Growth of metallic Au adsorbed islands on the Si(111)-(7 × 7) substrate

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Abstract. Au adsorbed(Au-Si) islands are formed by the deposition of Au atoms on the fabricated Si(111) surface, on which size selected Si nanoislands have been constructed. The growth of the Au-Si islands is subject to the substrate temperature, Ts. At Ts < 270 °C, the surface structure on Au-Si islands shows the Si(111) $\sqrt{3}$×$\sqrt{3}$-Au structure, and some Au atoms form hole-island pairs on the flat surface because the diffusion length of the Au atoms is too short to reach to the Si nanoislands (about 10 nm). At Ts > 280 °C, the diffusion length of Au atoms becomes larger than a mean distance between the Si islands. At Ts > 300 °C, the surface structure on the Au-Si islands shows the Si(111) 5×2-Au structure, and some of the islands grow along one of the <110> directions. The result means that the surface diffusion of Si atoms among the Au-Si islands is drastically enhanced, that hardly occurs at Ts < 270 °C.

1. Introduction

Low dimensional structures formed by metal adsorption on a semiconductor surface less than 1 monolayer(ML) are investigated by a lot of workers[1-6], because these nanostructures show unique electronic properties to the low dimensionality[7] and the quantum effects from electron confinement[8]. The properties change drastically depending on the adsorbates and their structures[9-14]. So the nanostructures have high potential as nanoparticles create nano-devices in the next generation[15,16]. To control the electronic property of the nanostructure, it is essential to investigate the formation process of the nanostructure.

We have studied the homoeptaxial growth of Si on the Si(111) 7×7 dimer adatom stacking-fault(DAS) structure. The unit cell of this surface structure is divided into two triangle subunits that are a faulted half-cell(FHC) and an unfaulted half-cell(UHC)[17]. Si nanoislands are formed at the initial stage of Si deposition with coverage($\theta$) of 0.1 bilayer(BL: 1 BL = 2 ML = 1.57×10$^{19}$ atm/m$^2$) on the Si(111) 7×7 DAS substrate. The size distribution of those islands shows several peaks at magic sizes by a restriction of lateral growth of Si layer on the FHC. The islands have a triangular shape, whose apex points to the [11$\bar{2}$] direction, and are surrounded by the FHC[18-22].

After an annealing, the islands transform to the stable shapes while the size of each island is maintained in the area surrounded by the FHC. The stable islands show a star-like shape composed of 92 atoms, a rounded shape(162 atoms) and a hexagonal shape(343 atoms)[23,24]. The size distribution of the islands can be controlled by the growth condition, i.e. the substrate temperature(Ts), the
annealing temperature($T_a$) and the growth rate. Under an optimized condition, we have achieved the selective formation of the rounded(R-) Si islands more than 70% of the total islands[25-27].

To form metallic nanoislands, we used the R-Si islands of the same size and metallized these by an additional deposition of Au atoms[28]. The surface on the Au adsorbed island shows a Si(111) $\sqrt{3}\times\sqrt{3}$-Au structure at $T_s = T_a = 270 \degree C$[28], and the surface shows metallic feature[11,29,30]. We also confirmed the metallic feature by a measurement with scanning tunnelling spectroscopy[31]. The deposited Au atoms combine with Si through the step site because the site is more active than a site on the flat surface. Therefore, the Au atoms combine with the Si atoms in the R-islands, i.e. the Au adsorbed structure does not grow on the flat surface but grow from the Si islands, selectively. So the metallic islands can be formed on the semiconductor surface. The size of the Au adsorbed(Au-Si) islands reflects to that of the prepared Si islands, because the Au-Si island is formed by absorption of Au atoms to the Si islands without diffusion of Si atoms[28].

In this report, we investigate the growth process of the Au-Si island at several growth conditions with a scanning tunnelling microscope (STM). We find that the reconstructed surface structure on the Au-Si island can be controlled by the growth condition at the Au deposition. This result means that the electronic property of the metallic nanoislands fabricated on the semiconductor surface will be controlled, because it depends on the reconstructed surface structure.

