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Phase Transition of In/Si(111) Surface Studied by Reflection High-Energy Positron Diffraction*

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We determined the structures of Si(111)-4×1-In and Si(111)-8×2-In surfaces that are formed at 293 K and 60 K, respectively, through the rocking curve analyses of reflection high-energy positron diffraction (RHEPD). The structure of Si(111)-4×1-In surface is in good agreement with the zigzag chain structure determined by the surface X-ray diffraction [O. Bunk *et al.*, Phys. Rev. B **59**, 12228 (1999)]. In the Si(111)-8×2-In surface, In atoms are displaced in two dimensional directions from the positions of zigzag chain structure. The structure of Si(111)-8×2-In surface determined here is compatible to the hexagon structure predicted by the first principles study [C. González, F. Flores, and J. Ortega, Phys. Rev. Lett. **96**, 136101 (2006)]. We determined the surface Debye-temperatures of 4×1 and 8×2 phases to be 80 K and 130 K, respectively.

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Keywords: Surface structure; Surface Debye-temperature; Reflection high-energy positron diffraction (RHEPD); Silicon; Indium

I. INTRODUCTION

Low-dimensional structures attract much attention due to their exotic properties. So far, the one-dimensional structure has been investigated mainly using bulk-like organic conductors [1]. Similar one-dimensional structures can be formed on crystal surfaces. Depositing one monolyer of In atoms on a Si(111) surface well-ordered In atomic chains are formed. This surface has a 4×1 periodicity at room temperature [2–5]. From the angle-resolved photoemission spectroscopy (ARPES) measurements, Abukawa *et al.* showed that the three surface bands termed m_1, m_2, and m_3 cross the Fermi level and thus the Si(111)-4×1-In surface is metallic [5]. Yeom *et al.* found an occurrence of ×2 modulation of the 4×1 structure along the chain direction below 100 K by ARPES [2]. Sakamoto *et al.* determined this phase transition temperature to be 130 K from the high-resolution electron-energy-loss spectroscopy (HREELS) measurements [6]. That is, the surface periodicity is transformed from the 4×1 to 8×2 at 130 K. Yeom *et al.* determined the detailed Fermi counters of the m_3 state [2]. They concluded that this transition is dominated by the Peierls instability. In fact, from the temperature dependence of surface electronic conductivity measured using the microscopic four-point probe method, Tanikawa *et al.* confirmed the metal-insulator transition associated with the In/Si(111) surface at around 130 K [7].

Bunk *et al.* determined the structure of the Si(111)-4×1-In surface to be the zigzag chain-like using the surface X-ray diffraction (SXRD) [8], as shown in Fig. 1(a). This structure model is supported by experimental [9] and theoretical studies [10, 11]. The band structure calculated with the zigzag chain structure shows an excellent agreement with the experiments [5, 10, 11]. The structure of the Si(111)-8×2-In surface is explained as the trimer structure [12–15], as shown in Fig. 1(b). However, the appearance of the insulator phase at low temperatures is hardly explained by the trimer structure [12]. Recently, González *et al.* proposed a new structure model for the Si(111)-8×2-In surface from the first-principles calculation [16], as shown in Fig. 1(c). This structure is composed of the In hexagons [16]. The appearance of the band gap and the change in the electrical conductivity may be explained by this structure [16, 17]. However, no experimental evidences indicating the formation of In hexagons have been obtained to date.

To determine the structures of the In/Si(111) surface we used the reflection high-energy positron diffraction (RHEPD). This method is a powerful tool for determining the structure of the first surface layer [18, 19]. When a positron beam is incident on a surface at small enough glancing angles, the total reflection takes place [18]. Having a positron beam with 10 keV, and a Si(111) surface the critical angle of the total reflection is estimated to be 2.0°. In the total reflection region, positrons do not penetrate into the bulk and hence the diffraction intensity is very sensitive to the structure of the first surface layer.

In this study, we performed the RHEPD experiments for the Si(111)-4×1-In and Si(111)-8×2-In surfaces. We determined these structures from the rocking curves and their analyses based on the dynamical diffraction theory. We also measured the temperature dependence of the RHEPD intensity and determined the surface Debye-temperatures.

