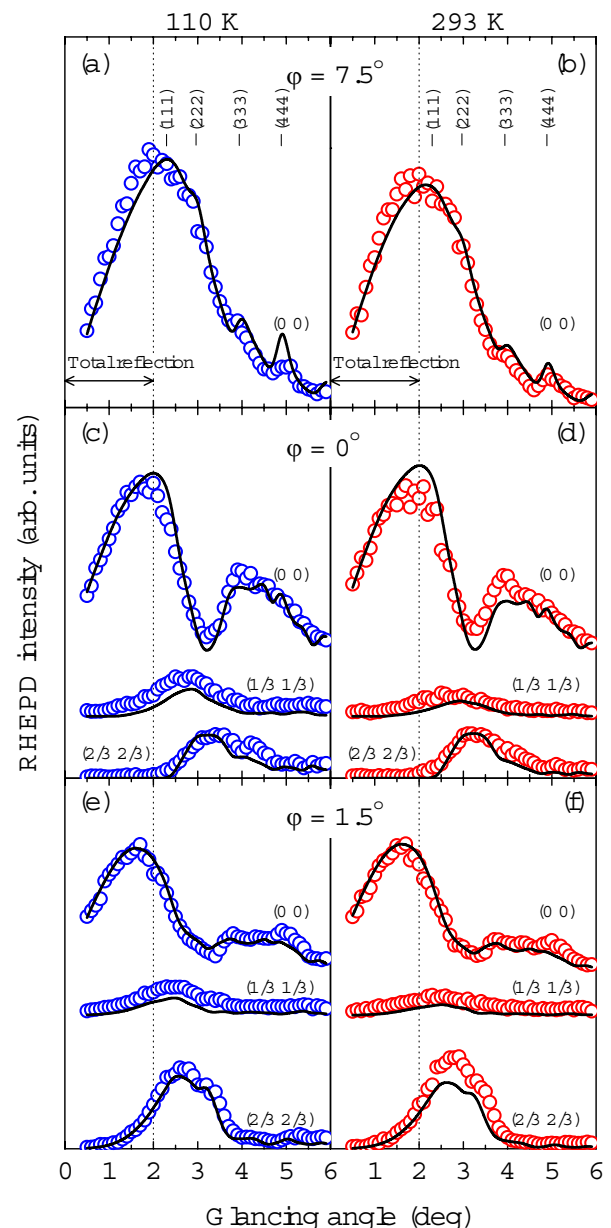


FIG. 2: RHEPD rocking curves from the Si(111)- $\sqrt{3} \times \sqrt{3}$ -Ag surface (a) and (b) under the one-beam condition ($\varphi = 7.5^\circ$), (c) and (d) under the many-beam condition at $\varphi = 0^\circ$, i.e., $[11\bar{2}]$ incidence and (e) and (f) under the many-beam condition at $\varphi = 1.5^\circ$, at 110 K (left) and 293 K (right). The circles denote the experiments. The solid lines represent the rocking curves calculated using the optimized IET model.

ture. Below it is shown that the observed temperature dependences of RHEPD intensities and the rocking curves are reproduced by the order-disorder phase transition.

In our preliminary STM observation, the average size of the domain divided by steps and defects was typically about 1000 Å. The coherence length of the present positron beam is estimated to be approximately 200 Å. Consequently, the interferences among positron waves scattered at neighboring anti-domains are negligible. This allows us to calculate the RHEPD intensities considering a single domain composed of both IET(+) and IET(-) at low temperature. The spot intensities ($I_{\text{hk}}^{\text{total}}$) are given

