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STM observation of initial stage of growth of Si-Mn films on Si(111)7 × 7 surface

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Recently, it has become very important to obtain knowledge about interactions between substrates and deposited materials in an atomic scale. In this study, we focused on the initial stage of Si-Mn films adsorbed on to a Si(111) substrate. A sample were prepared by depositing the Mn particles onto a cleaned Si(111) substrate by the pulsed laser deposition (PLD) method and the observation was performed with a scanning tunneling microscope (STM). First, we have observed adsorption site, size and shape of the particles at room temperature. Next, the change of the STM image at elevated temperature up to 200 ºC was observed. In this paper, we have discussed about the structure of clustered Mn particles on Si(111) substrate by comparing the result with particles of other kinds.

Key words: STM, PLD, Diluted magnetic semiconductor, Adsorption, Mn.

Introduction

Recently, the various kinds of technique for fabrication of ultra thin films have been developing in order to the miniaturized semiconductor, high performance semiconductor and optical devices. In particular, the DMS (diluted magnetic semiconductor) which have both properties of magnetic substance and semiconductors attract many attention in the field of high performance semiconductors and optical device. In the DMS, researches have been performed mainly on (Ga, Mn)As which is doped with Mn in GaAs[1], because it is said that the wider band gap materials produce higher Curie temperature DMS. However, the Curie temperature of fabricated film was lower than predicted value by about 100 ºC[2]. Eventually, the mechanism of the magnetic transformation in the DMS has not been well defined. Accordingly, in addition to the research on the wide band gap semiconductors, the mechanism are also studied how Mn particle is incorporated into the semiconductor lattice using Si which is widely used and whose property are well known. On the basis of this background, we tried to observe the initial stage in which Mn particles are interact with Si surface with the atomic scale resolution. We observed the Mn particle of Si(111) 7 × 7 surface deposited with the PLD(pulsed laser deposition) method and obtained the information related to the interaction between them.

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Experimental

Figure 1 shows the schematic drawing of the experimental setup. An ultra-high-vacuum chamber of which base pressure was less than 10^{-8} Pa was used.

We prepared Si(111) substrates according to the procedure of the high temperature flashing method in order to obtain a clean 7 × 7 surface structure as shown in Fig. 2. All experiments in the present study performed using the substrates with off-angles less than 0.14 degree, because wide reconstructed area is easy to obtain. The flashing condition were as follows: 3 ~ 4 seconds as 1080 ~ 1085 ºC, 10 times, followed by the final heating of 1 ~ 2 seconds at 1070 ~ 1075 ºC. We used a STM (scanning tunneling microscope) for the observation under condition of 10^{-8} Pa in the vacuum chamber. Subsequently, Mn particle was deposited to Si substrate by the PLD method. A metallic Mn plate was used for the target. In the PLD method, the distance between a target and a substrate was set at

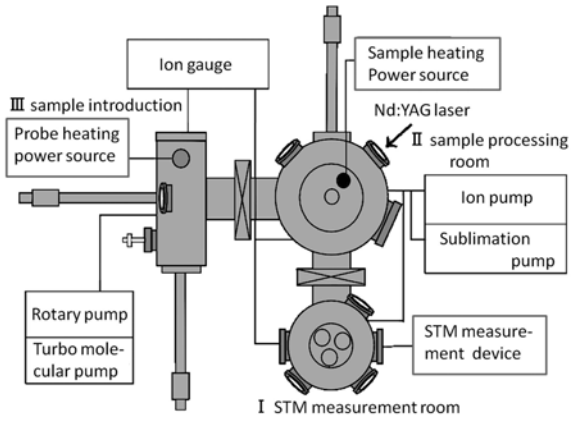

Fig. 1. A schematic drawing of the experimental setup.

