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Ga-rich GaAs(0 0 1) surfaces observed by STM during high-temperature annealing in MBE

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Abstract

Ga-rich GaAs (0 0 1) surfaces are successfully observed by scanning tunneling microscopy (STM) during high-temperature annealing in molecular beam epitaxy. With a substrate temperature of 550°C, reflection high-energy diffraction patterns and reflectance anisotropy spectra confirm a (4×2) Ga-stabilized surface. STM images clearly show alteration of the surface reconstructions while scanning. It is postulated that detaching and attaching of Ga adatoms may be the cause of this surface dynamics. For these conditions it is determined that $\zeta(4\times4)$, $\zeta2(4\times4)$ and $\zeta(4\times6)$ reconstructions co-exist on the surface. The $\zeta2(4\times4)$ reconstruction contains a Ga tetramer cluster.

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1. Introduction

The complexity and variety of surface reconstructions observed in semiconductors has been an intriguing problem in surface science. Recently, combined molecular beam epitaxy (MBE) and scanning tunneling microscopy (STM) systems have provided a very powerful technique for the real-space observation of semiconductor surfaces, especially GaAs(0 0 1), with extremely high resolution [1–5]. Avery et al. reported STM studies of MBE grown submonolayer islands in the pre-coalescence regime on the three low-index surfaces of GaAs [6,7]. In Ref. [7], the dynamics of the As-rich surface during growth was inferred by comparing room-temperature STM ‘snapshots’ with kinetic Monte Carlo simulations [7]. Ga-rich surfaces [8–10] are especially difficult to study due to a transition in surface reconstruction between high and low temperatures [11]. Therefore, if samples are cooled and transferred to a cleaner environment for STM analysis, the surfaces are no longer representative of the one at high temperature. STM analysis at high temperature needs to be

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performed. In this paper, the Ga-rich GaAs(0 0 1) surfaces were successfully observed by STM during high-temperature annealing in MBE.

2. Experimental procedure

Si-doped GaAs(0 0 1) 1° off ⟨1 1 1⟩A ($n = 2 \times 10^{18}\,\text{cm}^{-3}$) substrates were prepared by standard solvent cleaning and etching procedures, and then loaded into the MBE chamber. After the oxide was removed at 600°C under an As_4 flux of 2×10^{-5} Torr, an undoped GaAs buffer layer of 1.0 μm was grown at 580°C with the following conditions: As_4/Ga flux ratio ~30, growth rate 1.0 μm/h and background pressure of 2×10^{-7} Torr. This resulted in a smooth GaAs surface with single bilayer steps. The samples were then annealed at 550°C without As overpressure in order to produce a (4×2) phase surface as determined by reflection high-energy electron diffraction (RHEED) [12,13], as shown in Fig. 1(a). The reflectance anisotropy spectrum (RAS or RDS), shown in Fig. 1(b), also indicates a (4×2) Ga-stabilized surface. If the substrate temperature is higher than 550°C, for example, 610°C, RHEED pattern and RAS still show the (4×2) surface. However, if it is lower than 525°C, these are changed into $(2 \times 6)/(3 \times 6)$ pattern [14]. This $(2 \times 6)/(3 \times 6)$ pattern is continued until room temperature. Therefore, we need to observe STM at least at 550°C in order to compare with RHEED analysis and RAS measurement of (4×2) surface.

