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STM study of the Ga thin films grown on Si(111) surface

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Structural evolution of Ga thin films grown on the Si(111)-$\sqrt{3}\times\sqrt{3}$-Ga template have been investigated with a low-temperature scanning tunneling microscopy (STM). The first Ga layer exhibits a stripe structure along the base vectors of Si(111) lattices. Individual Ga dimers have been directly visualized from the high-resolution STM images of the first Ga layer. The second Ga layer reveals a pseudo 1×1 structure with respect to the Si(111). A new 5×5 phase has been found in the second Ga layer when annealing the sample to 120 °C. Further annealing to 150 °C leads to the formation of 6.3×6.3 phase, which is more stable than the 5×5 phase. The existences of a variety of superstructures of Ga films demonstrates the delicate balance between the interactions of Si(111)-Ga and Ga-Ga. These results shed important light on the epitaxial growth mechanism of Ga films on semiconductor surfaces.

1. Introduction

The adsorption of Group III metals on silicon surfaces have attracted intense interest in recent decades owing to the potential technological applications in optoelectronic and microelectronic devices [1,2]. Great attention was stimulated by the superstructural phases of the metals on silicon surface, which can be used as templates for the fabrication of novel nanostructures [3–5]. In particular, STM is widely used to reveal the geometric and electronic structures of the metals and organic molecules adsorbed on solid surfaces [6–18], owing to its atomic resolution.

Ga on the Si(111)–7×7 surface, as a typical group III metal adsorbed on silicon surfaces, has already been widely studied. It was observed that the structures of Ga strongly depend on Ga coverage and annealing temperature. The deposition of a small amount of Ga at room temperature (RT) leads to the formation of magic clusters [16–18]. When the Ga coverage increases to 1/3 monolayer (ML) and annealing temperature reaches to 550 °C, the $\sqrt{3}\times\sqrt{3}$-Ga R30° surface reconstruction appears with Ga atoms occupying the T4 sites [11,19] (1 ML is defined as the density of a bulk truncated Si(111) surface which is 7.85×10^{14} atoms/cm^2). Further increasing the Ga coverage up to 1 ML, various structures were observed, such as the phases of 6.3×6.3, 11×11, $6\sqrt{3}\times6\sqrt{3}$R30° and 1×1. The first three phases have been widely studied by low energy electron diffraction (LEED) [19–23] and STM [11–15]. However, the 1×1 phase was only observed from LEED measurements [22,23], the STM observation in real space is still lacking. Furthermore, Ga atoms in bulk prefer to form dimer, such as α-Ga, but there is no detailed observation of Ga dimer due to the standing orientation. Recently, a superconducting phase of a two-atom layer of hexagonal Ga film has been reported on GaN(0001) [9].

In this work, we report the direct STM observation of the Ga dimers in the first Ga layer grown on Si(111)-$\sqrt{3}\times\sqrt{3}$-Ga. The second Ga layer reveals a pseudo 1×1 structure with respect to the Si(111)–1×1, similar to the pseudo 1×1 structure of Ga bilayer grown on GaN(0001) [9]. Annealing the second Ga layer to 120 °C leads to the formation of a new 5×5 phase. Moreover, we found the new 5×5 reconstruction coexists with the previously reported 1×1 in the Ga bilayer, but it is less stable than the 6.3×6.3 phase.

2. Experiment

The experiments were performed in a Unisoku ultra-high vacuum LT-STM system with the base pressure maintained at 1.2×10^{-10} mbar. After degassed Si at 600 °C for 10 hours, it was flashed at 1200 °C several seconds to clean the surface, and at 900 °C to obtain an atomically cleaned Si(111)–7×7 surface. Ga atoms were thermally evaporated onto the Si substrate from a quartz crucible by controlling the current to the crucible. Annealing was done by resistively heating the sample and the temperature was measured by an infrared thermometer. Electrochemically etched tungsten tips, subsequently heated by electron beam, were used for STM imaging. STM images were obtained at liquid nitrogen temperature (78 K) under constant-current mode.