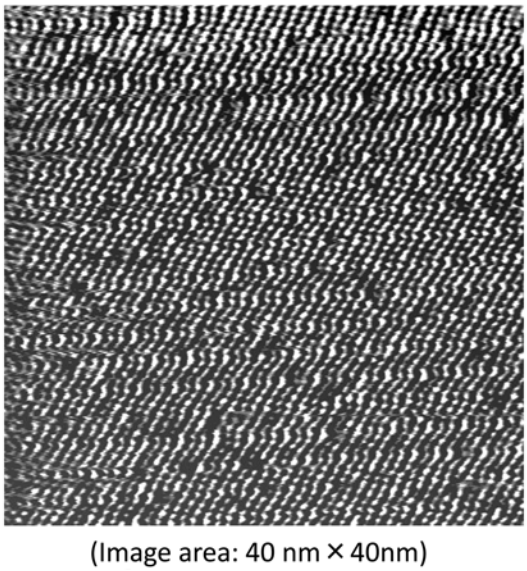

Fig. 2. STM image of reconstructed Si(111)7 × 7 surface used in this work.

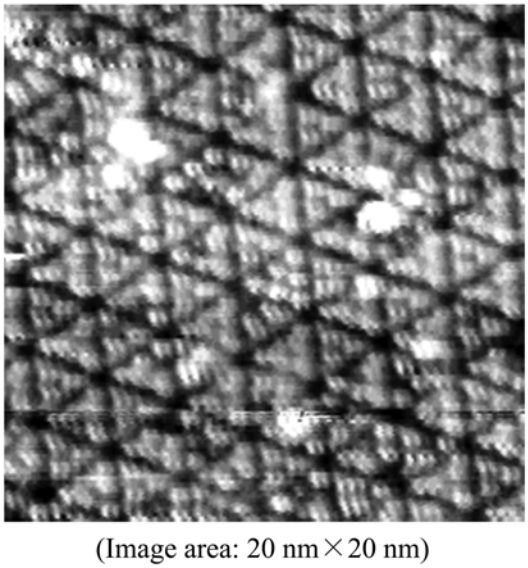

Fig. 3. The typical STM image of adsorbed Mn particles on the cleaned Si(111)7 × 7 surface.

20 mm, and the laser energy was 1.0 mJ/pulse, and the number of the laser shots varied from 1 to 8 were used.

After the deposition, the surface was observed with STM again, and the adsorption site, morphology and size were investigated in room temperature. Furthermore, the substrate was heated up to 200 ºC by applying a electrical current to the sample directly and observed the change. We also performed the similar experiments using Au particles for comparison.

Results and Discussion

Adsorption sites

Figure 3 shows the STM images obtained by the present experiments. We can observe Mn particle on the cleaned Si(111)7 × 7 surface. As discussed in the next section, not only the single atom of Mn as shown in Fig. 3, but also clusters which has larger size have been observed in the present study. The ratio of number of clusters against the all observed particles was about 20%. In this section we focus on the single atomic Mn particles only. Figure 4 shows the schematic drawing of the Si(111) DAS(dimer adatom stacking fault) model. Focusing on the adsorption sites, it was found that the particles were adsorbed on only four kinds of sites on the Si surface which is forming the DAS model structure: near the center of the half unit cell, on the center adatoms, on the corner adatoms, and near the central point between the center adatoms and the corner adatoms. In the present of paper, we referred to these four sites as site A, site B, site C, and site D, respectively. Table 1 shows an observation frequency for these sites. As shown Table 1, it was found that Mn particle were adsorbed on site B and site C which is on the adatoms more than site A and site D which is on

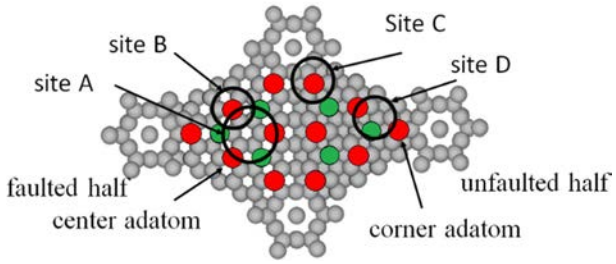

Fig. 4. The schematic drawing of the Si(111)7 × 7 DAS model.