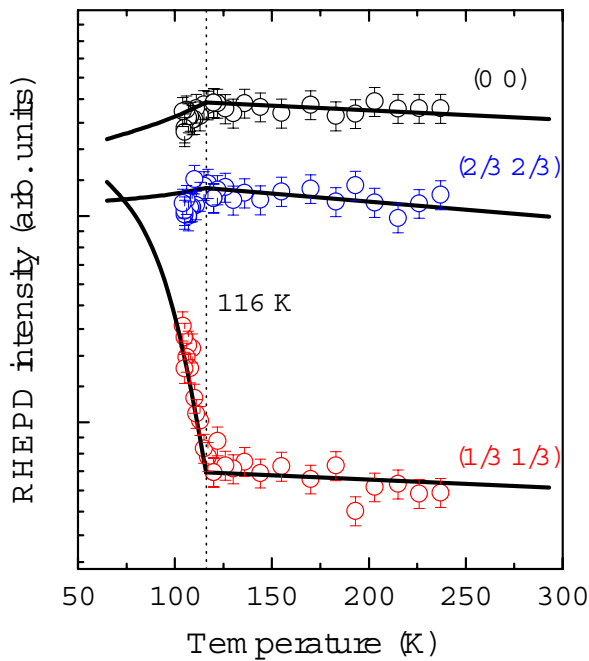


FIG. 3: Temperature dependence of the RHEPD intensity for the (00), (1/3 1/3), and (2/3 2/3) spots at $\theta = 2.0^\circ$ and $\varphi = 1.5^\circ$. The circles show the measured intensities. The solid lines denote the results of calculation based on the dynamical diffraction theory using Eqs. (1) and (2) assuming the order-disorder phase transition.

by

$$I_{\text{hk}}^{\text{total}}(f) = I_{\text{hk}}(f) + I_{\text{hk}}(1-f), \quad (1)$$

where f denotes the occupation probability of one of two IET sites. That is, $1-f$ represents that of the other IET site. Thus, $f = 1/2$ means completely disordered state and $f = 1$ and $f = 0$ mean completely ordered state. Also, $0 < f < 1/2$ and $1/2 < f < 1$ correspond to the partially disordered (or partially ordered) states. For example, regarding f as the occupation probability of the Ag atoms at the IET(+) site, $I_{\text{hk}}(f)$ and $I_{\text{hk}}(1-f)$ express the spot intensities from a single domain composed of the IET(+) and IET(-) structures at $f = 1$, respectively (see Fig. 4). The occupation probability of the Ag atoms at the IET(-) site increases with decreasing f to $1/2$. In this case, the Ag atoms occupy the IET(+) and IET(-) sites with each value of the occupation probability in the unit cell. This means that the Ag atoms at the IET(+) site are randomly replaced with the IET(-) sites and the occupation probabilities at the IET(+) and IET(-) sites correspond to f and $1-f$ at a certain moment, respectively. Figure 5 shows the RHEPD intensities as a function of f calculated based on the dynamical diffraction theory [18, 22]. In the calculation, the atomic coordinates, the Debye temperatures and absorption potentials associated with Ag and Si atoms determined later were used. It is a matter of course that $I_{\text{hk}}^{\text{total}}(f)$ is reversible with respect to $f = 1/2$. For the (1/3 1/3) spot intensity two contributions from $I_{\text{hk}}(f)$ and $I_{\text{hk}}(1-f)$ are separately drawn. It is found that the (1/3 1/3) spot intensity increases drastically as f increases from $1/2$ to 1. The intensities for the (00) and (2/3 2/3) spots, on the contrary, decrease gently