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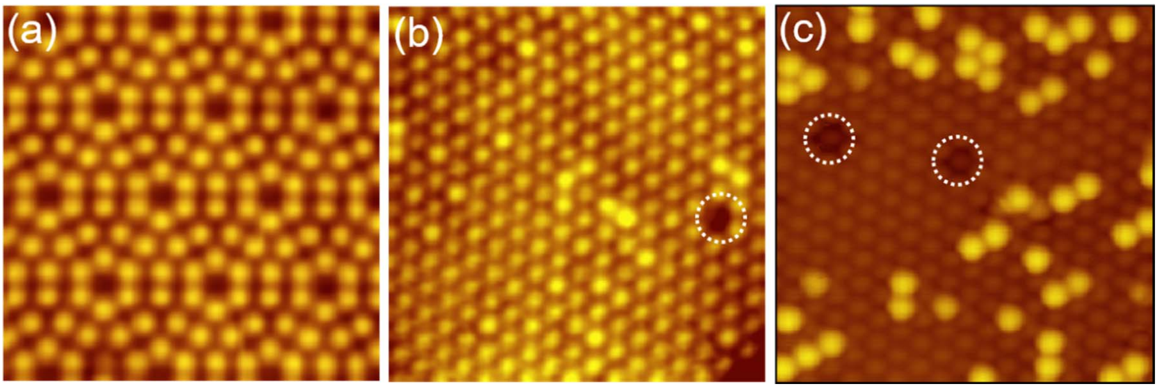

Fig. 1. (a) STM image of the Si(111)–7×7 surface (10×10 nm^2, 1.6 V). (b) STM image of the Si(111)-$\sqrt{3}\times\sqrt{3}$-Ga obtained by depositing ~1/3 ML Ga with subsequent annealing to 550 ℃ (10×10 nm^2, 2.5 V). (c) Excess Ga atoms (bright protrusions) on the Si(111)-$\sqrt{3}\times\sqrt{3}$-Ga surface (10×10 nm^2, −1.8 V). The white circles in (b) and (c) indicate the vacancies of Ga atoms.

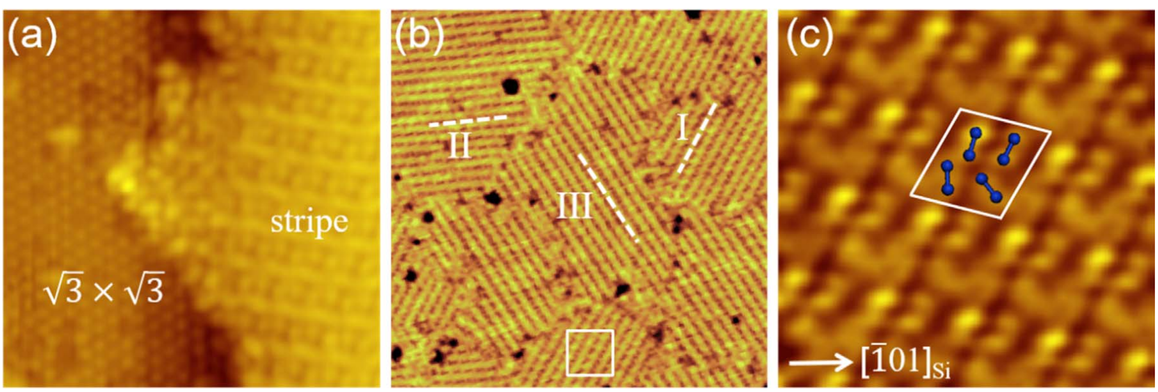

Fig. 2. (a) The STM image of Ga submonolayer, 15×15 nm^2, 2.2 V. (b) Three types of striped domains of the first Ga layer aligned at the principal axes of the Si(111) (50×50 nm^2, 2.0 V). (c) High-resolution STM image of the first Ga layer corresponding to the white box in Domain-I of (a) (6×6 nm^2, −1.2 V). A unit cell consisting of four Ga dimers is marked.

