Atomistic investigation of various GaN (0001) phases on the 6H-SiC (0001) surface

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A number of superstructures of the GaN (0001) surface have been investigated systematically by reflection high-energy electron diffraction, scanning tunneling microscopy, and first-principles theoretical calculations. The GaN-thin films are grown on the Si-terminated 6H-SiC (0001) surface by an N plasma-assisted molecular-beam epitaxy under the Ga-rich condition. While the as-grown GaN surface is revealed to be a featureless 1×1 structure, post-growth deposition of Ga at lower temperatures results in the formation of a series of ordered structures, such as 2×2, 4×4, 5×5, $5\sqrt{3}\times2\sqrt{13}$, $\sqrt{7}\times\sqrt{7}$, and 10×10 in the order of the increasing Ga coverage. An 1×1-Ga-fluid structure is obtained with the highest Ga coverage. Neither ordered structure nor smooth morphology has been observed under the N-rich regime. We conclude that the atomic structures of all these Ga-rich phases can be described best by a Ga-adatom scheme. We further show that the 5×5 and $5\sqrt{3}\times2\sqrt{13}$ phases are two configurations that exhibit a unique one-dimensional characteristic in the adatom arrangement. Their structures can be understood by Peierls distortion against Fermi-surface instability under the Ga-adatom scheme. [S0163-1829(99)10719-7]

I. INTRODUCTION

Group-III nitrides (AlN, GaN, InN, and their alloys) have been known for their enormous potential in the applications for optoelectronic devices operating in the spectral range from blue to ultraviolet.[1] Recent rapid development in blue light emission devices, such as light-emitting diodes and laser diodes fabricated by nitrides has greatly stimulated the interest in the study of these materials.[2] Due to the difficulty in making bulk materials, GaN thin films are obtained by epitaxial growth on other dissimilar materials with lattice mismatch. As any epitaxial growth of a thin film is essentially a surface process, a study of the film surface structure is of fundamental importance and it should subsequently help us to optimize the growth conditions for achieving high-quality films.

GaN crystallizes into two types of crystal structures: a stable hexagonal (wurtzite) GaN phase and a metastable cubic (zinc-blende) GaN phase. The hexagonal GaN is commonly grown by metallorganic chemical-vapor deposition (MOCVD), and molecular-beam epitaxy (MBE) on the basal plane of sapphire and 6H-SiC. Since there is no reversion symmetry in the bulk, the hexagonal GaN epitaxial film grown along the polar axis of the substrates always exhibits polarity; either the (0001) surface known as the Ga polarity or the (0001) known to be the N polar.[3] These two technologically important surfaces are found to possess some different properties, especially in their surface structures.[3,4] So far, a number reconstructions of the wurtzite GaN formed on sapphire and 6H-SiC have been reported, such as 1×1, 2×2, 2×3, 3×2, 3×4, 4×4, and 5×5, based on the reflection high-energy electron diffraction (RHEED) observations.[5,6] In those studies, both the surface polarity and its correlation with the surface structure are not understood. Recently, Smith and co-workers[7–10] carried out a careful scanning tunneling microscopy (STM) and RHEED study on the surface structures of the GaN films with the definite polarity; while the N-polar (0001) surface grown on sapphire by MBE exhibits the 3×3, 6×6, and $c(6\times12)$ reconstructions, the homoepitaxially grown Ga-polar (0001) surface was found to have different structures, such as 2×2, 5×5, and 6×4 reconstructions, demonstrating a strong influence of the surface polarity on the surface structure. Among these reconstructions, the 2×2 phase is believed to be the most important basis for the Ga-polarity film,[3,8] and an indicator of optimal conditions for smooth morphology during MBE growth. However, the fact that an exhaustive search of the 2×2 phase was not successful suggests that it is very difficult to access kinetically or might be stabilized by the presence of alien atoms.[10] *So far there is very limited information on the atomic structures of the Ga-polar GaN (0001) surface phases. Knowledge in this aspect is important for further understanding the unique properties of GaN.*

In this paper, we report a systematic STM study on the structures of the Ga-polar GaN (0001) surface grown on the Si-terminated 6H-SiC (0001) substrate. The long-range or-

dering of the surface is established by the RHEED pattern and further confirmed by STM. No ordered surface has been observed under the N-rich conditions and the films reported in this paper were prepared under the Ga-rich conditions. Post-growth Ga deposition on the as-grown surface followed by subsequent annealing at low temperatures results in the formation of a number of well-defined reconstructions with smooth morphology, which has allowed us to study them by STM. These reconstructions are 1×1, 2×2, $\sqrt{7}\times\sqrt{7}$, 4×4, 5×5, $5\sqrt{3}\times2\sqrt{13}$, 10×10, and most Ga-rich 1×1 fluid. Based on the obtained high-resolution STM images, preparation conditions and theoretical calculations, we will present a detailed discussion of the atomic structures of these phases.

II. EXPERIMENT

The experiments are performed in an UHV dual-chamber MBE-STM system that has advantage for the *in situ* study of the epitaxial films.[11] An atomically clean and flat 6H-SiC(0001) substrate surface (*n*-type-doped 2×10^{18} cm^{-3}, by Cree Research Corp.) is prepared by a two-step method of hydrogen etching followed by annealing under Si flux in UHV. The details of the preparation process have been described elsewhere.[12] The GaN film is grown by solid source MBE and atomic N is supplied from an EPI RF N plasma source. The growth starts with nitridation of the Si-terminated SiC (0001)-3×3 surface followed by an AlN buffer-layer deposition at 750 °C. Then, the substrate temperature is lowered to 650 °C and the GaN film is grown under the Ga-rich condition at a growth rate of ~1000 Å/h. The N plasma source is operated at 250 W with typical N pressure of $7.5\times10^{-5}\sim1.0\times10^{-4}$ Torr. After two hours of growth, a specular surface with interference color usually forms. The growth is terminated by turning off the N plasma followed by 2 ML Ga deposition at the growth temperature, and then the sample is quenched to room temperature. An (1×1) RHEED pattern is observed for the as-quenched surface. When about 1 ML Ga is deposited on the surface at room temperature followed by 10 min annealing at 200 °C, the 2×2 phase appears. Further annealing of the 2×2 surface results in the 4×4 and 5×5 phases. The $5\sqrt{3}\times2\sqrt{13}$, $\sqrt{7}\times\sqrt{7}$, and 10×10 are prepared in a similar manner (the conditions are described in later sections).

