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Fabrication of GaAs Quantum Dots on a Bilayer-GaSe Terminated Si(111) Substrate

Keiji UENO*, Koichiro SAIKI[1] and Atsushi KOMA

Department of Chemistry, School of Science, The University of Tokyo, 7–3–1, Hongo, Bunkyo-ku, Tokyo 113-0033, Japan

[1]*Department of Complexity Science and Engineering, Graduate School of Frontier Sciences, The University of Tokyo, 7–3–1, Hongo, Bunkyo-ku, Tokyo 113-0033, Japan*

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We have developed a novel method to fabricate self-assembled quantum dots (QDs) of compound semiconductors on a Si(111) substrate using the so-called 'droplet epitaxy' technique. In order to fabricate QDs on a Si substrate by droplet epitaxy, we examined the termination of a Si (111) surface with a bilayer-GaSe. This surface is formed by depositing 1 monolayer Ga on a Si(111)-7×7 surface and annealing in a Se flux at 520°C. Then Ga atoms are deposited to form Ga droplets on this surface, and the sample is annealed in an As flux to transform Ga droplets into GaAs QDs. It is revealed that GaAs QDs with a diameter as small as 10 nm and a height of 5 nm can be formed on the bilayer-GaSe/Si(111) substrate at a maximum density of 8.4×10^{10}cm^{-2}. Using this method a new technique will be available to fabricate QDs of many kinds of compound semiconductors on the Si(111) substrate.

KEYWORDS: quantum dot, droplet epitaxy, GaAs, GaSe, bilayer-GaSe, Si(111), surface termination

* e-mail address: kei@chem.s.u-tokyo.ac.jp

1. Introduction

Fabrication of semiconductor quantum dots (QDs) is of considerable interest because of the possibility of their application in high-performance optical and electronic devices.[1,2] Usually high-quality QDs of compound semiconductors are formed by self-organization during the Stranski-Krastanow (SK) growth mode.[3,4] In this case, however, the possible combinations of substrates and grown materials is limited, because the SK growth mode essentially requires an adequate amount of lattice mismatch between them. Furthermore, it is difficult to control sites and sizes of QDs freely in the case of the SK growth method, although it is important to fabricate such a novel electronic device as an integrated circuit of single-electron tunneling transistors.

Our approach to fabricate QDs of a compound semiconductor uses the so-called 'droplet epitaxy' technique. If a Ga flux, for example, is irradiated under ultrahigh-vacuum (UHV) condition on an inactive substrate surface at an appropriate substrate temperature, Ga atoms freely migrate on the surface and coalesce into a large number of nm-scale Ga droplets. When the migration is uniform, namely the surface energy is uniform on the substrate, these droplets are able to have highly uniform size and density. Then they can be transformed into GaAs nano-crystals by annealing in an As flux. Until now, QDs of III-V compound semiconductors (GaAs, InGaAs, InSb, etc.) have been fabricated on a S or Se-terminated GaAs(001) substrate by droplet epitaxy,[5–9] because it has low surface-energy, and deposited Ga atoms can migrate on it even at the substrate temperature as low as 150°C. However, this surface is not sufficiently stable against high-temperature annealing in the As flux, which is required to form high-quality III-As QDs. Such annealing seems to result in a reaction between the QDs and the substrate or in the unintentional doping of chalcogen atoms into QDs, and as a result the quality of QDs is inevitably degraded.

In order to fabricate high-quality QDs by droplet epitaxy, we examined a new type of a stable substrate surface: a bilayer-GaSe terminated Si(111) surface (hereafter abbreviate to 'BGS'). The structure of the BGS surface has been reported as shown in Fig. 1.[10–12] In this surface, each Si atom in the top and the second layers of the ideal Si(111) surface is

Fig.1

replaced by Se and Ga atoms, respectively. It has been reported previously [10,11,13–15] that an epitaxial film of GaSe, which has a two-dimensional layered structure, can be grown on the BGS surface in a similar manner to that of van der Waals epitaxy[16,17] in spite of the 2.2% lattice mismatch and different crystal structures. The authors reported that no covalent bonds existetd between the BGS surface and the grown GaSe film, and only weak van der Waals interaction was present. Furthermore, the substrate temperature could be raised to 500°C during the growth of GaSe. Therefore we expected the BGS surface to have low surface energy without any active dangling bonds that could disturb the creation of nanometer-scale Ga droplets, and to have sufficient stability against high-temperature annealing in As flux. In this paper we will present the fabrication results of GaAs QDs, and the possibility of intentional control of the density and the size of QDs on the BGS surface.