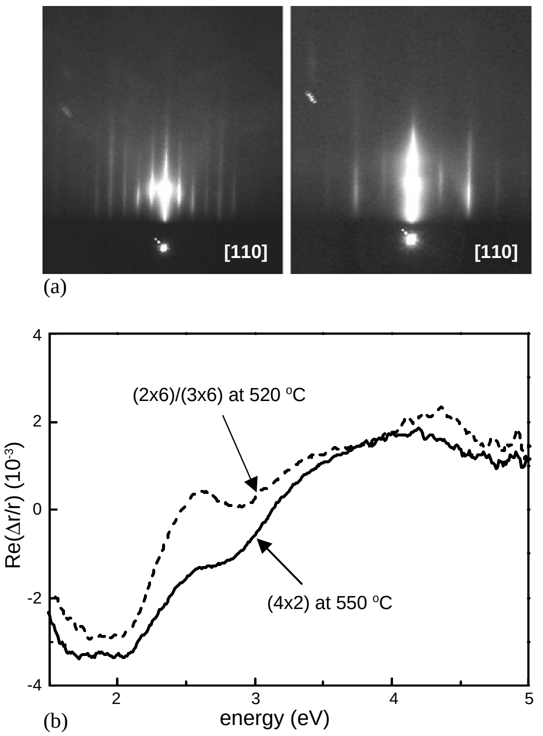

Fig. 1. (a) RHEED pattern, and (b) RAS spectrum of Ga-rich GaAs (0 0 1)-(4×2) surface with the substrate temperature of 550°C. For comparison, RAS spectrum of $(2 \times 6)/(3 \times 6)$ surface at 520°C is also shown.

3. Results and discussion

Under the same conditions as RHEED and RAS measurements, STM images were obtained at 550°C. The background pressure was 2×10^{-11} Torr. The STM images show steps and a few islands present on the surface. Fig. 2 shows the changes in the surface reconstruction observed by STM. Line scans and correlation functions of the surface confirm the clear $4\times$ periodicity in the $[1\,\bar{1}\,0]$ direction and show regions of the surface with a periodicity of $\times 3$ and $\times 4$ in [1 1 0]. By RHEED rocking-curve analysis, the optimized structure based on $\zeta(4 \times 2)$ by Lee et al. [8], which is basically the same as that proposed by Kumpf et al. [10], indicated a good agreement [14]. Therefore, these structures lead us to a good starting point to analysis these obtained STM images.

What are the possible surface reconstructions that are consistent with RHEED analysis, RAS measurement and the STM images? The STM data strongly point to a co-existence of reconstructions. One set of candidates is predicted as the $\zeta(4 \times 4)$, $\zeta 2(4 \times 4)$, and $\zeta(4 \times 6)$ reconstructions, as shown in Figs. 3(a)–(c), respectively. All models are based on $\zeta(4 \times 2)$ by Lee et al. [8] and satisfy electron-counting heuristics. The models differ in the presence and location of Ga atoms. At elevated temperatures, Ga adatoms can detach and diffuse to make Ga clusters [15]. These dynamics may be the cause for the changes shown in Fig. 2. Mobile Ga would result in different surface reconstructions on different parts of the surface as seen in Fig. 2.

In the $\zeta(4\times4)$ reconstruction shown in Fig. 3(a), 50% of the Ga dimers in $\zeta(4\times2)$ is missing and four As dangling bonds make two As dimers. Therefore, the STM images show that the trench is unfilled as indicated by a white arrow in Fig. 2(i). The $\zeta2(4\times4)$ reconstruction, shown in Fig. 3(b), does not make As dimers but depends on a Ga tetramer cluster that consists of four adatoms and is able to supply four electrons to the four As dangling bonds [16]. The STM image of this reconstruction would show that the trench is partially filled with the Ga clusters as indicated