III. RESULTS AND DISCUSSION

A. Surface polarity

One notes that there is no reversed symmetry center for the hexagonal crystal structure of wurtzite GaN; the (0001) polarity ends with a Ga-N bilayer with the N termination whereas the (0001) ends with a N-Ga bilayer with the Ga termination.[3] Such a polarity variation produces essentially different structures on the surface, and more importantly it results in different growth processes. In order to investigate the surface structure and to understand the epitaxial process, it is necessary to determine the film polarity first.

Our GaN thin film is assigned to have the (0001) Ga polarity based on the following considerations:

(I) *The initial stage of the film nucleation process.* When we deposit Ga and Al (from submonolayer to 3 ML) on the Si-terminated 6H-SiC (0001) substrate followed by low-temperature annealing (below 600 °C), not much change in the substrate structure and morphology is observed. Only some two-dimensional (2D) or 3D Al islands (depending on the amounts of Al deposited) or Ga droplets are distributed randomly on the surface. Annealing at higher temperatures (up to 700 °C) leads to desorption of all Al and Ga. One example is shown in Fig. 1. The deposited Al simply forms 2D islands, and the surrounding 3×3 structure of the SiC remains intact, suggesting a low reactivity of Al/Ga with the Si and the preferential N-Si bonding at the interface.[13]

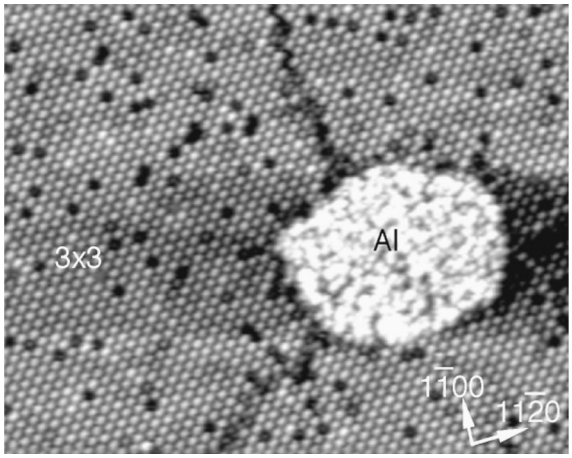

FIG. 1. Filled-state STM image of the 6H-SiC (0001) Si-3×3 surface deposited with 0.05 ML Al at room temperature, followed by annealing at 600 °C for 10 min. The Al forms two-dimensional islands on the 3×3 surface. No new surface reconstruction has been induced under various Al coverages and annealing temperatures. The tunneling current (It) is 40 pA and the bias voltage (Vs) is -3.0 V.

(II) *The observation of the different surface reconstructions compared with the (0001) surface.* If our film has the (0001) polarity, we should steadily observe the 1×1, 3×3, and 6×6 structures, as reported by Smith *et al.*[7] However, in spite of the very similar post-growth treatment conditions to Smith *et al.*, a completely different set of structures (2×2, $\sqrt{7}\times\sqrt{7}$, 4×4, 5×5, and $5\sqrt{3}\times2\sqrt{13}$, etc.) are observed, which are in agreement with the observations reported on the (0001) surface.[8]

We attempted to start the nitride growth with Al and Ga deposition for the (0001) polarity, but no good film was obtained. This is due probably to the intermixing Ga-Si and N-Si bonding, which results in poor crystallization. The po-

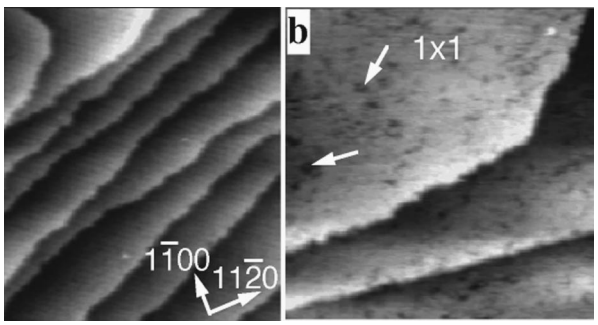

FIG. 2. Filled-state STM images of the as-grown 1×1 surface of GaN: (a) 1500 Å$\times$1500 Å, (b) 250 Å$\times$250 Å. The arrows indicate the defects on the surface. $It=80$ pA, $Vs=-2.8$ V.

larity of GaN/SiC has been examined by theory[14] and other experiments.[15] The results also support the present (0001) assignment. In addition, we performed chemical wet etching to check the epitaxial GaN films polarity.[8,16] Although a smooth morphology was observed, our result is presently inconclusive because of insufficient amounts of data with different polar surface. A study of the GaN surface on the C-terminated 6H-SiC (0001) is currently underway.

B. As-grown (1×1) surface

Figure 2(a) shows the morphology of the as-grown GaN surface obtained under the optimal growth conditions. The surface is characterized by a well-defined terrace-plus-step structure with a measured step height of 2.55 Å (corresponding to the bilayer height of the hexagonal GaN along the *c* axis). This surface is typical and the area extends to approximately 0.5 μm, indicating a smooth morphology, substantiating the advantage of the SiC substrate and AlN buffer layer. At the different film thickness the surface exhibits different interference color, another indication of the film quality. As no RHEED intensity oscillation is observed, which can be used to measure the film thickness, the film thickness is only estimated by an optical method developed by Christiansen, Carpini, and Tsong.[17] If the surface is prepared under the N-rich condition, the STM images show that the surface is always rough and contains many defects of bumps. According to the preparation conditions and the observed 1×1-RHEED pattern, this as-quenched surface should correspond to the bulk-terminated 1×1-Ga structure since the surface with 2 ML Ga is unstable theoretically.[7] The enlarged image of the surface is shown in Fig. 2(b). Despite the smooth morphology, no ordered structure is observed. Many dark holes (indicated by the arrows) with diameter of approximately 10 Å distribute randomly on the surface, indicating an incomplete full monolayer of Ga. Attempts to obtain better resolution images are unsuccessful. The Ga coverage of this surface should be close to but less than 1 ML, according to these observations.

