RHEED Rocking Curve Analysis of Si(111)√3 × √3-Ag Surface Phase Transition at Low Temperature *

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Si(111)√3 × √3-Ag surface structural phase transition from honeycomb chained triangles (HCT) structure to inequivalent triangles (IET) structure is investigated using reflection high-energy electron diffraction (RHEED) rocking curves. Rocking curves are measured during spontaneous heating process of a cooled (~120 K) sample up to room temperature. The rocking curves were analyzed using many-beam dynamical RHEED calculations with three kinds of structural models, HCT (Ag triangle stays at mirror symmetry position), IET (Ag triangle rotates by 6 degrees) and rotating-HCT (r-HCT; Ag atoms are randomly rotating between ±6° which maintains the mirror symmetry) structures. At room and low temperatures, r-HCT and IET structures give the best results respectively. Rocking curves between room and low temperatures are also reproduced by mixing of r-HCT and IET structures and the mixing ratio changes almost linearly with substrate temperature. It is obtained that r-HCT coverage is almost 100% at room temperature and IET coverage is about 60% at 120 K. It is also found that mixing ratio of IET/r-HCT structure meets 0.5 at about 150 K which is known as a transition temperature in previous reports.

Keywords: Reflection high-energy electron diffraction; Surface structure, morphology, roughness, and topography; Ag; Si(111)

I. INTRODUCTION

Many studies were reported[1–8] on phase transition of Ag induced Si(111)√3 × √3 structure at low temperature after Aizawa et al.[9] predicted existence of a stable IET (inequivalent triangles) structure using a first principal calculation in 1999. Before rising the IET structure, HCT (honeycomb chained triangles) structure[10–12] was believed to be a stable structure. The most important difference in those structures are their symmetry, the HCT has p3m1 while the IET has p3. The mirror symmetry breaking in the IET structure is caused by rotation of topmost Ag and Si triangles by 6 degrees. STM observation[1] clearly revealed the symmetry breaking at about 60 K. Most of the reports[7, 9, 13] concluded that the IET to the HCT phase transition was order-disorder transition as well as Si(001) c(4×2) to 2×1 phase transition[14]. Experimental evidence of order-disorder transition was reported by Matsuda et al.[7], in which photoemission spectroscopy showed mirror symmetry breaking even at room temperature. While in a photoelectron spectroscopic study by Uhrberg et al.[4], they concluded that symmetric structure maintained even at low as 100 K. X-ray diffraction (XRD)[6] study concluded that structural phase transition occurred at around Tc = 150 K because some Bragg intensities showed discontinuous changes at Tc and diffuse components appeared lower than Tc. We also reported[8] that reflection high-energy electron diffraction (RHEED) rocking curve changes continuously with substrate temperature, while temperature dependence of relative rod intensities show changes in gradients at about 150 K. It was mentioned that some kind of structural transition occurred at 150 K, however, theoretical analysis was not carried out in the previous report.

In this paper, many-beam dynamical RHEED analysis was carried out for rocking curves during the phase transition to clarify the phase transition mechanism.

II. EXPERIMENTAL

P-type Si(111) wafer with resistivity of 10–16 Ωcm was used as a substrate. The substrate was cleaned by acetone in an ultrasonic cleaner followed by several times of flash heating in an ultra-high vacuum chamber. Silver atoms were evaporated by a BN crucible and its deposition rate was 0.2 monolayer (ML)/min. Si(111)√3 × √3-Ag surface was obtained by 1 ML Ag deposition at 830 K of substrate temperature. The substrate was cooled down to 120 K by liquid N2 and RHEED rocking patterns were measured during spontaneous heating process of the substrate up to 290 K. The heating process took about 28 hours and about 100 rocking patterns were measured during the process. Incident electron energy was 10 keV and an incident azimuth was chosen at [112] direction. Base pressure of the vacuum chamber was ~1 × 10−8 Pa and pressure during Ag deposition was lower than 1 × 10−7 Pa. Details of the experimental apparatus used in this study is explained elsewhere[8].

