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Surface reconstruction of GaAs(0 0 1) nitrided under the controlled As partial pressure

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Abstract

Under the controlled As partial pressure, the nitridation process of GaAs(0 0 1)-(2×4) surface was studied using a scanning tunneling microscope (STM) combined with an electron cyclotron resonance plasma-assisted molecular beam epitaxy system. With either prolonging the nitridation time or decreasing the As partial pressure, the previously reported (3×3) structure with two dimers per surface cell ((3×3)-2D) was found to progressively convert into a new (3×3) structure characterized by one dimer per surface cell ((3×3)-1D). Reversely the exposure to arsenic transformed the structure from (3×3)-1D to (3×3)-2D, suggesting that the topmost layer is composed of As_2-dimers. Based on these STM images together with the X-ray photoelectron spectroscopy data, we propose the new As_2-dimer coverage models to explain both (3×3)-1D and -2D structures involving the exchange reaction of arsenic with nitrogen in the subsurface region of GaAs.

Keywords: Gallium arsenide; Gallium nitride; Nitrogen atom; Surface relaxation and reconstruction; Scanning tunneling microscopy; Reflection high-energy electron diffraction (RHEED); X-ray photoelectron spectroscopy

The nitridation of GaAs(0 0 1) surface was studied initially for the subsequent epitaxial growth of cubic GaN (β-GaN) on a large lattice-mismatched GaAs substrate (~20%) [1,2]. At the same time, atomic scale analyses of the nitridation process were performed by either reflection high-energy electron diffraction (RHEED) or scanning tunneling microscopy (STM) combined with molecular beam epitaxy (MBE) [3–7]. For the nitrided GaAs(0 0 1)-(2×4) surface, we have found that the initial (2×4) As_2-dimer phase reconstructs first to the intermediate (3×4) As_2-dimer phase and then is rearranged to the (3×3) with two dimers per surface cell, hereafter denoted as (3×3)-2D.

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However, the origin of (3×3)-2D dimers remains controversial, because the existence of N_2-dimers is energetically unfavorable due to the large distortion caused by a sizable mismatch of atomic radii and the high cohesive energy of N–N bonds in N_2 molecules. Total energy calculations also indicate that the chemisorption of a submonolayer arsenic significantly lowers the surface energy of the Ga-terminated GaN [8,9]. Such As atoms as an unintentional adsorbate come from the GaAs substrate itself and a residual atmosphere in the As-related MBE chamber.

To ascertain the atomic species of surface dimer, we investigated the influence of trace arsenic on the atomic arrangement of fully nitrided GaAs(0 0 1)-(2×4), i.e., GaAs:N(0 0 1)-(3×3) surfaces by varying either exposure time to active nitrogen (t_N) or As partial pressure during nitridation (ρ_{As}). The experiments were performed in a multiple-chamber ultra-high vacuum system composed of MBE, STM and X-ray photoelectron spectroscopy (XPS). The change in surface reconstruction during the GaAs growth, surface nitridation and the arsenic exposure of nitrided surface was monitored by RHEED equipped to the MBE chamber. Especially the electron cyclotron resonance plasma-assisted MBE for $Ga(As_{1-x}N_x)$ alloys was used to obtain the damage-less atomically smooth surface, since the plasma source is effective to produce the neutral N radicals. Except for the nitridation conditions of t_N and ρ_{As}, the preparation of the initial As-terminated GaAs(0 0 1)-(2×4) surfaces and the nitridation process inclusive of quenching procedures were the same as those in our previous paper [6]. The ρ_{As} throughout the experiments was precisely controlled in the range from 1×10^{-9} to 1×10^{-7} Torr by adjusting a heater current of As effusion cell. Filled-state STM images of the samples were taken at room temperature and background pressure below 1×10^{-10} Torr in a constant current mode with the sample bias voltage of −3.0 V and tunneling current of 0.7 nA. The surface concentrations and bonding states were analyzed from the photoelectron spectra of N 1s, Ga 3d and As 3d core levels using XPS with MgKα characteristic X-ray. The N 1s peak chosen from a viewpoint of photoionization cross section was deconvoluted from the energetically coincident Ga LMM Auger peaks.

