2 × 6 Surface Reconstruction of Sulfur-Terminated GaAs (001) Observed by Scanning Tunneling Microscopy

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We present scanning tunneling microscopy (STM) images of smooth, in situ prepared, Sulfur-terminated (S-terminated) GaAs(001) surface reconstruction. It is found that 2 × 6 surface reconstruction is dominant on the S-terminated GaAs(001) surface. This 2 × 6 reconstruction, which cell is containing five S-S adatom dimers, is determined by both STM and reflection high-energy electron diffraction. Atomic model, which is consistent with both the STM images and electron-counting heuristics, is also shown. Moreover, this 2 × 6 reconstruction is also observed in the case of (NH₄)₂Sₓ-treated surface.

1. Introduction

Surface treatments using sulfide solution such as Na₂S[1], (NH₄)₂S[2,3], and (NH₄)₂Sₓ[3] have great attentions since improved properties such as enhanced photoluminescence[4], increased sensitivity of Schottky-barrier height to the metal work function[2], and reduced band-gap surface states[3]. Moreover, this sulfur treated surface is an important element of droplet epitaxy which is a useful technique for fabricating quantum dot structures[5]. However, such surface reconstruction has not fully understood yet. Commonly, 2 × 1 surface reconstruction is understood as that of these chemically treated GaAs(001) surfaces by low-energy electron diffraction (LEED) and reflection high-energy electron diffraction (RHEED) studies[6,7]. However, these 2 × 1 reconstructions are rather diffused streaky patterns with diffused transmission spots, which is due to the surface roughness caused by the etching effect of the sulfide solutions. Moreover, there are few reports of scanning tunneling microscopy (STM) study of such surfaces[8]. Therefore, under these condition, it is hardly to say that 2 × 1 reconstruction is dominant on the S-terminated GaAs(001) surface.

Recently, we created the novel fabrication method for the sulfur-terminated (S-terminated) GaAs(001) surface by exposing S vapor in molecular beam epitaxy (MBE) system[9]. Using this method, we can form the S-terminated GaAs surface without exposing air and etching surface. Then, in this case, diffused 2 × 1 is not appeared by RHEED observation, only 2 × 6 form after exposing S vapor and annealing[9].

In this paper, we demonstrate, by STM observation, that 2 × 6 is dominant on the S-terminated GaAs(001) surface. And for comparison, a (NH₄)₂Sₓ-treated GaAs(001) surface was also observed by STM with same sample preparatory proceedings.

2. Experimental

In this work, there are two major system, MBE and STM systems which are separated by air. The MBE system is a conventional system (ANELVA-620) with a sample introduction chamber, in which a valved Knudsen cell charged with elemental S is installed.

Two Si-doped GaAs(100)1°off(111)B (n=2 × 10⁻¹⁸ cm⁻³) samples are prepared by standard solvent cleaning and etching procedures, and then loaded into the MBE chamber. A buffer layer of 0.2 μm was grown at 590 °C, enhancing smooth one-monolayer-stepped terraces. Then, the substrate temperature has decreased to room temperature with c(4 × 4) As-adsorbed surface.

Next, one sample was transferred into the sample introduction chamber and exposed to the S vapor which generates a chamber pressure of 4 × 10⁻⁴ Pa at room temperature for 3 min. The background pressure of the sample introduction chamber is 6 × 10⁻⁶ Pa. The other sample was taken out from MBE chamber and then immediately immersed in the (NH₄)₂Sₓ solution for 90 min at 60 °C. After blowing it dry, this sample again loaded into the MBE chamber. Then, these samples were transferred into the growth chamber and annealed at 370 °C for 30 min without the As molecular-beam flux. After the samples were cool down to about 10 °C, a protective layer of elemental As was deposited. The samples were, then, transferred from the MBE system through air to the STM apparatus.

The STM system (JEOL-JSTM4500VT) is a multichamber UHV system. There are a sample introduction chamber, a treatment chamber with RHEED, and a STM main chamber. The background pressure of both the treatment chamber and the STM main chamber is 1 × 10⁻⁸ Pa. In this treatment chamber, observing RHEED pattern, the samples were directly heated by an electric current and the temperature was measured with a optical pyrometer having a detection wavelength of 2 μm. Then, the sample was transferred to the STM main chamber without exposing air. In this
S-terminated in Vacuum \hspace{1cm} (NH$_4$)$_2$S$_x$-treated

Fig. 1  RHEED patterns and STM images of S-terminated in vacuum and (NH$_4$)$_2$S$_x$-treated GaAs(001) surfaces after annealing at 260 °C for 107 hours plus 370 °C for 168 hours with background pressure of 1 x $10^{-8}$ Pa. The STM image areas are 50 x 50 nm$^2$ for (b) and (e), 20 x 20 nm$^2$ for (c) and (f). Left bottom corner image of (c) is the magnification of 2 x 6 structures. (g) A proposed ball-and-stick model for 2 x 6 surface reconstruction.
study, STM measurements were performed in the constant current mode and the STM images were taken at sample bias voltage of -3 V relative to the tip and a constant tunneling current of 0.2 nA. The tips are an electrically etched tungsten wire.