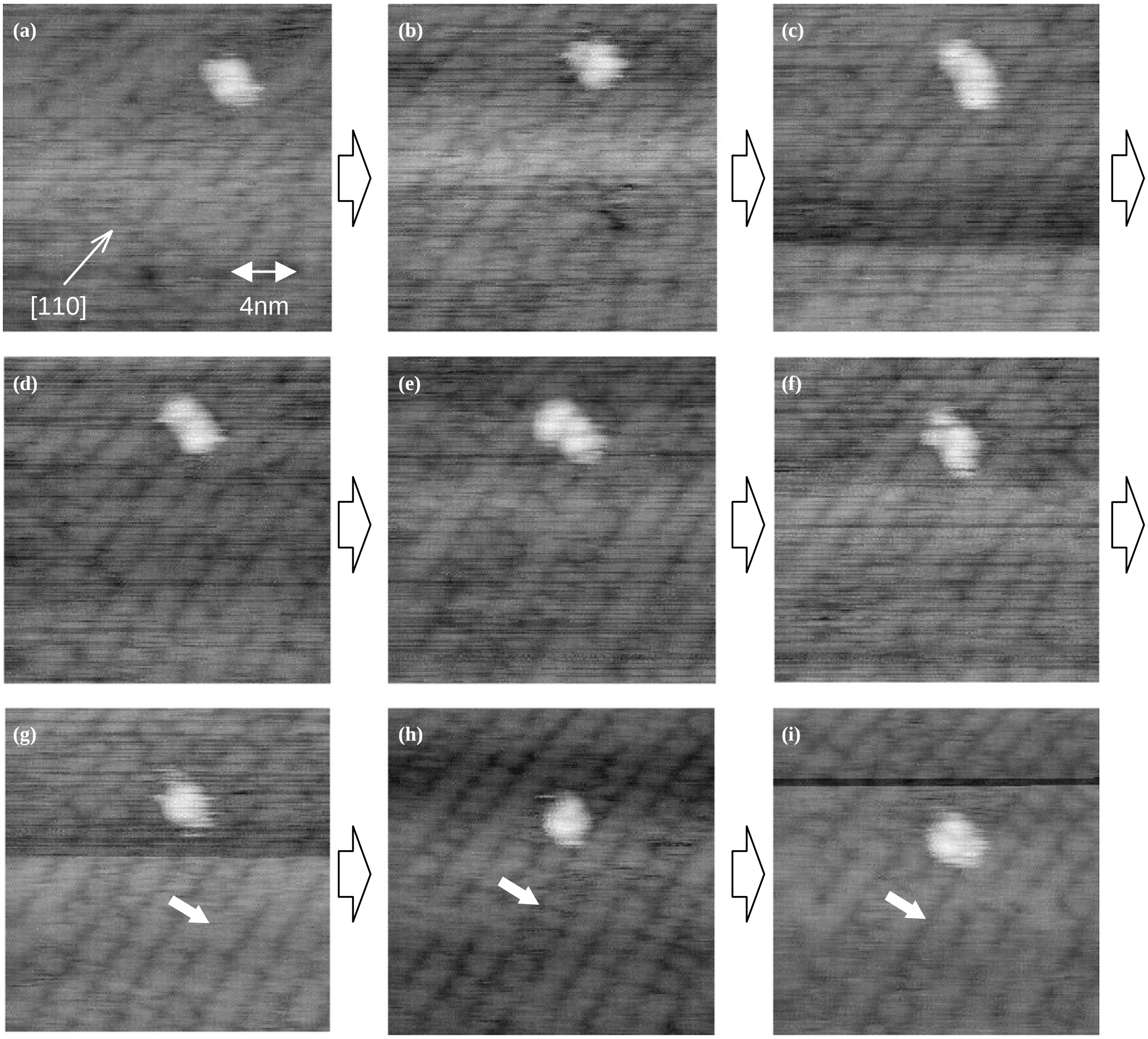

Fig. 2. (a)–(i) a series of STM images of Ga-rich GaAs (0 0 1) surface during annealing at 550°C with the background pressure of 2×10^{-11} Torr. Images were obtained in a constant current mode using a sample bias of -3.5 V (filled states) and tunneling currents of 0.2 nA. An island with lateral dimension of 2 nm, shown as white in the images, was used as a marker that does not change its position during scanning. Therefore, the images are drifting along the $[\bar{1}\,\bar{1}\,0]$ direction.