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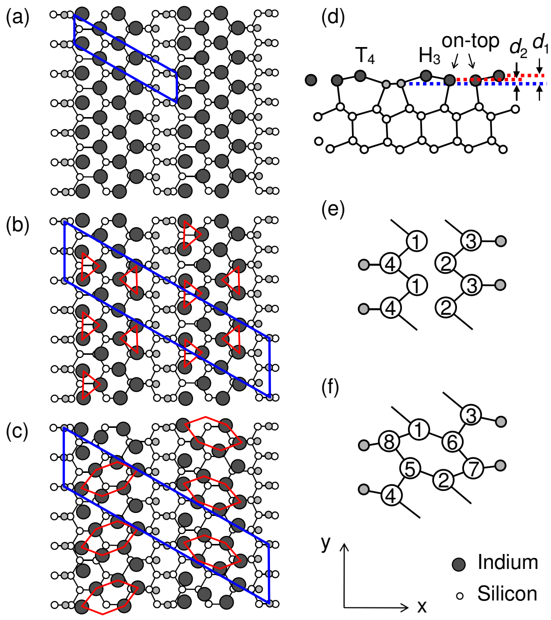

FIG. 1: Schematic drawings of (a) the zigzag chain (4×1) structure, (b) the trimer (8×2) structure, and (c) the hexagon (8×2) structure, for the In/Si(111) surface. Blue parallelograms indicate the unit cells. The side view of In/Si(111) surface is drawn in (d). The large black circles represent the In atoms. Filled and open circles indicate first layer Si atoms and deeper layer Si atoms, respectively. d_1 and d_2 denote the outer In arrays and inner In arrays from the substrate, respectively. In (e) and (f), four and eight parameters used in the optimization of the 4×1 and 8×2 structures are drawn, respectively. The x and y directions are $[11\bar{2}]$ and $[\bar{1}10]$, respectively.

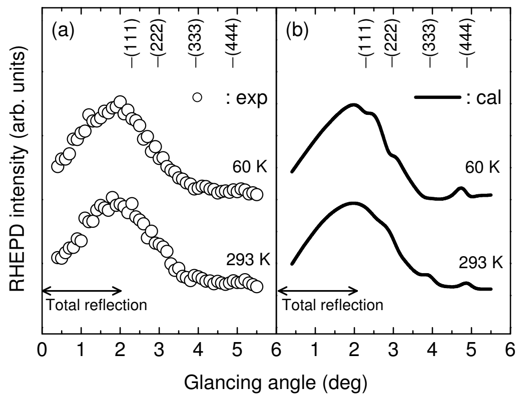

FIG. 2: RHEPD rocking curves (a) measured and (b) calculated from the Si(111)-4×1-In surface at 293 K and Si(111)-8×2-In surface at 60 K under the one-beam condition. The open circles indicate the measured intensities. The solid lines show the intensities calculated based on the dynamical diffraction theory. The incident positron beam energy is 10 keV. The total reflection region corresponds to $\theta < 2.0°$.

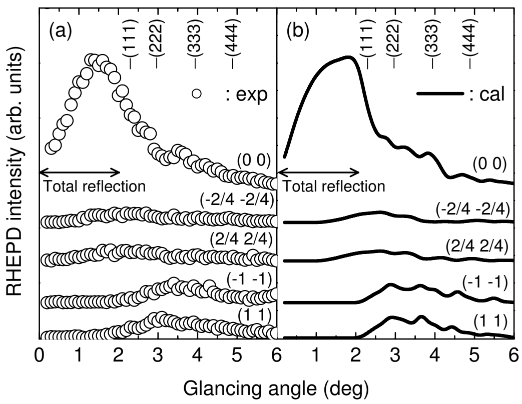

FIG. 3: RHEPD rocking curves (a) measured at 293 K and (b) calculated from the Si(111)-4×1-In surface. The open circles indicate the measured intensities. The solid lines show the intensities calculated based on the dynamical diffraction theory. The azimuthal angle of the incident positron beam corresponds to the $[1\bar{1}0]$ direction. The incident positron beam energy is 10 keV. The total reflection region corresponds to $\theta < 2.0°$.

II. EXPERIMENTAL PROCEDURE

Sample was cut from an n-type mirror-polished Si(111) wafer with a resistivity of 1-10 Ωcm. This was flashed at 1470 K in an ultra-high vacuum chamber (UHV) with a base pressure below 3×10^{-8} Pa to obtain a clean 7×7 surface. Depositing one monolayer of In atoms onto the Si(111)-7×7 surface at 600 K, and subsequent annealing for 1 minute, a Si(111)-4×1-In surface was obtained. The coverage of In atoms was calibrated with a formation of $\sqrt{3}\times\sqrt{3}$ (1/3 ML) structure. The sample was cooled down to 60 K using a cryostat refrigerator. The formations of the Si(111)-4×1-In surface at 293 K and the Si(111)-8×2-In surface at 60 K were checked from the reflection high-energy electron diffraction observations.