2. Experimental

The BGS surface and GaAs QDs were fabricated in an UHV molecular beam epitaxy (MBE) chamber with a base pressure of 3×10^{-8} Pa. A clean Si(111)-7 × 7 surface was obtained by the direct current heating process; heating at 600°C for 12 h, repeated flash heating from 850°C to 1200°C, and slow cooling (4°C/min) from 850°C to 700°C. After the substrate temperature was set to 520°C, 1 monolayer (ML) equivalent Ga atoms ($\approx 7.8 \times 10^{14}$atoms/cm^2) were evaporated from a Knudsen cell onto the clean Si(111)-7×7 surface. The intensity of the Ga flux measured by a nude ion gauge type monitor was 8×10^{-7} Pa, and the deposition rate was 0.25 ML/min. Then, the sample was annealed for about 2 minutes at 520°C in a Se flux at a typical intensity of 3×10^{-4} Pa.

After the substrate temperature was lowered to 150–300°C, Ga atoms were deposited onto the BGS surface. In addition to the substrate temperature, the deposition rate of Ga was also varied to change the QD density, as described later. Then the sample was annealed for 30 min in an As flux at a typical flux intensity of 3×10^{-4} Pa at the same substrate temperature as that used during the deposition of Ga.

During the fabrication of the BGS surface and GaAs QDs, surfaces were monitored by reflection high-energy electron diffraction (RHEED). After the growth of GaAs QDs the

sample was taken out of the MBE chamber and observed by an atomic force microscope (AFM) in air using the SEIKO Instruments SPI-3800/SPA-300 system. AFM images were collected in the noncontact mode by a Si cantilever.

3. Results and Discussion

Figure 2 indicates the evolution of RHEED images during the QD fabrication process. Fig.2 RHEED images of the BGS surface (a, b) show clear streaks, indicating the flatness of the surface. The top layer of the BGS surface has a sixfold symmetry, so that the streak interval in (a) observed along the $[11\bar{2}]$ azimuth of Si is $\sqrt{3}$ times larger than that in (b), which is observed along the $[10\bar{1}]$ azimuth by rotating the sample by 30° from (a). RHEED patterns of the BGS surface showed absolutely no change by the irradiation of the As flux at a substrate temperature as high as 450°C, which proves the stability of the BGS surface.

After 1.5 ML equivalent Ga atoms were deposited onto the BGS surface at a deposition rate of 0.25 ML/min at the substrate temperature of 250°C, some rings appeared on the streak pattern (c, d), indicating the formation of polycrystalline Ga droplets. Immediately after the start of annealing in the As flux, however, these rings vanished, and many spots appeared over the streak pattern of the BGS surface (e, f). Some twin spots could be observed between streaks. No ring or halo pattern existed after the irradiation of the As flux, which means that Ga droplets were almost completely transformed into epitaxial nano-crystals of GaAs. No change was observed in the streak image originating from the BGS surface except for the superimposition of the spotty pattern originating from GaAs QDs. Thus it is suggested that the bare BGS surface is exposed between QDs without being covered by the wetting GaAs layer.

When the sample was rotated by 60° from the $[11\bar{2}]$ azimuth, the same spotty RHEED pattern as (e) could be observed. Furthermore, faint streaks along the $\langle 111 \rangle$ azimuth are recognized in the RHEED image (f). Therefore it is suggested that grown GaAs dots have a threefold shape surrounded mainly by (111)A or (111)B facets. However, it is difficult to determine which facet really exists solely from the RHEED images.

