Structural Analysis of the Si(111) $\sqrt{21} \times \sqrt{21}$ -(Ag,Au) Surface by Reflection High-Energy Electron Diffraction Patterns *

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(Received 26 November 2007; Accepted 24 February 2008; Published 8 March 2008)

Reflection high energy electron diffraction (RHEED) patterns from the Si(111) $\sqrt{21} \times \sqrt{21}$ -(Ag,Au) surface are analyzed by kinematical calculations. The models including three, four, and five gold atoms in a unit cell are examined for the structural analysis. The best model is concluded that the surface atomic structure includes three gold atoms in the unit cell. [DOI: 10.1380/ejsnt.2008.84]

Keywords: Reflection high-energy electron diffraction (RHEED); Surface structure; Silicon; Gold; Silver

I. INTRODUCTION

The $\sqrt{21} \times \sqrt{21}$ structures on the Si(111) surface have been intensively studied by several method [1–13]. The $\sqrt{21} \times \sqrt{21}$ structures are formed by several combinations of adsorbed metals on the Si(111) $\sqrt{3} \times \sqrt{3}$ surfaces [1–8]. Ichimiya *et al.* [1, 3] measured coverage of gold deposited on the Si(111) $\sqrt{3} \times \sqrt{3}$ -Ag precisely. They determined that the coverage is 0.14 ML (1ML = 7.8×10^{14} atoms/cm²). The $\sqrt{3} \times \sqrt{3}$ pattern appears again for coverage more than 0.14 ML [1, 3]. This means that three gold atoms are in the $\sqrt{21} \times \sqrt{21}$ unit cell, because $0.14 \approx 3/21$.

Tong *et al.* [3] have shown that surface conductivity of the $\sqrt{21} \times \sqrt{21}$ structures is quite large in comparison with that of the Si(111) $\sqrt{3} \times \sqrt{3}$ surfaces. These surfaces show similar photoelectron spectra to these for the Si(111)($\sqrt{21} \times \sqrt{21}$)-(Ag,Au) [7]. According to the first principles calculations, the structure that gold atoms adsorb on the InEquivalent Triangle (IET) structure has the lowest surface energy [8].

For the $\sqrt{21} \times \sqrt{21}$ structure, various models of the atomic structure are proposed [1–6]. Most of the structure models have been determined by STM images. The first structural analysis has been carried out by Tajiri *et al.* [5] by Patterson analysis of grazing incidence X-ray diffraction intensities. They proposed the model with five gold atoms in the unit cell. Fukaya *et al.* [6, 13] measured reflection high-energy positron diffraction intensities for the Si(111) $\sqrt{21} \times \sqrt{21}$ -Ag surface at low temperatures [6] and the $\sqrt{21} \times \sqrt{21}$ -(Ag,Au) surface [13]. They have determined the structures by full dynamical calculations [14] that three adatoms are in the unit cell for the both structures.

In most cases, RHEED intensities must be analyzed by dynamical calculations for structure determinations. For weak diffraction spots, such as $\sqrt{21} \times \sqrt{21}$ spots, however, it is considered that dynamical diffractions between weak diffractions are able to ignore at surface regions. In the present work, we observed RHEED patterns from

the Si(111) $\sqrt{21} \times \sqrt{21}$ R($\pm 10.9^\circ$) (Ag,Au) surface for several glancing angles of the incidence. Since the diffraction spots due to the $\sqrt{21} \times \sqrt{21}$ reconstruction are very weak, it is possible to analyze the patterns by kinematical diffraction theory. We have compared measured intensities with those calculated by kinematical theory for the four models [1–4]. Only gold arrangement on the surface is determined by the kinematical analysis.