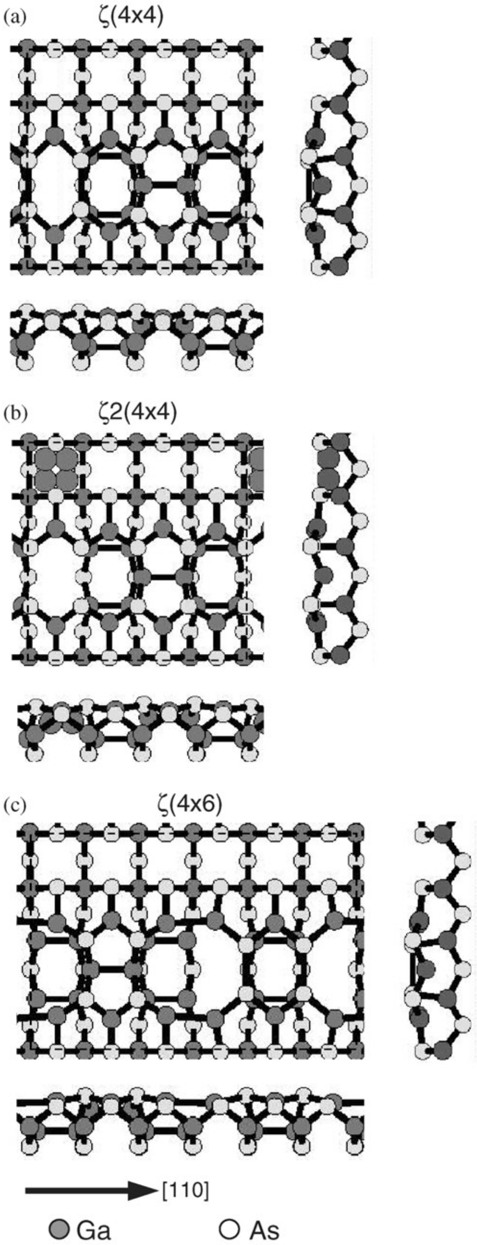

Fig. 3. Top and side views of (a) $\zeta(4\times4)$, (b) $\zeta2(4\times4)$, and (c) $\zeta(4\times6)$ surface reconstruction models corresponding to STM images as indicated by white arrows in Fig. 2 (i), (g), and (h), respectively. These models are all derived fundamentally from the $\zeta(4\times2)$ structure [8] and then modified accordingly to fulfill these STM images at 550°C and electron-counting rules.

by white arrow in Fig. 2(g). The $\zeta(4\times6)$ reconstruction, shown in Fig. 3(c), has two out of three Ga dimers missing as well as two As adatoms in each missing Ga dimer region. After restructuring, two Ga and two pairs of As form new dimers. This surface leads to STM images that show dark lines every three lattices units along [1 1 0] as indicated by white arrow in Fig. 2(h). Each of these reconstructions does not form large domains and is distributed randomly on the (0 0 1) surface. This reasonably explains why we do not observe the 1/4- and 1/6-order reflections in RHEED patterns obtained along the $[1\,\bar{1}\,0]$ direction. However, since all reconstructions are derived from the $\zeta(4\times2)$ structure, the surface dynamics associated with Ga motion [15] will produce transient regions with this symmetry. Therefore, it is natural to observe the 1/2-order reflection along the $[1\,\bar{1}\,0]$ direction.

From STM images, we can determine the average distribution of the $\zeta(4\times4)$, $\zeta2(4\times4)$, and $\zeta2(4\times6)$ reconstructions, which are 19%, 20%, and 61%, respectively. For this mixed surface structure, the occupancies of Ga dimers and cluster sites are determined to be 47% and 20%, which are closed to $45\pm13\%$ and $33\pm13\%$, respectively, obtained by the RHEED rocking-curve analysis [14]. The average coverage of surface Ga adatoms is 0.67 ML. These values are consistent with the results determined by surface X-ray diffraction using direct methods by Kumpf et al. [10].

4. Conclusion

We have used high-temperature STM, RHEED, and RAS to examine the GaAs (0 0 1) surface. We find the surface to contain several different co-existing reconstructions. These reconstructions are all derived fundamentally from the $\zeta(4\times2)$ structure. The mixed surface is consistent with electron counting rules and also agrees with X-ray and RHEED rocking-curve data.

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