3. Results and discussion

3.1. The structure of first Ga layer

Well-ordered $\sqrt{3}\times\sqrt{3}$-Ga R30° [Fig. 1(b)] is prepared by depositing 1/3 ML Ga atoms onto the Si(111)–7×7 [Fig. 1(a)] surface at RT and annealed subsequently at 550℃ for 30 minutes. 1/3 ML is the optimal coverage to form smooth $\sqrt{3}\times\sqrt{3}$-Ga surface. When the Ga coverage is less than 1/3 ML, the $\sqrt{3}\times\sqrt{3}$-Ga structure cannot completely cover full Si(111)–7×7 surface. When the coverage is over it, additional Ga atoms or clusters (bright protrusions) appeared on the Si(111)-$\sqrt{3}\times\sqrt{3}$-Ga surface [Fig. 1(c)]. This is consistent with the 2D-phase diagram investigated with LEED [23]. Fig. 1(b) is the high-resolution image of Ga film with ~1/3 ML coverage. The figure shows the orientations of $\sqrt{3}\times\sqrt{3}$ Ga rotate 30° with respect to the principal axes of the Si(111) lattice, and the atoms have almost the same brightness. There are a few individual Ga vacancies in $\sqrt{3}\times\sqrt{3}$ Ga inevitably, even when it has additional Ga atoms [marked by white circles in (b) and (c)].

Si(111)-$\sqrt{3}\times\sqrt{3}$-Ga is a better substrate to obtain high-ordered Ga monolayer than Si(111)–7×7, because the Ga atoms passivate the dangling bonds of Si(111)–7×7. Depositing Ga atoms on $\sqrt{3}\times\sqrt{3}$-Ga R30° surface at RT and annealed at 120 ℃, ordered Ga monolayer (around 0.28 nm high) is obtained. At low coverage, the Ga atoms form small two-dimensional clusters with random distribution. With the Ga coverage increasing, the cluster size increases. The structure of stripe and $\sqrt{3}\times\sqrt{3}$-Ga coexisting can be observed [Fig. 2(a)]. At the coverage of 4/3 ML, the growth of the first Ga layer is complete. As shown in Fig. 2(b), Ga monolayer exhibits the striped domains. The directions of domains are aligned at the base vectors of Si(111) surface. In other words, the striped domains have three equivalent domains. They arise from the strong interaction between substrate and Ga monolayer.

Fig. 2(c) is a high-resolution STM image of the first Ga layer. It shows that the promontories are located very close every two. The distance of two promontories obtained by measurement is 0.25 ± 0.01 nm, consistent with the distance of dimer bond [24]. The phase of Ga is commonly thought to contain both metallic and covalent bonds, and the Ga atoms like to be dimer, such as α-Ga. We conclude the stripes are composed with individual Ga dimers. A unit cell includes four dimers denoted by proposed model in Fig. 2(c). According to the different brightness of Ga atoms in dimers, we conclude that the dimers are slightly tilted in various angles resulting of the competition between the interactions of dimer-substrate and dimer-dimer. It should be pointed out that it is the first direct observation of the complete structure of Ga dimer by STM. Most experimental works used the diffraction method lacking the local structural information. Some STM observation of the Ga dimer was limited to the one atom of the Ga dimer because of the vertical alignment of the Ga dimer [10].

The striped domains are ordered, but all of the domain sizes are small (almost 900 nm^2) and there are some defects located at the domain boundaries [Fig. 2(b)]. To eliminate the defects and to increase the domain sizes, we anneal the sample to 150 ℃ for 40 minutes. However, it is found that the striped domains transform into the previously reported 6.3×6.3 phase. It implies that the striped domains only stable within a narrow temperature window.