II. EXPERIMENTAL

A p-type (B-doped), 10 Ω cm Si(111) wafer of size 3 mm $\times$ 20 mm $\times$ 0.3 mm was used as a substrate. A clean Si(111) surface was obtained by annealing at about 1250°C in UHV chamber. The Si(111) $\sqrt{3} \times \sqrt{3}$ -Ag surface was formed by silver deposition of 1 ML on the Si(111)7 $\times$ 7 surface at the substrate temperature of 500°C. Gold atoms are deposited on the Si(111) $\sqrt{3} \times \sqrt{3}$ -Ag surface from alumina cell heated by W wire. The deposition rate of gold atoms is 0.5 ML/min. The Si(111)($\sqrt{21} \times \sqrt{21}$)R $\pm 10.9^\circ$ (Ag,Au) structure was formed by gold deposition of 0.15 ML on the Si(111)($\sqrt{3} \times \sqrt{3}$)R30°-Ag surface at room temperature [1]. For gold deposition more the 0.15 ML, we obtained the $\sqrt{3} \times \sqrt{3}$ structure up to 0.33 ML.

The electron beam scattered and diffracted on the crystal surface focus on fluorescent screen. The diffraction patterns were taken on the fluorescent screen by a digital camera (Nikon D50). All experiments were carried out in an ultrahigh vacuum (UHV) system with a base pressure of 1×10^{-8} Pa equipped with a RHEED apparatus with an electron gun operated at 10 kV.

III. RESULTS AND DISCUSSION

Figure 1 shows RHEED patterns from the Si(111)($\sqrt{21} \times \sqrt{21}$)-(R $\pm 10.9^\circ$)-(Ag,Au) surface at several glancing angles. The orientation of the incident beam is [11 $\bar{2}$]. The $\sqrt{21} \times \sqrt{21}$ spot intensity distribution of RHEED patterns from the surface are nearly the same at various glancing angles of the incidence. Therefore it is considered that dynamical diffraction effect does not take place for the most of the diffraction spots of the $\sqrt{21} \times \sqrt{21}$ excepting the integral and the $\sqrt{3} \times \sqrt{3}$ spots, and kinematical analysis are effective for the $\sqrt{21} \times \sqrt{21}$ spots.

*This paper was presented at 6th International Symposium on Atomic Level Characterizations for New Materials and Devices, Kanazawa, Japan, 28 October-2 November, 2007.

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FIG. 1: RHEED patterns from the Si(111) ($\sqrt{21} \times \sqrt{21}$)R $\pm 10.9^\circ$ (Ag,Au) structure at several glancing angles. The incident glancing angles are (a) 2.7° , (b) 3.3° and (c) 3.9° . The orientation of the incident beam is $[11\bar{2}]$.

FIG. 2: Schematic RHEED spot intensities obtained from an experimental RHEED pattern at incident glancing angle of 2.7° . The sizes of the blue solid circles show logarithmic intensities of fractional diffraction spots. The red solid circles are integral and $\sqrt{3} \times \sqrt{3}$ order spots.

FIG. 3: Structural models of the $\sqrt{21} \times \sqrt{21}$. (a) The model by Ichimiya *et al.* [1]; model 1, (b) The model by Tong *et al.* [3]; model 2, (c) The model by Nogami *et al.* [2]; model 3, (d) The model by Tajiri *et al.* [4]; model 4.

In Fig. 2, average intensities of the RHEED patterns are shown schematically by sizes of blue solid circles for the $\sqrt{21} \times \sqrt{21}$ spots. The strong intensities of the integral and $\sqrt{3} \times \sqrt{3}$ order spot intensities are shown by red solid circles. The intensity distribution is compared with calculated ones for four structural models of the $\sqrt{21} \times \sqrt{21}$ shown in Fig. 3. In these four models, numbers of the gold atoms in the unit cell are different.

