Observation of Initial Stage of Nano-Scale Au Thin Film on Si(111)7×7 Surface by the PLD Method

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Abstract

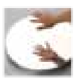
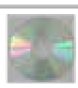
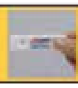
As an important information for fabrication of atomic scale Au thin film which is used for biosensors, we have observed morphology of Au particles absorbed on the Si(111)7x7 surface, which is supposed to be the initial stage of Au thin film formation. Au particles were adsorbed on the Si cleaned surface using PLD method, and the adsorbed particles were observed using the scanning tunneling microscope. As the number of laser shot was increased in the PLD method, size of the adsorbed particle became larger. The larger particle were seemed to form clusters which are aggregation of particles from which each particles are distinguished, so we call this type of clusters film-shaped clusters. In this work we have mainly analyzed this type of clusters. As a result the film-shaped clusters were found to have a structure of nearly monoatomic layer. The particles in the clusters were close gathered in nearly the 3-fold structure with an inter atomic distance of 0.864 nm. We proposed a model for the cluster structure by modifying Au(111) face so that the each observed particles consists of 3 Au atoms.

Keywords: STM, PLD, Adsorption, Au, thin film glowth

1. INTRODUCTION

Recently, metallic thin films have been utilized in various fields from scientific equipments to household goods applying their electromagnetic, mechanical, and chemical properties. Table 1 shows examples of such metallic thin film. Especially, extremely thin metallic films which are several nanometers thick are used for the biosensors, so it is necessary to use special techniques for fabrication and characterization. Typically, since the metallic thin film of Au which are approximately 10 nm thick, it is necessary to be flat at the atomic scale, so the roughness of the only 1~2 nm have to be avoided. The observation of the initial stage of growth is important because atomically flat thin film must be flat in their initial stages as well.

Table 1. Examples of metallic film.

Field	Application	Metal materials	Film thickness	Example
Optical thin films	Mirror, Filter	Al Ag Cr	Several µm or less	
Optical discs	Storage medium	Al Au Ag	3 µm or less	
Semiconductor devices	Electrode, Wiring	Al Cu	100 nm or less	
biosensors	Sensor surface	Au Ag	10～80 nm	

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Therefore, our interest has been focused on the clusters consisting of atoms of from several to tens on the Si(111) clean surface. The purpose of this work is to observe morphology of Au clusters on the Si(111) surface, which is the initial stage of film formation with the scanning tunneling microscope (STM) in order to obtain important informations for ultra-thin film formation at atomic scale.

2. EXPERIMENTAL

Figure 1 shows experimental set-up. The equipment consists of three ultrahigh-vacuum chambers referring to Chamber-I~III. Base pressure of these three chambers was less than 10^{-8} Pa. First, we introduced a Si substrate and an Au target from an introduction port of the Chamber-III which is a chamber of sample introduction. Next, the Si substrate and the Au target were moved together to the Chamber-II which is a preparation chamber. The high temperature flashing was carried out in order to obtain Si(111)7x7 surface here. The flashing conditions were as follows: 10 times of heating of which duration was 1~2 seconds at 1080~1085℃ followed by the final heating of 3~4 seconds at 1070~1075℃. After the cleaning process, the substrate was moved to the Chamber-I, and we checked with STM if the cleaned surface was formed. After the confirmation of the surface, we adsorbed Au particles are adsorbed by the PLD method in Chamber-II. Figure 2 shows the schematic drawing for the set up of the PLD method. In the PLD method, the pulsed laser beam was focused on to a target and the ablation phenomena were caused. The ablated materials were deposited onto the substrate surface and consequently, the thin film of the target materials can be fabricated. In spite of such a simple

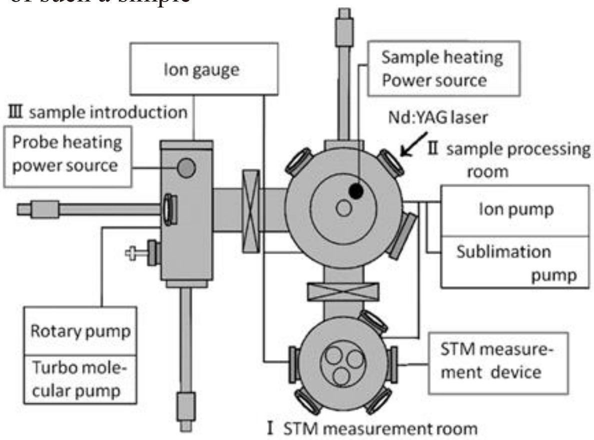


Fig. 1. Experimental set up.

