

Initial Stage of Nitridation of GaAs(001): Atomic Scale View

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The nitridation process of an As-terminated GaAs(001)- $\beta 2(2 \times 4)$ surface was studied by time-resolved reflection high-energy electron diffraction (RHEED) and *in situ* scanning tunneling microscopy (STM). On the intermediate nitrided surface, a (3×4) -ordered phase was formed by the rearrangement of the As-dimer pairs at 520°C. This phase reverted back to the (2×4) -ordered phase below 400°C (reverse reconstruction by the re-adsorption of As atoms). We propose a model to explain this behavior.

KEYWORDS: N-for-As exchange reaction, nitridation of GaAs(001) surface, GaAs(001)- $\beta 2(2 \times 4)$ As, GaAs(001)- (3×4) As, GaAs(001)- (3×3) N, RHEED, STM

1. Introduction

Special attention has been paid to GaN because it has enormous potential for applications in optoelectronic devices in the short-wavelength region, high-frequency electronic devices and for various other uses.¹⁾ For these applications, it is essential to grow high-quality GaN and related materials. However, we cannot find good substrates that are lattice-matched with GaN. For example, in the case of GaAs(001) substrates, the lattice mismatch is as high as 20% (0.565 nm for GaAs; 0.51 nm for GaN). Despite this, we can utilize this lattice-mismatch effect to grow self-organized nanometer-scale structures such as quantum dots.²⁾ Unfortunately, few studies have been conducted on the atomistic process of GaN growth.

In the case of nitridation on compound semiconductor surfaces, there are several experimental findings that suggest that the exchange reaction plays an important role. Gemmeren *et al.*³⁾ studied the nitridation of the InAs(110) surface at room temperature (RT) by X-ray photoelectron spectroscopy (XPS) and found that the N-for-As anion exchange reaction took place. Gwo *et al.*⁴⁾ also observed the N-for-As exchange reaction by the reflection high-energy electron diffraction (RHEED) measurement during the nitridation of GaAs(001) surface at 565°C and obtained scanning tunneling microscopy (STM) images showing that N atoms replace all As atoms at the topmost layer and form dimers at the final stage. These dimers most likely form the 3×3 reconstruction at the first layer of the nitrided GaAs(001) surface. Kasu *et al.*⁵⁾ also studied the nitridation of the InAs(001) surface and found that the nitrogen radicals replace As atoms at the topmost layer of As-stabilized surface at 100°C, whereas they bond mainly with the topmost In atoms on an In-stabilized surface at 350°C. Aksenov *et al.*⁶⁾ measured the temporal change of Auger electron spectroscopy (AES) spectra during nitridation of the GaAs(001)- (2×4) surface at 300–400°C and found the clear chemical shifts of the Auger transitions of Ga, As and N. However their exposure was quite large so it is very difficult to discuss the initial stage. Collins *et al.*⁷⁾ also observed a similar temporal change in the RHEED intensity due to the Sb-for-As anion exchange reaction on the InAs(001) surface.

Here we extend our former work⁴⁾ by examining the intermediate nitridation stage of GaAs(001)- $\beta 2(2 \times 4)$ surface

using *in situ* RHEED and STM techniques. We attempted to replicate the same experimental conditions as before. Unfortunately, we modified several parts in our plasma source and therefore could not realize the exact same conditions. This results in slightly different temporal dependence, especially, the absolute value of time. The overall behavior was the same as before and we discuss the atomistic view of the nitridation of the GaAs(001)- $\beta 2(2 \times 4)$ surface by taking account of both experimental results in this paper.

2. Experimental

Experiments were performed in a multiple chamber ultra-high vacuum system composed of an MBE chamber for nitridation of GaAs and an STM chamber for observing the atomic arrangement.⁴⁾ The MBE system used in our study is equipped with a compact ECR microwave (2.45 GHz) plasma source to provide the active nitrogen flux and a valved cracker for introducing As₄ flux. After degassing at 300°C and removing the surface oxide layer at 600°C, an Si-doped GaAs buffer layer (~100 nm) was grown at 565°C. This surface exhibited an atomically flat and well-ordered As-terminated $\beta 2(2 \times 4)$ -reconstructed surface.⁸⁾ Prior to nitridation, high-purity (99.9998%) N₂ gas was introduced through a variable leak valve at a pressure of around 2.0×10^{-3} Pa into the ECR plasma source. During nitridation, the input power of the ECR plasma source was kept at 265 W, the substrate temperature was 520°C, and both the Ga cell shutter and the As cracking cell valve were closed. Under these conditions, the ECR plasma mainly consists of neutral nitrogen radicals with less ionized species and is very suitable for nitriding the surface without roughening.⁴⁾ *In situ* RHEED observation was performed with two incident beam directions, one along the $[\bar{1}10]$ direction ($[\bar{1}10]$ RHEED) of GaAs(001) substrate and the other along the $[110]$ direction ($[110]$ RHEED).