C. 2×2 and 4×4 phases

The 4×4 phase is prepared by annealing the 2×2 phase at 350 °C–400 °C for about 5 min. Expecting Ga desorption from the surface, the 4×4 phase should be less Ga-rich than the 2×2 phase. The 2×2 structure is characterized with uniformly distributed bright spots with a separation of 6.4 Å along the close-packing directions, while the 4×4 phase forms by a missing array of every second bright spots from the 2×2 phase. Their atomic structures have been discussed in detail based on atomically resolved STM images and first-principles total-energy calculations elsewhere.[18] It is our conclusion that both of them can be understood by the Ga adatom model (see Fig. 3); the 2×2 and 4×4 adatom models are energetically favorable under Ga-rich and less Ga-rich conditions, respectively. The bright spots are assigned to be due to the tunneling from the states derived from the Ga adatom adsorbed on the T_4 site of the bulk 1×1-Ga surface (Fig. 2). Here, we show a case where the 2×2 and 4×4 phases coexist (Fig. 3). According to our adatom model, the Ga-surface coverage of the 2×2 and 4×4 phases is 1.25 and 1.18 ML, respectively. It is important to note that the model

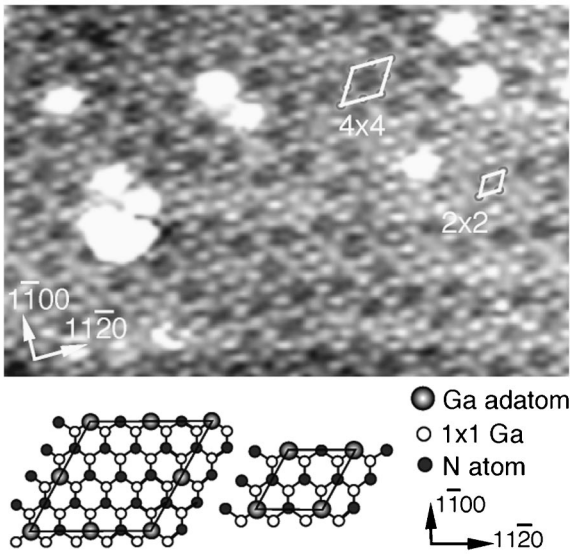

FIG. 3. Filled-state STM image (120 Å×80 Å) of the mixed 4×4 and 2×2 phases with highlighted unit cell of 4×4 and 2×2. $It = 80$ pA, $Vs = -3.0$ V. The schematic is the ball-to-stick model for the 2×2 and 4×4 reconstructions proposed in Ref. 18. The right one is the 2×2 model. Ga-adatom (big shadowed circle) bonds with 1×1 Ga atoms (small white circle) at the *T*4 position. The small black circles represent N atom layer under 1×1 Ga layer. The 4×4 model (left one) is similar to that of 2×2 except that one adatom at center is missed.

of the 4×4 phase as shown in Fig. 3 does not satisfy the electron counting model; there are three extra electrons in a 4×4 unit cell, each of them occupies one dangling bond of a Ga adatom. Our calculations indicate that the configuration is stabilized by a static-electrical repulsive interaction among the charged Ga adatoms.[18] As seen in the following, such an interaction might also play an important role in surface energy minimization of the other Ga-rich phases. We did observe a N-rich 2×2 phase by RHEED when the as-grown surface was bombarded by N plasma for 20 min and annealed at 500 °C–600 °C for 10 min. When the sample is cooled down to room temperature, the 2× streak in the RHEED pattern becomes very weak. This 2×2 phase was also observed by Smith *et al.*[10] While their STM image shows only some local 2×2 ordering, ours (not presented here) reveals a rough morphology and featureless structure, and even the step cannot be resolved. These results suggest that the N-rich 2×2 phase is stable only under some extreme condition, and is difficult to access kinetically. The theoretical investigations conclude that the 2×2 structure with the N adatom on the H_3 site is energetically favorable under the N-rich condition.[7,18] We, therefore, conclude that the observed N-rich 2×2 phase corresponds to the structure described by this N-adatom model.

D. 5×5 phase

The preparation condition for the 5×5 reconstruction is very similar to that for the 4×4 phase. Actually no distinct boundary in preparing these two phases has been established in our experiment, suggesting that their surface stoichiometry should be nearly identical. The surface exhibits a very sharp streaky ''5×'' RHEED pattern along the [1120] azi-

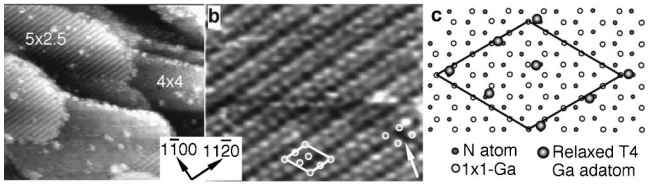

FIG. 4. Filled-state images and the proposed model for the 5×5 structure. (a) 600 Å×490 Å and (b) 100 Å×80 Å are taken at $It = 80$ pA, $Vs = -3.1$ V. (c) Top view of the ''5×5'' model proposed in Ref. 18. The Ga-adatom (large black circle) bonding with bulk 1×1 Ga atoms (small white circles) relaxes at $T4$ position and cause a variation in the spot location in the image. The small black circles represent N atom layer under 1×1 Ga layer.

muth while there is a strong background when the electron beam is incident along the [1100] azimuth. As shown in Fig. 4(a), the 5×5 structure consists of regular linear chains along the [1120] direction. The distance among the chains along the [$\bar{0}$110] direction is determined to be 15.8 Å, corresponding to $5\mathbf{a}_0$ [$\mathbf{a}_0 = 3.19$ Å, the in-plane lattice constant of the GaN (0001) surface]. A small amount of the 4×4 domain is often seen in the STM image of the 5×5 surface. A high-resolution [Fig. 4(b)] further reveals that each chain is actually a doublet, composed of two lines with a distance of 6.38 Å (2×) along the [0110] direction. The lines consist of individual bright spots. These bright spots are separated with either 2× or 3× or 2.5× of the lattice constant with an average separation of 2.5× (~7 Å) which results in a one-dimensional disorder along the [1120] direction. Therefore, the 5×5 can be best described as a ''5×2.5'' structure.[18] According to the line profile measurement, the contrast of the 5×5 phase is only 0.15 Å higher than that of the 4×4 phase. This contrast difference is typical of pure electronic effect. Based on the 4×4 adatom model (Fig. 3), preparation conditions and STM observations, we propose a model shown in Fig. 4(c).[18] The bright spots as seen in the high resolution image [Fig. 4(b)] are attributed to the tunneling