Table 1. Mn observation frequency of Mn single atom particles for site.

Site A[%]	Site B[%]	Site C[%]	Site D[%]
15 ± 10	36 ± 13	35 ± 15	14 ± 4.3

the space between adatoms. A reason for this tendency is considered to be as follows: the isolated Mn atom which has dangling bonds prefer to bind to the adatoms which also have a dangling bonds.

Shape and size of an adsorbed particles

We considered that the particles relatively larger size which is about 20% of the observed particles as clusters, so we tried to estimate the structure of them. This analysis was proceeded in comparison with the result for Au particles. We observed about 60 particles which are considered to be clusters out of about 150 observed particles. Solid manganese has the bcc (body-centered cubic) structure, while solid gold has the fcc (face-centered cubic) structure. Considering this fact, structure of clusters which contained atoms from 2 to 5 were assumed as shown in Fig. 5. In Fig. 5, examples for Mn clusters were illustrated. The solid line drawn in the figure are nominal atomic size which are

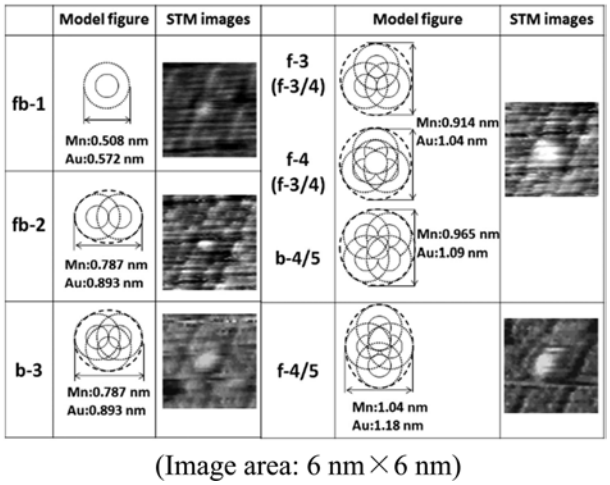

Fig. 5. Structure of clusters assumed that they have either the bcc or fcc structure.

Table 2. Observation frequency of Mn and Au clusters.

	Mn[%]	Au[%]
fb-1	52 ± 14	62 ± 8.9
fb-2	35 ± 17	23 ± 4.9
b-3	4.0 ± 4.2	3.0 ± 2.1
b-4/5 f-3/4	6.0 ± 4.6	6.0 ± 3.3
f-4/5	3.0 ± 0.7	6.0 ± 3.1

conventionally estimated from interatomic distance in crystalline solid. The previous research[3] suggested that the diameter of an isolated atom observed in the STM is about twice of the conventional atomic size, so we indicate this size by using dotted lines in Fig. 5. In the case of clusters, it is considered that the observed size became like broken lines in the Fig. 5 since these dotted lines were overlapped.

For example, in the case of a cluster consisting of 3 atoms which is basically having the bcc structure, it is considered that the clusters may have a structure denoted as b-3 in Fig. 5. On the other hand, in the case of a 3-atom-cluster which is basically having the fcc structure, it is considered the clusters may have a structure denoted as f-3 in Fig. 5. Furthermore, if one more atom is added to f-3 structure, it becomes a structure which should be called as f-4, however, these two structures cannot be distinguished by the resolution of the present STM observation, so we call this structure as f-3/4. In the case of a single atom and a 2-atom-cluster, since they are unrelated to either the structures, we denoted them as fb-1 and fb-2, respectively as shown in Fig. 5. From the similar consideration, a 4-atom-cluster and a 5-atom-cluster are denoted as b-4/5 and f-4/5, respectively as shown in Fig. 5. We measured the size of the particles in the STM images, and tried to classify the particles according to this classification.