After nitridation, we quickly shut off the valve used for introducing N₂ gas and quenched the sample to 400°C. The sample temperature was kept at 400°C until background pressure below 1.3×10^{-7} Pa (about 30 min) to minimize the As adsorption on the nitrided surface. Then the sample was quenched to room temperature (RT) and transferred to the STM chamber while keeping the pressure at 1.3×10^{-8} Pa. All STM images shown here were obtained under 1.3×10^{-8} Pa at RT in constant tunneling current mode.

3. Results and Discussion

Figure 1 shows the temporal change in the $[\bar{1}10]$ RHEED intensity during nitridation. We can see 1/4-order peaks at the initial surface as expected and the intensity of the 1/4-order peaks decreases with respect to the nitrogen exposure time. At around 135 s of nitridation, 1/3-order peaks begin to grow. At 180 s of nitridation*, only 1/3-order peaks are clearly seen. Figure 2 shows the temporal change in the $[110]$ RHEED intensity during nitridation under the same conditions as in Fig. 1. We can see 1/2-order peaks at the initial surface and the intensity of the 1/2-order peaks decreases until around 60 s of nitridation and then 1/3-order peaks begin to grow. After 120 s of nitridation, only 1/3-order peaks exist.

Figures 1 and 2 provide several findings on the surface structural change during nitridation: (1) At 120 s of nitridation, the $3\times$ -reconstruction along the $[\bar{1}10]$ direction is formed whereas the $\times 3$ -reconstruction along the $[110]$ direction is not formed yet. In other words, the (3×4) reconstruction is appeared. (2) After 120 s of nitridation, the $\times 4$ -reconstruction along the $[110]$ direction changes to the $\times 3$ -one, while the $3\times$ -reconstruction along the $[\bar{1}10]$ direction lasts. Then, the fully nitrided surface structure changes into the (3×3) phase. These results indicate an anisotropic

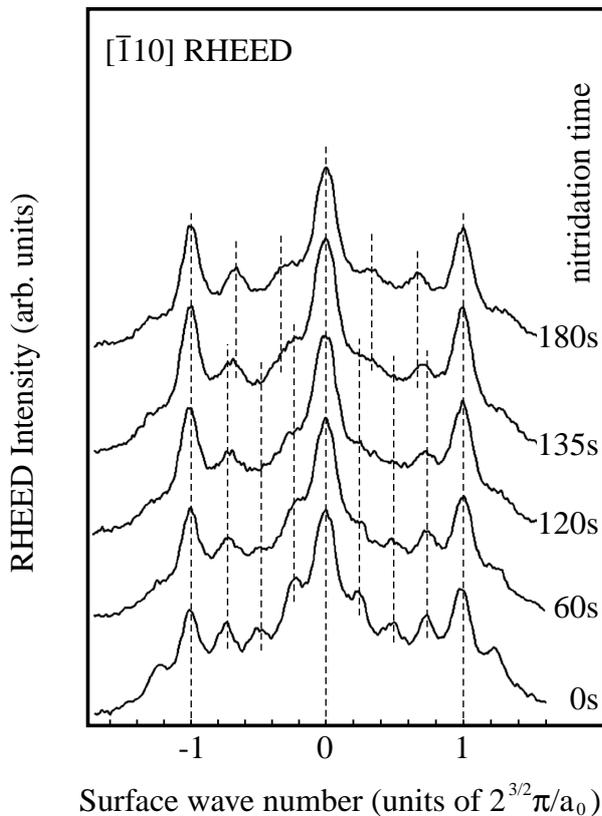


Fig. 1. Temporal change in the $[\bar{1}10]$ RHEED intensity during nitridation of the As-terminated GaAs(001)- $\beta 2(2 \times 4)$ surface. Dotted lines represent how the 1/4-order and 1/3-order peaks behave with respect to the nitrogen exposure time.