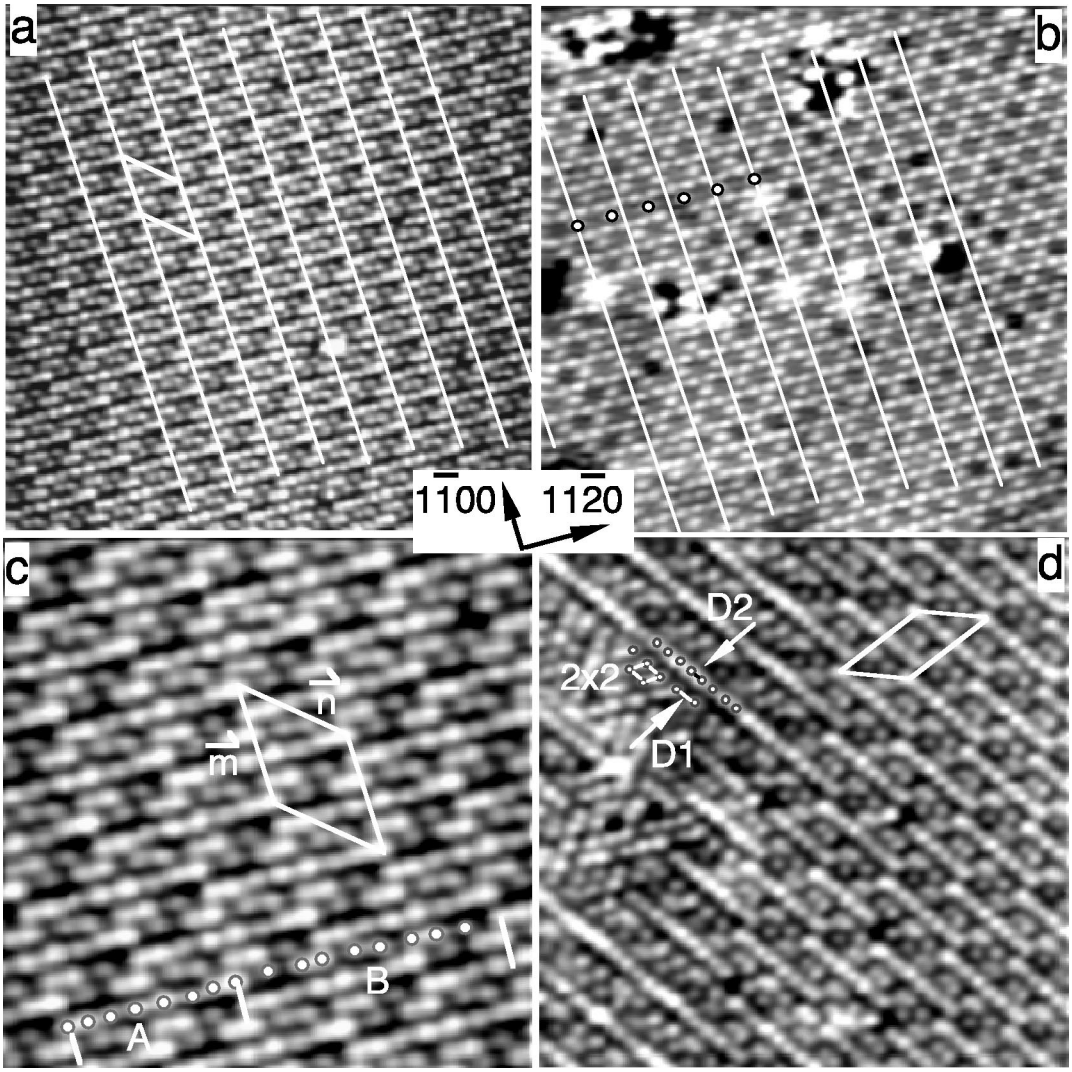

FIG. 5. (a) Filled-state STM image (200 Å×200 Å) of the $5\sqrt{3}\times\sqrt{13}$ phase. The parallel white lines have the periodicity of L along the [11$\bar{2}$0] direction, which is equal to the projection of the vector $\vec{n}$ on this direction. $It = 80$ pA, $Vs = -3.0$ V. (b) Filled STM image of the 4×4 structure with the same scale as that in (a). The circles stand on the 4×4 lattice position, implying that $5\times 4\mathbf{a}_0$ is equal to 4L, thus $L = 5\mathbf{a}_0$, $It = 80$ pA, $Vs = -2.8$ V. (c) Zoom-in STM image of the $5\sqrt{3}\times 2\sqrt{13}$ phase. $\vec{m}$, $\vec{n}$ are the basal vectors of the $5\sqrt{3}\times 2\sqrt{13}$. (d) Filled-states STM image of the $5\sqrt{3}\times 2\sqrt{13}$ showing the transition region.

from the filled states derived from the Ga adatoms. We note that the surface coverage is 1.16 ML Ga for the model and that is does not satisfy the auto-compensation rule.[18]