Using a highly parallel positron beam with energy of 10 keV, the RHEPD experiments were carried out. The details of the apparatus were described elsewhere [20]. The diffraction patterns were monitored using a microchannel plate assembly with a phosphor plane. In the measurements of rocking curves, the glancing angle (θ) of the incident positron beam was changed from 0.1° to 6.0° at an interval of 0.1° by tilting the sample.

III. RESULTS AND DISCUSSION

Figure 2(a) displays the rocking curves of the specular spots measured from the Si(111)-4×1-In surface at 293 K and Si(111)-8×2-In surface at 60 K under the one-beam condition (7.5° off-oriented from the $[11\bar{2}]$ direction), in which the diffraction intensities depend on the surface interlayer distance because of the suppressed simultaneous reflections parallel to the surface [21]. At both temperatures, the broad peaks including the total reflection, the (111), and the (222) Bragg reflections are observed. The shape of the rocking curves does not change according to the temperature. This result suggests that the positions of In atoms from the substrate are conserved during the transition from the 4×1 to 8×2 phases [22].

To determine the vertical positions of In atoms from the substrate the rocking curves under the one-beam condition were analyzed using the dynamical diffraction theory [23]. The Debye-temperature of Si layers was assumed to be 610 K [24]. The Debye-temperatures of In layers were assumed to be 80 K for the 4×1 phase and 130 K for the 8×2 phase as determined in the subsequent sec-

TABLE I: Vertical distances of outer In arrays (d_1) and inner In arrays (d_2) from the substrate for the Si(111)-4×1-In and Si(111)-8×2-In surfaces. The parameters of the In atoms are shown in Fig. 1(d). The unit of the displacements is given in Å.

	This work (60 K)	This work (293 K)	SXRD [8] (4×1)	LEED [9] (4×1)	Theory [10] (4×1)	Theory [11] (4×1)	Theory [14] (4×1)
d_1(Å)	0.98	0.76	0.86	0.87	0.77	0.76	0.95
d_2(Å)	0.70	0.34	0.49	0.45	0.33	0.39	0.66

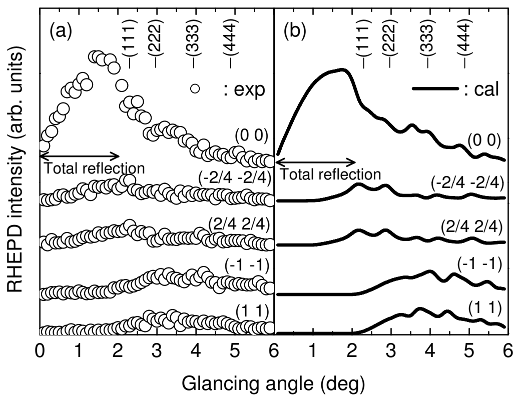

FIG. 4: RHEPD rocking curves (a) measured at 60 K and (b) calculated from the Si(111)-8×2-In surface. The open circles indicate the measured intensities. The solid lines represent the intensities calculated using the optimized hexagon structure. The azimuthal angle of the incident positron beam corresponds to the [1$\bar{1}$0] direction. The incident positron beam energy is 10 keV. The total reflection region corresponds to $\theta < 2.0°$.

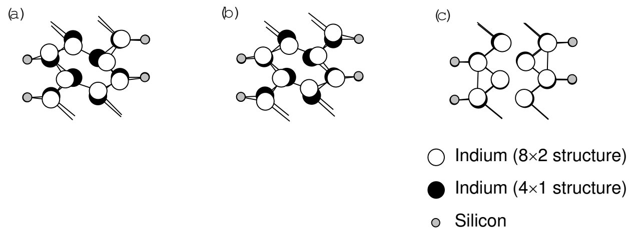

FIG. 5: Schematic drawings of (a) the structure obtained in this study, (b) the hexagon structure, and (c) the trimer structure, for the Si(111)-8×2-In surface. To show the displacements of the In atoms from the 4×1 structure, the zigzag chain structures are also drawn (denoted as black circles).

tion. The absorption potentials for the Si and In layers were assumed to be 1.70 and 0 V, respectively [24, 25]. The distances of outer In arrays (d_1) and inner In arrays (d_2) from the substrate (see Fig. 1(d)) were adjusted so as to minimize the reliability factor defined in Ref. [24] between the measured and calculated curves.