*The duration time (180 s) of intensity change differs from that of the previous study (35 s).⁴⁾ As described in the introduction, this may be due to different experimental conditions in the plasma source and a substrate temperature of 520°C.

nitridation process.

Figure 3 shows a typical STM image of nearly fully nitrided GaAs(001) surfaces, i.e., 150 s of nitridation. We can see several characteristic features: a (3×3) -ordered phase (the area marked by A), a bright $2\times$ -ordered row along the $[\bar{1}10]$ direction (B), a bright $3\times$ -ordered row along the $[\bar{1}10]$ direction (C), a bright phase consisting of neighboring $2\times$ -ordered or $3\times$ -ordered rows (D and E). The first two phases A and B are the same as those seen in the previous study.⁴⁾ It should be noted here that there are many $2\times$ -ordered rows along the $[\bar{1}10]$ direction in the STM image, although the $[110]$ RHEED exhibits no 1/2-order peaks after 120 s of nitridation, as shown in Fig. 2. This may become clear when we take the fast Fourier transform (FFT) of the STM image. In fact, the FFT image showed no clear $2\times$ spots along the $[\bar{1}10]$ direction only clear $3\times$ spots. This feature can be explained by the fact that these $2\times$ -ordered rows are too small to exhibit RHEED spots.

In the present study, we find the $3\times$ -ordered rows (C) with almost the same height and the same direction as the $2\times$ -ordered rows (B). This fact suggests that the origin of these $3\times$ -ordered rows could be the same as that of the $2\times$ -ordered rows. In Fig. 3, we cannot find the clear long-range order for these bright rows (B and C) along the $[110]$ direction, but in other areas we can observe several neighboring bright rows whose distances are 1.6 nm, i.e., they form a (2×4) -ordered phase (D) and a (3×4) -ordered phase (E). Here, we assume that the $2\times$ -ordered rows are formed by the remaining As-dimer rows on the GaAs(001)- $\beta 2(2 \times 4)$ sur-

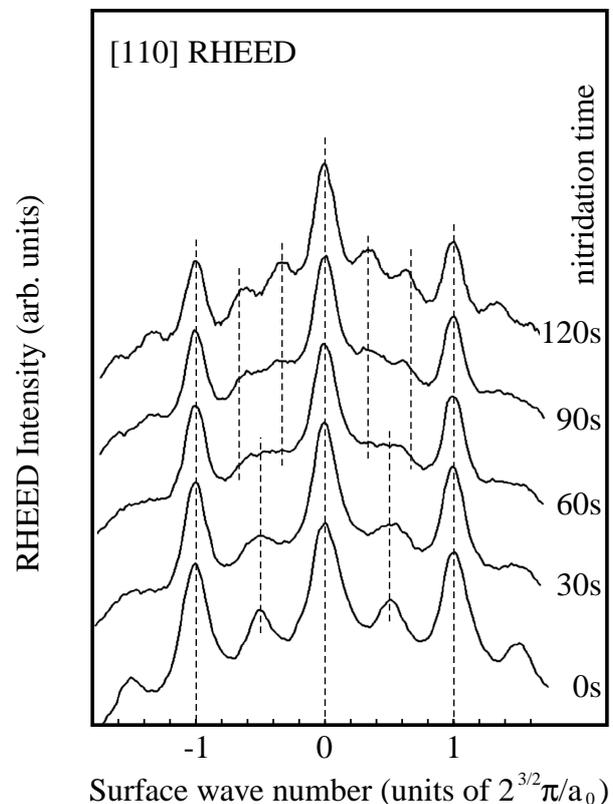


Fig. 2. Temporal change in the $[110]$ RHEED intensity during nitridation of the As-terminated GaAs(001)- $\beta 2(2 \times 4)$ surface. Dotted lines represent how the 1/2-order and 1/3-order peaks behave with respect to the nitrogen exposure time.