Fig. 1 shows the filled-state STM images of the GaAs:N(0 0 1)-(3×3) surfaces nitrided for (a) $t_N = 240$ s and (b) $t_N = 330$ s under the As background pressure below 3×10^{-9} Torr. Despite of the similarities between their (3×3) RHEED patterns, the STM images reveal changes in the atomic arrangement caused by the further nitridation under As-deficient conditions. In Fig. 1(a), small domains with a high degree of disorder can be classified into three kinds labeled I–III. Compared with the STM images of starting (2×4) surface not shown here, straight rows labeled I,

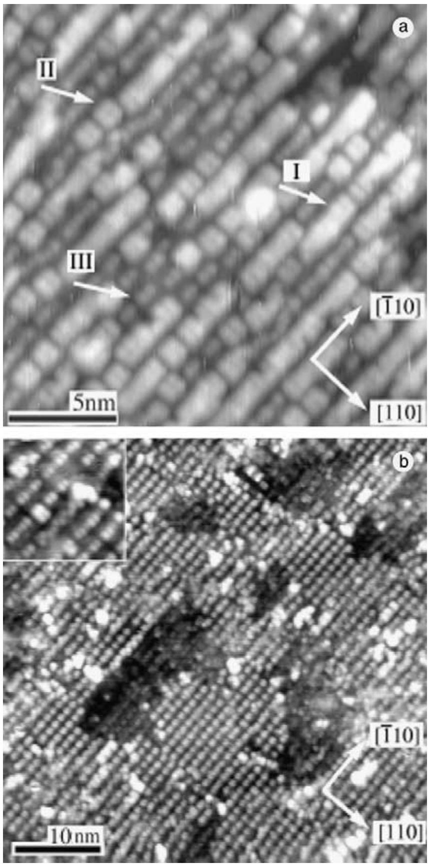


Fig. 1. STM images of the GaAs:N(0 0 1)-(3×3) surfaces nitrided under the As background pressure below 3×10^{-9} Torr; (a) $t_N = 240$ s and (b) $t_N = 330$ s. Arrows in (a) represent three characteristic structures: (I) remaining (2×4), (II) (3×3)-2D and (III) (3×3)-1D. An inset of (b) is the magnified image.

run along [−1 1 0] azimuth, correspond to the 2×-ordered rows of As-terminated (2×4) unit cells. Adopting the β2-phase of (2×4) reconstruction composed of two As_2-dimers and two missing dimers, this structure is identified with the remained rows of two As_2-dimers even after $t_N = 240$ s. The square-like protrusions labeled II contain a group of four maxima being ascribable to the adjacent two dimers parallel to the [−1 1 0] direction. Such units aligned along the [−1 1 0] azimuth with a 1.2 nm periodicity constitute the 3×-ordered rows of (3×3)-2D observed by Gwo et al. [5].

In contrast to (3×3)-2D, the structure labeled III consists of a pair of equivalent protrusions, suggesting a dimerization between the same atomic species along [−1 1 0] azimuth. Each dimer arranges with threefold periodicity of 1.2 nm along both [1 1 0] and [−1 1 0], and forms domains exhibiting a new (3×3) reconstruction with one dimer per surface cell, which is called (3×3)-1D hereafter. We note that these reconstructions occur on the same terrace, since the differences in height among them are much smaller than the interlayer atomic distances for GaAs(0 0 1) and GaN(0 0 1). Either local electronic differences or internal stress rather than the topographic effect may be responsible for the depression feature of both (3×3). In particular, the [−1 1 0] dimerization direction of (3×3)-1D/-2D indicates that a likely candidate for dimer species is either anion of arsenic or nitrogen, though the N 1s XPS signal was not measurable due to very weak intensity below our detection limit. The removal of either dimer from (3×3)-2D could establish the (3×3)-1D accompanied with a considerable number of kinks being recognizable in a series of short rows along [−1 1 0]. It should be mentioned that the actually observed (3×3) RHEED pattern is attributable to a statistical lateral distribution of both (3×3) small domains. This is confirmed by the fast Fourier transformation (FFT) of the STM images.