In this classification, although the structure of f-3/4 and b-4/5 were clearly different, they were not able to distinguish in the present size measurement accuracy. The observation frequency of these Mn particles and Au particles were summarized in Table 2. The structures which were mostly observed were b-4/5 and f-3/4 for both Mn and Au, however, we could not make any decision for structure by this information. On the other hand, it was found that the Mn and Au have a tendency to avoid forming the fcc and bcc, respectively, when one paid attention to the structure of the lowest observation frequency: f-4/5 in Mn and in Au b-3. This is supposed to be attributed by structure of of solid phase of each material. Paradoxically, according to this idea, concerned with b-4/5 and f-3/4 mentioned above, Mn and Au may have the structures of b-4/5, f-3/4, respectively.

Change of particle size and substrate at elevated temperature

Figures 6(a) and (b) shows the the images which surface adsorbed Mn and Au particles at elevated temperature up to 200 ºC. In the case of Mn, many defects were observed on the substrate surface while the almost no change in the case of Au. Besides, in the case of Mn, the particle size became larger. The counted number of defects per single image were summarized in Table 3. The defects observed on the Mn adsorbed surface were mainly the absence of the site B adatoms. On the other hand, the case of Au neither the surface nor particle changed.

The process of forming the defects in the case of Mn should be supposed as follows: a Mn atom adsorbed on an adatom approached and reacted chemically with a Si adatom on the site B as a result strong lattice vibration

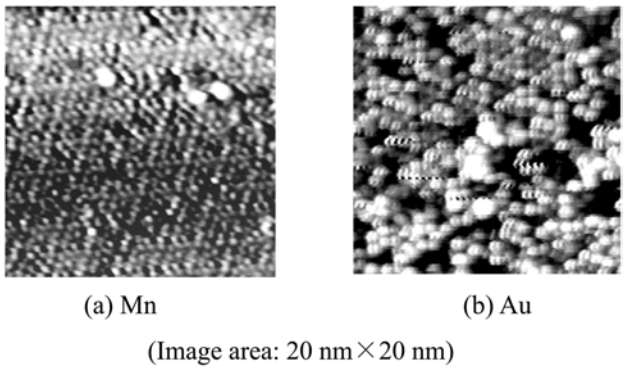

Fig. 6. STM images of surface adsorbed particles with Mn and Au. The sample temperature was rised up to 200 ºC after the deposition.

Table 3. The number of defects per single image.

	RT	75 ºC	150 ºC	200 ºC
Mn	28	53	142	135
Au	34	35	41	43

by heating. So we consider the large particles in Fig. 5(a) is certain compound of Mn and Si. On the other hand, in the case of Au, such a reaction did not arise since reactivity of Au to other materials was not stronger them Mn.

Conclusions

We observed the Mn particle of Si(111)7 × 7 surface deposited with the PLD method and obtained the information related to their interaction. Besides, change of adsorbed particles and substrate with rising temperature are also observed.

The Mn particle were found to be adsorbed on only four kinds of sites in the DAS model of Si at room temperature. It was also found that single atoms of Mn were have a tendency to adsorb on adatom which has a dangling bond rather than other sites which does not have. The structure of the clustered Mn particle was suggested to be attribute of its metallic solid. The size of Mn particle adsorbed on the surface became larger and defects on the surface of substrate increased by heating at only 150 ^{o}C. These facts are supposed to be due to the lattice vibration and chemical reaction between Mn and Si driven by thermal energy. These information is considered to be useful for understanding the mechanism for fabricating the DAS ultra thin films.

References

1. Tomasz Dietl: “Spintronics And Ferromagnetism In Wide-Band-Gap Semiconductors”.
2. K.ANDO, R.SHIODA, T.HAYASHI, M.TANAKA, A.TWARDOWSKI: “Crystallographic and Electronic Structures of III-V Based Diluted Magnetic Semiconductor $Ga_{1-X}Mn_XAs$”, Vol. 63, p. 29-35, 1999.
3. Y.OKAZAKI, A.YOKOTANI: “Observation of the Initial Stage Thin Film Formation Process by PLD Method”, No. 39, p. 173-178, 2010.