E. $5\sqrt{3}\times 2\sqrt{13}$ phase

The $5\sqrt{3}\times 2\sqrt{13}$ phase is prepared by deposition of about 2 ML Ga on the as-grown 1×1-Ga surface followed by annealing at 400 °C for 10 min, suggesting that the surface is slightly more Ga rich than 4×4. The STM image [Fig. 5(a)] reveals that the structure consists of chains made from regularly arranged spots and paired spots along the $[11\bar{2}0]$ direction. The unit cell of this structure is depicted in the zoom-in image [Fig. 5(c)] with one mesh vector indicated by $\vec{m}$ along the $[1\bar{1}00]$ direction. Because its structure shown by the STM image is rather complicated and the surface unit cell is further rotated, we show a STM image of the 4×4 phase in Fig. 5(b) in order to analyze the detail of the structure. The chains are separated by 6.4 Å ($2\times$) along the close-packing direction. Since the base vector $\vec{m}$ is perpendicular to the $[11\bar{2}0]$ (chain) direction, the chain separation along the $\vec{m}$ direction is $\sqrt{3}\mathbf{a}_0$, which results in a $5\sqrt{3}\mathbf{a}_0$ unit cell size of the surface in this direction. The unit cell along the $\vec{n}$-vector direction includes three chains and extends $5\mathbf{a}_0$ along the $[11\bar{2}0]$ close-packing direction [this is determined by superimposing the white lines in Fig. 5(a) to the same scale image of the 4×4 phase in Fig. 5(b)]. By looking at this grid, we find that four times the line spacing in Fig. 5(a) is exactly equal to five times (63 Å) ''$4\times$ periodicity'' in Fig. 5(b). So the surface as shown in Fig. 5(a) is $5\sqrt{3}\times 2\sqrt{13}$ reconstructed.

The striking feature of the $5\sqrt{3}\times 2\sqrt{13}$ phase is that it is composed of chains that have an one-dimensional unit cell of $25\mathbf{a}_0$ along the $[11\bar{2}0]$ direction. The unit cell of each chain consists of 16 spots and these spots are divided into two parts: Parts *A* and *B*, as indicated in Fig. 5(c). Part *A* takes $10\mathbf{a}_0$ and includes paired spots at the both ends and 4 individual spots in between. Part *B* takes $15\mathbf{a}_0$ region and includes 2 paired spots and 4 single spots. Figure 5(d) shows another $5\sqrt{3}\times 2\sqrt{13}$ domain, which is rotated by 120° with respect to that shown in Fig. 5(c). At the boundary area one observes some spots with the locally 2×2 ordering [a 2×2 unit cell is indicated in Fig. 5(d)]. At the upper-left and lower-left corners, the linear chains forming the 5×5 structure are also visible. If the individual spots are removed, the surface transforms into the 5×5 phase. Therefore, the surface coverage of the $5\sqrt{3}\times 2\sqrt{13}$ should be close to or between the 2×2 and 5×5 phases. The contrast variation among the spots in the $5\sqrt{3}\times 2\sqrt{13}$ structure is less than 0.3 Å and we conclude that these spots come from the same layer atoms. Based on our study of the 2×2 and 5×5 phases, the spots in the images are believed to be the tunneling from the dangling bonds of Ga adatoms.

We propose a ball-to-stick model for the $5\sqrt{3}\times 2\sqrt{13}$ in Fig. 6. Due to the formation of the paired-spots, it is not possible for all the bright spots to take the normal lattice sites. The observation may be explained by the occupation of the different adsorption positions (T_4, H_3, or bridge site) for the Ga atoms. According to the theoretical calculations, however, the H_3 site and the bridge site are not energetically favorable,[18,19] and thus, the model displayed in Fig. 6 is rather tentative. Recalling that there is also a nonlattice-site occupation of the bright features on the 5×5 surface, another possibility is the relaxation of the T_4 Ga adatoms. Further noting that both the 5×5 and $5\sqrt{3}\times 2\sqrt{13}$ phases exhibit an anisotropic one-dimensional structure, the observation might be explained by a coherent Peierls distortion of the adatom arrangement along the close-packing $[11\bar{2}0]$ direction.[20,21] In all quasi-one-dimensional structures where a metallic chain forms, it is unstable. It is energetically favorable to lower the surface energy by an atomic relaxation. Therefore, we believe that the nonlattice-site occupation of some of the bright spots as seen in the STM images [Figs. 5(a) and 4] can be best understood by the adatom relaxation associated with this Peierls distortion. A detailed study of the fully relaxed atomic geometry is underway currently and will be reported elsewhere.[22]

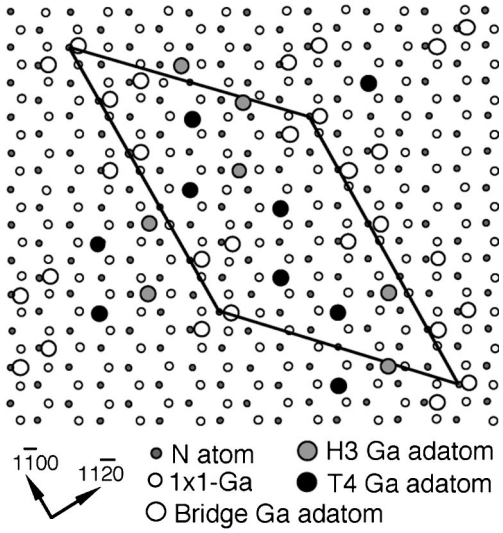

FIG. 6. The top view of the tentative model proposed for the $5\sqrt{3}\times 2\sqrt{13}$ phase. The white small ball represents the bulk 1×1 Ga atom. The large white, gray, and black balls represent the adatoms adsorbed at the bridge, *H*3 and *T*4 sites, respectively. The small black circles represent the N atom layer under the 1×1 Ga layer.

F. *L*-($\sqrt{7}\times\sqrt{7}$) phase

A phase exhibiting the locally ordered $\sqrt{7}\times\sqrt{7}$ structure forms during the preparation of the 2×2 structure if the amount of the deposited Ga is slightly more than those for the 2×2 or 4×4. Figure 7(a) shows a typical STM image of the $\sqrt{7}\times\sqrt{7}$ structure coexisting with the 4×4 phase. Many experiments were attempted to prepare the single-domain-ordered $\sqrt{7}\times\sqrt{7}$ surface by, for example, deposition of more Ga or annealing at different temperatures. However, the long-range-ordered $\sqrt{7}\times\sqrt{7}$ structure was not achieved even the whole surface was covered with this structure. The surface shows a 1×1-RHEED pattern, implying that the local ordering is an intrinsic property of the $\sqrt{7}\times\sqrt{7}$ phase. Thus we call it as *L*-$\sqrt{7}\times\sqrt{7}$. This structure is stable in a wide range of temperature and Ga coverage, and *L*-$\sqrt{7}\times\sqrt{7}$ is thought to be another characteristic reconstruction of the

