Structure and phase transition of low-dimensional metals on Si(111) surfaces studied by reflection high-energy positron diffraction

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Structure and phase transition of low-dimensional metals on Si(111) surfaces studied by reflection high-energy positron diffraction

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Abstract. We investigated the surface phase transitions of Si(111)-4×1 and Si(111)-√3×√3-Ag surfaces using reflection high-energy positron diffraction (RHEPD). We measured the rocking curves of RHEPD at above and below their phase transition temperatures. By means of the intensity analyses based on the dynamical diffraction theory, we discuss the structural changes upon the phase transitions.

1. Introduction

Phase transition is one of the main topics in the condensed matter physics. The surface phase transition takes place within a few layers of the crystal surface. For instance, clean Si(001)-2×1 superstructure undergoes a c(4×2)-2×1 phase transition below 200 K [1]. This phase transition is confirmed as the order-disorder phase transition [1]. That is, asymmetric dimer atoms are thermally flipping above 200 K, leading to the 2×1 periodicity. By depositing foreign atoms on a crystal surface, it is possible to fabricate various kinds of low-dimensional structures. The low-dimensional structure shows various intriguing properties such as Peierls instability, quantum well state, and Rashba effect. To explore these properties, it is very important to study atomic coordinates of the low-dimensional structure. In particular, the structure analyses of the topmost surface are needed.

Reflection high-energy positron diffraction (RHEPD) is a surface sensitive tool to study the atomic coordinates and thermal vibrational amplitudes of the topmost surface [2,3]. In 1998, we developed RHEPD apparatus and succeeded in the observation of RHEPD patterns [4]. Since positrons have a positive charge, the total reflection takes place at grazing incidence [2]. At the total reflection condition, the incident positron is mostly reflected at the topmost surface. Figure 1 shows the penetration depth of the incident positron beam into the Si surface as a function of the glancing angle. The penetration depth was calculated by solving the simple Schrödinger equation using a step-like potential. In this case, the critical angle (θ_c) of the total reflection condition can be determined via the Snell's equation [2]:

$$\theta_c = \arcsin\left(V_0/E\right)^{1/2}, \quad (1)$$

where V_0 and E are the inner potential of the crystal and the accelerating voltage of the incident positron beam. When V_0 = 12 V for the Si crystal and E = 10 kV, the critical angle of the total reflection is estimated to be 2.0° using equation (1). In particular, in the total reflection region, the

penetration depth is quite small, which is less than 2 Å. Thus, the RHEPD is very sensitive to the topmost surface structure.

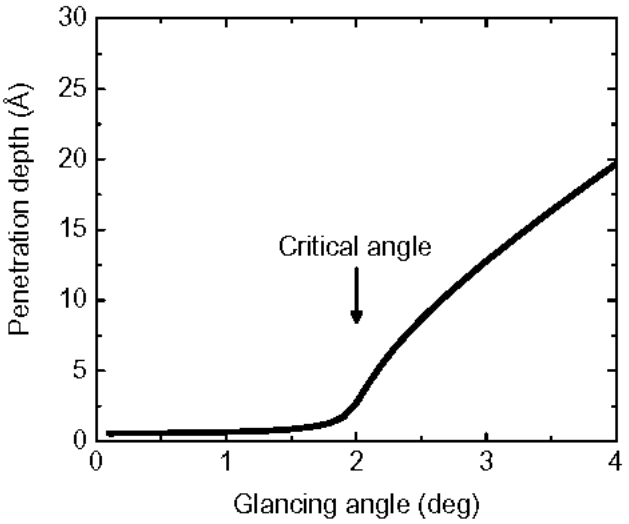

Figure 1. Penetration depth of the positron beam into the Si(111) surface as a function of the glancing angle. The critical angle of the total reflection region is estimated to be 2.0° when the accelerating voltage of the incident positron beam is 10 kV.

In this study, using the RHEPD, we investigated the surface structures at above and below the phase transition temperature. We will show two recent results concerning the phase transitions of one- and two-dimensional metals of In/Si(111) and Ag/Si(111) surfaces.