The model 1 by Ichimiya *et al.* [1] includes three gold atoms in the unit cell as shown in Fig. 3(a). The model 2 which includes four gold atoms in the unit cell proposed by Tong *et al.* [3] is shown in Fig. 3(b). For the model 3 by Nogami *et al.* [2] and the model 4 by Tajiri *et al.* [4], unit cell includes five gold atoms as shown in Fig. 3(c) and Fig. 3(d). Since the substrate structures formed by the silver and silicon triangles keep the $\sqrt{3} \times \sqrt{3}$ framework, these atomic arrangement do not contribute to $\sqrt{21} \times \sqrt{21}$

spots except $\sqrt{3} \times \sqrt{3}$ spots by kinematical calculations. Therefore the kinematical analysis is able to be done for gold arrangements on the surface. Figure 4 shows the calculated results of the intensities for gold arrangements for these four models. The calculated results are shown simultaneously for the two domains rotated $\pm 10.9^\circ$ as well as the experimental results. For model 1, the $\sqrt{21} \times \sqrt{21}$ spot intensities are the same excepting $\sqrt{3} \times \sqrt{3}$ and integral spots, while the spots have several intensities for the other three models, models 2, 3 and 4.

In order to obtain the best model, we calculate the reliability factors (R -factor) as follows:

$$R = \frac{\sqrt{\sum_{h,k} (I_{\text{cal}} - I_{\text{obs}})_{h,k}^2}}{\sum_{h,k} (I_{\text{cal}})_{h,k}} \times 100[\%] \quad (1)$$

The results are shown in Table I. The model 1 has the smallest value of the R -factor. Therefore we conclude that the $\sqrt{21} \times \sqrt{21}$ structure include the gold arrangement shown in Fig. 3(a). The model determined includes three gold atoms in the $\sqrt{21} \times \sqrt{21}$ unit cell; the gold coverage is $1/7$ monolayer. This result is consistent to the coverage of gold atoms in the surfaces of 0.15 ML. This value is in very good agreement with the result obtained by Ichimiya *et al.* [1] who have measured precisely deposition rate of gold atoms on the surface. This result is also nearly the same as the result obtained for Si(111) $\sqrt{21} \times \sqrt{21}$ -Ag surface at low temperatures and $\sqrt{21} \times \sqrt{21}$ -(Ag,Au) by Fukaya *et al.* [7, 13]. By kinematical calculations, the RHEED intensities from the $\sqrt{21} \times \sqrt{21}$ surface are insensitive to the rotation of the gold trimers. In order to determine the orientation and sites of gold atoms on the Si(111) surface, it is needed to analyze the intensities by dynamical calculations. In the case of the kinematical analysis of diffraction spot intensities, one uses ordinarily the Patterson function. In the present case, however, the Patterson analysis leads incorrect result because dynamical diffraction takes

FIG. 4: Calculated intensities for the four models: (a) model 1, (b) model 2, (c) model 3, (d) model 4. The sizes of the circles show logarithmic intensities. The large open circles are integral and $\sqrt{3} \times \sqrt{3}$ order spots.

TABLE I: Values of the R -factors.

	Model 1	Model 2	Model 3	Model 4
R -factor	14 %	21 %	20 %	25 %

place for some diffraction spots. Therefore the Patterson method was not adopted in this structural analysis.

In the present work, we adopted the four models already proposed. Another possible model with three gold atoms in a unit cell is only one model that three gold atoms arrange on a line. This model is, however, very strange from the symmetry of Si(111) surface. Therefore in the present stage, we ignore this model.

IV. CONCLUSION

The Si(111) $\sqrt{21} \times \sqrt{21}$ -(Ag,Au) surface was obtained by gold deposition of 0.15 ML ($\approx 1/7$ ML) on the Si(111) $\sqrt{3} \times \sqrt{3}$ Ag surface. RHEED patterns from the surface have been compared with patterns calculated by the kinematical diffraction theory for the four structure models already proposed which include three, four and five gold atoms in a unit cell. The best model is concluded that the structure includes three gold atoms in a unit cell. This model is in good agreement with that determined by Fukaya *et al.* [7, 13] and the number of gold atoms in a unit cell is consistent to the coverage of 0.15 ML.

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