Rocking curves were obtained from measured rocking patterns by choosing one diffraction spot in the pattern. Therefore it is possible to obtain rocking curves for dif-

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different spots at an experiment. These rocking curves were analyzed using RHEED dynamical intensity calculations with multi-slice method[15]. Parameters used in the calculations are shown in Fig. 1. As shown in the figure, 4 layers of substrate Si and topmost Si/Ag triangles were took into account. In addition to the atomic positions, mean square displacements(\(\langle u^2 \rangle\)) for Ag (normal/parallel to the surface) and Si (isotropic) were also used as parameters. Surface normal positions (z coordinates) of Ag and Si1 were measured from bulk positions of Si2 and those for other atoms (Si2 ∼ Si5) were measured from respective bulk positions. Surface parallel components for Ag, Si1 and Si2 were represented by triangle radius \(r\) and rotation angle \(\theta\) as denoted in the lower part of Fig. 1. Those components for other atoms (Si3 ∼ Si5) were fixed as its bulk positions. In the calculation, 3 structural models were assumed, HCT[10, 16], IET[1, 9] and rotating-HCT (r-HCT) structures. The HCT structure has \(p\bar{3}m\) symmetry with triangle rotation angle \(\theta\) (see Fig. 1) of 0 degree. The IET structure has \(p\bar{3}\) symmetry with \(\theta\) of 6 or −6 degrees (which causes breaking of mirror symmetry in the HCT structure). The r-HCT structure has \(p31m\) symmetry with \(\theta = \pm 6\) degrees in which Ag/Si triangle is thermally rotated between two stable angles (each site has 0.5 ML of coverage in the calculation). It should be noted that in the IET structure, 3 Ag atoms which compose a triangle rotate to the same direction (synchronous rotation), while in the r-HCT, they rotate randomly (random rotation) which maintains the mirror symmetry on average. To determine optimal structure, Pendry \(R\) factor was used as an index. The \(R\) values were calculated for 1 ∼ 5° of incident angle range for 00-rod rocking curves, because reliability of experimental intensities outside this range is relatively poor. In the optimization, atomic positions were changed by ∼0.05 Å step and mean square displacements were changed by ∼0.002 Å² step. 21 beams were used in the calculations.

III. RESULTS AND DISCUSSION

Figure 2 shows experimental rocking curves and optimized calculated results at substrate temperature of 290 K and 130 K. The r-HCT and the IET structure was used for 290 K and 130 K curves respectively. Values of \(R\) factors for respective curves are 12 % and 13 %. The IET structure did not reproduce the rocking curve at 290 K at all. In addition, either of the r-HCT nor the HCT structure did not reproduce the rocking curve at 130 K. While the HCT structure can be optimized for the rocking curve at 290 K with \(R = 19\) %. However, \(R\) factor for the HCT structure is significantly worse than that of the r-HCT structure. Therefore it is concluded that the r-HCT and the IET structures are optimal structures for room and low temperature phases respectively, i.e., Ag atom randomly rotates at room temperature.

Optimized parameters used in the calculation is shown in Table I. In the table, XRD results[16, 17] and two kinds of first principle calculation (FPC) results[9, 18] are also shown for comparison. As shown in the table, difference in atomic positions between high (r-HCT) and low
temperature, while surface normal component $<u^2>$ at 130 K are shown in Table II. Optimized parameters for substrate temperature of 290 K and changed as a parameter as well as other structural parameters. 416 http://www.sssj.org/ejssnt (J-Stage: http://ejssnt.jstage.jst.go.jp)

mally, decreases with decreasing substrate temperature. Nor-

previously reported results. In contrast, the IET temperature phases are small which agrees with (IET) temperature phases are small which agrees with previously reported results. In contrast, $<u^2>$ of Ag atoms were drastically changed. Surface parallel component $<u^2>_{Ag//p}$ increases with decreasing substrate temperature, while surface normal component $<u^2>_{Ag//n}$ decreases with decreasing substrate temperature. Normally, $<u^2>$ should decreases with decreasing substrate temperature, so that behavior of surface parallel component seems abnormal. Substrate temperature dependence of $<u^2>_{Ag}$ is discussed later. Comparing respective parameters with the other reports, vertical position of Ag layer is slightly lower and Si triangle size is slightly larger. The other parameters agree within calculation error ($\sim 0.05$ Å) except for deeper Si positions. Since rocking curves are insensitive to deeper atomic positions, it is considered that accuracy of those values are lower than that of XRD results. At present, it is difficult to conclude which value is accurate.