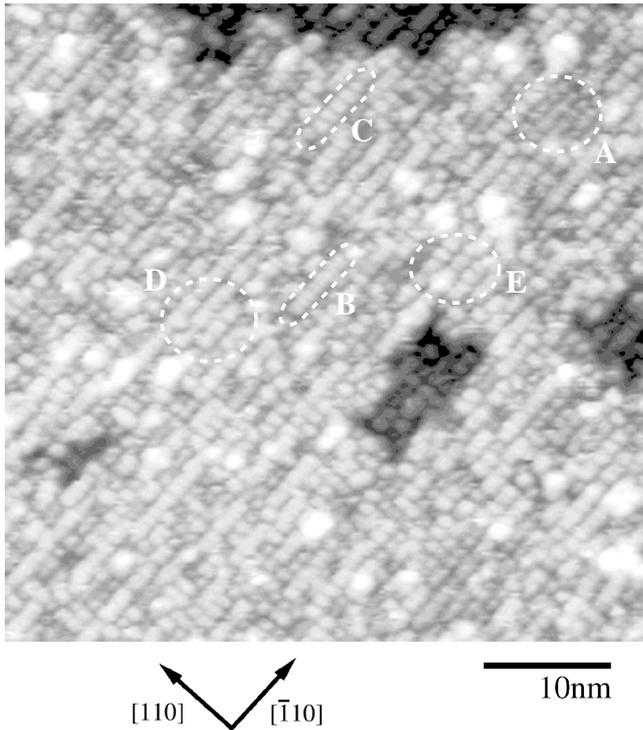


Fig. 3. A typical STM image of GaAs(001)-β2(2 × 4) surfaces nitrified for 150 s. The sample bias voltage is -3.0 V and the tunneling current is 0.2 nA (filled-state imaging). Dashed circles represent the characteristic phases: (3 × 3) phase (A), bright 2 × -ordered phase (B), bright 3 × -ordered phase (C), neighboring bright 2 × - (D) and 3 × - (E) ordered rows. The crystallographic directions and the imaging size are shown in the inset.

face and the 3 × -ordered rows are reconstructed from these 2 × -ordered rows. According to the temporal change of RHEED and this assumption, we assume that the reconstruction process of GaAs(001)-β2(2 × 4) surface during nitridation is composed of two successive processes. In the first process, the initial As-terminated β2(2 × 4) surface reconstructs from (2 × 4)-ordered As-dimer phase to (3 × 4)-ordered As-dimer phase. In the second process, this intermediate (3 × 4)-ordered As-dimer phase is rearranged so as to form the (3 × 3)-ordered N-dimer phase. In Fig. 4, we draw an atomistic model of these three phases. The (2 × 4) phase stands for the GaAs(001)-β2(2 × 4) surface and the (3 × 3) phase is the same as that proposed previously.⁴⁾ In the intermediate (3 × 4) phase, the As-dimer pairs, whose origin is that of the (2 × 4) phase, exist at the topmost layer and rearrange with 3 × -ordering along the [1̄10] direction. When the N atoms form bonds with the Ga atoms of the second layer, large tensile strains are induced. These large strains may stabilize this (3 × 4) phase. However, we cannot determine the adsorption site of the N atoms and the atomic arrangement on the “trench” (missing dimer row region in the (2 × 4) phase) with only our present data.

To examine the stability of the bright 2 × -ordered rows in the phase B, we measured their length and frequency in the STM image. The results are summarized in Fig. 5, together with the data taken from the former work.⁴⁾ In this plot, we can see a peak at 4 units of As-dimer pairs. This indicates that the bright rows most probably consist of four As-dimer pairs. The existence of characteristic length suggests that the