2. Experiment

The experiment was performed in an ultra high vacuum(UHV) chamber equipped with a STM and an electron beam evaporation source(base pressure: $1.5\times10^{-8}$ Pa). The deposition of Si and Au atoms and STM observation can carry out in the UHV chamber. Other experimental details and the growth condition of the size selected Si nanoislands have been described in elsewhere[23-27].

Au-Si islands prepared by two step processes: First, the size selected Si islands were prepared by a deposition of Si with $\theta = 0.05$ BL at $T_s = 330 \degree C$ on the Si(111) 7×7 DAS substrate, and an annealing at $T_a = 410 \degree C$ for 10 min at the pressure below 1.0×10$^{-7}$ Pa. The STM image from the surface shows that R-Si islands are formed more than 70% in the Si islands[25-27]. Second, in order to form the Au-Si islands, Au atoms were deposited about $\theta = 0.07$ ML on the Si fabricated surface at $T_s = 250 \sim 370 \degree C$ at the pressure below 3.0×10$^{-7}$ Pa and the sample was annealed at $T_a = T_s$ for 5 min. Hence the composition of the Si and Au atoms is kept a constant value(Si : Au = 1 : 0.7) in this experiment. After the deposition, we carried out the STM observation with a constant current mode at room temperature.

3. Result and Discussion

Figure 1(a) shows a typical STM image of the Si(111) surface after the deposition of Au atoms at $T_s = T_a = 280 \degree C$, on which two kinds of reconstructed surface structures are formed at this condition. One surface structure is a Si(111) $\sqrt{3}\times\sqrt{3}$-Au structure and another structure is a Si(111) 5×2-Au structure as shown in figure 1(b) and 1(c), respectively. We should note that the 7×7 DAS structure on the substrate is preserved even after the Au deposition and the Au atoms combine with the Si islands and the step edges. This means that Au atoms are adsorbed through the edge sites. The result is the same as we reported in the previous paper at $T_s = 270 \degree C$ [28], at which only the $\sqrt{3}\times\sqrt{3}$-Au structure is observed.

Although the formation of two surface structures was also reported by Shibata et al.[32,33], a hole and an island are always formed a pair on a flat Si(111) surface by the deposition of Au. The hole-island pair is formed by excess Si atoms, when the Au atoms combine with the Si atom on the flat surface[32]. The amount of excess atoms leading the hole-island pair depends on the composition of each reconstructed surface structure, where the atomic composition is 1 : 0.76(Si : Au) for the $\sqrt{3}\times\sqrt{3}$ structure and 1 : 0.45 for the 5×2 structure, respectively[34,35]. In the present study, the substrate surface keeps the 7×7 DAS structure, because almost of Au atoms are consumed to combine with the Si in the islands. However, we can see a few holes near the islands, because the ratio of Au to Si coverage on the substrate(1 : 0.7) is higher than the mean value of two compositions.
Figure 1. (a) STM image(90×90 nm$^2$) of the Si(111) surface after the deposition of Au atoms at $T_s = T_a = 280 \, ^\circ$C. (b) Au-Si island showing Si(111) $\sqrt{3}\times\sqrt{3}$-Au structure. (c) Au-Si island showing Si(111) 5×2-Au structure.

Figure 2. (a) STM image(100×100 nm$^2$) of surface after the deposition of Au atoms at $T_s = T_a = 250 \, ^\circ$C. The $\sqrt{3}\times\sqrt{3}$ structure is formed on the islands, preferentially. (b) Size distribution of the Au-Si islands($N_0 = 421$) for figure 2(a). The size of the islands is expressed by the number of FHC, which have been covered with the islands. Two STM images of an R-Si island(upper left) and an Au-Si island(upper middle) for $n = 3$ and a schematic view(upper right) are also shown.