As described above, the r-HCT and the IET structures are optimal structures for room and low temperature phases respectively. The next problem is the phase transition mechanism how the IET structure changes to the r-HCT structure. There are two possibilities to explain the transition, one is the IET structure changes to r-HCT structure at critical temperature, and another is the r-HCT structure gradually replaces the IET structure as raising the substrate temperature. As reported before[8], temperature dependence of the rocking curve did not show sudden change in its shape. Therefore it is considered that the second assumption is probable. To confirm this assumption, rocking curves between low and high temperatures were calculated with a mixture model of the IET and the r-HCT structures (Fig. 3). In the calculation, all structural parameters as well as a mixing ratio $\xi = IET/r-HCT$ were optimized. The $R$ factors varies around $11 \pm 1\%$ over the temperature range. In addition to better $R$ factors, experimental curves were well reproduced by the calculations as shown in the figure (i.e. peaks A and B in the figure) which ensures that the surface consists of two different structures around the phase transition temperature.

Optimized parameters used in the calculations shown in Fig. 3 is listed in Table II. As shown in the table, atomic positions were scarcely changed as same as the optimized parameters for single phase cases (Table I). As mentioned above in the case of single phase calculation, behavior of parallel components $<u^2>_{Ag//p}$ increases with decreasing the substrate temperature. On the contrary, it stays constant in the case of mixed phase calculation. In the mixed phase case, $\xi$ at 130 K is far from unity but is about 60 %, i.e. 40 % of the surface is still r-HCT structure. The r-HCT model corresponds to large lateral thermal vibration model, therefore, it is considered that larger $<u^2>_{Ag//p}$ value in the single phase case compensate ignorance of r-HCT phase at 130 K, i.e. $<u^2>_{Ag//p}$ in the single phase case is artificial but not real value. On the other hand, mean square displacement of Si atom $<u^2>_{Si}$ seems to increase at low temperature in the mixture case. Optimized value of $<u^2>_{Si}$ for 130 ~ 260 K almost stays $0.3 \times 10^{-2}$ Å$^2$, and it has $0.5 \times 10^{-2}$ and $0.1 \times 10^{-2}$ at respective ends of the temperature range. Since calculation step for $<u^2>_{Si}$ is $0.2 \times 10^{-2}$, it is difficult to say the difference in $<u^2>_{Si}$ is significant. In addition to 00-rod rocking curve optimization, fractional rods optimization...
TABLE I: Optimized parameters for r-HCT (290 K) and IET (130 K) calculations and comparison with XRD experimental and first principle calculation (FPC) reports.

| Parameter   | This work | XRD [16, 17] | FPC 1 [9] | FPC 2 [18] |
|-------------|-----------|--------------|-----------|------------|
|             | h-HCT IET | HCT IET      | HCT IET   | HCT IET    |
| r_{Ag} [Å]  | 2.83 2.85 | 2.85 2.85    | 2.82 2.82 | 2.81 2.80  |
| r_{Si} [Å]  | 1.50 1.50 | 1.41 1.45    | 1.47 1.49 | 1.43 1.45  |
| r_{Si2} [Å] | 2.30 2.30 | 2.15 2.09    |           |            |
| z_{Ag} [Å]  | 2.82 2.87 | 3.05         | 3.02 3.01 | 2.86 2.93  |
| z_{Si} [Å]  | 2.25 2.25 | 2.25         | 2.29 2.29 | 2.24 2.24  |
| z_{Si2} [Å] | -0.05 -0.05 | 0.00       |           |            |
| z_{Si3a} [Å] | 0.05 0.05 | 0.05         |           |            |
| z_{Si3b} [Å] | -0.10 -0.10 | -0.26     |           |            |
| z_{Si4a} [Å] | 0.05 0.05 | 0.05         |           |            |
| z_{Si4b} [Å] | -0.10 -0.10 | -0.18     |           |            |
| z_{Si5} [Å] | -0.10 -0.10 | 0.00       |           |            |
| <u^2>_Ag/p | 0.5 1.1  |             |           |            |
| <u^2>_Ag/n | 1.7 0.8  |             |           |            |
| <u^2>_Si  | 0.1 0.1  |             |           |            |