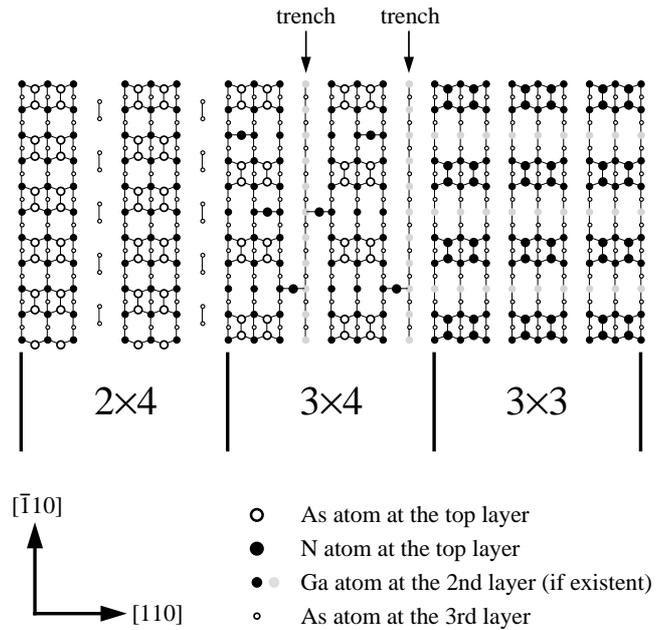


Fig. 4. An atomistic model for (2 × 4), (3 × 4) and (3 × 3) phases in nitrified GaAs(001)-β2(2 × 4) surface. The various circles represent atom sites, as indicated in the lower half. In the (3 × 4) phase, the trenches might be occupied by the Ga atoms at the second layer.

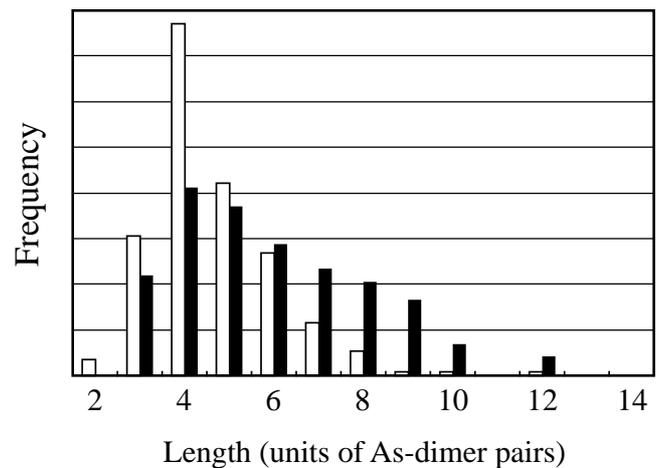


Fig. 5. Histogram of the distribution of the bright 2 × -ordered row length calculated from the STM image shown in Fig. 3 (black) and the previous work (white).⁴⁾

stabilized mechanism is related to surface atomic configuration. In Fig. 6, we draw three possible types of surface atomic arrangements of the 2 × -ordered As-dimer pair rows (X, Y, Z) surrounded by the (3 × 3) phase which is composed of the N-dimer pairs. In the case of X, both sides of the 2 × -ordered As-dimer pairs match with the neighboring 3 × -ordered N-dimer pairs as marked by α and β with leaving three Ga atoms of the second layer at both ends. In the cases of Y and Z, the 2 × -ordered As-dimer pairs do not match at one end as shown by γ and δ with leaving extra exposed Ga atoms just below these pairs. These Ga atoms may be unstable due to the existence of dangling bonds. This could be a reason why the peak positions appeared at 4 units of As-dimer pairs in Fig. 5. The peak is broader for the present data than for the previous data. This may be due to the lower density of surrounding N-

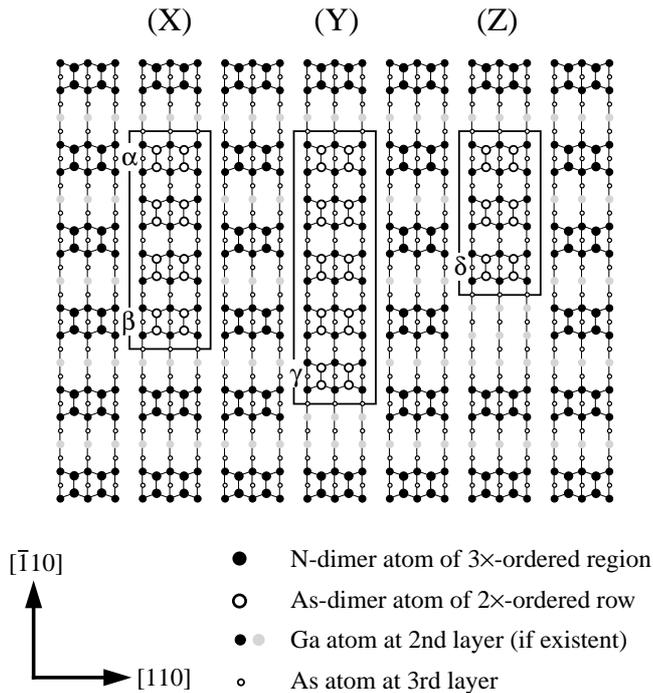


Fig. 6. Three possible types of surface atomic arrangement of the $2\times$ -ordered As-dimer pair rows surrounded by the (3×3) N-dimer region. In case X, the As-dimer pairs match with the N-dimer pairs at positions α and β and in cases Y and Z, they do not, as shown by γ and δ .

dimers which is caused by the less nitrated condition of this surface.