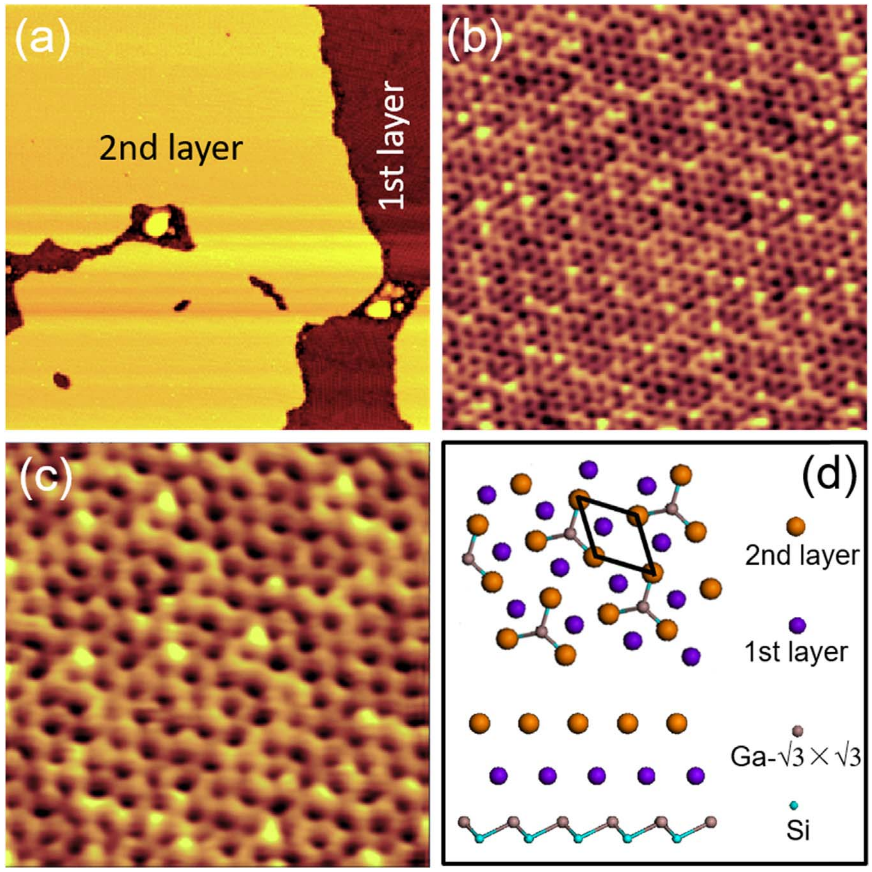

Fig. 3. (a) Morphology of the second Ga layer grown on the first Ga layer (150×150 nm^2, 1.5 V). (b) STM image of the second Ga layer, showing the pseudo 1×1 structure (10×10 nm^2, −1.5 V). (c) Close-up view of the 1×1 phase of the second Ga layer (5×5 nm^2, −1.5 V). (d) Schematic top (top panel) and section (bottom panel) views of the 1×1 phase. The unit cell of 1×1 Ga phase is displayed.

3.2. The structure of second Ga layer

Further depositing Ga atoms on the striped Ga monolayer at RT and annealed subsequently at 120 °C for 40 minutes, the islands of second Ga layer with a height of 0.28 nm appeared on top of Ga monolayer. With the Ga coverage increasing, Ga bilayer is obtained including three phases: 5×5, 1×1 and 6.3×6.3. The phase of 1×1 is consistent with the reported results studied by LEED. The 5×5 structure is a new phase, which is different from any surface structure reported so far on Ga/Si(111) surface. The three phases in Ga bilayer are not equally distributed. 1×1 phase occupies the most of the area, and the phases of 5×5 and 6.3×6.3 are fewer.

Fig. 3(a) shows the atomically resolved image of hexagonal 1×1 phase. Via the measurement, a lattice constant of 0.38 nm is obtained, very close to the parameter of Si(111)−1×1. Furthermore, the orientation of 1×1 phase is along the principal axis of Si(111) substrate. Therefore, we ascribe this phase to the pseudomorphic 1×1 structure with respect to the Si(111) substrate, similar to case of pseudo 1×1 structure of a two-atom layer of hexagonal Ga film on GaN(0001). Schematic model of 1×1 phase is shown in Fig. 3(b).

As shown in Fig. 4, the 5×5 phase presents a fascinating periodic structure. The building block is a Ga heptamer with six atoms located at the vertices of a hexagon and one atom located at the center, constitute a flower-like pattern [Fig. 4(c)]. The lattice constant is measured to be ~1.92 nm, five times of the lattice constant of 1×1 phase or Si(111)−1×1. Furthermore, we find the distance between adjacent Ga atoms is $\sqrt{3}$ times of the lattice constant of the 1×1 phase. Thus the 5×5 phase can be regarded as a modified superstructure of Si(111)-$\sqrt{3}\times\sqrt{3}$-Ga surface. Moreover, we noticed that there are many Ga vacancy defects in the 5×5 phase, which would destroy the long-range ordering of the 5×5 superconstructure. Similar to the case of pseudo 1×1 phase, the orientation of 5×5 reconstruction is also along the Si(111) lattices. Schematic model of the 5×5 phase is shown in Fig. 4(b). When the Ga bilayer further annealed at 150 °C, both the 5×5 and 1×1 phases transform to the stable 6.3×6.3 phase, indicating that they are metastable phases.