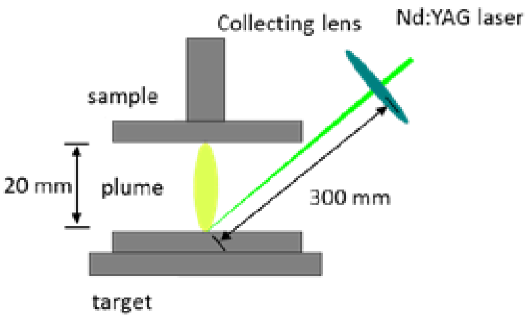


Fig. 2. Schematic drawing of the set up of the PLD method.

apparatus, it is possible to supply particles in atomic level if the irradiation condition was properly selected. In this study, we used the second harmonic of Nd:YAG laser (λ =532 nm) with a laser energy of 0.2 mJ/pulse. The laser was focused on the surface of Au target using a lens with a focal length of 300 mm. The distance between the target and the substrate was set at 20 mm. Laser pulses of 4-20 shots were irradiated before the observation. We moved the substrate to the Chamber- I again, and observed the morphology of adsorbed Au particles with STM.

3. RESULTS AND DISCUSSION

3.1 Morphology of adsorbed particles

Figure 3 shows an STM image of Au particles adsorbed on a Si(111)7x7 surface after irradiation of 7 shots of the laser pulses. In the STM images, particle images brighter than Si adatoms are Au particles. As the number of laser shot was increased in the PLD method, size of the adsorbed particle became larger. Among the adsorbed particle, small particles surrounded by the blue circle in Fig. 3 is supposed to be a single atom which is adsorbed on Si surface. Particles surrounded by both the yellow and the red circles are clusters which consists of plural atoms. Two types of clusters were observed, namely grain-like clusters (the yellow) and film-shaped clusters (the red). Figure 4(a), (b) and (c) show enlarged images of typical examples of the particle and the clusters Fig. 3. Fig. 4(a) shows the image of the monoatomic particle which has been reported in previously by authors[1]. It has been indicated that this type of particles prefer to adsorb onto the Si adatoms. Fig. 4(b) shows the image of particles which consist of 2~5 atoms. Authors have already reported that this type of particles have structures based on fcc structure just like the bulk metallic Au[1]. So in this paper, we mainly treated the film-shaped clusters shown Fig. 4(c). Detailed discussion has been made in the next section.

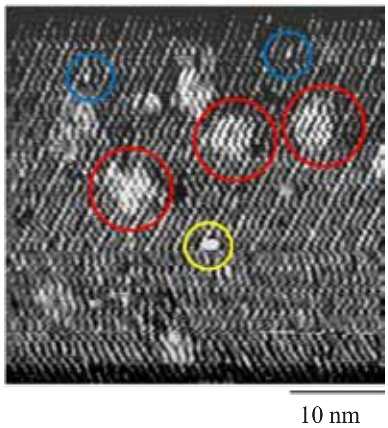
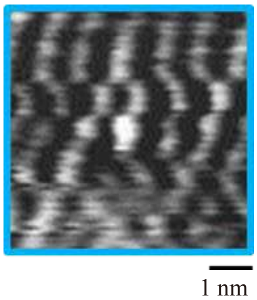
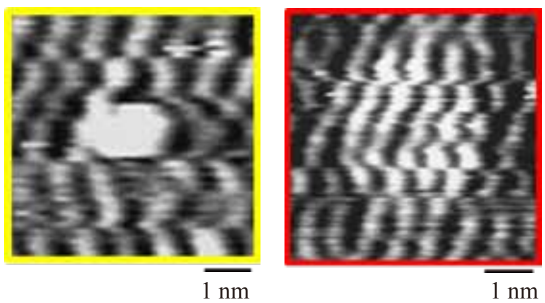


Fig. 3. STM image of Au particles adsorbed on Si(111)7x7 surface after irradiation of7shots of laser pulses.