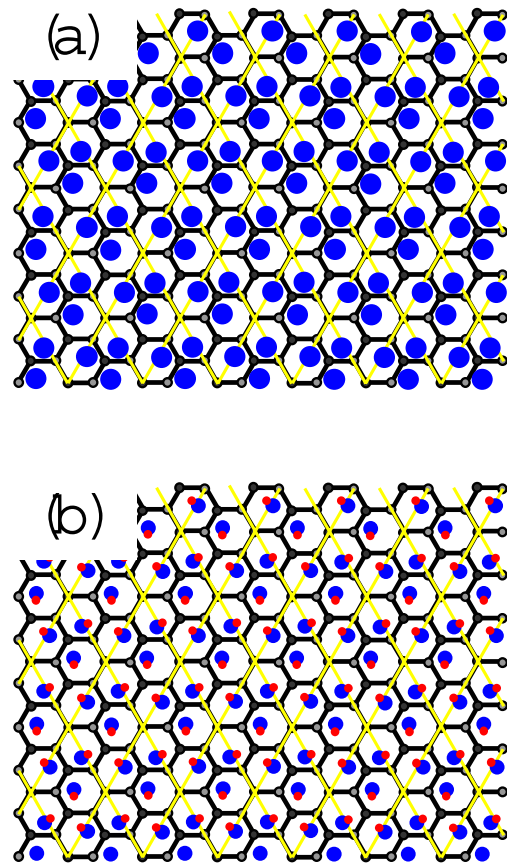


FIG. 4: Structure models of the original IET(+) domain (a) at $f = 1$ and (b) at $f = 0.7$ below T_c . Blue and red circles, whose sizes represent the magnitude of the occupation probability, indicate the Ag atoms situated at IET(+) and IET(-) sites, respectively. Yellow lines show the unit cell. At $f = 0.7$, the Ag atoms randomly occupy the IET(-) site with $f = 0.3$.

with increasing f . Such an opposite behavior is similar to the experiments shown in Fig. 3. That is, assuming that the occupation probability changes as a function of temperature below T_c because of ordering/disordering, the observed temperature dependences (Fig. 3) are reasonably reproduced.

From the relationship between the order parameter and the critical exponent for the phase transition, the occupation probability is given by

$$f = \frac{1}{2} + A \left| 1 - \frac{T}{T_c} \right|^\beta, \quad (2)$$

where β is the critical exponent and A denotes the arbitrary coefficient. Solid lines in Fig. 3 represent the best fit of the temperature dependences using Eqs. (1) and (2). β and T_c were determined to be 0.5 and 116 K, respectively. The value of β is consistent with the ideal one predicted by mean field approximation. This means that the phase transition is second-order and the Ag atoms are randomly situated at the IET(+) or IET(-) sites in the domain.

The existence of the IET structure at room temperature is supported by the ARPES spectra [14]. Also, since the surface structure does not change at the phase transition temperature, the STM image at room temperature is considered to exhibit the time-average of the thermally fluctuating

TABLE I: Optimum r_{Ag} and ϕ_{Ag} for the IET model of the Si(111)- $\sqrt{3} \times \sqrt{3}$ -Ag surface obtained from the analyses of rocking curves and temperature dependent diffraction intensities.

Parameter	Present (110 K)	Present (293 K)	XRD (50 K) [9]	Theory [7]
r_{Ag} (Å)	2.78 ± 0.09	2.74 ± 0.08	2.85	2.82
ϕ_{Ag} (°)	65.8 ± 1.5	64.8 ± 1.3	65.1	66

