

Structural analysis of Si(111)- $\sqrt{21} \times \sqrt{21}$ -(Ag, Au) surface by using reflection high-energy positron diffraction

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Abstract

The Au adsorption induced $\sqrt{21} \times \sqrt{21}$ super-lattice structure on the Si(111)- $\sqrt{3} \times \sqrt{3}$ -Ag structure has been investigated using reflection high-energy positron diffraction. The height of the Au adatom was determined to be 0.59 Å from the underlying Ag layer from the rocking curve analysis with the dynamical diffraction theory. The adatoms were preferentially situated at the center of the large Ag triangle of the inequivalent triangle structure of the Si(111)- $\sqrt{3} \times \sqrt{3}$ -Ag substrate. From the intensity distribution in the fractional-order Laue zone, the in-plane coordinate of the Au adatoms was obtained.

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1. Introduction

The deposition of noble metal (Cu, Ag, and Au) or alkali metal (Na, K, and Cs) atoms on the Si(111)- $\sqrt{3} \times \sqrt{3}$ -Ag surface leads to the formation of $\sqrt{21} \times \sqrt{21}$ super-lattice structures [1–4]. The $\sqrt{21} \times \sqrt{21}$ structures have a high electrical conductivity as compared to the Si(111)- $\sqrt{3} \times \sqrt{3}$ -Ag surface [1,2]. The band structures have been extensively studied by photoemission spectroscopy [5–9] and optical second-harmonic generation [10]. Among the $\sqrt{21} \times \sqrt{21}$ structure family, the surface structures induced by Au and Ag atoms were expected to be the same [11]. Several structure models have been proposed of the $\sqrt{21} \times \sqrt{21}$ structures. In early studies, Nogami et al. [12] and Ichimiya et al. [13] proposed the coordinates of the Au atoms using scanning tunneling microscopy (STM), respectively, as shown in Fig. 1a and b. In the Nogami model, five Au atoms in the unit cell are situated at the center of the Ag triangle of the Si(111)- $\sqrt{3} \times \sqrt{3}$ -Ag substrate. In the Ichimiya model, three Au atoms are located at the center of the Si tri-

mer. Tong et al. also proposed the structure model using STM, as shown in Fig. 1c [14]. The model contains four Ag atoms at the center of the Ag triangle. Tajiri et al. performed the structure analysis using surface X-ray diffraction (Fig. 1d) [15]. In the Tajiri model, five Au atoms are included in the unit cell, similar to the Nogami model. Recently, we observed the Si(111)- $\sqrt{21} \times \sqrt{21}$ -Ag surface using the reflection high-energy positron diffraction (RHEPD) [16]. We determined the surface structure in the case of the Ag adatoms, as shown in Fig. 1e. Three Ag atoms on the center of the large Ag triangle of the inequivalent triangle (IET) structure surround the Si trimer. We also found that the height of the Ag atoms from the underlying Ag layer is considerably low (~ 0.53 Å).

RHEPD is a surface-sensitive tool to determine the surface structure [17,18]. Since the positron has a positive charge, the total reflection takes place at grazing incidence.¹ In the total reflection condition, the incident

¹ The critical angle (θ_c) at which the total reflection takes place is given in the form $\theta_c = \arcsin \left(\frac{V_0}{E} \right)^{\frac{1}{2}}$ (Snell's equation) [18], where E and V_0 are the accelerating voltage of the incident positron beam and the mean inner potential of the crystal, respectively. In the case of $E = 10$ kV and $V_0 = 12$ V for the Si(111) surface, θ_c is equal to 2.0°.

