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Metal Co-Adsorption Induced $\sqrt{21} \times \sqrt{21}$ Superstructure on Si(111) Surface Studied by Reflection High-Energy Positron Diffraction*

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The Ag adsorption induced $\sqrt{21} \times \sqrt{21}$ superstructure on the Si(111)-5 × 2-Au structure at high temperature, namely $\sqrt{21} \times \sqrt{21}$-(Au,Ag), has been studied using reflection high-energy positron diffraction. The profiles of the rocking curves and the intensity distributions in the diffraction pattern are similar to those from the Ag or Au adsorption induced $\sqrt{21} \times \sqrt{21}$ superstructure ($\sqrt{21} \times \sqrt{21}$-Ag and $\sqrt{21} \times \sqrt{21}$-(Ag,Au)) on the Si(111)-$\sqrt{3} \times \sqrt{3}$-Ag structure below room temperature. Assuming all of the adsorption atoms as the Ag atoms, we analyzed the atomic structure of the $\sqrt{21} \times \sqrt{21}$-(Au,Ag) surface on the bases of the dynamical diffraction theory. We found that the structure model is almost the same as the $\sqrt{21} \times \sqrt{21}$-Ag and $\sqrt{21} \times \sqrt{21}$-(Ag,Au) surfaces.
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Keywords: Surface structure; Reflection high-energy positron diffraction; Total reflection; Silicon; Gold; Silver

I. INTRODUCTION

Due to the deposition of small amount of the noble metal atoms such as Ag and Au on the Si(111)-$\sqrt{3} \times \sqrt{3}$-Ag surface, the $\sqrt{21} \times \sqrt{21}$ superstructures are formed, accompanied with a drastic increase in the surface electronic conductivity [1, 2]. The atomic structures of the $\sqrt{21} \times \sqrt{21}$-Ag and the $\sqrt{21} \times \sqrt{21}$-(Ag,Au) surfaces have been extensively investigated by using various surface techniques [3–8]. These $\sqrt{21} \times \sqrt{21}$ structures are considered to be almost the same. Figure 1 shows one possible structure model of the $\sqrt{21} \times \sqrt{21}$ surface [7, 8]. In this model, three adatoms in the unit cell are located on the center of the large Ag triangle of the inequivalent triangle (IET) structure [9] and form the triangular shape, surrounding the Si trimer. It should be noted that these $\sqrt{21} \times \sqrt{21}$ structures are constructed using the $\sqrt{3} \times \sqrt{3}$-Ag surface as a template. Recently, Matsuda et al. discovered that the deposition of Ag atoms on a Si(111)-5 × 2-Au surface also leads to the formation of the $\sqrt{21} \times \sqrt{21}$ superstructures ($\sqrt{21} \times \sqrt{21}$-(Au,Ag)) [10]. That is, it is possible to make the $\sqrt{21} \times \sqrt{21}$ superstructures without the template of the $\sqrt{3} \times \sqrt{3}$-Ag surface. The atomic coordinate of the new $\sqrt{21} \times \sqrt{21}$ superstructure is unknown. We investigated the $\sqrt{21} \times \sqrt{21}$-(Au,Ag) superstructure by using a reflection high-energy positron diffraction (RHEPD).

The RHEPD is a surface sensitive tool to study the surface structure [11]. When the positron beam is incident on the crystal surface below the critical angle, the total reflection takes place [12]. The critical angle of the total reflection is evaluated via the Snell's low [12]. When the mean inner potential and the accelerating voltage are 12 V and 10 kV, respectively, the critical angle is estimated to be 2.0°. In the total reflection region, the incident positron beam does not almost penetrate the bulk. Thus, the diffracted intensity is very sensitive to the topmost surface. In this study, we determined the atomic coordinate of the $\sqrt{21} \times \sqrt{21}$-(Au,Ag) superstructure by means

