Site-resolved electronic structure of Al nanocluster fabricated on Si(111)7 × 7 surface

Hisashi Narita, Mitsuru Kakeya, Akio Kimura, and Masaki Taniguchi
Graduate School of Science, Hiroshima University, Kagamiyama 1-3-1, Higashi-Hiroshima, Hiroshima 739-8526, Japan

Masashi Nakatake, Tian Xie, Shan Qiao, and Hirofumi Namatame
Hiroshima Synchrotron Radiation Center, Hiroshima University, Kagamiyama 2-313, Higashi-Hiroshima, Hiroshima 739-0046, Japan

(Rceived 12 November 2005; Accepted 7 December 2005; Published 16 February 2006)

We have done scanning tunneling microscopy (STM), scanning tunneling spectroscopy (STS) as well as current imaging tunneling spectroscopy (CITS) of an Al nanocluster periodic array of a submonolayer-Al/Si(111) system. To understand the formation mechanism of this system in detail, a phase diagram of the Al/Si(111) has been carefully produced. Among several structural phases, the nanocluster phase appears for the deposition thickness of 0.24-0.5 ML at a substrate temperature of 550°C. It has been confirmed that these growth conditions should be carefully chosen to produce the well-defined nanocluster. The site-resolved STS spectra of Al nanocluster at 78 K show an insulating energy gap of 3.3 eV. In the CITS images, we have found different features of space-resolved tunneling current for the filled and empty states, which markedly depend on atomic sites and also on inequivalent half-unit cells. [DOI: 10.1380/ejssnt.2006.208]

Keywords: Scanning tunneling spectroscopy; Aluminum; Silicon(111)

I. INTRODUCTION

Over the past few decades, the fabrication and the phase transition, the electronic state of various kinds of metal species on a Si substrate have been investigated by using angle-resolved photoemission spectroscopy (ARPES) and low energy electron diffraction (LEED) techniques. Recently, scanning tunneling microscopy (STM) has enabled us to understand the structural and electronic properties of the nano-sized exotic surface phases in more detail.

The submonolayer-Al/Si(111) system is well known to show four different surface phases (nanocluster (α-7 × 7), √3 × √3R30°, √7 × √7R19.1°, γ-phase). For each structural phase, people have tried to determine atomic structures using several experimental tools like STM, LEED, ARPES, and also with a help of theoretical calculation. In the case of √3 × √3R30°, numerous attempts have been made to decide Al adsorption site, and it was concluded that the Al atom is adsorbed on T4 site [1–8]. The α-phase has been understood as a quasi-periodic incommensurate system [2, 3, 11–18], in which Al substitutes for outermost Si atom. Recently, a reasonable structure model (ZS model) of the γ-phase is reported by Saranin, et al. [5], using the photoelectron spectroscopy, which was revised later by Hamers, et al. [9] with the bias-dependent STM results. However, Kotlyar [10] recently proposed a new structural model. The γ-phase has been understood as a quasi-periodic incommensurate system [2, 3, 11–18], in which Al substitutes for outermost Si atom. Recently, a reasonable structure model (ZS model) of the γ-phase is reported by Saranin, et al. [19] on the basis of the high resolution STM. Moreover, they clarified that the γ-phase has two types of the domain walls containing a larger or smaller Al density called as "heavy" or "light" γ-phase, respectively.

The Al nanocluster array can be realized with well-controlled conditions of metal deposition and substrate temperature. The present study is mainly focused on this nanocluster phase. The structural model of the cluster was first proposed by Kotlyar, et al. [20] and a more accurate structure was explored later by Jia, et al. [21]. It has been proposed that this nanocluster contains six Al atoms forming a triangle and three Si atoms displaced toward the center of a HUC as shown in Fig. 1(a).

Although the former studies have been dedicated to the structure, little is known about the electronic states. The purpose of the present study is to clarify the local electronic structure of the Al nanocluster array on the Si(111)7 × 7 reconstructed surface using scanning tunneling spectroscopy (STS) and current imaging tunneling spectroscopy (CITS) [22] techniques depending on various atomic sites within the cluster.

FIG. 1: Structural model of Al nanocluster given by Jia, et al. [21].

This paper was presented at International Symposium on Surface Science and Nanotechnology (ISSS-4), Saitama, Japan, 14-17 November, 2005.

