Atomic-level in situ real-space observation of Ga adatoms on GaAs(0 0 1)(2 × 4)-As surface during molecular beam epitaxy growth

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Abstract

We study in situ scanning tunneling microscopy (STM) observations of Ga adatoms on the molecular beam epitaxy (MBE) growth front, GaAs(0 0 1)(2 × 4)-As surface, with a system in which STM and MBE are completely one. It is found that Ga adatoms are self-organized about one unit cell far from the B-step edge and on a missing dimmer row. Moreover, the three Ga adatoms form a trigonal surface structure. And this trigonal changed to a tetragonal structure with the addition of one Ga atom. © 1999 Published by Elsevier Science B.V. All rights reserved.

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1. Introduction

The combined molecular beam epitaxy (MBE) and scanning tunneling microscopy (STM) system has proven to be a very powerful technique for the observation of real-space semiconductor surfaces, especially GaAs(0 0 1), with extremely high lateral and vertical resolution [1–5]. Recently, Avery et al. reported STM studies of submonolayer islands in the precoalescence regime grown by MBE on the three low-index surface of GaAs [6,7]. However, the growth dynamics of the step edges of these surfaces are still poorly understood at the atomistic level. Since, using this combined system, samples need to be cooled and transferred to a cleaner environment for STM analysis, the step edges, especially B-step edges which provide the most active sites on GaAs(0 0 1) [8–10], are evolved and no longer representative of the true growth dynamics. Moreover, reflection high-energy diffraction (RHEED) is well known as a real-time in situ surface observation technique for the MBE growth. However, the RHEED patterns show not real-space but reciprocal lattice images of surface reconstructions. These patterns are good for the 2D, layer by layer growth, however in the 3D cases,
dots growth etc., there are many missing information, especially that of atomic-level 3D structures. In this paper, we study atomic-level in situ real-space observations on the MBE growth front, \((2 \times 4)\beta2\) As-adsorbed surface [11], with a system in which STM and MBE are completely one, the so-called, “scanning tunneling molecular beam epitaxy (STMBE) system”.

2. Experimental procedure

In order to achieve STMBE operation, we must solve a lot of problems. For STM observation, we need to prepare a stable environment with reduction of vibrations and noises. However, the conventional MBE system involves many noise sources like LN\(_2\) bubbling, vacuum pumps, radiation noises from material sources, etc. In order to overcome these problems, we designed a novel sample holder with wide clearances around hold pins, shown in Fig. 1a, and a novel STM docking mechanism (b). Using this holder, we can perform the STMBE operation free from most of the MBE vibrations and noises, and normal MBE growth on detaching STM from MBE by this docking mechanism. Moreover, the STM unit is protected from material source depositions and radiation from substrate and source heaters by a special shield (c).

The Si-doped GaAs(001) 1° off \(<111>\)A \((n = 2 \times 10^{18} \text{ cm}^{-3})\) sample was prepared by standard solvent cleaning and etching procedures, and then loaded into the STMBE chamber. After the oxide was removed at 600°C with the As\(_4\) flux of

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**Fig. 1.** Ordinary combined STM and MBE, and new STMBE systems. The STMBE system has (a) a novel sample holder with wide clearances around hold pins, (b) a STM docking mechanism, and (c) a special shield which protects STM unit from material source depositions and heater radiation.
$2 \times 10^{-5}$ Torr, an undoped GaAs buffer layer of 1.0 μm was grown at 580°C at the As$_4$/Ga flux ratio, growth rate, background pressure of $\sim$30, 1.0 μm/h, and $2 \times 10^{-7}$ Torr, respectively, resulting in smooth one-GaAs-layer-stepped terraces. The samples were then annealed at 580°C for 5 min under a constant As pressure in order to produce a (2 $\times$ 4)$\beta$2 phase surface [12]. By RHEED monitoring of the (2 $\times$ 4)$\beta$2 As-adsorbed surface it was found that the substrate temperature has decreased from 580 to 200°C, in under 5 min, whereas the desorption of As atoms from surface reconstruction did not occur and the adsorption from a background was prevented. At the same time, an As$_4$ cell’s shutter was closed and the heater of an As$_4$ cell was turned off, resulting in the rapid reduction of the background pressure, especially that of As, to less than $8 \times 10^{-10}$ Torr. Then, the images were obtained in constant current mode using sample biases of $-3.0$ V (filled states) and tunneling currents of 0.2 nA.

3. Results and discussion

Fig. 2 shows one of the filled-state STM images of GaAs(0 0 1)(2 $\times$ 4)$\beta$2 As-adsorbed surface at 200°C after the supply of Ga at a rate of 0.1 monolayer (ML)/s for no more than 1 s. The images are obtained with noticeable thermal drift caused by the temperature difference between the substrate (200°C) and the radiant heat from the Ga cell (750°C) during the supply of Ga for no more than 1 s. However, in Fig. 2, the clear missing dimer rows and unit cells, and even two humps along the [1 1 0] direction in each unit cell can be observed [11].