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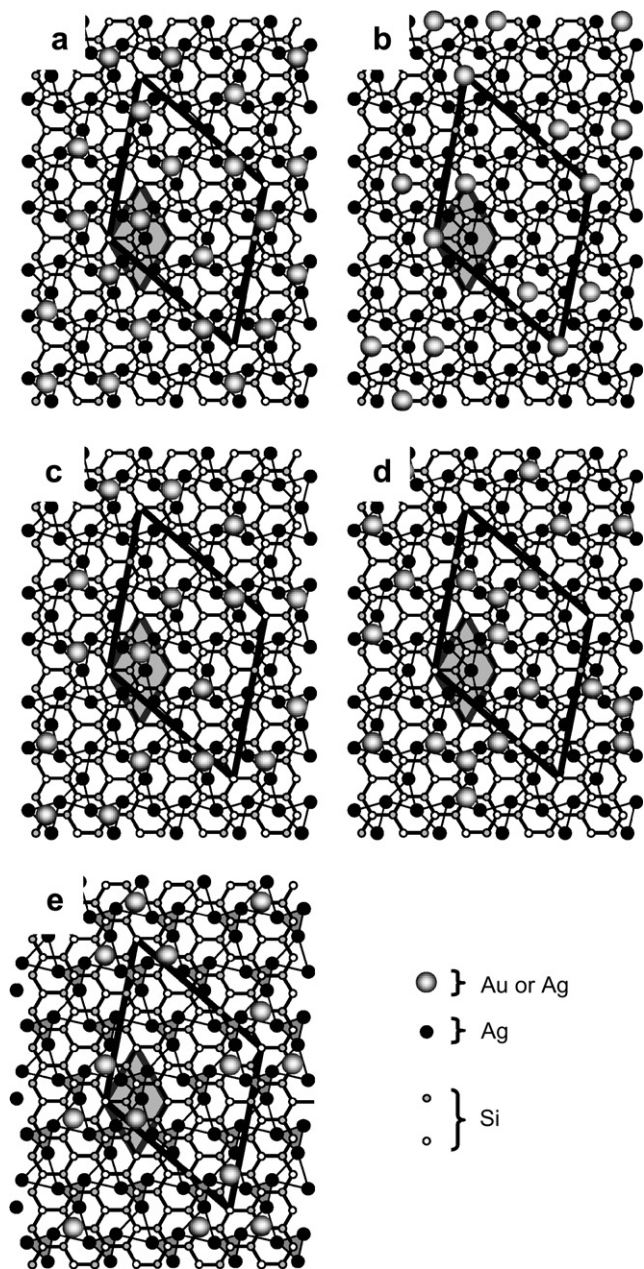


Fig. 1. Schematic drawings of the structure models for the Si(111)- $\sqrt{21} \times \sqrt{21}$ -(Ag, Au) or Si(111)- $\sqrt{21} \times \sqrt{21}$ -Ag surface. (a) Nogami model [12], (b) Ichimiya model [13], (c) Tong model [14], (d) Tajiri model [15], and (e) our model [16]. Large and small diamonds represent the unit cells of the $\sqrt{21} \times \sqrt{21}$ and $\sqrt{3} \times \sqrt{3}$ structures, respectively. Large and middle circles indicate the additional Ag or Au atoms and the underlying Ag atoms, respectively. The other circles show the inner Si atoms. In these figures, the Si trimers are not displayed. The underlying structures in (a)–(d) correspond to the honeycomb chained triangle (HCT) structure for the Si(111)- $\sqrt{3} \times \sqrt{3}$ -Ag surface. In (e), the underlying structure is composed of the inequivalent triangle (IET) structure.

positrons are mostly reflected by the topmost surface layer without penetrating the bulk layers. Therefore, we are able to determine the adatom height and the thermal vibrational amplitude by means of the intensity analysis using the totally reflected positrons [19,20].

In this paper, we investigated the $\sqrt{21} \times \sqrt{21}$ structure induced by the deposition of Au atoms on the Si(111)- $\sqrt{3} \times \sqrt{3}$ -Ag surface using the RHEPD. We measured the diffraction patterns and rocking curves at various conditions and determined the adsorption site of the Au atoms by means of the intensity analysis based on the dynamical diffraction theory. We will report the structure model of the Si(111)- $\sqrt{21} \times \sqrt{21}$ -(Ag, Au) surface.

2. Experimental procedure

The substrate ($15 \times 5 \times 0.5 \text{ mm}^3$) was cut from the mirror polished *n*-type Si(111) wafer with a resistivity of 1–10 $\Omega \text{ cm}$. The Si(111) substrate was rinsed in ethanol before introducing into a chamber. The sample was heated at 1470 K in 10 s a few times by passing a direct current in a ultra high-vacuum chamber. The sharp 7×7 spots were observed by using reflection high-energy electron diffraction. The Si(111)- $\sqrt{3} \times \sqrt{3}$ -Ag surface was prepared by the deposition of Ag atoms on the Si(111)- 7×7 surface held at 770 K. By the deposition (0.14 monolayer) of Au atoms on the Si(111)- $\sqrt{3} \times \sqrt{3}$ -Ag surface at room temperature, the Si(111)- $\sqrt{21} \times \sqrt{21}$ -(Ag, Au) surface was produced. The coverage of Au corresponds to three atoms per the $\sqrt{21} \times \sqrt{21}$ unit cell. The deposition rate was preliminary estimated from the formation of the Si(111)- 5×2 -Au surface (about 0.5 ML).