(a) Monoatomic particles.



(b) Grain-like clusters. (c) Film-shaped clusters.

Fig. 4. Enlarged images of typical example of Fig. 3.

3.2 Structure of film-shaped clusters

The STM image was basically constructed by the height information from the applied voltage to piezoelectric devices. However, it is difficult to analyze the raw data directly because they contain noise and drifted signal to produce an image distortion. Therefore we tried to re-measure the height information from the obtained STM image from the brightness distribution confirming the quality of the image. Figure 5 shows a schematic drawing of the Si(111)7x7 DAS model. In this figure, the adatoms in the first layer and the rest atoms in the second layer were filled with pink red color, respectively. The dashed line in the figure stands for a line that two of corner holes in the DAS model were connected. Fig. 6(a) shows the STM image which was used to confirm the validity of measurement by measuring the height the adatom from the corner hole. The dashed blue line in Fig. 6(a) is corresponding to the dashed blue line in Fig. 5. The height distribution obtained from brightness STM image of Fig. 6(a) was shown by the blue curve in Fig. 7. The abscissa stands for the horizontal distance, and the ordinate stands for the relative value of height information. In Fig. 7, a schematic drawing of the cross sectional view when Si(111)7x7 DAS was cut along the blue dashed line in Fig. 5 was also shown in the same scale. Generally in STM image, since atoms are observed with a diameter of approximately 2 times larger than that of so-called atomic size estimated by hard sphere model, the dashed lines in Fig. 7 express the size which is expected to observe with STM. Considering this fact, the blue curve in Fig. 7 was successfully agreed with the profile of the cross section of the Si(111)7x7 DAS model. Next, we carried out similar the height measurement for the image in Fig. 6(b). The observed particles in the cluster were arranged basically in the 3-fold structure. Figure 6(b) shows the STM image which was used to estimate the highest point of the cluster from the corner hole by measuring the height of the corner hole, the adatom and the cluster. We measured the height distribution between positions denoted A and B in Fig. 6(b), and estimated the height of the Si adatom and the highest point clusters measured from the corner hole. The obtained distribution between the positions denoted C and D in Fig. 6(b) was also shown in Fig. 7 by the red curve. The circles filled with yellow in Fig. 7 show the size of Au atom of 0.288 nm in diameter. In Fig. 7, two kind of cases were illustrated: an Au atom was adsorbed and two Au atoms were vertically accumulated on the Si adatom. As described before, the size of 2 times larger them the atom was illustrated by the dashed lines surrounding the yellow circle. Comparing these heights, we recognized the highest point of the film-shaped cluster approximately 0.67±0.01 nm which is higher than the case of single Au atom (0.62nm), but lower than the case of two Au atoms (0.84nm). Consequently, these results imply thickness of the film-shaped cluster is nearly monoatomic or so.

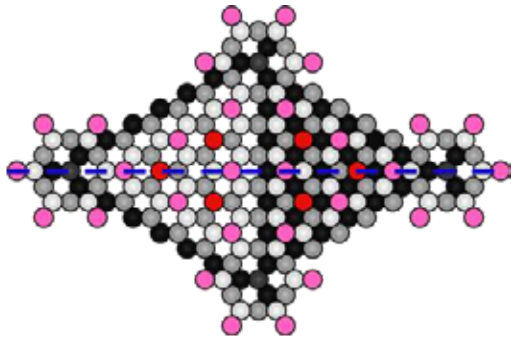


Fig. 5. Si(111)7x7 DAS model.

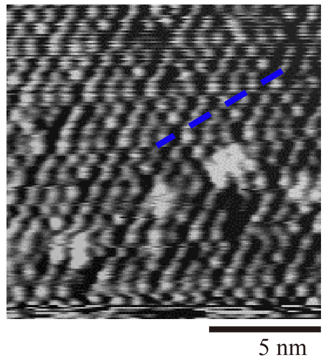


Fig. 6(a). STM image used for measurement of the height of the adatom from the corner hole.