Furthermore we found that the prolonged exposure to active nitrogen led to a well-ordered array of (3×3)-1D, and simultaneously to a complete disappearance of (3×3)-2D and As-terminated (2×4) rows, as shown in Fig. 1(b). The single domain of (3×3)-1D structure clearly seen in an inset of magnified image impresses us as an advanced stage in nitridation of the GaAs(0 0 1) surface. The etching traces pointed out by Xue et al. [7] might be caused by the evaporation of As atoms decomposed from the GaAs surface, because the nitridation conditions of low ρ_{As} and high sample temperature ($T_s = 525$ °C) promote such behaviors. The vacancy islands partly retrieved the (3×3)-1D are associated with a precursor of surface portions etched by exposing the (1 1 1) crystal planes with the slowest nitridation rate described by Okumura et al. [10]. We add a few words that no appreciable change in the STM images was observed against the exposure to dry O_2 gas of $\sim 1\times10^7$ Langmuir, demonstrating the surface passivation by nitridation.

Taking into account that (3×3)-1D with lower dimer coverage is a further nitrided phase, the surface dimers in (3×3)-2D are assigned not to N–N but to As–As. However, the STM image obtained for (3×3)-1D displays no evidence for the existence of surface As_2-dimers, though the predominant formation of (3×3)-1D in consequence of the further nitridation is focused on the transition from (3×3)-2D to (3×3)-1D. With the purpose of observing the opposite transformation from (3×3)-1D to (3×3)-2D, we adsorbed the As atoms on the (3×3)-1D surface as follows. After checking the (3×3)-1D structure by STM, the sample was transferred back to the MBE chamber and heated up to 450 °C. While keeping the background pressure at around 1×10^{-9} Torr, the As cell heater was raised up to 200 °C and its shutter was opened for 300 s to expose the (3×3)-1D surface to As_4 flux. Fig. 2 shows the STM image of this surface on which two kinds of atomic arrangements composed of (3×3)-1D and (3×3)-2D are observed. More precisely, the (3×3)-1D surface labeled A is partly converted to (3×3)-2D surface labeled B which was absent before exposure to arsenic. The domain area of (3×3)-2D was found to increase with the exposure time, and one of two dimers in (3×3)-2D seems to be that in (3×3)-1D, indicating that exposure to arsenic induces the transformation from (3×3)-1D to (3×3)-2D. It should be noticed here that no nitrogen atoms are present in the environment during exposure to arsenic, and two dimers in (3×3)-2D exhibit the same contrasts and the same

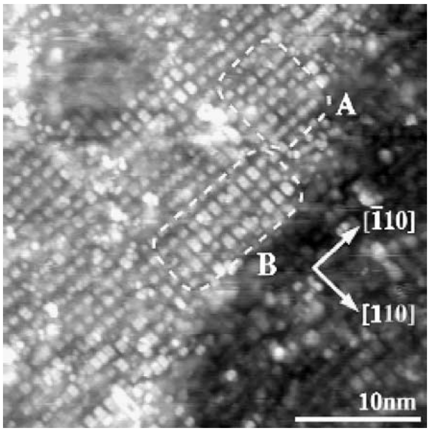
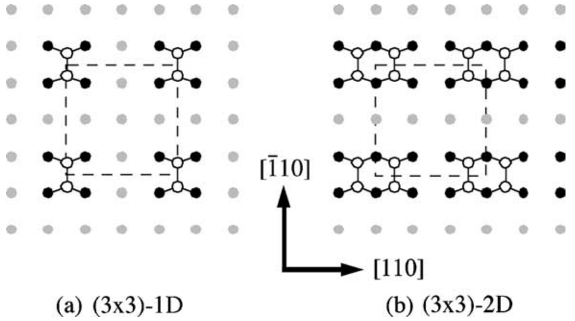


Fig. 2. STM image of the GaAs:N(0 0 1)-(3×3)-1D surface after exposure to As_4 flux at $\rho_{As} \sim 1 \times 10^{-9}$ Torr. The exposure time and substrate temperature were 300 s and 450 °C, respectively. Addition of another adjacent dimer to the (3×3)-1D structure labeled A gives rise to the (3×3)-2D structure labeled B.