Figure 3 indicates an AFM image of this sample surface. Each QD does not appear Fig.3

to be spherical, but seems to be surrounded by some facets as predicted by the RHEED observation. The resolution of the noncontact AFM, however, was not sufficient to trace the real structure of QDs precisely. QDs formed at 250°C with the Ga deposition rate of 0.25 ML/min have 30–40 nm diameter and 10–15 nm height with an average dot density of 1.2×10^{10}cm^{-2}. Standard deviation of the diameter of QDs shown in Fig. 3 is about 0.2 nm. Rough calculation of the number of Ga atoms included in these GaAs QDs agrees well with the amount of deposited Ga atoms (1.5 ML equivalent).

It is usual for the Si(111)-7×7 surface cleaned by the direct current heating to have many defects. They may remain as irregular sites even after the bilayer-GaSe termination, and Ga droplets may be selectively formed at these sites. If Ga atoms can freely migrate on the BGS surface without being trapped at these active sites, Ga droplets are formed through the two-dimensional nucleation process.[18,19] In this case, the density of GaAs QDs can be changed by varying the substrate temperature or the deposition rate of Ga. If active trap sites exist on the BGS surface, on the contrary, the density of QDs will not be reduced below the density of trap sites. To verify the density of the active defect, the substrate temperature or the deposition rate at the stage of the Ga deposition was varied, and the change of the density of GaAs QDs was measured using AFM.

Figure 4 indicates AFM images of GaAs QDs fabricated on BGS surfaces at two different substrate temperatures. When the substrate temperature was raised to 300°C with the same deposition rate of Ga atoms (0.25 ML/min), the average density of GaAs QDs decreased to 1.5×10^{9}cm^{-2} (Fig. 4(a)). In this case the diameter of each QD was increased to about 60–80 nm. However, when the substrate temperature was lowered to 200°C the average density of GaAs QDs increased to 8.4×10^{10}cm^{-2} (Fig. 4(b)), and the diameter of each QD was decreased to about 10–20 nm. The dependence of the average dot density on the substrate temperature for the Ga deposition is summarized in Fig. 4(c). As is clearly shown in the graph, the log of the dot density linearly increases against $1/T$ without having the lowest limit of the dot density at higher temperatures.

Fig.4

The density of GaAs QDs also varied against the change of the deposition rate of Ga atoms. When the Ga deposition rate was decreased to 0.16ML/min at the substrate temperature of 250°C, the average density of GaAs QDs was decreased to 3.3×10^{9}cm^{-2}, as

shown in an AFM image in Fig. 5(a). However, when the Ga deposition rate was increased to 1.25 ML/min, the average density was increased to 2.9×10^{10}cm^{-2}, as indicated in Fig. 5(b). If Ga atoms were trapped at active sites on the BGS surface and formed droplets, their density would be hardly decreased when only the deposition rate was reduced. Therefore it is concluded that the density of trap sites is lower than the order of 10^9cm^{-2}, and the majority of Ga droplets shown in AFM images are formed through the two-dimensional nucleation process. Fig.5

It is also suggested from these results that the density and the size of GaAs QDs can be intentionally controlled. As shown above, the Ga droplet density can be set to a fixed amount by adjusting the substrate temperature and the deposition rate. Once Ga droplets are formed on the BGS surface, successively deposited Ga atoms freely migrate on the BGS surface and are incorporated into the pre-existing droplets. Therefore the size of GaAs QDs can be controlled by adjusting the total amount of Ga atoms without changing the density of QDs. By examining in detail the dependence of the QD density on the substrate temperature and the deposition rate in a wide range, it is possible to evaluate the adsorption energy, diffusion energy and two-dimensional clustering energy of Ga atoms on the BGS surface. This process will be described elsewhere, since it is not in the scope of the present paper.