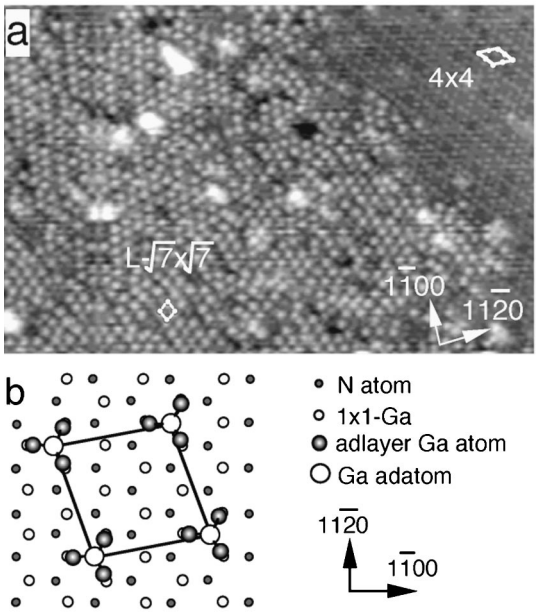

FIG. 7. (a) Filled-state STM image of the mixed L-$\sqrt{7}\times\sqrt{7}$ and 4×4 structures with highlighted unit cells. $It=80$ pA, $Vs=-2.3$ V. (b) The top view of the proposed model. The small black circles represent the N atom layer under the 1×1 Ga layer (the small white circles).

(0001) surface. The image contrast of L-$\sqrt{7}\times\sqrt{7}$ is higher than the neighboring 4×4 by as much as 1.0 Å. Thus, it is reasonable to speculate that it involves one more layer of Ga on the surface. A tentative model is proposed in Fig. 7(b). The gray circle represents the adlayer Ga atoms, which bond to the 1×1 Ga atoms of the N-Ga bilayer. One extra adatom (white circle) is bonded with three adlayer Ga adatoms forming a tetramer. The atomic configuration in the second and/or deeper surface layers is unknown, for example, the second-layer adatoms between the tetramers may be missing. Further study, such as the surface coverage measurement and theoretical simulation, is necessary for the establishment of a complete structure model.

G. 10×10 phase

By depositing another 1–2 ML Ga on the L-$\sqrt{7}\times\sqrt{7}$ surface and annealing at 350 °C for 10 min, a 10×10 phase is obtained. Figure 8(a) shows a typical image of this structure. Usually it coexists with the L-$\sqrt{7}\times\sqrt{7}$ structure with the contrast higher by 1.6 Å than the surrounding L-$\sqrt{7}\times\sqrt{7}$. According to the preparation condition, the 10×10 phase involves three layers of Ga on the bulk-terminated 1×1 Ga surface. as clearly seen in the high-resolution STM image [Fig. 8(b)], this structure is characterized by a unique honeycomb structure consisting of 18 bright spots in a unit cell: the inner ring contains six spots while the outer ring 12 spots. The overall arrangement of the spots is very similar to what appears on the Si (111)-7×7 surface. From the large-scale image [Fig. 8(a)], we observe many fractional rings that are located at the 10×10 island edges. Assuming that the 10×10 phase is more energetically stable than the L-$\sqrt{7}\times\sqrt{7}$ surface, the local-ordered characteristic of the $\sqrt{7}\times\sqrt{7}$ may be understood by a phase transition to the 10×10 phase under the Ga-rich conditions. Its atomic model is schematically shown in Fig. 8(c). The small white circle represents the

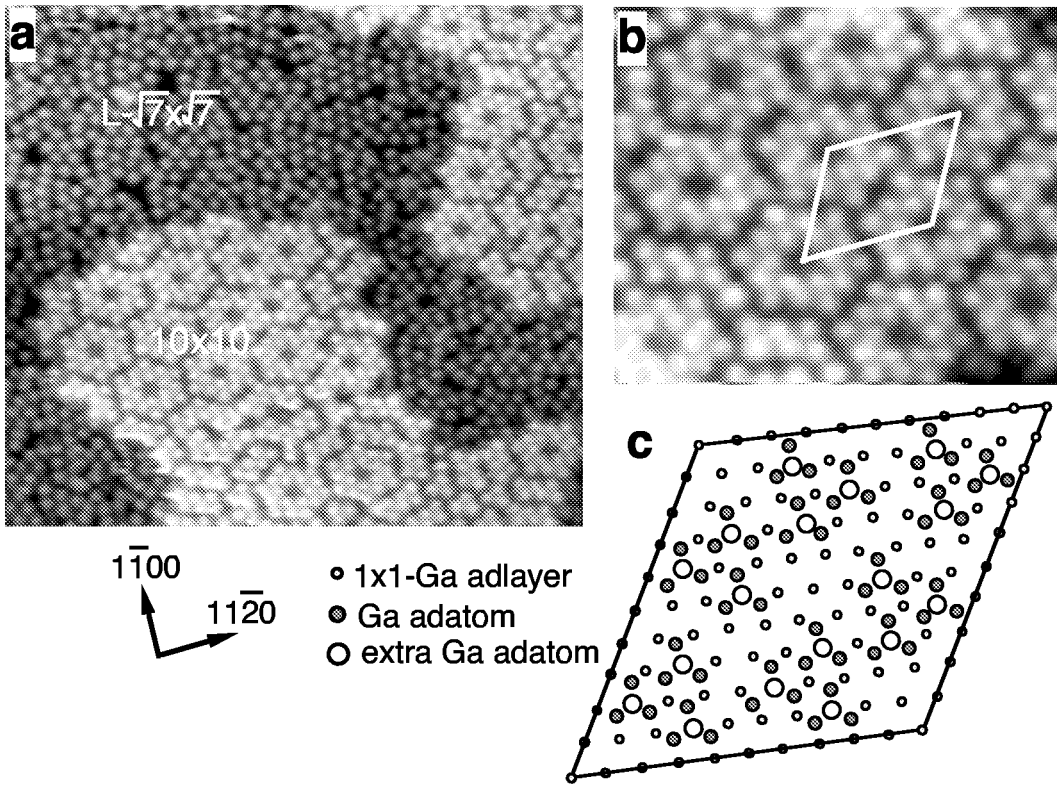

FIG. 8. Filled-state STM images of the 10×10 phase. (a) Large-scale scan (200 Å×200 Å). The 10×10 phase coexists with the L-$\sqrt{7}\times\sqrt{7}$ phase. (b) Zoom-in image (80 Å×80 Å) with highlighted unit cell. (c) The schematic model.