Figure 2(a) shows the STM image from the surface after the deposition of Au atoms at $T_s = T_a = 250 \, ^\circ$C. At the lower temperature, the surface on the Au-Si islands shows only the $\sqrt{3}\times\sqrt{3}$ structure, because the activation energy of the $\sqrt{3}\times\sqrt{3}$ structure formation is less than that of the 5×2 structure[32]. But the DAS structure(bright contrast) remains partly on some islands as indicated by arrows. The imperfection is due to a lack of Au supply by surface diffusion. In Figure 2(a), a lot of small hole-island pairs are also formed at a mean space of ~10 nm. Since the migrated Au atoms create the hole-island pairs, the diffusion length of the Au atom is estimated to 10 nm at 250 °C.
Figure 2(b) shows the size distribution of the Au-Si islands, where the number density ($N_n$) of the islands showing a size of $n$ is normalized by the total number density ($N_0$). The size of the island is expressed by the number of FHCs, which have been covered with the islands. The distribution shows some peaks at $n = 1, 3$ and $6$. The peak at $n = 1$ corresponds to the small hole-island pair islands, and two peaks at $n = 3$ and $6$ reflect to the size distribution of Si islands before the Au deposition. The result suggests that the Si atoms don’t migrate between islands at the lower temperature, as reported in the previous paper [28].

At elevated temperature, $T_s = T_a = 370 \, ^\circ C$, the 5×2 structure is preferentially formed on the Au-Si islands. Since the coverage of the Au atom is kept at 0.07 ML that is higher than the composition of Au in the 5×2 structure, we can see some holes beside the islands. The size distribution at 370 °C is plotted in Figure 3(b). Some of the islands are grown during the Au deposition, and make additional peaks at $n = 5$ and $9$ in the size distribution. From the shapes of the islands, both islands are grown from the R-Si islands ($n = 3$) and the hexagonal Si islands ($n = 6$) at the higher temperature as shown by inset of figure 3(b). Since the growth direction is one of the $<1\overline{1}0>$ directions in both islands, the preferential growth direction of the 5×2 structure will be the $<1\overline{1}0>$ directions. The enlargement is caused by the Au deposition, because the size distribution of the Si nanoislands does not change by annealing even at $T_a = 410 \, ^\circ C$, as described in a part of sample preparation.

![Figure 3](image3.png)

**Figure 3.** (a) STM image(85×85 nm$^2$) of surface after the deposition of Au atoms at $T_s = T_a = 370 \, ^\circ C$. The 5×2 structure is formed on the Au-Si islands and some holes beside the islands are created. (b) Size distribution of the islands ($N_0 = 362$) for figure 3(a). The growth shapes of the Au-Si islands are drown in the upper part schematically.

Since the enlargement of the islands during Au deposition relates to the formation of the 5×2 structure, the detachment of Si atoms from the islands is suppressed at temperature below 270 °C. The Si migration occurs at temperature above 280 °C and the surface diffusion of Si atoms among the Au-Si islands is enhanced above 300 °C, drastically, above which the 5×2 structure is preferentially formed on the Au-Si islands.

In summary, the growth of Au-Si islands from Si islands is subject to the substrate temperature, $T_s$, that has great influences on the diffusion of Au and Si atoms and the reconstruction of the surface. In the lower temperature range $T_s = T_a < 260 \, ^\circ C$, the diffusion length of Au atom is too short to reach the Si islands (less about 10 nm). However a part of the Si islands is metallized by the reached Au atoms and the $\sqrt{3} \times \sqrt{3}$ structure is formed on the part even in the low $T_s$. In the range, $280 \, ^\circ C < T_s = T_a < 300 \, ^\circ C$, the diffusion length of Au atoms becomes larger than the mean distance between the islands and all Au atoms combine with Si atoms in the Si islands. The 5×2 structure is also formed in addition to the $\sqrt{3} \times \sqrt{3}$ structure on the Au-Si islands. We think the reconstruction of the 5×2 structure needs
high thermal energy because many bond breakings and re-bonding are essential to construct the 5×2 structure compared to the 3×3 structure. Above 300 °C, the 5×2 structure is preferentially formed on the islands, and some of the Au-Si islands are grown along one of the <110> directions. In the high T_s, the surface diffusion of Si atoms among the islands is drastically enhanced, and then the growth of the islands during Au deposition is occurred.

The results make possible to form size selected metallic nanoislands on semiconductor substrate, and the electronic structure of the metallic islands can be altered by a choice of the surface structure that will be changed drastically by growth conditions and adsorbates.