As shown in Fig. 5(a), steps could be often recognized on the BGS surface. However, no preferential growth of GaAs QDs has been observed at these steps. Figure 6 indicates a wide-area AFM image of GaAs QDs fabricated at 300°C. Long-range corrugation exists on the BGS surface, which originates from the step-bunching during the cleaning process of the Si(111) surface. GaAs QDs, however, seem to be randomly distributed on the surface. Although the exact structure of the step edge of the BGS surface is not known yet, it is clearly concluded that steps on the BGS surface do not disturb the migration of Ga atoms. Fig.6

The inactiveness and the low trap density of the BGS surface will enable the site-control of QDs. If the surface energy of a BGS surface can be locally increased, Ga droplets will be formed selectively at these 'activated' sites. Therefore we can expect to control the position of QDs by locally desorbing Se atoms and exposing dangling bonds on the BGS

surface just before the deposition of Ga atoms. It has already been reported that the control of the position of QDs is also possible in the case of the SK growth mode by locally etching the substrate surface.[20,21] In this case, however, the control of the QD position is achieved via the change of the distortion or the migration energy, so that QDs are fromed *around* etched positons and the accuracy of the position control is limited. In our case, on the contrary, QDs can be formed *just at* positions where dangling bonds are exposed. Previously we have succeeded in excavating a GaSe film and fabricating nano-scale grooves using an AFM cantilever.[22] We are now trying to modify the BGS surface using a scanning tunneling microscope under the UHV condition so as to adsorb Ga atoms selectively at modified sites.

We are also attempting to fabricate QDs of other compound semiconductors. Preliminary experiments have revealed that In droplets can also be formed on the BGS surface, and they can be transformed into InAs QDs. We think the inactiveness of the BGS surface will also enable us to form droplets of such III- or II- column metals as Al, In or Zn, Cd, Hg, and to transform them into QDs of III-V or II-VI semiconductors by annealing in fluxes of V- or VI-column elements such as N, P, As, Sb or O, S, Se, Te, respectively.

4. Conclusions

We have developed a novel method to fabricate self-assembled quantum dots of GaAs on a Si(111) substrate, by terminating its surface by bilayer-GaSe. By using the droplet epitaxy technique on this surface, GaAs nano-crystals with an average size of as small as 10 nm diameter and 5 nm height can be formed on the BGS surface with the density of $8.4\times10^{10}\text{cm}^{-2}$. It was revealed that the density and the size of GaAs QDs can be controlled by changing the substrate temperature and the Ga flux intensity at the formation stage of Ga droplets. This method will open a new way to fabricate site-controlled QDs of many kinds of compound semiconductors on the Si(111) substrate.

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Figure captions

Fig. 1. Structure of a bilayer-GaSe terminated Si(111) surface.

Fig. 2. Evolution of RHEED images during the fabrication of GaAs QDs: a clean BGS surface (a, b), after the deposition of 1.5 ML equivalent Ga (c, d), and after annealing in the As flux (e, f). RHEED images were observed along $[11\bar{2}]$ azimuth (a, c, e), and along $[10\bar{1}]$ azimuth (b, d, f) of the Si(111) substrate, respectively. Ring patterns observed in (b) and (f) are the halo of the direct beam, not the diffraction pattern of the sample surface.

Fig. 3. An AFM image of GaAs QDs fabricated on a BGS surface. Ga droplets were formed at the substrate temperature of 250°C with the deposition rate of 0.25 ML/min. Deposited amount of Ga atoms was 1.5 ML equivalent.

Fig. 4. AFM images of GaAs QDs fabricated on BGS surfaces at different substrate temperatures with the Ga depositon rate of 0.25 ML/min. Deposited amount of Ga atoms was 1.5 ML equivalent.

Fig. 5. AFM images of GaAs QDs fabricated on BGS surfaces with different deposition rates of Ga atoms at the substrate temperature of 250°C. Deposited amount of Ga atoms was 1.9 ML equivalent in (a), and 5.0 ML equivalent in (b).

Fig. 6. A wide-area AFM image of GaAs QDs fabricated on a BGS surface that has long-range corrugation due to the step bunching.