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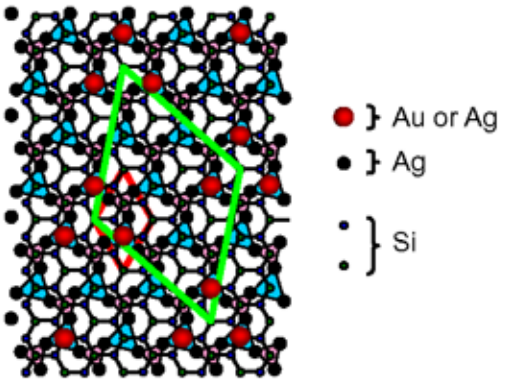

FIG. 1: Schematic drawing of one possible structure for the Si(111)-$\sqrt{21} \times \sqrt{21}$-Ag and Si(111)-$\sqrt{21} \times \sqrt{21}$-(Ag,Au) surfaces. Green and red diamonds denote the unit cells of the $\sqrt{21} \times \sqrt{21}$ and $\sqrt{3} \times \sqrt{3}$ structures, respectively. The underlying structure is composed of the inequivalent triangle (IET) structure for the Si(111)-$\sqrt{3} \times \sqrt{3}$-Ag surface. Red and black circles indicate the Ag or Au adatoms and the underlying Ag atoms, respectively. The small circles indicate the inner Si atoms.

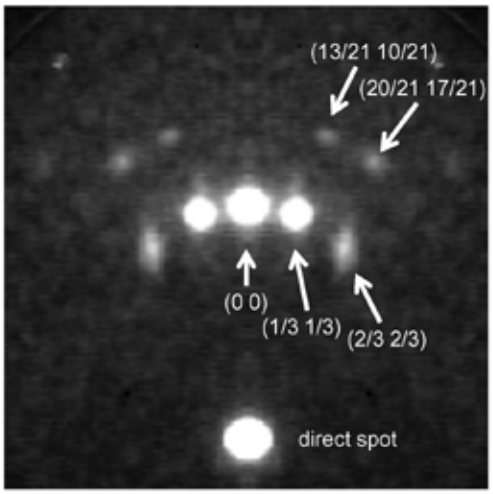

FIG. 2: RHEPD pattern from the Si(111)-$\sqrt{21} \times \sqrt{21}$-(Au,Ag) surface at room temperature. The glancing angle and the incident azimuth are 2.7° and the [11$\bar{2}$] direction, respectively. The pattern corresponds to the superimposition of the left and right parts.

of the intensity analyses of the RHEPD.

II. EXPERIMENTAL PROCEDURE

The substrates ($15 \times 5 \times 0.5$ mm^3) were cut from a mirror polished n-type Si(111) wafer with a resistivity of 1-10 Ωcm. They were introduced into a ultra-high vacuum (UHV) chamber with a base pressure below 3×10^{-8} Pa and flashed at 1200°C in a few seconds several times to from a 7×7 reconstruction. The formation of the 7×7 structure was confirmed with reflection high-energy electron diffraction (RHEED). At first step, 0.4 monolayers (ML) of the Au atoms were deposited onto the Si(111)-

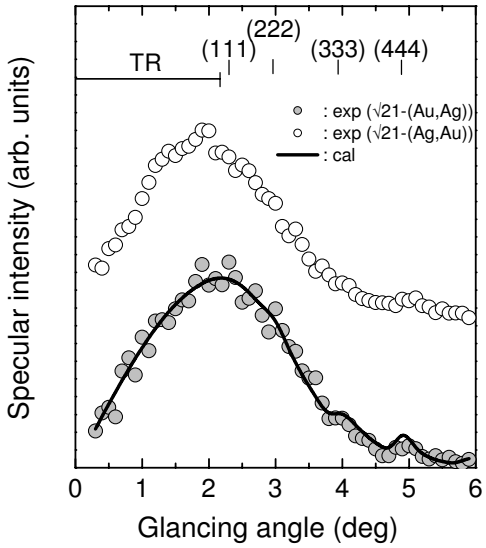

FIG. 3: RHEPD rocking curve from the Si(111)-$\sqrt{21} \times \sqrt{21}$-(Au,Ag) surface under the one-beam condition. For the sake of the comparison, the rocking curve from the Si(111)-$\sqrt{21} \times \sqrt{21}$-(Ag,Au) surface is also plotted. The circles denote the experimental curve. The solid line indicates the calculated curve using the optimized adatom height. TR stands for the total reflection region.