Corresponding author: narimac@hiroshima-u.ac.jp
Corresponding author: mkiok@hiroshima-u.ac.jp
II. EXPERIMENTAL

The experiments were carried out in an ultrahigh vacuum (UHV) chamber with a base pressure of $1.0 \times 10^{-10}$ mbar, and using a low-temperature scanning tunneling microscope (Omicron LT-STM). We employed highly Sb-doped Si(111) wafers and the surface was chemically treated by a modified RCA cleaning method [23] and then immediately introduced into the UHV chamber. A clean Si(111)$7 \times 7$ surface was obtained by a standard flashing procedure up to $1250^\circ$ C after outgassing at $500^\circ$ C for several hours. Subsequently, Al was carefully deposited using a well-outgassed home-made evaporator with an AlN crucible showing a high thermal conductivity. All of the STM, STS and CITS images were obtained at $78$ K using an STM tip made of chemically etched tungsten wire. We have prepared an Al nanocluster periodic array by $0.24$ ML ($1$ ML = $7.8 \times 10^{14}$ atoms/cm$^2$) Al deposition. For the STS spectrum, the normalized conductance ($dI/dV$) / ($I/V$) could be adopted, however, a divergence of intensity due to a negligible tunneling current in the energy gap region would be expected. Therefore we have modified the conductance using a corrected $I/V$ denoted as $I/V = \sqrt{(I/V)^2 + 0.02}$, which was originally introduced by Prietsch, et al. [24].

III. RESULTS AND DISCUSSION

A. Sample preparation

Figure 2 shows the phase formation diagram of the Al/Si(111) system obtained in our experiment. These results are almost consistent with that of Nishikata, et al. [11] and Hamers, et al. [3]. The phase formation diagram makes it clear that the each phase of sub-monolayer Al/Si(111) system has a different feature of appearance scale for the film growth condition.

For the Al deposition coverage above 0.5 ML, $\gamma$-phase can be formed above $T_s \sim 500^\circ$ C. We have found the two different growth modes for the $\gamma$-phase, which can be separated at $T_s \sim 600^\circ$ C in Fig. 2. Several reports have been devoted to the structural study of $\gamma$-phase for $T_s < 700^\circ$ C [9, 19], but little attention has been paid to the morphology in a large scale. Fig. 3 shows the filled state STM images of the $\gamma$-phase with two different morphologies in $200 \times 200$ nm$^2$ range. One is the $\gamma$-phase Al below $T_s = 600^\circ$ C, where the well-known "patchwork" is observed as shown in Fig. 3(a). In contrast, a flat feature of the film grown in Frank-van der Merve (FM) mode is recognized in Fig. 3(b) if the substrate temperature is above $600^\circ$ C, which is newly found in the present experiment. Here, it must be noted that these films in Figs. 3(a) and 3(b) are not purely Al films, but they are identified as silicide films as suggested by Liu, et al. for the higher substrate temperature [25].

Below the Al coverage of 0.5 ML, $\sqrt{3} \times \sqrt{3}$, $\sqrt{7} \times \sqrt{7}$ and $\alpha$-7$ \times $ 7 phases can be realized depending on the substrate temperature. Among them, the $\sqrt{7} \times \sqrt{7}$R19.1$^\circ$ have the small formation range compared to the other phases. It can be recognized that the formation range of the Al nanocluster phase is also quite narrow, which is surrounded by the other phases. Thus, it is needed for the growth condition of the nanocluster phase to be accurately controlled regarding the substrate temperature and Al deposition.

B. Local electronic structure of Al nanocluster

Figure 4(a) shows the filled state STM image of the well-ordered Al nanocluster array. Triangle-shaped bright spots are found on the faulted half-unit cell (FHUC) as well as on the unfaulted half-unit cell (UFHUC) of the
FIG. 3: Filled state STM images of two types $\gamma$-phases observed at 78 K. (a) The patchwork $\gamma$-phase prepared with 1.1 ML-Al deposition at 550°C ($V_s = -2.5$ V: 200 × 200 nm²). (b) The $\gamma$-phase grown in the Frank-van der Merve (FM) mode prepared with 0.55 ML-Al deposition at 700°C ($V_s = -2.0$ V: 200 × 200 nm²).

FIG. 4: (a) Filled state STM image of Al nanocluster array observed at 78 K ($V_s = -2.0$ V: 15 × 15 nm²) (b) (c) STS spectra of ($dI/dV$)/($I/V$) for various atomic sites inside Al nanocluster obtained at 78 K. The insets show the expanded STM images of Al nanocluster observed at 78 K for the filled state (left) and at RT for the empty state (right).