(a) (3x3)-1D (b) (3x3)-2D

Fig. 3. Structural models proposed for the GaAs:N(0 0 1) surfaces of (a) (3×3)-1D and (b) (3×3)-2D, where the respective topmost layers consist of one and two As_2-dimers per surface cell. Open, filled and gray circles represent the topmost As atoms, the underlying Ga atoms and the exposed Ga atoms, respectively. The incorporated N atoms not shown here partly replace the As atoms in the subsurface region.

separations to each other. Therefore we can conclude that both one dimer in (3×3)-1D and two dimers in (3×3)-2D consist of the same atomic species which could be not N atoms but As atoms.

Based on these STM data, the (3×3)-2D structure is formed by adding another As_2-dimer to the adjacent to the As_2-dimer in (3×3)-1D structure. Fig. 3 illustrates such atomic arrangements of (a) (3×3)-1D and (b) (3×3)-2D structures. Each As atom forms bonds with two underlying Ga atoms and dimerizes along [−1 1 0] azimuth. In this figure, only As_2-dimers in the topmost layer and Ga atoms in the second layer are depicted, but the existence of N atoms is still uncertain. To grapple with this problem, we analyzed the (3×3)-1D surface using XPS and detected the N 1s signal. As for (3×3)-1D shown in Fig. 1(b), the signal intensity ratios of N 1s/Ga 3d and As 3d/Ga 3d were obtained 0.02 and 0.88, respectively. By assuming a submonolayer N coverage to avoid a mathematical complexity [11,12], the surface N content of (3×3)-1D was roughly estimated to be 0.2 ± 0.1 monolayer (ML). Though the noticeable chemical shifts in the XPS spectra were unobservable due to a small amount of nitrogen, a slight increase (∼6%) in the full width at half maximum for Ga 3d peak and no change for As 3d peak suggest the formation of Ga–N bonds. The N atoms substituted for As atoms in the subsurface region should bond with the nearest-neighbor Ga atoms. The reason is that heat of formation of GaN (6.81 eV) is much larger than that of GaAs (5.55 eV) [13]. Most of XPS and Auger electron spectroscopy studies support the formation of Ga–N bonds through the product of a crystalline GaN layer [10,14,15]. In either case, the N content in the third or deeper As layer is comparable to the above estimated submonolayer one. If the N atoms of (3×3)-1D uniformly distribute only in the third As layer of GaAs and the intensity of N 1s XPS signal is diminished by a monomolecular overlayer of GaAs, the incorporated N content is calculable from the surface N coverage of 0.2 ML using an attenuation factor of $\exp(-2d/\lambda_{N1s})$. Here, d is the plane distance for GaAs(0 0 1) and $\lambda_{N\,1s}$ the escape depth of N 1s photoelectron. By introducing $d = 0.14$ nm and $\lambda_{N1s} = 1.96$ nm, the N content of 0.23 ML in the third As layer was obtained, which turns out to be within the numerical errors of ±0.1 ML.