7×7 surface held at 600 °C using a electron beam evaporator to produce the 5×2-Au structure. Here, 1 ML corresponds to 7.83×10^{14} cm^{-2}. Then, the substrate temperature was reduced to 460 °C and the Ag atoms were deposited onto the 5×2-Au surface until the 5×2 pattern in the RHEED was changed into the $\sqrt{3} \times \sqrt{3}$ pattern. When the substrate temperature decreased to room temperature, clear $\sqrt{21} \times \sqrt{21}$ pattern appeared.

The experiments were carried out in a UHV chamber equipped with a positron source of ^{22}Na and electromagnetic lens system [13]. The accelerating voltage of the incident positron beam was set at 10 kV. The diffraction pattern was enhanced using a micro channel plate with a phosphor plane and taken with a charge coupled devise camera. The glancing angle of the incident positron beam was varied from 0.3° to 6.0° at 0.1° step by rotating the sample. The measurements of the pattern and rocking curves were performed at room temperature.

III. RESULTS AND DISCUSSION

Figure 2 displays the RHEPD pattern measured from the $\sqrt{21} \times \sqrt{21}$-(Au,Ag) surface. The incident azimuth and the glancing angle correspond to the [11$\bar{2}$] direction and 2.7°, respectively. The patterns clearly show the fractional-order spots indexed by (13/21 10/21) and (20/21 17/21), resulting from the $\sqrt{21} \times \sqrt{21}$ periodicity. The intensity distribution in the pattern is similar to those from the $\sqrt{21} \times \sqrt{21}$-Ag and the $\sqrt{21} \times \sqrt{21}$-(Ag,Au) surfaces. We also confirmed the formation of the $\sqrt{21} \times \sqrt{21}$-(Au,Ag) superstructure with the RHEPD.

Figure 3 shows the RHEPD rocking curves measured from the $\sqrt{21} \times \sqrt{21}$-(Au,Ag) surface. The incident az-

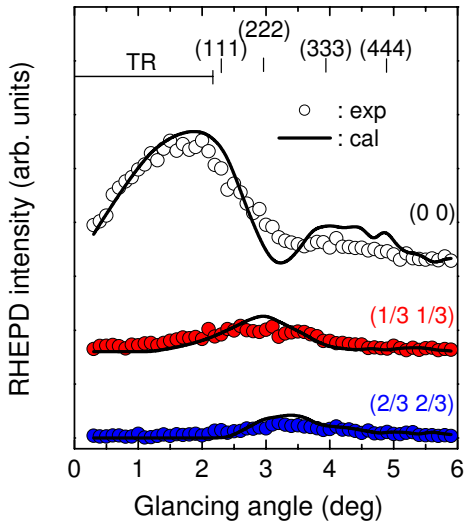

FIG. 4: RHEPD rocking curves from the Si(111)-$\sqrt{21} \times \sqrt{21}$-(Au,Ag) surface at the [11$\bar{2}$] direction. The open circles denote the experimental curves. The solid lines indicate the curves calculated using the optimized structure.

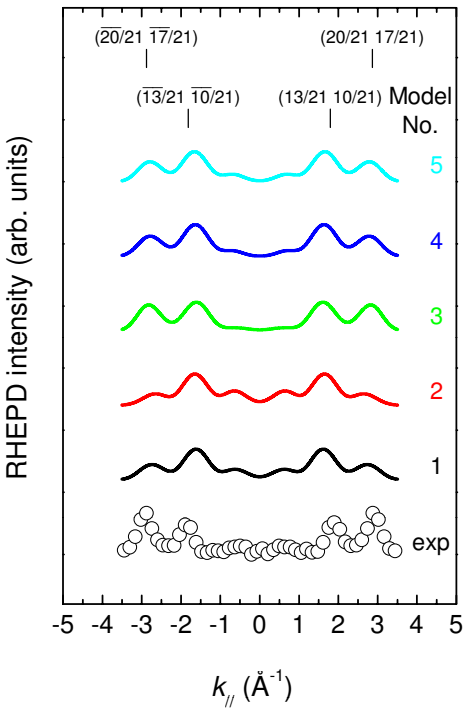

FIG. 5: Line profiles of the 1/7th Laue zone in the $\sqrt{21} \times \sqrt{21}$ pattern. The open circle shows the experimental line profile extracted from Fig. 2. The solid lines show the line profiles calculated using various structure models. Each model number corresponds to the structure in Fig. 6 of Ref. [8].