References
[1] Grandidier B, Niquet Y M, Legrand B, Nys J P, Priester C and Stiévenard D 2000 Phys. Rev. Lett. 85 1068
[2] Evans D A, Alonso M, Cimino R and Horn K 1993 Phys. Rev. Lett. 70 3483
[3] Yeom H W, Ahn J R, Yoon H S, Lyo I -W, Jeong H and Jeong S 2005 Phys. Rev. B 72 035323
[4] Blaha P, Carmelo J M P, Martelo L M, Sacramento P D, Dressel M and Jacobsen C S 2003 Phys. Rev. B 68 125111
[5] Vitali L, Ramsey M G and Netzer F P 1999 Phys. Rev. Lett. 83 316
[6] Kocán P, Sobotík P, Ošt’ádal I and Kotrla M 2004 Phys. Rev. B 69 165409
[7] Crain J N and Himpsel F J 2003 Appl. Phys. A 82 431-38
[8] Barke I and Hovel H 2003 Phys. Rev. Lett. 90 166801
[9] Riikonen S and Sanchez-Portal D 2005 Phys. Rev. B 71 235423
[10] Ahn J R, Byun J H, Koh H, Rotenberg E, Kevan S D and Yeom H W 2004 Phys. Rev. Lett. 93 106401
[11] Zhang H M, Balasubramanian T and Uhrberg R I G 2002 Phys. Rev. B 66 165402
[12] Tong X, Ohuchi S, Sato N, Tanikawa T, Naga T, Matsuda I, Aoyagi Y and Hasegawa S 2001 Phys. Rev. B 64 205316
[13] Schneider Wolf-Dieter 2002 Surf. Sci. 514 74-83
[14] Martinez-Gila A, Rotaa A, Maroutiana T, Bartenliana B, Beauvillaina P, Moyenb E and Hanbückenb M 2004 Superlattices and Microstructures 36 235-43
[15] Terabe K, Hasegawa T, Nakayama T and Aono M 2005 Nature 433 47
[16] Ono Y, Takahashi Y, Yamazaki K, Nagase M, Namatsu H, Kurihara K and Murase K 2000 Appl. Phys. Lett. 76 3121
[17] Takayanagi K, Tanishiro Y, Takahashi S and Takahashi M 1985 Surf. Sci. 164 367
[18] Shigeta Y, Endo J and Maki K 1996 J. Crystal Growth 166 617-21
[19] Shigeta Y, Endo J, Fujino H and Maki K 1996 Surf. Sci. 357/358 414-17
[20] Shimada W and Tochihara H 1994 Surf. Sci. 311 107
[21] Shigeta Y, Endo J and Maki K 1995 Phys. Rev. B 51 2021-24.
[22] Voigtländer B and Weber T 1996 Phys. Rev. Lett. 77 3861-64
[23] Shigeta Y, Fujino H and Maki K 1999 J. Appl. Phys. 86 881
[24] Shigeta Y 2000 Surf. Rev. Lett. 7 61
[25] Suzuki M and Shigeta Y 2003 Surf. Sci. 539 113-19
[26] Negishi R and Shigeta Y 2003 J. Appl. Phys. 93 4824
[27] Negishi R, Suzuki M and Shigeta Y 2004 J. Appl. Phys. 96 5013-16
[28] Negishi R, Mochizuki I and Shigeta Y 2006 Surf. Sci. 600 1125-58
[29] Murayama M, Nakayama T and Natori A 2001 Surf. Sci. 493 626-32
[30] Kadohira T, Nakamura J and Watanabe S 2004 e-J. surf. Sci. Nanotech. 2 146-50
[31] Mochizuki I, Negishi R, and Shigeta Y to be published elsewhere.
[32] Shibata A, Kimura Y and Takayanagi K 1992 Surf. Sci. Lett. 273 L430-34
[33] Shibata A and Takayanagi K 1993 Jpn. J. Appl. Phys. 32 1385-88
[34] Khramtsova E A, Sakai H, Hayashi K and Ichimiya A 1999 Surf. Sci. 433-435 405-09
[35] Grozea D, Bengu E and Marks L D 2000 Surf. Sci. 461 23-30