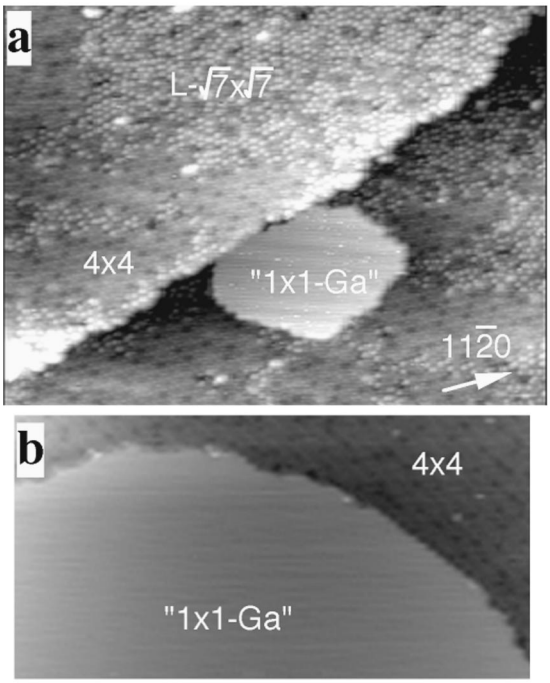

FIG. 9. (a) Filled-state STM image (450 Å×360 Å) displaying the coexisted 4×4, L-$\sqrt{7}\times\sqrt{7}$, and ''1×1-Ga'' fluid structures. $It = 80$ pA, $Vs = -2.0$ V. (b) Zoom-in STM image (150 Å×80 Å) of the ''1×1-Ga'' fluid. In the upper part of the image, the 4×4 phase is visible.

1×1 Ga adatom, which sits on the top of the bulk 1×1 Ga atoms. The gray circles are the Ga adatoms bonding with three Ga atoms in the Ga adlayer. The outmost Ga adatom (the large white circle) stands on these three adatoms (the gray circle). The current model is simply based on the STM image. Other models, for example, one similar to the dimer adatom stacking fault (DAS) model of the Si (111)-7×7 surface may also satisfy the STM images presented here.

H. ''1×1-Ga'' fluid structure

The 1×1-Ga fluid is the most Ga-rich phase and almost always coexists with all other phases described above, except for the as-grown 1×1 surface. The STM image [Fig. 9(a)] obtained during preparation of the 2×2 surface exhibits the coexisting 4×4, $\sqrt{7}\times\sqrt{7}$, and ''1×1-Ga'' phases. This ''1×1-Ga'' was also reported by Smith *et al.*,[9] and its structure is very different from the previous 1×1 as-grown surface. While in the latter case, some defects are always present [Fig. 2(b)], the ''1×1-Ga'' surface is seen to be atomically flat [Fig. 9(b)]. No STM image resolving the atomic structure has been achieved. Line-profile measurements indicate that it is higher than the 4×4 surface by 2.1 Å. Since theoretically the 2×2 is 1.78 Å higher than the bulk 1×1 Ga layer,[23] the height of ''1×1-Ga'' is about 3.88 Å above the 1×1 Ga layer. This corresponds to 1.9 ML. This surface is metallic as the tunneling is stable even when the bias voltage is less than 0.2 V and the obtained STM image at low-bias voltage is similar to that obtained at higher-bias voltage. Sometimes the ''1×1-Ga'' structure covers several thousand angstroms of the surface. If this structure is nitrided at 500 °C for 10 min, no obvious change is observed and only the edge of the ''1×1-Ga'' islands becomes brighter than the inside area. On the contrary, all other structures disappear after the same treatment. These observations clearly indicate that ''1×1-Ga'' is a stable phase as long as the surface is very Ga-rich. A fluidlike and discommensurate Ga bilayer structure has been modeled for the ''1×1-Ga'',[9] which explains our observations well. The observations imply a very low solubility of the N into the bulk Ga. From the viewpoint of epitaxial growth, the Ga flux may never be oversupplied to maintain smooth surface morphology, which may partially explain why a flat morphology results under the Ga-rich conditions.

While the above mentioned surface structures are obtained by deposition of some amount of Ga on the as-grown surface, attempts to prepare an ordered N-induced structure have not been successful. The STM images showed a rough surface where it was difficult even to find a terrace. This may be attributed to a lower mobility of N atom on the Ga face of GaN,[19] resulting in a difficulty for N atoms to find favorable sites. Assuming a stable growing front surface, it is not surprising to observe a smooth surface morphology with larger Ga atom diffusivity. On the other hand, the very strong cohesive energy of N_2 makes the N adatoms thermodynamically unstable against evaporation as N_2,[24] and eliminates the local kinetic pathway to the formation of an N-rich phase despite a global N-rich growth environment. Thus, some theoretically predicted N-rich structures are difficult to access kinetically. This situation distinguishes the GaN surface from all traditional III-V surfaces. Considering theoretical studies,[18,19,24] the present observations that various Ga-rich phases are stable on the GaN (0001) surface (this case seems to hold true for the N-polar surface as well), clearly illustrate that the growth under the Ga-rich conditions is necessary to achieve a quality film.[25,26]

IV. SUMMARY

A series of phases belonging to the GaN (0001) surface, such as 2×2, 4×4, 5×5, $5\sqrt{3}\times 2\sqrt{13}$, $\sqrt{7}\times\sqrt{7}$, 10×10, and 1×1-Ga fluid, have been documented and discussed with high-resolution STM images. The results are summarized as follows:

(1) On the Si-terminated 6H-SiC (0001) substrate, the GaN/AlN films has the (0001) surface polarity. When the initial nucleation process of the film starts with the Al deposition and thus the Si-Al bonding for the (0001) polarity, the undesirable film morphology results, probably due to a mixed interface bonding.