Si(111)7 × 7 surface. Note that this cluster is periodically arranged forming a honeycomb lattice. The present STM image at low temperature in Fig. 4(a) is consistent with the reported result at room temperature by Kotlyar, et al. [20] and Jia, et al. [21].

We have also carried out STS measurement for three atomic sites (cluster-Si, corner-Al, and edge-Al) inside the cluster on FHUC and UFHUC as shown in Figs. 4 (b) and 4(c). These STS spectra have been obtained for the same sample surface using the same tip, and estimated by averaging 10 spectra of each atomic site over several unit cells. The STS spectra of several sites in the Al nanocluster indicate an insulating energy gap of 3.30 eV at 78 K. One can notice that the filled state ($dI/dV$)/($I/V$) spectra show the different features for the different atomic sites. There appear two peak structures at the sample biases ($V_s$) of -1.83 and -2.73 V in the ($dI/dV$)/($I/V$) spectra of Si site in the cluster (cluster-Si). Both of the two different STS spectra on the corner-Al and edge-Al also show a shoulder at $V_s = -2.06$ V and a peak at $V_s = -2.83$ V. The STS intensity on the cluster-Si site for $V_s > -1.9$ V is comparable to that for the Al sites, while the intensity is larger on the Al sites than on Si sites for $V_s < -1.9$ V.

In the empty state (Fig. 4(c)), the STS intensity for the cluster-Si site on the FHUC is slightly higher than that on the UFHUC in the bias range of +2.40 V to +2.80 V, while, for the higher sample bias, the situation changes and the intensity on the UFHUC is higher than that on the FHUC, where the difference is distinctly large above +3.00 V. These results indicate that the cluster-Si is strongly affected by the stacking fault of the substrate located below the Al nanocluster.

To understand the observed feature of STS images in terms of the lateral local electronic structure, we have carried out a current imaging tunneling spectroscopy (CITS) under the same conditions such as the distance between...
FIG. 5: Filled state CITS images of Al nanocluster with the sample bias ($V_s =$ -2.01 (upper) and -2.65 V (bottom) observed at 78 K.

The (d$I$/d$V$)/($I/V$) commonly reflects the density of states of sample, but the present STS spectra cannot be simply reproduced by the calculated electronic band structure of Al cluster array [26]. The calculation shows that the Si and Al sp states are located in the limited region from -1.5 to +1.0 eV relative to the Fermi energy. However, the present STS spectra on both the Si and Al sites within the cluster show the peaks at the similar sample bias around $V_s =$ -2.7 ~ -2.8 V, where the intensity on the Al site is larger than those on the Si site as shown in Fig. 4(b). This suggests that the density of electronic states derived from the Al site in the cluster is located around -2.7 ~ -2.8 eV below EF. It is also clarified that the ringlike feature observed in the filled state CITS image at $V_s =$ -2.65 V comes mainly from the Al derived state. From these results, we suppose that the bonding state between the Al and second layer Si atoms of the substrate reasonably explains the observed CITS feature as schematically represented in Fig. 6.

Finally, we have observed inequivalent features in the positive sample bias region of the STS spectra and the CITS images on the different HUCs only for the Si site, while, in the negative bias region, no recognizable difference is observed. Figures 7(a) and 7(b) show the empty state CITS images at $V_s =$ +2.74 V and +3.06 V. The asymmetry of the STS intensities with a formula $(D_F - D_U)/(D_F + D_U)$ [$D = (d$I$/d$V$)/($I/V$)] of the different cluster-Si sites within the FHUC (F) and UFHUC (U) is plotted in Fig. 7(c). It is found that the asymmetry shows a positive feature at the lower sample bias below +2.90 V, while it is negative above it and this asymmetry is turned out to be more remarkable as temperature decreases. The origin of this difference is not exactly clear, however, it might come from the different electronic potentials in the Al nanoclusters on the different HUCs.

IV. CONCLUSIONS

We have investigated the local electronic structure of an Al nanocluster fabricated on a Si(111)7 × 7 surface by STM, STS and CITS techniques. It has been clarified that the (d$I$/d$V$)/($I/V$) shows a significant gap of 3.3 eV at 78 K. The ring-shaped structure in the filled state CITS image has been newly observed for $V_s <$ -1.9 V, which originates from the Si-Al bonding state between adsorbed Al and second layer Si atoms around the cluster. Moreover, the distinct difference in (d$I$/d$V$)/($I/V$) in the empty state CITS images on the two inequivalent HUCs indicates the presence of different surface potentials.