2. Experimental procedure

Samples with a dimension of 5×25×0.5 mm^3, which were cut from a mirror-polished *n*-type Si(111) wafer (resistivity: 1-10 Ωcm), were used. After transferring them into a ultra-high vacuum (UHV) chamber with a base pressure of 5×10^{-8} Pa, they were heated at 673 K for several hours and then flashed at 1473 K for a few seconds several times to obtain clean 7×7 reconstructed surfaces. To make Si(111)-4×1-In surfaces, 1 monolayer (ML: 1 ML = 7.83×10^{14} cm^{-2}) of In atoms were deposited on the Si(111)-7×7 surface at 673 K using an electron beam evaporator. To prepare Si(111)-√3×√3-Ag surfaces, 1 ML of Ag atoms were deposited on the Si(111)-7×7 surface at 773 K. The substrate temperature (*T*) was calibrated with an infrared radiation thermometer and a thermo couple attached near the sample.

Experiments were carried out in the UHV chamber equipped with a ^{22}Na positron source (3.7GBq) and electromagnetic lens system [5]. The positron beam was accelerated at 10 kV. The glancing angle (θ) of the incident positrons was adjusted by rotating the sample. The diffraction patterns were observed using a micro channel plate with a phosphor plane and a CCD camera. The sample was cooled down by using a cryostat.

3. Results and discussion

3.1. 8×2-4×1 phase transition of In/Si(111) surface

The 4×1 structure is composed of the zigzag chains of In atoms at room temperature [6], as represented in figure 2(a). Since angle-resolved photoemission spectroscopy (ARPES) measurements show the electronic band dispersions characteristic of one-dimensional systems, the 4×1-In structure is

known as a quasi-one-dimensional atomic chain [7]. When the substrate temperature is reduced, the 4×1 structure is transformed to a 8×2 structure [8]. The phase transition temperature was determined to be 130 K using a high-resolution electron energy loss spectroscopy [9]. From the ARPES [8] and surface electrical conductivity measurements [10], it was found that the surface undergoes the metal-insulator transition at 130 K according to the 8×2-4×1 phase transition. Although the phase transition has been extensively investigated by many researchers, the atomic configuration of the 8×2 phase is still in debate. Especially, the atomic positions are not confirmed experimentally. Therefore, the phase transition mechanism is not fully clarified.

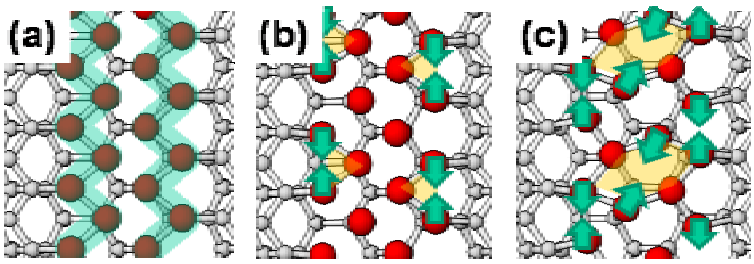

Figure 2. Structure models of (a) zigzag chain, (b) trimer, and (c) hexagon for In/Si(111) surface. Red and gray circles denote the In and Si atoms, respectively. Arrows indicate the possible displacements of In atoms from the zigzag chain to trimer or hexagon structures.