The proposed structural models for (3×3)-1D and -2D are consistent with the recent first-principles total-energy calculations for the clean and As-covered GaN(0 0 1) surfaces [8]. In contrast to the N-terminated surface with energetically unfavorable N_2-dimers, the Ga-terminated one can be stabilized by the Ga metallic bonds, since the Ga atoms on GaN have approximately the same distance as in bulk Ga due to a small radius of N atom. That surface is further stabilized by the chemisorption of a submonolayer As atoms. In fact, both topmost layers shown in Fig. 3 consist of only arsenic and the As coverage decreases from 0.44 ML for (3×3)-2D to 0.22 ML for (3×3)-1D with prolonging t_N or increasing the nitrogen content. Because of a comparatively high vapor pressure of arsenic at the nitridation temperature of 525 °C, even the surface As_2-dimers on the starting (2×4) and the free As atoms segregated from the bulk are regarded as an arsenic source. The dimerization and atom missing to minimize the surface energy are commonly observed at the reconstructed surfaces of GaAs(0 0 1). However, neither model in Fig. 3 satisfies the electron counting rule [16] which requires the autocompensation involving the charge transfer from cation to anion dangling bonds. This is probably related to a rise of electrostatic energy and strain energy contributions to the surface energy, since there is a large difference in the electron negativity and atomic radius between As and N atoms.

To further elucidate the effect of trace As, we compared the STM images of sample surfaces nitrided under various ρ_{As} in a constant time ($t_N = 330$ s). Fig. 4 shows the domain area ratios among three structures of (2×4), (3×3)-2D and (3×3)-1D against ρ_{As} in the range of 3×10^{-9}–1×10^{-7} Torr. The depressed area under low ρ_{As}, which is similarly observed in Fig. 1(b), was excluded statistically. Obviously, with decreasing ρ_{As} the area of (3×3)-1D as an advanced nitridation phase increases, while those of (3×3)-2D and (2×4) decrease. The fact that low ρ_{As} encourages the growth of (3×3)-1D phase at the sacrifice of (3×3)-2D agrees with our models. In other words, high ρ_{As} suppresses the formation of (3×3)-1D, because the atmospheric As atoms arriving at the surface necessarily hinder the superficial reaction between impinging N radicals and exposed Ga atoms, and also the penetration of N atoms leading to the nitridation in the subsurface region [4,10].

In summary, the surface reconstruction of GaAs(0 0 1) nitrided under the controlled As partial pressure has been studied using high-resolution STM in combination with RHEED and XPS. By varying either t_N or ρ_{As}, the initial As-terminated (2×4) surface was found to change to two kinds of (3×3). One is the (3×3)-1D consisted of one dimer per surface cell, and the other (3×3)-2D of two dimers. The former (3×3)-1D surface predominantly formed during the further nitridation in an As-free atmosphere converted to the latter (3×3)-2D after exposure to As atoms. From these results, we reasoned that both surface dimers in (3×3)-1D/-2D are not N–N but As–As. Considering the incorporated N atoms confirmed by XPS, the proposed models for As_2-dimer coverage of (3×3)-1D/-2D are explicable as follows. The incoming N atoms partly substitute the As atoms in the subsurface region, and then bond with Ga atoms. This phenomenon toward the formation of β-GaN should energetically prefer the Ga-terminated surface to the N-terminated one. According to the theoretical calculations, such Ga-terminated surface is further stabilized by a submonolayer As coverage, resulting in the formation of As_2-dimers on (3×3)-1D/-2D.

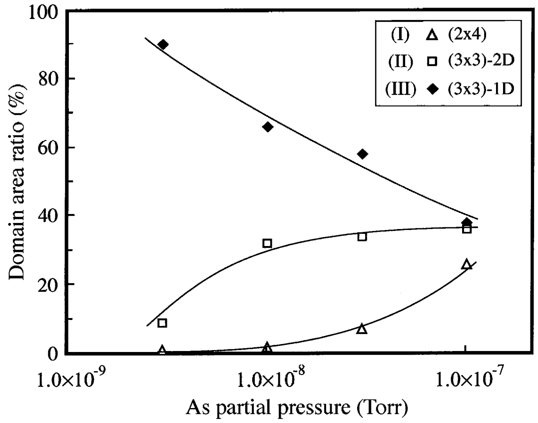


Fig. 4. Area ratios of three reconstructed domains against the ρ_{As}: (I) (2×4), (II) (3×3)-2D and (III) (3×3)-1D. The GaAs(0 0 1)-β2(2×4) surfaces were nitrided under the various ρ_{As} in the range of 3×10^{-9}–1×10^{-7} Torr in a constant time ($t_N = 330$ s).

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