TABLE II: Optimized parameters used in the calculation at 290 K and 130 K of Fig. 3.

| Parameter   | 290 K | 130 K |
|-------------|-------|-------|
| r_{Ag} [Å]  | 2.83  | 2.85  |
| r_{Si} [Å]  | 1.50  | 1.50  |
| r_{Si2} [Å] | 2.30  | 2.30  |
| z_{Ag} [Å]  | 2.82  | 2.82  |
| z_{Si} [Å]  | 2.25  | 2.25  |
| z_{Si2} [Å] | 0.00  | 0.00  |
| z_{Si3a} [Å] | 0.08  | 0.08  |
| z_{Si3b} [Å] | -0.10 | -0.10 |
| z_{Si4a} [Å] | 0.05  | 0.05  |
| z_{Si4b} [Å] | -0.10 | -0.10 |
| z_{Si5} [Å] |       |       |

with large beam number (> 30) should be carried out to discuss parameter values in detail (however, it requires far more computational resources).

To confirm calculation reliability, fractional order rod rocking curves were calculated using the parameters obtained by 00-rod optimization shown in Table II. Figure 4 shows comparison between experimental and calculated rocking curves for 1/3/3, 2/3/3 and 11-rods at 290 K and 130 K. Although those curves were not optimized to experimental ones, peak positions and its shapes are reproduced by the calculations appreciably. However, because of the small number of beams used in the calculation (= 21), experimental and calculated intensities does not agree sufficiently especially for 11-rod which is relatively far from 00-rod. From the above results, it is considered that the parameters in Table II is practically correct and experimental rocking curves can be explained by mixture phase of the IET and the r-HCT structures.

Temperature dependence of the normal component of mean square displacement of Ag atoms <u^2>_Ag/n and mixing ratio of IET/r-HCT ξ are shown in Fig. 5. As shown in the figure, <u^2>_Ag/n increases with increasing the substrate temperature. The value <u^2>_Ag/n = 1.7 × 10^{-2} Å^2 at room temperature is considerably large as compared with normal surface atoms (< 1 × 10^{-2} Å^2). It is considered that rotating Ag atom also vibrates in vertical direction with quite large amplitude. As described above, ξ is almost 0 (surface is covered with r-HCT structure) at room temperature and about 0.6 at lowest temperature in this experiment (~ 120 K). It is also obvious that ξ changes linearly with the substrate temperature.

It was reported[8] that gradients of relative rod intensities changed at about 150 K. It was also reported[6] that Bragg component of a 4/3/4 spot in XRD showed discontinuous change and diffuse component appeared at about 150 K, which suggests that the transition temperature is around 150 K. From Fig. 5, the mixing ratio becomes almost half at 150 K, which agrees with the transition temperature obtained in previous works. Hence, it is considered that transition temperature corresponds to the temperature that dominant structure changes between IET and r-HCT. However, calculated relative rod intensities with parameters in the Table II only shows monotonic decrease with temperature but not kinks in gradients at around 150 K. Therefore it is considered that changes in

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IV. CONCLUSION

In conclusion, it was found that the optimal structure of Si(111)√3 × √3-Ag at room temperature is the r-HCT structure, in which Ag atoms are randomly fluctuating between ±6° of rotation angle. Because of the random fluctuation, mirror symmetry (p31m) is maintained on average. At sufficiently low temperature, it is confirmed that the IET structure is optimal. Atomic positions for both surfaces are very similar to each other, while normal component of mean square displacement of Ag atom increases linearly with increasing substrate temperature. Rocking curves at intermediate temperature range were reproduced by mixture model of the IET and the r-HCT structures and the mixing ratio also changes linearly with substrate temperature. Therefore it is concluded that the r-HCT structure gradually replaces the IET structure with increasing substrate temperature. It is also found that a known transition temperature 150 K corresponds to the temperature at which dominant structure exchanges between IET and r-HCT.

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