The experiment was carried out in a UHV chamber equipped with a positron source of ^{22}Na and magnetic lens system. The detail of the apparatus was described elsewhere [21]. The accelerated voltage of the incident positron beam was set at 10 kV. In the measurement of the rocking curve, the glancing angle (θ) was varied from 0.2° to 6.0° at a step of 0.1° by rotating the sample holder. The sample was cooled down to 110 K using liquid nitrogen. The temperature was measured using a thermocouple attached near the sample holder.

3. Results and discussion

Fig. 2 shows an example of the RHEPD pattern from the Si(111)- $\sqrt{21} \times \sqrt{21}$ -(Ag, Au) surface. The azimuth of the incident beam corresponds to the $[1\bar{1}2]$ direction. The glancing angle is set at 2.7° . We can clearly observe the fractional-order spots indexed by $(8/21\ 11/21)$, $(13/21\ 10/21)$, and $(20/21\ 17/21)$. The intensity distribution in the pattern from the Si(111)- $\sqrt{21} \times \sqrt{21}$ -(Ag, Au) surface is similar to that from Si(111)- $\sqrt{21} \times \sqrt{21}$ -Ag surface [16]. This indicates that the atomic coordinates of these structures are similar to each other.

The determination of the atomic coordinate of the Si(111)- $\sqrt{21} \times \sqrt{21}$ -(Ag, Au) surface proceeded at three steps, as described in detail in Ref. [16]. Firstly, in order to determine the height of the Au adatoms, we measured the RHEPD rocking curve under the one-beam condition. The specular spot is dominant under the one-beam condition and the intensity can be expressed by the atomic

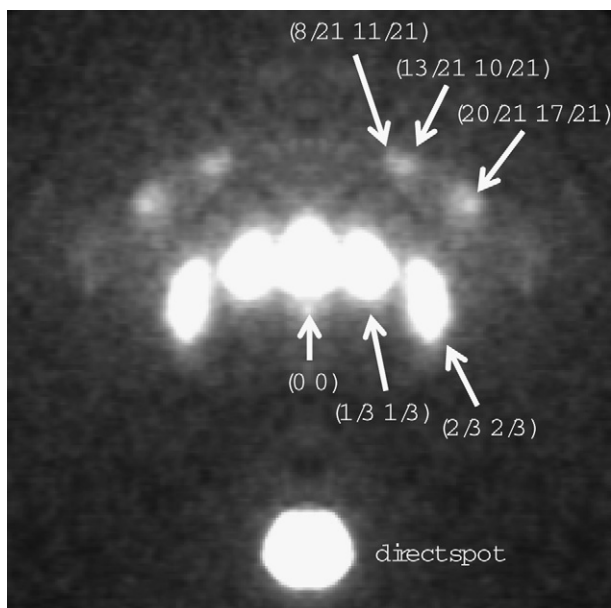


Fig. 2. RHEPD pattern from the Si(111)- $\sqrt{21} \times \sqrt{21}$ -(Ag,Au) surface at $\theta = 2.7^\circ$ at temperature of 110 K. The incident azimuth corresponds to the $[1\bar{1}2]$ direction.

positions normal to the surface, because the simultaneous reflections in the direction parallel to the surface are significantly suppressed [22]. Fig. 3a shows the RHEPD rocking curve measured from the Si(111)- $\sqrt{21} \times \sqrt{21}$ -(Ag,Au) surface at 110 K. For the sake of the comparison, the RHEPD rocking curve from the Si(111)- $\sqrt{3} \times \sqrt{3}$ -Ag surface, which is the surface structure before the Au deposition, is also displayed. The rocking curve from the Si(111)- $\sqrt{21} \times \sqrt{21}$ -(Ag,Au) surface is almost the same as that from the Si(111)- $\sqrt{3} \times \sqrt{3}$ -Ag surface. The rocking curve is constructed from the considerable large peak including the total reflection, 111 and 222 Bragg reflections. Also, the small peaks from the 333 and 444 Bragg reflections are identified. In the RHEPD measurement at total reflection condition, we can estimate the adatom height from the dip position in the profile [18]. The position of the dip changes according to the height. The high atomic position gives low dip glancing angle. In the measured curve, the dip structure can not be obviously found. Therefore, it is considered that the height of the Au adatoms is sufficiently low.