Figure 7 shows a typical STM image of partially nitrated GaAs(001)- $\beta 2(2\times 4)$ surfaces, i.e., 60 s of nitridation. Experimental conditions except for nitridation time are the same as that in Fig. 3. Although the [110] RHEED exhibited weak $1/3$ -order peaks as shown in Fig. 2 just after nitridation, they changed to diffuse $1/2$ -order peaks during sample cooling and, in fact, we did not observe a clear $3\times$ -ordered structure in the STM image at RT, as seen in Fig. 7. This suggests that the reverse process of the reconstruction from the nitrated GaAs(001)- (3×4) surface to As-terminated GaAs(001)- $\beta 2(2\times 4)$ surface occurs due to the re-adsorption of As atoms on the surface. This process is characteristic of the partially nitrated surface. On the other hand, the fully nitrated surface remains unchanged clear 3×3 RHEED patterns for several minutes even at 520°C and with As_4 flux. In other words, once the 3×3 phases are formed, the reverse process rarely occurs. This means that the existence of the intermediate 3×4 phase is essential for the reverse process. In our model for the 3×4 phase (Fig. 4), the As-dimer pairs remain at the topmost layer and keep the $\times 4$ -ordering along the [110] direction, which could make the reverse process easier. As mentioned above, the strains induced by the N incorporation can stabilize this 3×4 phase. Therefore, the desorption of N atoms after stopping N irradiation directly makes the As-dimer pairs on the (2×4) surface unstable. As atoms from the MBE chamber can easily adsorb on the surface. In this way, the reverse process may proceed and an As-terminated $\beta 2(2\times 4)$ surface is formed.

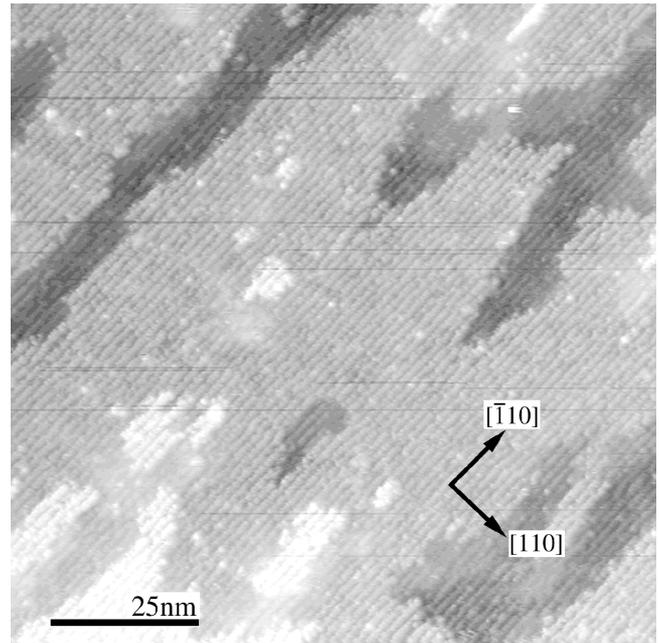


Fig. 7. A typical STM image of partially nitrated GaAs(001)- $\beta 2(2\times 4)$ surfaces nitrated for 60 s. The sample bias voltage is -3.0 V and the tunneling current is 0.2 nA (filled-state imaging). The surface is uniformly covered by the 2×4 reconstruction without $3\times$ -ordered phase. The crystallographic directions and the image size are shown in the inset.

4. Summary

We studied the intermediate stage of the nitridation process of the As-terminated GaAs(001)- $\beta 2(2\times 4)$ surface using time-resolved RHEED analysis and *in situ* STM observation. We found characteristic structures on the intermediate nitrated surface: $2\times$ -ordered As-dimer pair rows, $3\times$ -ordered As-dimer pair rows and (3×4) regions. All of these structures were determined by the rearrangement of the As-dimer pairs. We also found the reverse reconstruction from the (3×4) phase to the (2×4) phase on the intermediate nitrated surface. We proposed a model to explain these findings. However, to confirm this model, we need more systematic experimental data as well as theoretical calculations.

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