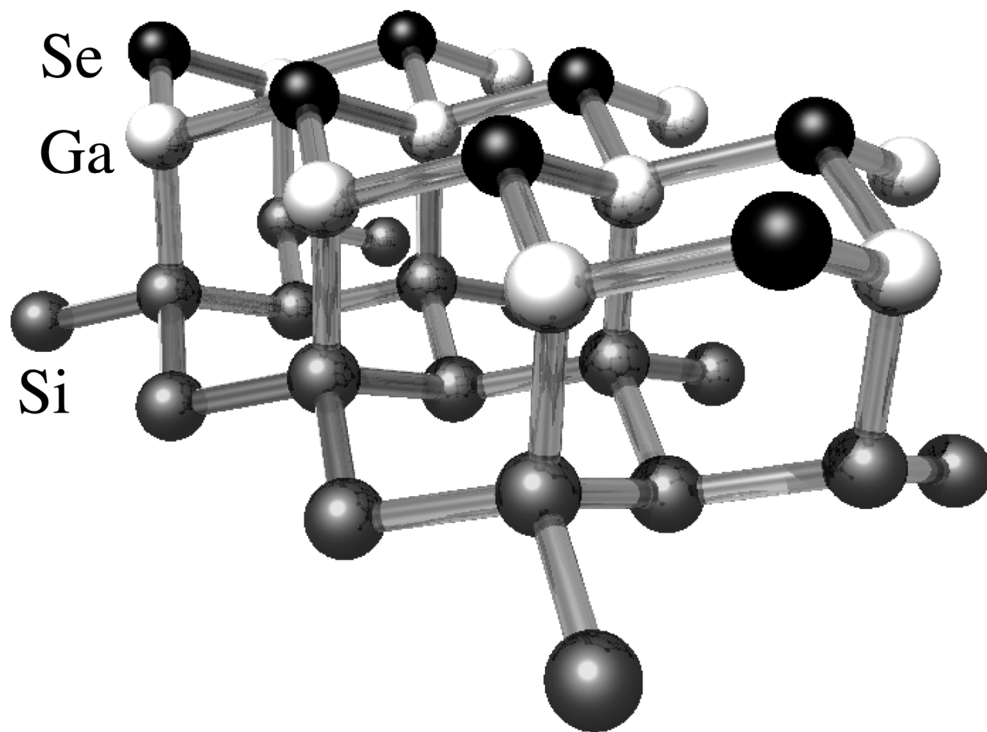


Fig. 1