We calculated the RHEPD intensity based on the dynamical diffraction theory [23,20]. We used the atomic positions of the inequivalent triangle (IET) structure determined from the first-principles calculations [24] of the Si(111)- $\sqrt{3} \times \sqrt{3}$ -Ag substrate. The thermal vibrational amplitudes of the Ag (8.90×10^{-2} Å) and Si (5.16×10^{-2} Å) atoms determined in the RHEPD observation [25,26] were used. As regards the Au adatoms, the amplitude was assumed to be the same as the underlying Ag atoms. The absorption potential (V_{ei}) resulting from the electronic excitations such as one-electron excitation and plasmon was taken to be 1.70 V for Si atoms [27]. As regards the Au and Ag atoms, the value of V_{ei} was assumed

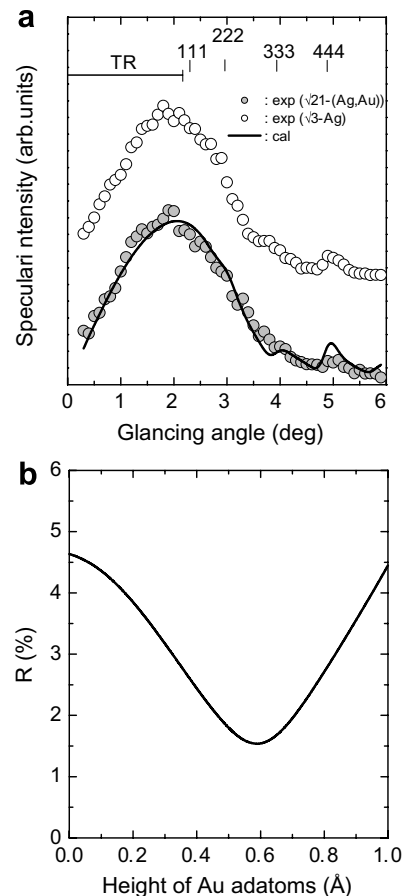


Fig. 3. (a) RHEPD rocking curves from the Si(111)- $\sqrt{21} \times \sqrt{21}$ -(Ag,Au) surface and the Si(111)- $\sqrt{3} \times \sqrt{3}$ -Ag surface under the one-beam condition at 110 K. The circles indicate the measured curve. The solid line shows the calculated curve using the adatom height of 0.59 Å. TR denotes the total reflection region. (b) Reliability factor (R) as a function of the Au adatom height.

to be 0 V, because the influence of the electronic excitations on the RHEPD intensity from the topmost surface layer is negligibly small [19].

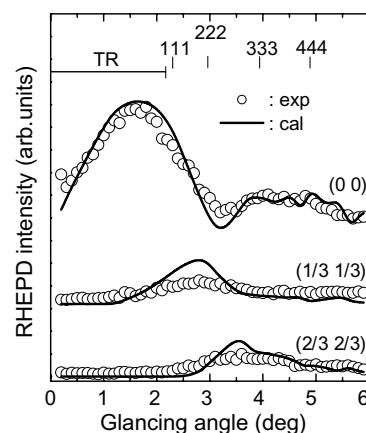


Fig. 4. RHEPD rocking curves from the Si(111)- $\sqrt{21} \times \sqrt{21}$ -(Ag,Au) surface at the $[1\bar{1}2]$ direction at 110 K. The open circles denote the measured curve. The solid lines show the calculated curves using the best fit model (see text).

Table 1
Reliability factors between the measured and calculated rocking curves using various models

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 (%)	2.70	3.37	3.52	4.37	3.35	4.33	4.29	4.94	6.43	4.00

Fig. 3b shows the reliability factor (R) between the measured and calculated curves using various Au adatom heights from the underlying Ag layer. The R was defined in Ref. [20]. The value of R becomes the minimum around 0.59 Å. The solid line in Fig. 3a shows the calculated curve using the height of 0.59 Å and is in good agreement with the measured curve. Therefore, the Au adatom height for the Si(111)- $\sqrt{21} \times \sqrt{21}$ -(Ag,Au) surface is found to be 0.59 ± 0.11 Å. The value is compatible to that for the Si(111)- $\sqrt{21} \times \sqrt{21}$ -Ag surface, where the height was determined as 0.53 Å [16].

Secondly, we measured the RHEPD rocking curves at the $[11\bar{2}]$ azimuth to determine the adsorption site of the Au adatoms on the Si(111)- $\sqrt{3} \times \sqrt{3}$ -Ag substrate. Fig. 4 shows the RHEPD rocking curves for the (00), (1/3 1/3), and (2/3 2/3) spots from the Si(111)- $\sqrt{21} \times \sqrt{21}$ -(Ag,Au) surface along the $[11\bar{2}]$ direction at 110 K. As compared to the curves from the Si(111)- $\sqrt{21} \times \sqrt{21}$ -Ag surface [16], the corresponding rocking curves are almost the same except for a slight shift of the peak positions in the total reflection region of the (00) curve.