Ga adatoms are relatively found near not A- but B-type step edges, especially at the positions indicated by white arrows in Fig. 2. Ito and Shiraishi calculated migration potentials of Ga adatoms near A- and B-type step edges [13]. They found that the A-step edge does not affect the migration potential significantly compared with that of the B-step edge. Moreover, based on RHEED observations during migration enhanced epitaxy (MEE) on misoriented GaAs(0 0 1) substrates, Yamaguchi and Horikoshi point out that the difference in critical temperature for the step growth can be explained by the different characteristics between A- and B-type steps; the B-type steps, unlike A-type steps, provide active sites for Ga adsorption [8–10]. The STMBE result well agrees with these theoretical and RHEED studies.

Moreover, there are many small spots in the missing dimer rows on the terraces. These spots are not like the filled trench structure with two Ga and four As atoms [6] but their heights are about middle between the top and second As dimers. According to a set of scannings, it is found that many of these spots change their positions even at 250 s after the supply of Ga atoms. It seems that these spots still migrate in the missing rows, probably, due to the effect of the heating of 200°C and scannings with the sample bias of $-3.0$ V. The ECMC simulation indicates adsorption sequences near B-type step edges [14]. According to this simulation, Ga adatoms change their sites in the missing row in order to minimize the number of electrons in the Ga dangling bonds. Therefore, these spots might be related to Ga adatoms which migrate along the missing rows. Including these spots as Ga adatoms, the total number of Ga adatoms agree well with the supplied Ga atoms of about 0.1 ML which corresponds to about 0.8 atom in one unit cell. Moreover, the sizes of these spots are small compared with the Ga adatoms near B-type step edges. This is due to the minimization of electrons in the Ga dangling bonds and, because we observed the filled-state images, the Ga adatoms in the missing rows are almost invisible. On the other hand, near B-type step edges, there are clear bright spots which indicate that many electrons still remain in the Ga dangling bonds, resulting in the creation of more active sites near the B-type step edges. This also agrees with former theoretical [13,14] and RHEED [8–10] studies.

Fig. 3 show (a) 3D and (b) plane-view filled-state STM images of Ga adatoms near the B-type stepped terrace observed at 25 (left), 250 (center) and 500 s (right) after the supply of Ga at 200°C. Fig. 3a and Fig. 3b are the zoom-in images from a series of scannings like Fig. 2. As shown in the top image of Fig. 3, the Ga atoms form a dimer-like surface
structure with two Ga adatoms about one unit cell far from the B-step edge and on a missing dimer row indicated by the arrow. Then, with the addition of one Ga atom, this dimer-like structure changed into a trigonal-like surface structure. After 250 s, as shown in the right image, this trigonal changed into a tetragonal-like structure with the addition of one more Ga atom. It seems that this position attracts the Ga atoms since the lowest migration potential value on a stepped GaAs(0 0 1)(2 × 4)b2 surface was located at the position of one unit cell far from the B-step edge and on a missing dimer row [13].

Fig. 3c shows a model of this self-organizing process of Ga adatoms. As shown in Fig. 3a, the Ga adatom (A) occupied the most stable lattice site which agrees well with this theoretical prediction [13]. And the Ga adatom (B) was attracted by the step-edge As atom which had a sp3-like dangling bond [9]. Then, the third Ga adatom (C) occupied the site where the number of electrons in the Ga dangling bonds was decreased [14]. Moreover, the fourth Ga adatom (D) breaks the As dimer, forming the tetragonal-like structure. In these cases, the Ga adatoms were clearly observed by the filled-state STM images (—3.0 V) of GaAs(0 0 1)(2 × 4)b2 surface after the supply of 0.1 ML Ga at 200 °C. White arrows indicate typical Ga adatoms near the B-step edge.

Fig. 2. Filled-state STM images (—3.0 V) of GaAs(0 0 1)(2 × 4)b2 surface after the supply of 0.1 ML Ga at 200 °C. White arrows indicate typical Ga adatoms near the B-step edge.
Fig. 3. (a) 3D and (b) plane-view filled-state STM images (−3.0 V) of Ga adatoms near the B-type stepped terrace observed at 25 (left), 250 (center) and 500 s (right) after the supply of 0.1 ML Ga at 200°C. And (c) a model of this self-organizing process of Ga adatoms. Ga and As atoms are indicated by filled and unfilled circles, respectively.
imaging. Therefore, many electrons still remain in these Ga dangling bonds, resulting in more attraction of other Ga adatoms. On the other hand, a Ga adatom in the next missing dimer row, indicated by a white arrow shown in Fig. 3b, even follows this model (c) but was not clear. In this case, however, the Ga adatoms seem to behave more ideally. The second adatom located just next to the first one, whose position agrees well with the theoretical calculation [14] and the dangling bonds of these two Ga adatoms are completely empty, satisfying electron counting (local-charge neutrality) heuristics. Therefore, this site did not attract other Ga adatoms even after 250 s (right).

4. Conclusions

We successfully observed the Ga adatoms on the MBE growth front, GaAs (0 0 1)(2 × 4)-As surface, with a system in which STM and MBE are completely one. It is found that Ga adatoms are self-organized about one unit cell far from the B-step edge and on a missing dimmer row. This position agreed well with the theoretical prediction. Moreover, the three Ga adatoms form a trigonal surface structure. And this trigonal changed to a tetragonal structure with the addition of one Ga atom. It seems that the surface reconstruction strongly affects the self-organizing process of Ga adatoms.

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