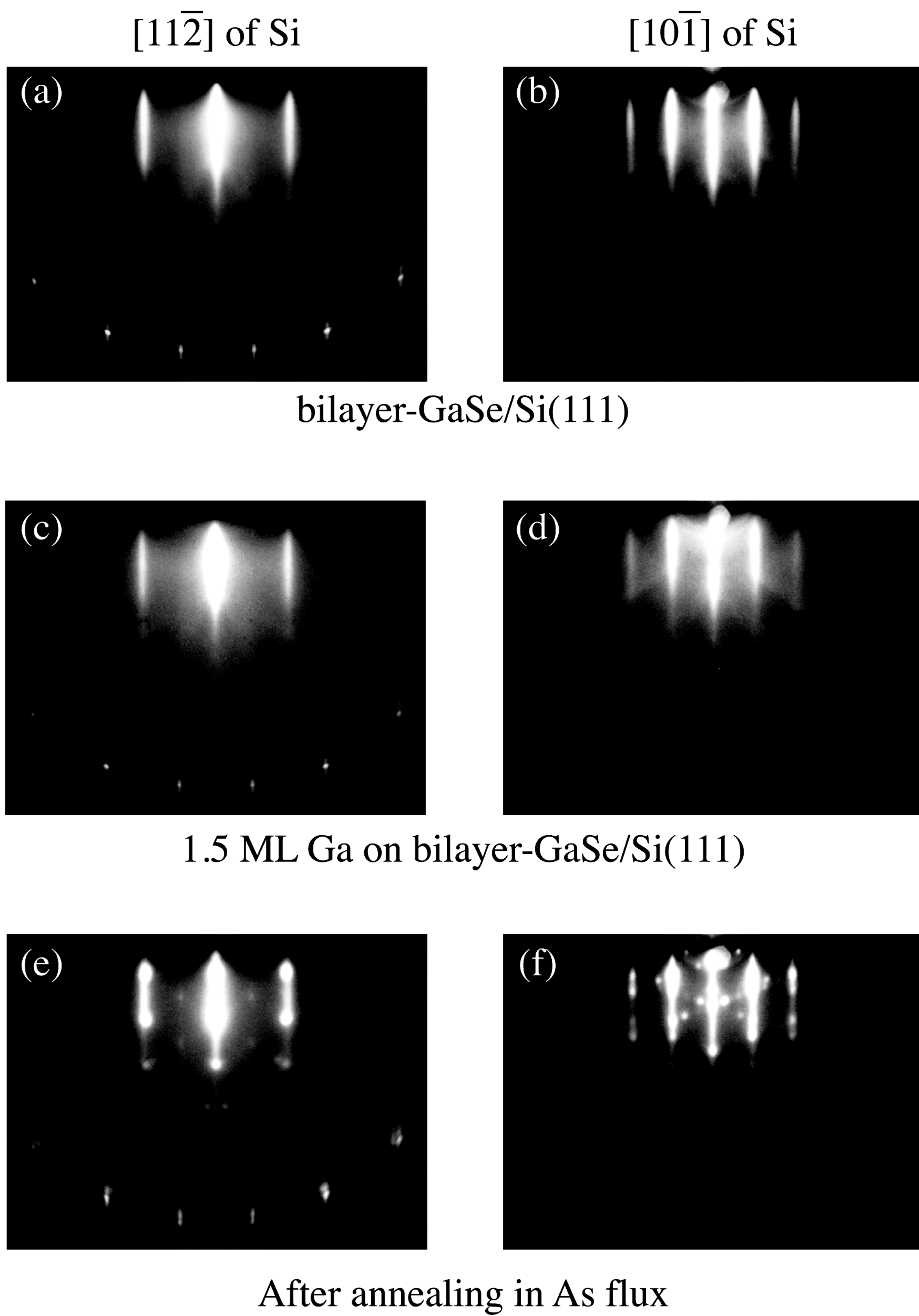
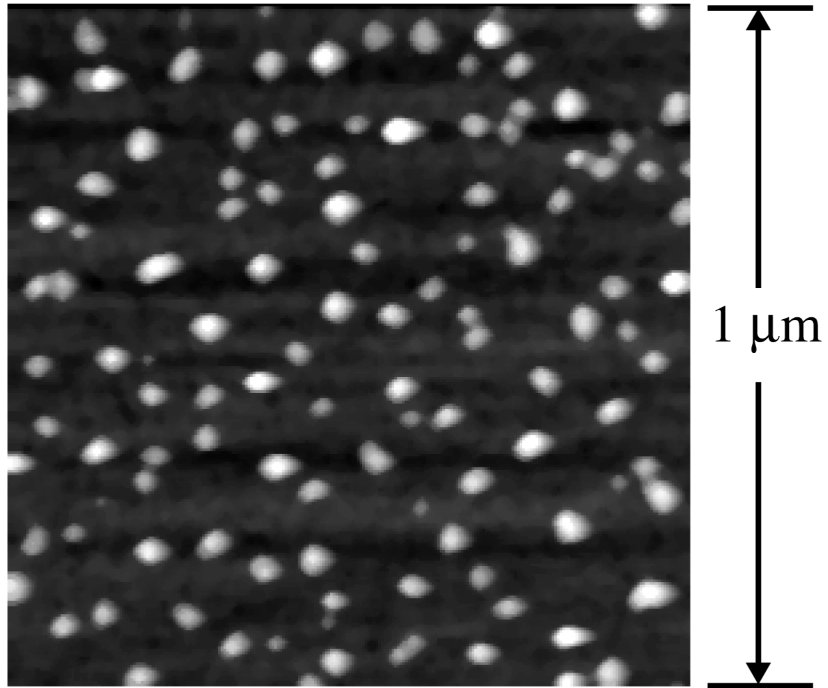