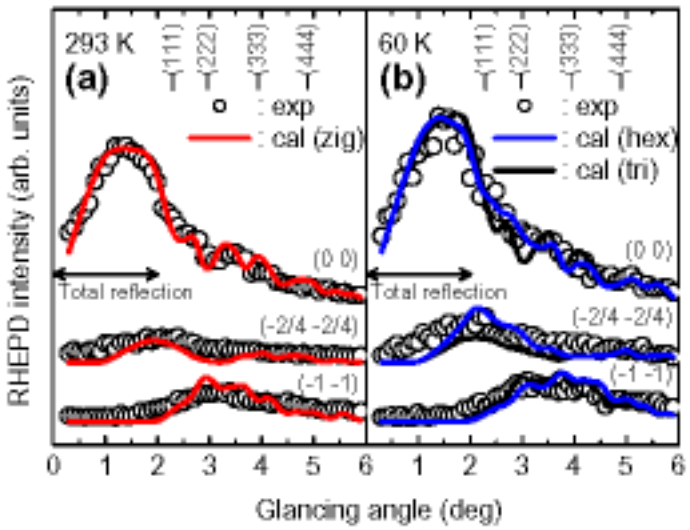

Figure 3. Rocking curves from (a) the Si(111)-4×1 surface at 293 K and (b) 8×2 surface at 60 K. The open circles and solid lines denote the measured and calculated curves, respectively. The accelerating voltage of the positron beam is set at 10 kV. The incident azimuth of the positron beam corresponds to the $[1\bar{1}0]$ direction.

Figures 3(a) and 3(b) show the RHEPD rocking curves from the Si(111)-4×1 surface at 293 K and 8×2 surface at 60 K along the $[1\bar{1}0]$ direction, respectively. As for the Si(111)-4×1 surface, small peaks are observable in the shoulder of the rocking curve for the (0 0) spot in the range of θ = 2.5°-

4.5°. The intensity for the (-2/4 -2/4) spot is relatively weak. When the 4×1 structure is transformed to the 8×2 structure, the total reflection peak becomes sharp. The small peaks in the shoulder disappear. Furthermore, the intensity for the (-2/4 -2/4) spot increases. These changes indicate the atomic displacements of In atoms according to the phase transition.

We investigated the atomic positions of the 4×1 and 8×2 structures from the rocking curve analyses. We calculated the rocking curves based on the dynamical diffraction theory [11]. As for the 4×1 structure, we used the atomic positions of the zigzag chain model determined by surface x-ray diffraction [6] in the calculations. The solid lines in figure 3(a) show the calculated rocking curves using the zigzag chain structure. The calculated curves can well reproduce the small peaks in the shoulder of the rocking curve for the (0 0) spot and the relatively weak intensities for the (-2/4 -2/4) spot. The calculated curve is in good agreement with the measured curve for each spot. Therefore, we also confirmed that the 4×1 structure is composed of the zigzag chains of In atoms.

As for the 8×2 phase, two different structure models, trimer (figure 2(b)) [12,13] and hexagon (figure 2(c)) [14,15] structures have been proposed theoretically. First of all, we calculated the RHEPD intensity based on the dynamical diffraction theory using the trimer model as represented by the black lines in figure 3(b). The small peaks apparently appear in the shoulder of the rocking curve for the (0 0) spot in the range of θ = 2.5°-4.5°. The feature is not consistent with the measured curve. Then, we optimized the displacements of In atoms to minimize the difference between the measured and calculated curves based on the trimer configurations, as denoted by the arrows in figure 2(b). As a result, the measured curves for the Si(111)-8×2 surface cannot be reproduced by considering the trimer model.

Similarly, we optimized the displacements of In atoms to minimize the difference between the measured and calculated curves based on the hexagon configurations, as denoted by the arrows in figure 2(c). The blue lines in figure 3(b) show the calculated rocking curves using the optimized hexagon model. The calculated curve is in good agreement with the measured curve for each spot. In particular, the calculated curve can well reproduce the shape of the rocking curve in the θ range between 2.5° to 4.5°. We found that the optimum atomic positions are close to the values calculated by González *et al*. [14,16,17]. Therefore, we confirmed experimentally that the 8×2 structure is composed of the hexagons of In atoms. The electronic band structures calculated using the 8×2 structure of the optimized hexagons is found to be semiconducting, as calculated by González *et al*. [14,17]. The band gap of the optimized hexagon structure is estimated to be 60-202 meV. This value is in good agreement with the previous experimental results [18]. Very recently, it was found from the reflection anisotropy spectroscopy [19] and first-principles calculations [20] that the spectrum of the 8×2 phase at low temperature can be well explained by considering the hexagon model.