In Fig. 2(b), the solid lines show the calculated rocking curves. These are in good agreement with the measured curves at both temperatures. The vertical positions of the In atoms are listed in Table I. The vertical positions of both inner and outer In arrays are independent of temperature. This feature is consistent with the result of low-energy electron diffraction (LEED) [9], *ab-initio* calculations [14], and reflectance anisotropy spectroscopy (RAS) [26]. That is, d_1 = 0.95-0.98 Å and d_2 = 0.66-0.70 Å. Comparing to the previous studies [8–11, 14], the above values seems to be slightly higher.

To determine the atomic positions parallel to the surface, we measured the rocking curves along the [1$\bar{1}$0] direction. Figures 3(a) and 4(a) show the rocking curves measured from the Si(111)-4×1-In surface at 293 K and the Si(111)-8×2-In surface at 60 K, respectively. When the temperature decreases from 293 K to 60 K, the shape of the (0 0) rocking curve is slightly changed in the glancing angle range of $2.5° < \theta < 4.5°$. The peak intensities of the (-2/4 -2/4) and (2/4 2/4) spots at around $\theta = 2.0°$ increase (see Fig. 4). The change in the rocking curve with temperature indicates the structural transformation of In atoms due to the phase transition.

We calculated the rocking curves of Si(111)-4×1-In surface at 293 K by moving the positions of four In atoms (In_1 through In_4) in Fig. 1(e) until the differences between experimental and calculated curves are minimized. The Debye-temperature for In atoms was assumed to be 80 K, which is determined in the subsequent section. The solid lines in Fig. 3(b) show the calculated rocking curves. The calculated curves are in good agreement with the measured curves (Fig. 3(a)). Table II lists the positions of four In atoms in the unitcell. For comparison, the values obtained by SXRD results of Bunk *et al.* [8] are also listed. The present result is in good agreement with that by SXRD [8]. Thus, we confirmed that the surface structure of the Si(111)-4×1-In at 293 K is composed of In zigzag chains.

Similarly to the above procedure, the rocking curves from the Si(111)-8×2-In surface were calculated. The positions of eight In atoms (In_1 through In_8) shown in Fig. 1(f) were moved in the calculation. The Debye-temperature of the In atoms was assumed to be 130 K, as determined in the subsequent section. The solid lines in Fig. 4(b) show the calculated rocking curves. The calculated curves are in good agreement with the measured ones. Table III lists the positions of In atoms and the reliability factors (R). We adopted the reliability factor defined in Ref. [24]. For comparison, the values obtained by the first-principles calculations of González *et al.* [16] and López-Lozano *et al.* [15] are also listed. The values in parentheses represent the displacements from the position of the zigzag chain structure by Bunk *et al.* [8]. The deviations from the theoretical calculation [16] are less than 0.26 Å except for the y-direction of In_3 and In_6 (see also Fig. 5).

We measured the temperature dependences of the RHEPD intensities from the Si(111)-4×1-In and Si(111)-8×2-In surfaces to determine the surface Debye-temperature of the In layers. Figure 6 shows the temperature dependence of the (0 0) spot intensity from the In/Si(111) surface in the temperature range from 60 to 247 K at $\theta = 2.0°$. The (0 0) spot intensity gradually de-

TABLE II: Positions of In atoms for the Si(111)-4×1-In surface determined through the rocking curve analyses. The actual atomic coordinates (x, y) are related to the ideal (bulklike) atomic position under In_1. The labeling of the In atoms is shown in Fig. 1(e). The unit of the atomic positions is given in Å.

	This work (293 K)		SXRD [8]	
	x	y	x	y
In_1	0.55	0.16	0.36	0.02
In_2	2.92	1.77	2.86	1.92
In_3	5.28	0.04	5.09	0.02
In_4	11.3	-5.61	11.4	-5.74

TABLE III: Positions of In atoms for the Si(111)-8×2-In surface determined through the rocking curve analyses and the reliability factors (R). The actual atomic coordinates (x, y) are related to the ideal (bulklike) atomic position under In_1. The labeling of the In atoms is shown in Fig. 1(f). The values of parentheses are the displacements from the zigzag chain structure determined in the SXRD study. The unit of the displacements is given in Å.