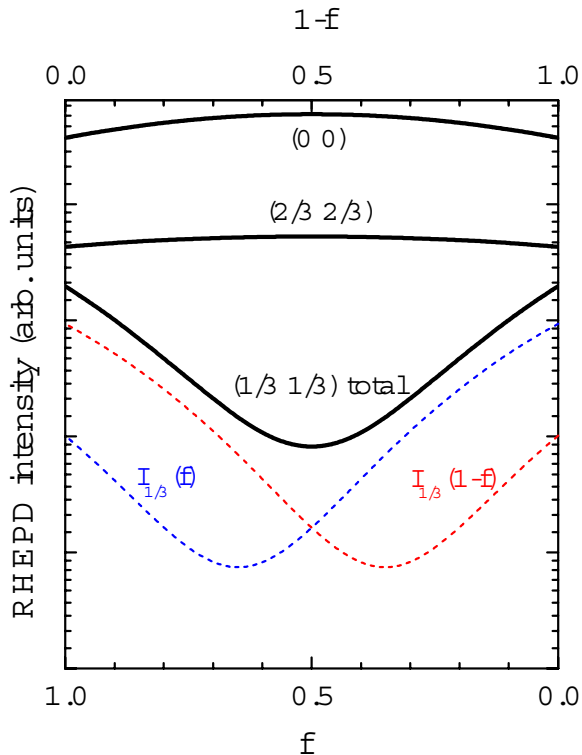


FIG. 5: Calculated RHEPD intensities for (00), (1/3 1/3), and (2/3 2/3) spots as a function of the occupation probabilities of the IET(+) and IET(-) sites.

tuated structure between two IET configurations [11, 13]. Consequently, for the Si(111)- $\sqrt{3} \times \sqrt{3}$ -Ag surface, the order-disorder phase transition occurs within IET structure around 120 K.

Based on the above conclusion, we calculated the rocking curves using the dynamical diffraction theory to determine the atomic coordinates of the Si(111)- $\sqrt{3} \times \sqrt{3}$ -Ag surface [18, 22, 23]. In one-beam condition, the following parameters are needed: (i) the absorption potentials resulting from the electronic excitations, (ii) the Debye temperatures and (iii) the interlayer distances, for both Ag and Si layers. We assumed theoretical absorption potential and interlayer distances for underlying Si atoms [7, 24]. The Debye temperatures for Ag and Si layers

were determined to be 140 K and 610 K from the temperature dependent diffraction intensities, in a similar way for the Si(111)- 7×7 surface [18, 23]. Varying the rest two unknown parameters (the electronic absorption potential and the distance between Ag and the first Si layers defined as d_{Ag} in Fig. 1), the optimum rocking curves were found so as to minimize the reliability factor [18]. Solid lines in Fig. 2(a) and 2(b) represent the calculated best rocking curves. d_{Ag} was determined to be 0.78 Å at 110 K and 0.74 Å at 293 K. These are in good agreement with those determined by experimental [25, 26] and theoretical [7] studies. The thermal shift of d_{Ag} is thus very small. The electronic absorption potential for the Ag layer is negligibly small (~ 0 V) for both 110 K and 293 K. This implies that the electronic excitations by fast positrons are rather suppressed similarly to the result for the Si(111)- 7×7 surface [17].

Using the electronic absorption potential and interlayer distance for Ag layer obtained above and varying the distance (r_{Ag}) and the rotation angle (ϕ_{Ag}) defined in Fig. 1(b), we subsequently calculated the best rocking curves for $\varphi = 0^\circ$ and $\varphi = 1.5^\circ$. Here we also assumed $f = 0.5$ at 293 K and $f = 0.75$ at 110 K considering the above-mentioned results. Solid lines in Figs. 2(c) to 2(f) represent the calculated rocking curves. It is seen that the experimental rocking curves are well reproduced by the calculation. Table I summarizes the obtained parameters. We got $r_{\text{Ag}} = 2.74 \pm 0.08$ Å and $\phi_{\text{Ag}} = 64.8 \pm 1.3^\circ$ at 293 K, and $r_{\text{Ag}} = 2.78 \pm 0.09$ Å and $\phi_{\text{Ag}} = 65.8 \pm 1.5^\circ$ at 110 K. These again suggest that topmost Ag atoms are not displaced accompanying the phase transition. The obtained parameters are in good agreement with the XRD at 50 K [9] and theory [7].

IV. CONCLUSION

In conclusion, we investigated the phase transition of the Si(111)- $\sqrt{3} \times \sqrt{3}$ -Ag surface using the RHEPD. From the temperature dependent diffraction intensities, we found that the Si(111)- $\sqrt{3} \times \sqrt{3}$ -Ag surface undergoes the order-disorder phase transition. The atomic structure of the topmost Ag layer is well described by the IET model both below and above the critical temperature of the phase transition.

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