imuth was set at 7.5° away from the [11$\bar{2}$] direction, which is called one-beam condition. Under the one-beam condition, the diffraction intensity is very sensitive to the change in the normal-components of the atomic positions because the simultaneous reflections parallel to the surface are sufficiently suppressed [14]. In the rocking curve, the broad peak composed of the total and the (111) reflections is observed at low glancing angles. The profile of the curve is also similar to that from the $\sqrt{21} \times \sqrt{21}$-Ag [8] or $\sqrt{21} \times \sqrt{21}$-(Ag,Au) surface [15]. Thus, the stacking of the deposited metal atoms is nearly the same as the $\sqrt{21} \times \sqrt{21}$-Ag and $\sqrt{21} \times \sqrt{21}$-(Ag,Au) surfaces. Figure 4 shows the RHEPD rocking curves measured from the $\sqrt{21} \times \sqrt{21}$-(Au,Ag) surface along the [11$\bar{2}$] direction. The rocking curves are also similar to that from the $\sqrt{21} \times \sqrt{21}$-Ag or $\sqrt{21} \times \sqrt{21}$-(Ag,Au) surface. These results suggest that the surface structure resembles the other $\sqrt{21} \times \sqrt{21}$ family.

To investigate the detailed atomic structure, we analyzed the rocking curves and the pattern on the bases of the dynamical diffraction theory. The procedure followed the Refs. [8, 15]. In this study, to the first approximation, we did not distinguish the species of the adsorption atoms. That is, we substituted the Ag atoms for the Au atoms in the intensity analyses. Moreover, we assumed that the surface structure is composed of the IET structure [9] and the adatoms of 0.14 ML in a similar way to the $\sqrt{21} \times \sqrt{21}$-Ag and $\sqrt{21} \times \sqrt{21}$-(Ag,Au) surfaces. To determine the adatom height on the IET structure, we analyzed the rocking curve under the one-beam condition so as to minimize the difference between the measured and the calculated curves. The goodness of the fit was justified with a reliability factor (R) defined in Ref. [16]. The intensity calculations were based on the dynamical diffraction theory [17]. We used the atomic positions of the IET structure determined by the first-principles calculations [9]. The thermal vibrational amplitudes of the Ag and Si atoms were taken to be 8.90×10^{-2} Å and 1.42×10^{-1} Å at room temperature, respectively [8]. The absorption potentials of the Ag and Si atoms were set at 0 V and 1.70 eV, respectively [18].

The solid line in Fig. 3 shows the rocking curve calculated using the optimized value of the adatom height. The calculated curve is in good agreement with the measured one. In the optimization, we found that the adatom height is 0.35 Å from the underlying Ag layer of the IET structure. The value of 0.35 Å is relatively low and compatible to the adatom heights for the $\sqrt{21} \times \sqrt{21}$-Ag and $\sqrt{21} \times \sqrt{21}$-(Ag,Au) surfaces.

Next, we determined the adsorption sites of the adatoms to analyze the rocking curves of (0 0), (1/3 1/3), and (2/3 2/3) spots at the [11$\bar{2}$] incidence. As mentioned in previous study [8], using the rocking curves at the [11$\bar{2}$] incidence, we are able to distinguish the three different adsorption sites of the adatoms, i.e., (i) the center of the large Ag triangle, (ii) the center of the small Ag triangle, and (iii) center of the Si trimer (see Fig. 1). The results of the analyses are listed in Table I. The value of R shows the minimum for the model where the all adatoms are located at the center of the large Ag triangle. The solid lines in Fig. 4 represent the rocking curves of (0 0), (1/3 1/3), and (2/3 2/3) spots using the optimized model. The calculated curves are in good agreement with the measured ones. We found that all of the adatoms are situated at the center of the large Ag triangle.