	This work (60 K)		Theory [16]		Theory [15]	
	x (Δx)	y (Δy)	x (Δx)	y (Δy)	x (Δx)	y (Δy)
In_1	0.34	-0.53	0.60	-0.66	0.44	-0.07
	(-0.03)	(-0.55)	(0.23)	(-0.68)	(0.07)	(-0.09)
In_2	2.87	2.53	2.62	2.64	2.77	2.02
	(0.01)	(0.60)	(-0.24)	(0.72)	(-0.09)	(0.10)
In_3	5.30	0.15	5.05	0.59	5.12	-0.10
	(0.21)	(0.13)	(-0.04)	(0.57)	(0.03)	(-0.12)
In_4	11.2	-6.49	11.5	-6.32	11.4	-5.60
	(-0.21)	(-0.75)	(0.05)	(-0.58)	(-0.04)	(0.14)
In_5	-0.47	-3.94	-0.22	-4.01	0.24	-3.74
	(-0.84)	(-0.12)	(-0.59)	(-0.19)	(-0.13)	(0.08)
In_6	3.71	-2.17	3.45	-1.72	2.97	-2.00
	(0.85)	(-0.25)	(0.59)	(0.20)	(0.11)	(-0.08)
In_7	5.11	-4.12	5.26	-4.05	5.02	-3.67
	(0.02)	(-0.30)	(0.17)	(-0.23)	(-0.07)	(0.15)
In_8	11.3	-9.37	11.2	-9.32	11.5	-9.74
	(-0.07)	(0.21)	(-0.17)	(0.26)	(0.06)	(-0.16)
R	2.1 %		2.1 %		2.9 %	

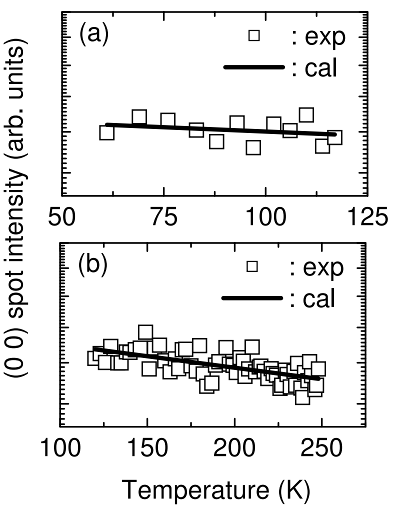

FIG. 6: Temperature dependence of the RHEPD intensities from (a) the Si(111)-8×2-In surface and (b) the Si(111)-4×1-In surface. Open squares indicate the measured intensities of (0 0) spot at the [1$\bar{1}$0] direction. The glancing angle is 2.0°, which satisfies the total reflection condition. The solid line shows the calculated intensity using the surface Debye-temperature of 130 K and 80 K at 8×2 phase and 4×1 phase, respectively.

creases with increasing temperature for both phases. The slope of the intensity with temperature for the 4×1 phase is larger than that for the 8×2 phase. We calculated the temperature dependence of the (00) spot intensity with changing the surface Debye-temperature of the In layers so as to minimize the difference between the measured and the calculated intensities.

As a result, we obtained the surface Debye-temperatures of 80 K and 130 K for the In layers of the Si(111)-4×1-In and Si(111)-8×2-In surfaces, respectively. As shown in Fig. 6, the calculated temperature dependence of the intensity is in good agreement with the measured one in each temperature region. The surface Debye-temperature of 80 K at 4×1 phase is smaller than that at 8×2 phase. This suggests that the thermal vibrational amplitude of the In atoms for 4×1 phase is much larger than that for 8×2 phase. The vibrational amplitudes of the In atoms are estimated to be 0.24 Å at 300 K and 0.07 Å at 60 K by using the above Debye-temperature of 80 K and 130K, respectively.

IV. SUMMARY

The structures of the Si(111)-4×1-In and Si(111)-8×2-In surfaces were determined from the analyses of the RHEPD rocking curves. The vertical positions of In atoms are almost the same for both phases. The Si(111)-4×1-In at 293 K is composed of In zigzag chains. The Si(111)-8×2-In surface at 60 K is composed of In hexagons.

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