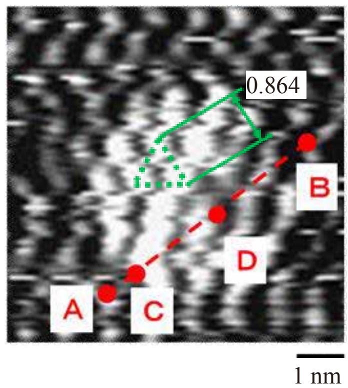


Fig. 6(b). STM image used for measurement of the highest point of the cluster from the corner hole.

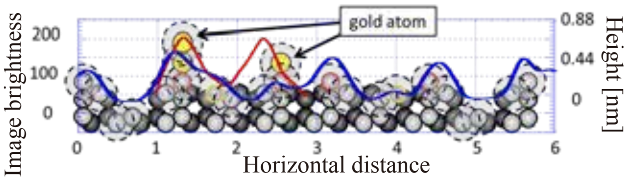
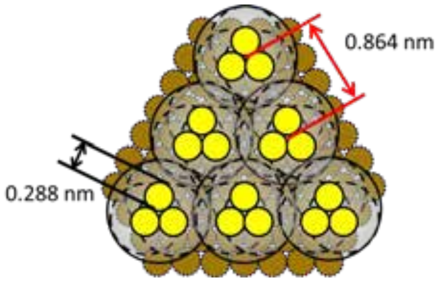
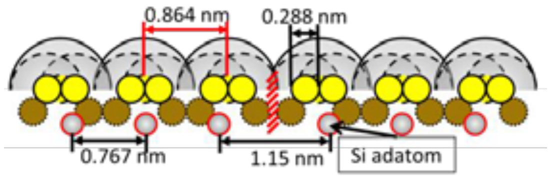


Fig. 7. The height distribution obtained from brightness STM image.

Considering the fact obtained from the analysis, we tried to reveal the structure of this type of clusters. Although the particles in the STM image are observed as if each particles were distinguished, but each particles were not considered to be single atoms,

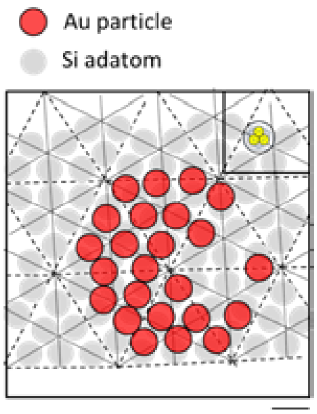


(a) Top view.



(b) Side view.

Fig. 8. Proposed structure of film-shaped clusters of Au.



1 nm

Fig. 9. A schematic drawing of position of the atoms and the particles consistiong of the cluster show in Fig. 6(b).

because their diameter were too large compared to the atom. As shown in Fig. 6(b), the distance between the particles was 0.864 nm, so the diameter of particle was 0.864 nm assuming closed packed. This diameter was similar to the diameter of grain-like clusters consisting of three Au atoms[1]. Considering these fact and 3-fold structure, we considered a model based on the (111) face of the fcc stucture with nearly monoatomic layer. The proposed structure was shown in Fig. 8. In figure 8(a) and (b), the top view and the side view were shown, respectively. The Au atoms in the first layer and the second layer were filled with yellow and brown, respectively. In this model, observed each particles consist of three Au atoms (diameter 0.288 nm) arranging at distance periodicity of 0.864 nm. In the small limited area, the proposed structure was consistent with the observed facts. However, this periodicity is not matched with that of the adatom as shown in Fig. 8. This fact give rise to a defects. Figure 9 schematically shows the relation between positions Si adatoms and Au particles observed in STM image in Fig. 6(b). The Au particles and the Si adatoms were filled with red and gray, respectively. As shown in this figure, the particles of the cluster are not always arranged exactly on the Si adatoms. While the Au roughly take particles the 3-fold structure, they also have undoubted disordering structure. It is considered that this disordering is due to the difference of a periodicity of the Au particles and Si adatoms.

4. SUMMARY

As an important information for fabricate atomic scale thin film, we have observed morphology of Au clusters formed on the Si(111)7x7 surface by the PLD method. The results obtained in this study are as follows:

1) The observed film-shaped clusters were found to have a structure of nearly monoatomic layer.
2) The structure of the film-shaped cluster has been successfully proposed by assuming the each particles of the cluster consist of 3-Au atoms.

It is expected that the flat Au thin film in atomic scale can be formed by covering with many of these film-shaped clusters.

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