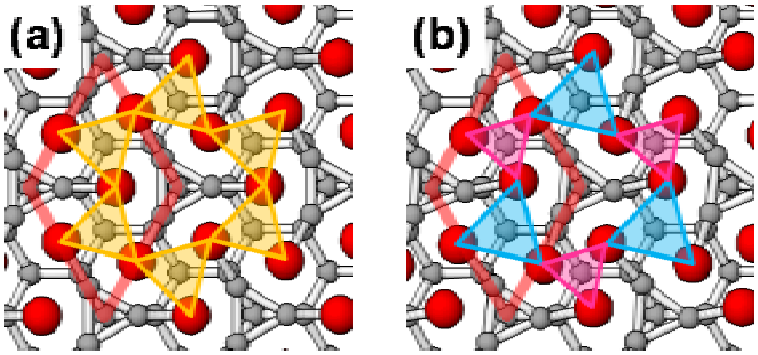

Figure 4. Schematic drawings of (a) honeycomb chained triangle (HCT) and (b) inequivalent triangle (IET) models for the Si(111)-√3×√3-Ag surface. Red and gray circles denote the Ag and Si atoms, respectively. Parallelogram indicates the √3×√3 unit cell.

3.2. √3×√3-√3×√3 phase transition of Ag/Si(111) surface

The Si(111)-√3×√3-Ag surface is one of the most extensively studied surfaces by using several surface techniques. Nowadays it becomes a typical prototype as two-dimensional metal/semiconductor systems [21]. In 1988, the framework of √3×√3-Ag superstructures has been revealed as the honeycomb chained triangle (HCT) by surface x-ray diffraction (see figure 4(a)) [22]. In 1999, this structure was slightly modified. The inequivalent triangle (IET) structure has been confirmed as the grand state structure by using the first-principles calculations and low-temperature scanning tunneling microscopy (figure 4(b)) [23]. In the IET model, the topmost Ag atoms are slightly shifted about 0.15 Å from that in the HCT model. The IET structure contains small and large Ag triangles in the unit cell of √3×√3. According to the mirror symmetry along the $[11\bar{2}]$ direction, two types of the IET structures, i.e., IET(+) and IET(-), exist. There is no difference of the surface energy between the IET(+) and IET(-) structures. When the temperature is elevated above 120 K, the STM image is changed, having the mirror symmetry along the $[11\bar{2}]$ direction [24]. To explain the change in the STM image with temperature, two different mechanisms of the phase transition have been reported, displacive phase transition from the IET to HCT structure [25,26] and order-disorder phase transition of the IET structure [27-31]. The phase transition mechanism of the Si(111)-√3×√3-Ag surface is still controversial.

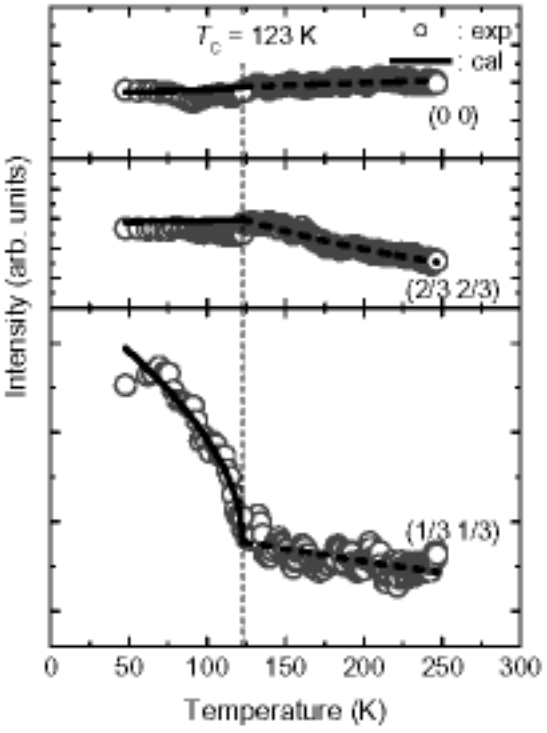

Figure 5. Temperature dependence of the RHEPD intensities from the Si(111)-√3×√3-Ag surface. The azimuthal angle of the incident positron beam corresponds to 1.5° away from the $[11\bar{2}]$ direction. The glancing angle is set at 2.0°, which satisfies the total reflection condition. The open circles denote the measured intensities. The solid lines indicate the calculated intensities using equation (3).