Acknowledgments

This work was partly supported by a Grant-in-Aid for Scientific Research from the Ministry of Education, Culture, Sports, Science and Technology (No: 17340112) and by Iketani Science and Technology Foundation (No: 0171067-A).
FIG. 7: (a) (b) Empty state CITS images with $V_s = +2.74 \text{ V}$ and $+3.06 \text{ V}$ obtained at 78 K. (c) Normalized difference in $(dI/dV)/(I/V)$ intensities with formula $(D_F - D_U)/(D_F + D_U)$ [$D = (dI/dV)/(I/V)$] of Si sites within FHUC (F) and UFHUC (U).

[1] J. E. Northrup, Phys. Rev. Lett. 53, 683 (1984).
[2] J. R. Chelikowsky, Phys. Rev. B 16, 3618 (1977).
[3] R. J. Hamers, Phys. Rev. B 40, 1657 (1989).
[4] T. Kinoshita, S. Kono and T. Sagawa, Phys. Rev. B 32, 2714 (1985).
[5] G. V. Hansson, R. Z. Bachrach, R. S. Bauer and P. Chiaradia, Phys. Rev. Lett. 46, 1033 (1981).
[6] R. I. G. Uhrberg, G. V. Hansson, J. M. Nichols, P. E. S. Presson, and S. A. Flodstrom, Phys. Rev. B 31, 3805 (1985).
[7] B. N. Dev, S. M. Mohapatra, K. C. Mishra, W. M. Gibson and T. P. Das, Phys. Rev. B 36, 2666 (1987).
[8] M. Kelly, G. Margaritondo, J. Anderson, D. J. Frankel and G. J. Lapeyre, J. Vac. Sci. Technol. A 4, 1396 (1986).
[9] R. J. Hamers, Phys. Rev. B 40, 1657 (1989).
[10] V. G. Kotlyar, T. V. Kasyanova, E. N. Chukurov, A. V. Zotov and A. A. Saranin, Surf. Sci. 545, L779 (2003).
[11] K. Nishikata, K. Murakami, M. Yoshimura and A. Kawazu, Surf. Sci. 269/270, 995 (1992).
[12] J. J. Lander and J. Morrison, Surf. Sci. 2, 533 (1964).
[13] A. V. Zotov, E. A. Khramtsova, S. V. Ryzhkov, A. A. Saranin, A. B. Chub and V. G. Lifshits, Surf. Sci. 316, L1034 (1994).
[14] E. A. Khramtsova, A. V. Zotov, A. A. Saranin, S. V. Ryzhkov, A. B. Chub and V. G. Lifshits, Appl. Surf. Sci. 82/83, 576 (1994).
[15] T. Michely, M. C. Reuter and R. M. Tromp, Phys. Rev. B 53, 4105 (1996).
[16] R. Gröger and P. von Blanckenhagen, Thin Solid Films 281/282, 73 (1996).
[17] R. Gröger and M. R. Barczewski, Surf. Sci. Interface Anal. 32, 154 (2001).
[18] Y. Sugawara, S. Orisaka and S. Morita, Appl. Surf. Sci. 157, 239 (2002).
[19] A. A. Saranin, V. G. Kotlyar, A. V. Zotov, T. V. Kasyanova, M. A. Cherevik and V. G. Lifshits, Surf. Sci. 517, 151 (2002).
[20] V. G. Kotlyar, A. V. Zotov, A. A. Saranin, T. V. Kasyanova, M. A. Cherevik, I. V. Pisarenko and V. G. Lifshits, Phys. Rev. B 66, 165401 (2002).
[21] J. F. Jia, X. Liu, J. Z. Wang, J. L. Li, X. S. Wang, Q. K. Xue, Z. Q. Li, Z. Zhanuy and S. B. Zhang Phys. Rev. B 66, 165412 (2002).
[22] R. J. Hamers, J. E. Demuth and R. M. Tromp, Phys. Rev. Lett. 56, 1972 (1986).
[23] W. Kem and D. A. Puotinen, RCA Rev. 31, 187 (1970).
[24] M. Prietsch, A. Sansavar and R. Ludeke, Phys. Rev. B 43, 11850 (1991).
[25] H. Liu, Y. F. Zhang, D. Y. Wang, M. H. Pan, J. F. Jia and Q. K. Xue, Surf. Sci. 571, 5 (2004).
[26] L. Zhang, S. B. Zhang, Q. K. Xue, J. F. Jia and E. G. Wang, Phys. Rev. B 72, 033315 (2005).