3. Results and discussion

STM images were obtained after annealing at 260 °C for 107 hours plus 370 °C for 168 hours shown in Fig.1. The first annealing temperature is for removing the As protective layer[10] and the second annealing temperature is for making Ga-S bond dominant over As-S and S-S bonds[11], resulting only S atoms remaining on Ga-stabilized surface. During the annealing process, the pressure was maintained in the 10⁻⁸ Pa range. RHEED patterns for both cases are also shown in Fig.1.

In the case of the sample terminated by the S vapor in vacuum, the RHEED pattern shows 2 × 6 with clear half order streaks in the direction of <110> and sharp 1/6ths streaks and weak other fractional order streaks (2/6ths, 3/6ths, 4/6ths, and 5/6ths) in the direction of <110> shown in Fig.1(a). And by STM, we observed smooth and large terraces which width corresponded to the sample miscut of 1°, shown in Fig.1(b). Clear ordered structures with a 2a₀(σ₈=0.4nm) periodicity are shown along the <110> direction and dark lines across the <110> direction. Height of the dimer, which corresponds to the height from dark region to bright region in the same terrace, is 0.10 nm which is good agreed with the value from theoretical calculation of Ga-S height of 0.11 nm [12]. In Fig.1(c) at higher resolution, the distribution of the separation of the dark lines along the <110> direction is 2a₀(4%), 3a₀(29%), 4a₀(19%), 5a₀(15%), 6a₀(30%), and 7a₀(3%). According to this results, it seems that 2 × 5 and 2 × 6 structures are dominant, however, there are many 3a₀ × 3a₀ (marked by white arrow), surrounded by random separations. Because these 2 × 3 structures are an intermediate phase between the 2 × 6 S-stabilized and the 4 × 6 Ga-stabilized surface structures [13], this 3a₀ × 3a₀ can be counted as 6a₀, resulting in the distribution of 2a₀(4%), 3a₀(3%), 4a₀(22%), 5a₀(17%), 6a₀(51%, including 3a₀+3a₀: 15%), and 7a₀(3%). This result shows that the 2 × 6 structure is dominant, which is agreed with the RHEED observation.

On the other hand, in the case of the (NH₄)₂Sₓ-treated GaAs(001) surface shown in Fig.1(e), there are many steps and islands caused by the etching effect of the sulfide solution [4]. This surface roughness made RHEED pattern rather diffused streaky patterns with diffused transmission spots, shown in Fig.1(d). However, from Fig.1(f) at higher resolution, on the narrow terraces, 2 × 6 surface reconstruction was observed (area A). In addition, 2 × 2 surface reconstruction with three S atoms and other 2 × 6 structures were also appeared (area B), which structure was never observed on the sample terminated by the S vapor in vacuum. Probably, this region is considered to be composed of two S layers [8].

Left bottom corner image of Fig.1(g) shows the magnification of the 2 × 6 structure, which cell is containing five S-S adatom dimers and one missing dimer. Figure 1(g) shows a proposed ball-and-stick model for the observed 2 × 6 structure. Electron counting (local-charge neutrality) model clarifies that this 2 × 6 surface reconstruction is dominant on the S-terminated GaAs(001) surface. Ohno and Shirasaki revealed that monolayer of S combined to the outermost Ga atom of the substrate surface, and the S atom occupied the bridge site on the surface with two dangling bonds containing 1.75 electrons each [12]. So, two S atoms with four dangling bonds contain 7 electrons in total. In order to form the S-S dimer, 6 electrons need, which means 1 electron per one dimer are exceeded. So, the electron counting model shows that 2 × 1 structure by S-S dimers is not stable. However, if one missing dimer exist, in order to occupy the remainder of four Ga dangling bonds containing 0.75 electrons each, 5 electrons need, resulting that five S-S dimers and one missing, 2 × 6 structure, satisfies electron counting heuristics.

5. Conclusions

We successfully observed, in situ prepared, S-terminated GaAs(001) surface by STM. It is found that the 2 × 6 surface reconstruction is dominant on the S-terminated GaAs(001) surface. This 2 × 6 reconstruction, which cell is containing five S-S adatom dimers, is determined by both STM and RHEED. Atomic model for 2 × 6 reconstruction is consistent with both the STM images and electron-counting heuristics. Moreover, in the case of the (NH₄)₂Sₓ-treatment, despite the rough surface caused by the etching effect, there is the 2 × 6 reconstruction was also observed.

References