Figure 5 shows the temperature dependence of the RHEPD intensity from the Si(111)-√3×√3-Ag surface in the temperature range from 48 K to 247 K. The RHEPD intensities of (0 0), (1/3 1/3), and (2/3 2/3) spots were measured at 1.5° away from the [$11\bar{2}$] azimuth under the total reflection condition (θ = 2.0°). Above 123 K, the intensities for the (0 0), (1/3 1/3), and (2/3 2/3) spots slightly decrease with increasing the temperature. The intensity change with temperature follows the Debye-Waller like attenuation. However, below 123 K, the (0 0) and (2/3 2/3) spot intensities slightly decrease with decreasing the temperature. Very interestingly, the (1/3 1/3) spot intensity drastically increases with decreasing the temperature. These intensity changes cannot be explained by the displacive phase transition from the HCT to IET structure. We found that these intensity changes can be reproduced by considering the order-disorder phase transition of the IET structure, as described below.

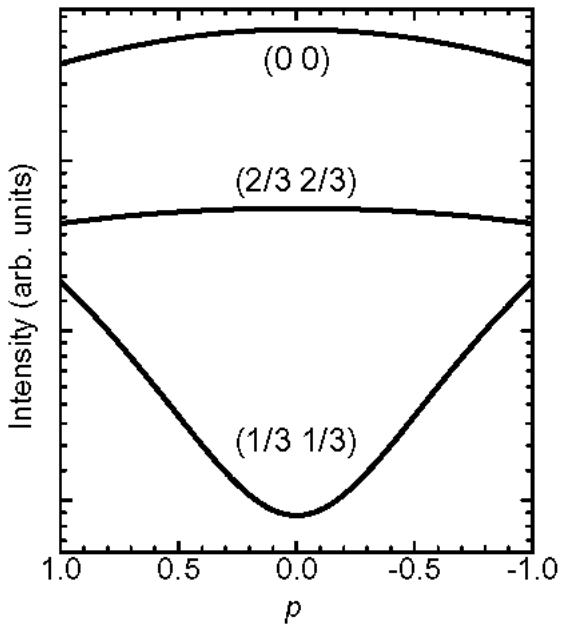

Figure 6. Calculated RHEPD intensities for (00), (1/3 1/3) and (2/3 2/3) spots as a function of the order parameter (p). p of 0.0 and 1.0 or –1.0 mean the completely disordered and completely ordered states, respectively. The calculations were done based on the dynamical diffraction theory.

Assuming n_+ and n_- to be the fraction of the IET(+) and IET(-) phases, respectively, the order parameter (p) is expressed by

$$p = \frac{n_+ - n_-}{n_+ + n_-}. \tag{2}$$

In the completely ordered state, p = 1 or p = -1. On the other hand, in the completely disordered state, p = 0. By considering these states, we calculated the RHEPD intensity based on the dynamical diffraction theory as a function of p. The detail of the RHEPD calculation was described in the previous paper [32]. Figure 6 represents the RHEPD intensities for the (0 0), (1/3 1/3), and (2/3 2/3) spots with p. When p changes from 0 to 1 or -1, the intensities for the (0 0) and (2/3 2/3) spots decrease slightly. On the contrary, the intensity for the (1/3 1/3) spot drastically increases with p. Assuming that p depends on the substrate temperature, p is given by

$$p \propto \left|1 - \frac{T}{T_c}\right|^{\beta}, \tag{3}$$

where T_c and β denote the phase transition temperature and critical exponent, respectively. From the fitting between the measured and calculated intensities, we obtained β = 0.28. The value of β is slightly larger than that (0.125) expected from the two-dimensional Ising model. The result suggests that the Si(111)-√3×√3-Ag surface system cannot be expressed by the simple two-dimensional Ising model. The calculated intensities using β = 0.28 can well reproduce the measured intensities, as shown by the solid lines in figure 5. Therefore, we found that this phase transition can be explained by the order-disorder phase transition.

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