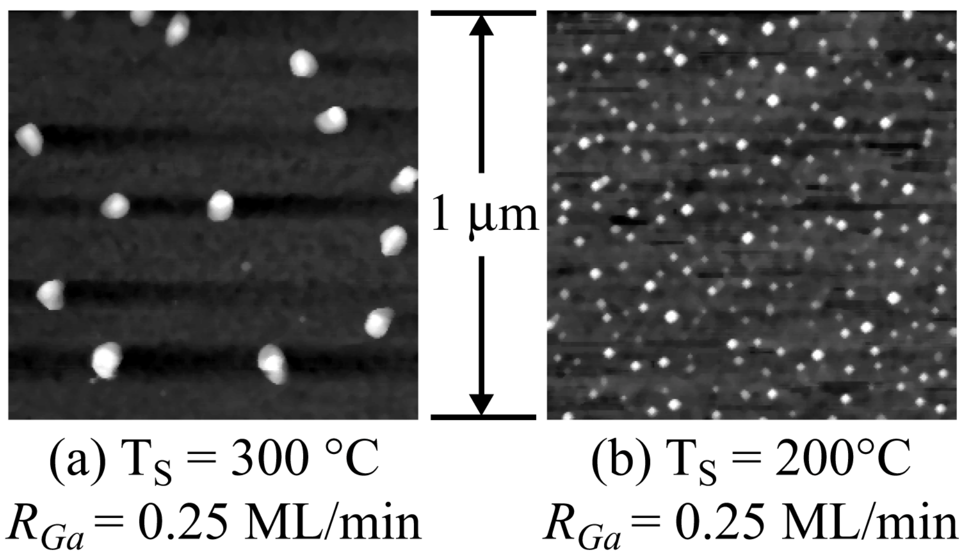
Fig. 2



Ts = 250 °C

R_{Ga} = 0.25 ML/min

Fig. 3



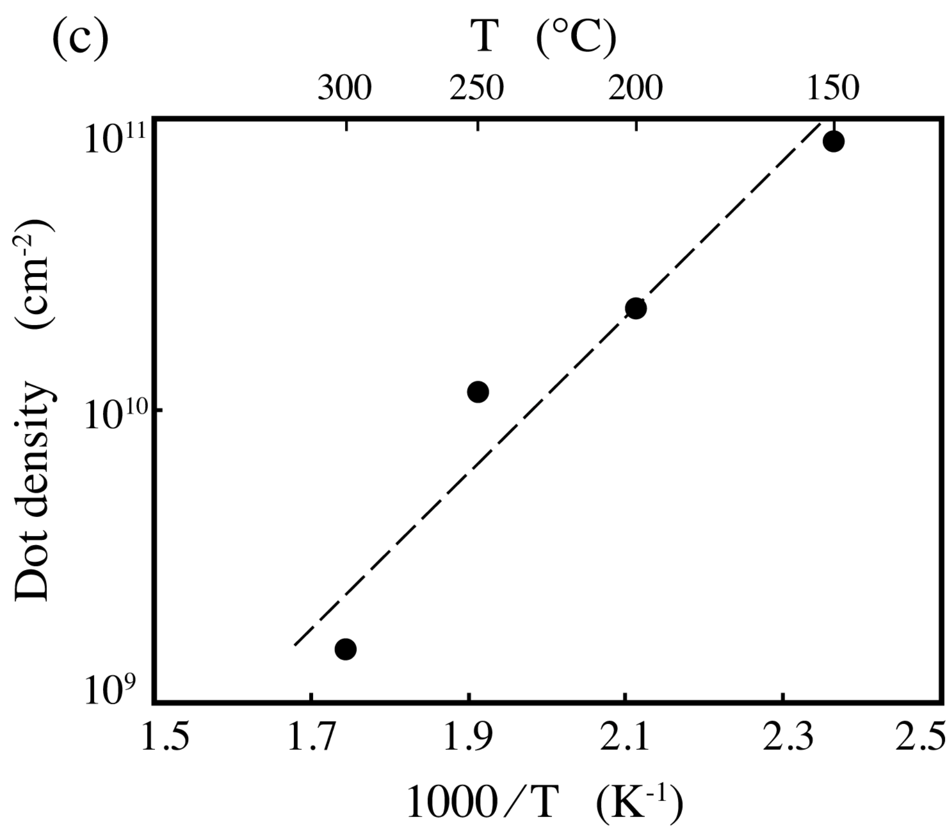