Finally, we calculated the line profile of the 1/7th Laue zone using the possible models to determine the coordi-

TABLE I: Reliability factors between the measured and the calculated rocking curves with changing the number of adatoms at the possible adsorption sites. Three different adsorption sites of the adatoms on the IET structure are considered.

Structure model No.	1	2	3	4	5	6	7	8	9	10
Large Ag triangle	3	2	2	1	1	1	0	0	0	0
Small Ag triangle	0	0	1	2	1	0	1	2	3	0
Si trimer	0	1	0	0	1	2	2	1	0	3
R (%)	2.91	3.36	3.28	4.10	3.16	3.45	3.67	4.64	6.03	3.24

nate of the adatoms situated at the center of the large Ag triangle. For the possible models, five different structures are considered, as shown in Fig. 6 of Ref. [8]. We calculated the line profiles of the 1/7th Laue zone using the remaining five models. The solid lines in Fig. 5 show the line profile calculated using each model. We can notice that the peak heights of the (13/21 10/21) and (20/21 17/21) spots are changed depending on the structure model. As shown in Fig. 5, the line profile for the model 3 is similar to the experimental profile. Consequently, the structure model of the $\sqrt{21} \times \sqrt{21}$-(Au,Ag) surface corresponds to that drawn in Fig. 1. However, there is a small difference between the intensities of the (13/21 10/21) and (20/21 17/21) spots.

One possible reason of the small discrepancy might result from the assumption that all of the adsorption atoms are taken to be the Ag atoms. Considering the structure model obtained in this study, the bond length between the adatoms and the underlying layer atoms is estimated to be 2.30 Å. The value of 2.30 Å is considered to be slightly short as compared to be the bulk (2.89 Å) [19] and ionic atoms (2.37-2.65 Å) [20]. It is considered that the intensity analysis without the inclusion of the 0.4 ML Au atoms leads to the small discrepancy. To identify the adsorption sites of the Au atoms, it will be necessary to measure the band structure and the core-level shift using the photoemission spectroscopy.

Recently, new structure model with respect to the Si(111)-$\sqrt{21} \times \sqrt{21}$-Ag surface has been proposed using the first-principles calculations [21]. The optimum number of the adatoms on the $\sqrt{3} \times \sqrt{3}$-Ag surface is consistent with our results [8, 15]. The theoretical calculations indicated the immersion of the adatoms into the $\sqrt{3} \times \sqrt{3}$-Ag substrate. From the rocking curve analysis, we found that the adatom height from the underlying Ag layer is 0.53-0.59 Å [8, 15]. The height of the adatoms has the same tendency toward the immersion. However, the theoretical calculations suggested that the adatoms were situated at the center of the small Ag triangle and hence the adsorption of the adatoms results in the large distortions of the underlying Ag configurations. The large distortions should bring about the drastic changes in the rocking curves from the $\sqrt{21} \times \sqrt{21}$-Ag surface, which is in contrast to our results [8, 15]. To clarify the difference between the structure models, more experimental and theoretical studies are needed.

IV. SUMMARY

W e investigated the $\sqrt{21} \times \sqrt{21}$-(Au,Ag) superstructure resulting from the Ag atoms adsorption on the Si(111)-5 × 2-Au surface at high temperature by using the RHEPD. Comparing to the other $\sqrt{21} \times \sqrt{21}$ family studied in previous study, the atomic coordinate of the $\sqrt{21} \times \sqrt{21}$-(Au,Ag) structure is nearly the same as those of the $\sqrt{21} \times \sqrt{21}$-Ag and the $\sqrt{21} \times \sqrt{21}$-(Ag,Au) structures. It is considered that the surfaces showing the $\sqrt{21} \times \sqrt{21}$ periodicity have identical atomic structure.

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