4. Conclusions

In summary, the structures of first and second layers of Ga films grown on Si(111)-$\sqrt{3}\times\sqrt{3}$-Ga template have been clarified with a LT-STM. The first Ga layer presents a striped structure aligned at the directions of Si(111)−7×7 lattice. Individual Ga dimers have been directly observed from the high-resolution STM images of the first Ga layer. The second Ga layer reveals a pseudo 1×1 structure with respect to the Si(111)−1×1. Annealing the second Ga layer to 120 °C leads to the formation of a new 5×5 phase. Moreover, we found the new 5×5 reconstruction is less stable than the 6.3×6.3 phase. The existences of a variety of superstructures of Ga films demonstrates the delicate balance between the interactions of Si(111)-Ga and Ga-Ga.

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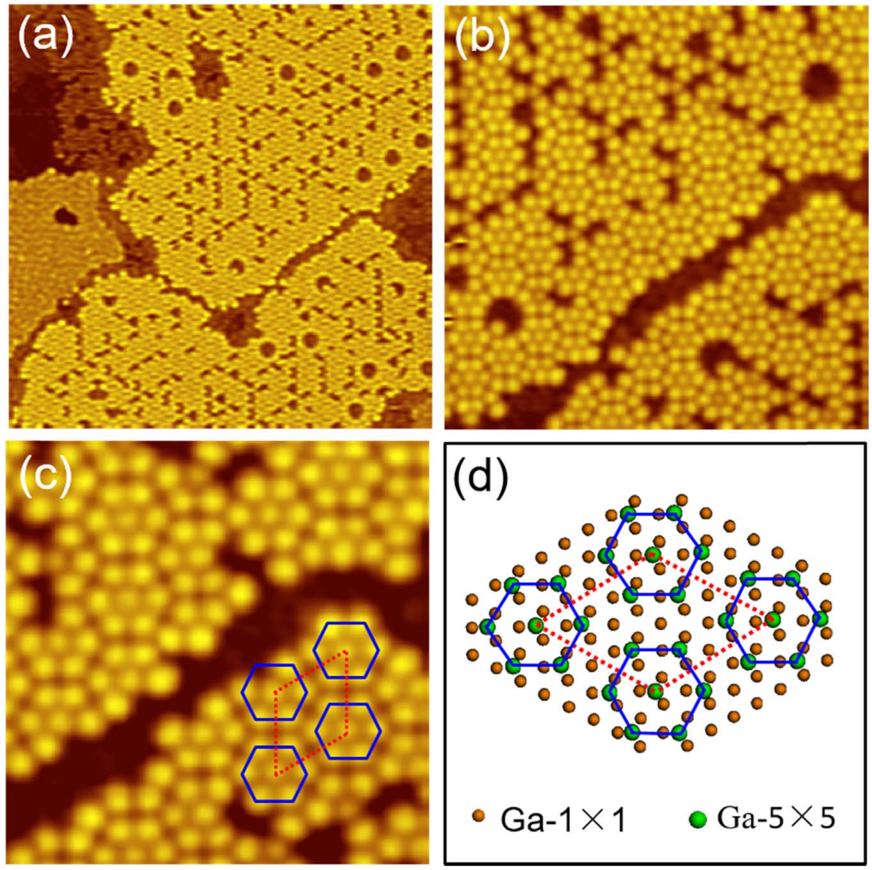

Fig. 4. (a) The 5×5 phase appeared in the second Ga layer after annealing to 120 ℃ (50×50 nm^2, −1.3 V). (b) Close-up view of the 5×5 phase (20×20 nm^2, −1.3 V). (c) High-resolution image of the 5×5 phase (10×10 nm^2, −1.3 V). (d) Schematic structure of the Ga 5×5 phase.

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