Fig. 4

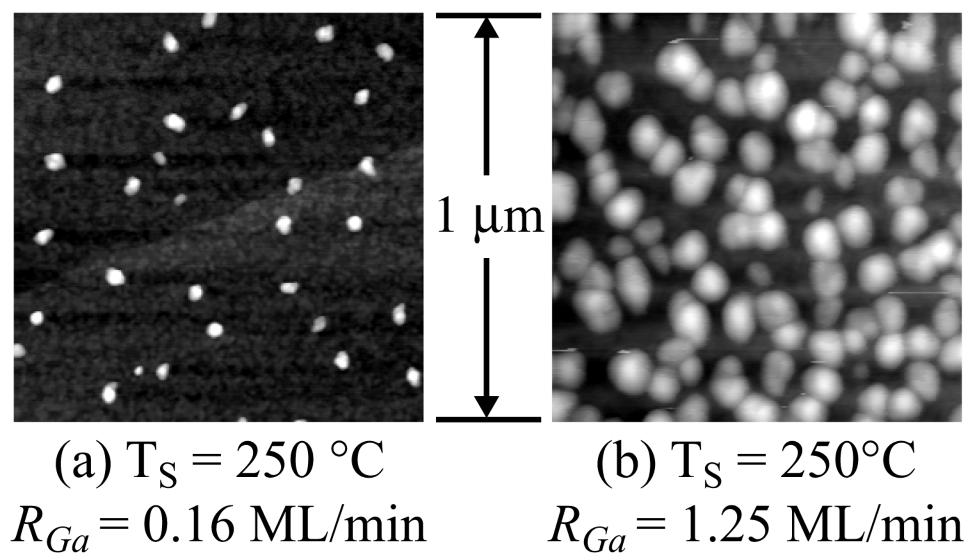
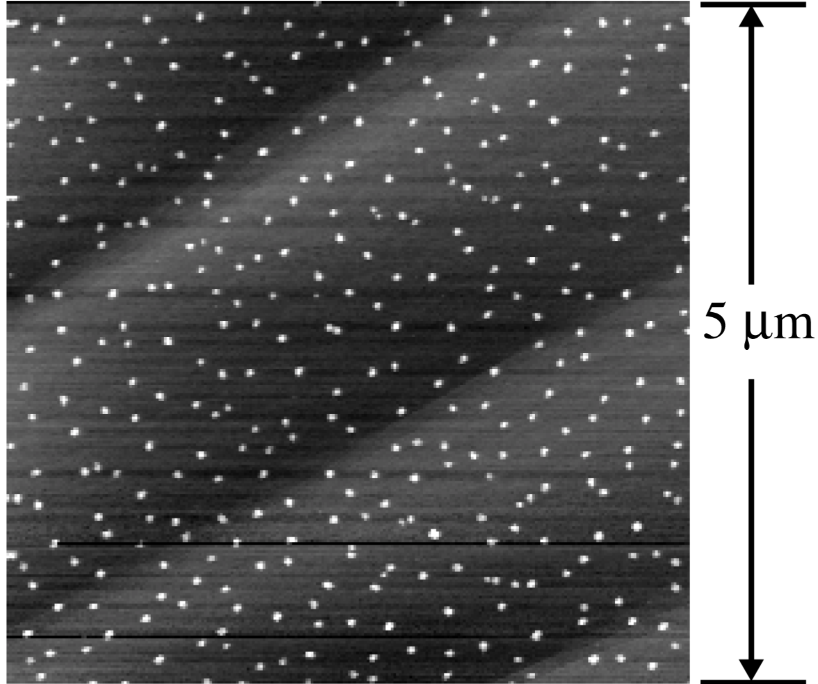


Fig. 5



Ts = 300 °C

R_{Ga} = 0.25 ML/min

Fig. 6