In a similar way of the Si(111)- $\sqrt{21} \times \sqrt{21}$ -Ag surface [16], we consider three different sites on the IET structure, i.e., center of the large Ag triangle, center of the small Ag triangle, and center of the Si trimer. From the simulations, it was found that the RHEPD intensities for the (00), (1/3 1/3), and (2/3 2/3) spots are very sensitive to the distribution of the Au adatoms over the three possible adsorption sites. Table 1 displays the reliability factors of RHEPD rocking curves when the distribution of three Au adatoms over the three possible adsorption sites is changed. It is found that when all of three Au atoms are situated at the center of the large Ag triangle of the substrate, the calculated rocking curve agrees with the measured one. Moreover, the value of R is slightly improved when the double domain structure of the Si(111)- $\sqrt{21} \times \sqrt{21}$ -(Ag,Au) surface is considered.

Finally, we measured the line profile of the 1/7th Laue zone in the RHEPD pattern to determine the atomic coordinate of the Au adatoms within the center of the large Ag triangle. Fig. 5 shows the line profile of the 1/7th Laue zone, which was extracted from the pattern in Fig. 2. The intensity for the (20/21 17/21) spots is slightly higher than those for (8/21 11/21) and (13/21 10/21) spots. The intensities for the spots other than these spots are considerably small. Considering the structure models where all of the three atoms adsorb at the center of the large Ag triangle, five different models are possible, as described in Ref.

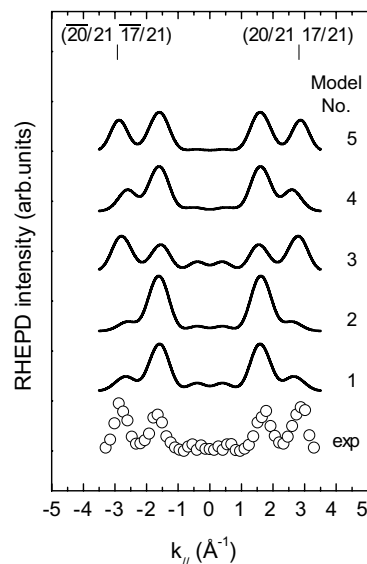


Fig. 5. Line profile of the 1/7 order Laue zone in the RHEPD pattern. The open circle denotes the line profile extracted from the measured pattern (Fig. 2). The solid lines show the intensity distribution calculated using the structure models. The number of the model corresponds to that of the structure sketched in Fig. 6 of Ref. [16].

[16]. We calculated the RHEPD intensities of the 1/7 Laue zone using these five structures. The detail of the structure models was described in the previous paper [16]. The profile of the intensity calculated using the model 3 is in good agreement with the measured one. The model 3 corresponds to the structure model sketched in Fig. 1e. The surface structure of the Si(111)- $\sqrt{21} \times \sqrt{21}$ -(Ag,Au) is composed of three Au adatoms surrounding the Si trimer on the Si(111)- $\sqrt{3} \times \sqrt{3}$ -Ag surface. Consequently, the structure is the same as the Si(111)- $\sqrt{21} \times \sqrt{21}$ -Ag structure except for the height of Au adatoms.

The bond length between the Au and Ag atoms for the Si(111)- $\sqrt{21} \times \sqrt{21}$ -(Ag,Au) surface can be estimated to be 2.35 Å, because the height of the Au atoms is determined as 0.59 Å from the rocking curve analysis. When the bond length is evaluated using the atomic radius in the bulk [28], the value corresponds to 2.89 Å. This value is not consistent with our result. Considering the ionic radius [9], the bond length is estimated to be 2.37–2.65 Å. The lower limit of the estimation is in well accordance with the value determined in this study. Thus, the adatom is ionized and hence the doping of the electrons into the Si(111)- $\sqrt{3} \times \sqrt{3}$ -Ag substrate leads to the relatively high electrical conductivity.

4. Summary

In summary, we measured the rocking curves and the pattern form the Si(111)- $\sqrt{21} \times \sqrt{21}$ -(Ag,Au) surface by using the RHEPD. By means of the intensity analysis based on the dynamical diffraction theory, the surface structure model was proposed. The Au adatoms are situated at the center of the large Ag triangle. Three Au adatoms in the unit cell aggregate and surround the Si trimer. Their height is considerably low (0.59 Å). We found that the Si(111)- $\sqrt{21} \times \sqrt{21}$ -(Ag,Au) surface structure is the same as the Si(111)- $\sqrt{21} \times \sqrt{21}$ -Ag surface.

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