(2) All ordered surface phases are found to be Ga-rich and their structures can be understood by the Ga-adatom scheme. No stable N-rich phase has been observed. Theoretically predicted N-rich phases might be difficult to access kinetically.

(3) Auto-compensation, one of the guiding rules for conventional III-V compound semiconductor surface reconstructions, may not be strictly satisfied on the GaN surface. In many cases, the surface energy of GaN can be lowered by static-electrical repulsion interaction among charged adatoms and Peierls distortion.

(4) To achieve the smooth surface morphology, material growth under the Ga-rich conditions is suggested. Since the N-rich growth conditions lead to a morphology instability, new processes to manipulate the growth kinetics and ener-

getics, for example, use of surfactants, are very important in order to decrease the N-vacancy defects, which are usually believed to cause high-background carrier concentration in nitrides. This partially explains why MBE has been less successful than MOCVD where H-radicals might play a crucial role in stabilizing surfaces. Our attention is presently placed on this direction.

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[1] S. Strite and H. Morkoç, J. Vac. Sci. Technol. B **10**, 1237 (1992).
[2] S. Nakamura, M. Senoh, S. Nagahama, N. Iwasa, T. Yamada, T. Matsushita, H. Kiyoku, Y. Sugimoto, T. Kozaki, H. Umemoto, M. Sano, and K. Chocho, Appl. Phys. Lett. **72**, 211 (1998); Jpn. J. Appl. Phys., Part 2 **37**, L309 (1998).
[3] E. S. Hellman, MRS Internet J. Nitride Semicond. Res. **3**, 11 (1998).
[4] V. M. Bermudez, D. D. Koleske, and A. E. Wickenden, Appl. Surf. Sci. **126**, 69 (1998).
[5] M. E. Lin, S. Strite, A. Agarwal, A. Salvador, G. L. Zhou, N. Raguchi, A. Rockett, and H. Morkoç, Appl. Phys. Lett. **62**, 702 (1993); W. C. Hughes, W. H. Rowland, Jr., M. A. L. Johnson, S. Fujita, J. W. Cook, Jr., J. F. Schetzina, J. Ren, and J. A. Edmond, J. Vac. Sci. Technol. B **13**, 1571 (1995); O. H. Hughes, D. Korakakis, T. S. Cheng, A. V. Blant, N. J. Jeffs, and C. T. Foxon, *ibid.* **16**, 2237 (1998).
[6] K. Iwata, H. Asahi, S. J. Yu, K. Asami, H. Fujita, M. Fushida, and S. Gonda, Jpn. J. Appl. Phys., Part 2 **35**, L289 (1996).
[7] A. R. Smith, R. M. Feenstra, D. W. Greve, J. Neugebauer, and J. E. Northrup, Phys. Rev. Lett. **79**, 3934 (1997).
[8] A. R. Smith, R. M. Feenstra, D. W. Greve, M. S. Shin, M. Skowronski, J. Neugebauer, and J. E. Northrup, Appl. Phys. Lett. **72**, 2114 (1998).
[9] A. R. Smith, R. M. Feenstra, D. W. Greve, M. S. Shin, M. Skowronski, J. Neugebauer, and J. E. Northrup, J. Vac. Sci. Technol. B **16**, 2242 (1998).
[10] A. R. Smith, V. Ramachandran, R. M. Feenstra, D. W. Greve, A. Ptak, T. Myers, W. Sarney, L. Salamanca-Riba, M. Shin, and M. Skowronski, MRS Internet J. Nitride Semicond. Res. **3**, 12 (1998).
[11] Q. K. Xue, Q. Z. Xue, Y. Hasegawa, I. S. T. Tsong, and T. Sakurai, Jpn. J. Appl. Phys., Part 2 **36**, L1486 (1997).
[12] Q. Z. Xue, Q. K. Xue, Y. Hasegawa, I. S. T. Tsong and T. Sakurai, Appl. Phys. Lett. (to be published).
[13] S. Y. Ren and J. D. Dow, Appl. Phys. Lett. **69**, 251 (1996).
[14] R. B. Capaz, H. Lim, and J. D. Joannopoulos, Phys. Rev. B **51**, 17 755 (1995); R. D. Felice, J. E. Northrup, and J. Neugebauer, *ibid.* **54**, R17 351 (1996).
[15] S. Stemer, P. Pirouz, Y. Ikuhara, and R. F. Davis, Phys. Rev. Lett. **77**, 1797 (1996).
[16] M. Seelmann-Eggebert, J. L. Weyher, H. Obloh, H. Zimmermann, A. Rar, and S. Porowski, Appl. Phys. Lett. **71**, 2635 (1997).
[17] J. W. Christiansen, D. D. Carpini, and I. S. T. Tsong, Nucl. Instrum. Methods Phys. Res. B **15**, 218 (1986).
[18] Q. K. Xue, Q. Z. Xue, R. Z. Bakhtizin, Y. Hasegawa, I. S. T. Tsong, T. Sakurai, and T. Ohno, Phys. Rev. Lett. (to be published).
[19] T. Zywietz, J. Neugebauer, and M. Scheffler, Appl. Phys. Lett. **73**, 487 (1998).
[20] R. E. Peierls, *Quantum Theory of Solids* (Clarendon, Oxford, 1955).
[21] C. B. Duke, Chem. Rev. **96**, 1237 (1996).
[22] Q. K. Xue, Q. Z. Xue, Y. Hasegawa, I. S. T. Tsong, T. Sakurai, and T. Ohno (unpublished).
[23] J. Fritsch, O. F. Sankey, K. E. Schmidt, and J. B. Page, Phys. Rev. B **57**, 15 360 (1998).
[24] J. Neugebauer, T. Zywietz, M. Scheffler, J. E. Northrup, and C. G. V. D. Walle, Phys. Rev. Lett. **80**, 3097 (1998).
[25] K. H. Ploog, O. Brandt, H. Yang, and A. Trampert, J. Vac. Sci. Technol. B **16**, 2229 (1998).
[26] E. J. Tarsa, B. Heying, X. H. Wu, P. Fini, S. P. DenBaars, and J. S. Speck, Jpn. J. Appl. Phys., Part 1 **82**, 5472 (1997).