RAPID COMMUNICATIONS

PHYSICAL REVIEW B VOLUME 52, NUMBER 4 15 JULY 1995-II

Surface reconstructions of zinc-blende GaN/GaAs(001) in plasma-assisted molecular-beam epitaxy

O. Brandt, H. Yang, B. Jenichen, Y. Suzuki,* L. Däweritz, and K. H. Ploog

Paul-Drude-Institut für Festkörperelektronik, Hausvogteiplatz 5-7, D-10117 Berlin, Germany

(Received 17 April 1995; revised manuscript received 30 May 1995)

We identify the growth conditions required for the synthesis of purely cubic GaN films on GaAs(001) by means of plasma-assisted molecular-beam epitaxy. It is shown that it is the surface stoichiometry which governs the phase composition and which thus has to be tightly controlled in order to avoid nucleation of hexagonal grains. Such control over the surface stoichiometry is achieved by investigating the surface reconstructions of zinc-blende GaN under both static and dynamic conditions by *in situ* reflection high-energy electron diffraction.

GaN is, because of its large ionicity, one of the most extreme representatives of compound semiconductors which, at equilibrium, condense in the wurtzite structure only.[1] It was, consequently, thought to be virtually impossible to force any of the group-III nitrides into the metastable zinc-blende modification. This belief was substantially hardened by the lack of substrate materials with a reasonably close lattice match,[2] which otherwise could provide the required epitaxial constraint. In striking contrast to these considerations, researchers using molecular-beam epitaxy (MBE) have recently demonstrated the synthesis of the zinc-blende modification of GaN on various, highly mismatched cubic substrates.[3] It seems, however, that the hexagonal phase often coexists with the cubic one.[4] Though this phenomenon might appear as natural given the preference of GaN for the hexagonal phase, it is of both fundamental interest and of great technological importance to investigate the mechanisms that govern the phase purity of GaN on a cubic substrate.

It is the aim of this paper to identify the conditions for the synthesis of purely cubic, epitaxial GaN films on (001) GaAs. We present results suggesting that the phase purity of GaN films is determined by the surface stoichiometry during growth. Our data furthermore indicate that problems common to both modifications of GaN, such as the high background electron concentration and the dominating yellow midgap luminescence, are also critically dependent on surface stoichiometry. To improve control over growth, we investigate the surface reconstructions and the associated growth kinetics of GaN films grown on (001) GaAs by plasma-assisted MBE. Three distinct reconstructions of cubic (001) GaN are observed. We identify the reconstruction obtained under near-stoichiometric conditions as the one under which zinc-blende single-phase growth is achieved.

Growth on GaN films is carried out on (001)-oriented (offcut $<0.1°$), semi-insulating GaAs substrates in a custom-designed solid-source MBE chamber. Active N is generated by a high voltage ($\simeq 1.5$ keV) plasma glow discharge. The plasma power is kept constant for all experiments at 30 W. The surface of the growing crystal is monitored *in situ* by reflection high-energy electron diffraction (RHEED), using an incident angle between 1° and 2° and an acceleration voltage of 15 keV. RHEED patterns are recorded by a charge-coupled device camera connected to an image processing system. The Ga flux is determined by RHEED oscillations during GaAs growth under N_2 background pressure.[6] The N flux is determined by evaluating the growth rate via the layer thickness as measured by scanning electron microscopy (SEM) for films grown under Ga-rich conditions.

Growth is initiated on the (2×4) reconstructed GaAs surface by closing As and simultaneously opening the N shutter. The presence of an As background pressure in the initial stage of growth promotes the nucleation of a cubic template, an observation which resembles the finding of Cheng *et al.*[3] It is not, however, necessary to provide an As flux throughout growth as reported by these authors. Furthermore, the same effect is achieved by using N-rich conditions during nucleation of the first $\simeq 5$ ML. Ga excess in this stage, however, inevitably leads to nonepitaxial, columnar growth of hexagonal crystallites whose c axis is oriented along [001]. In either case, the RHEED pattern invariably switches to an apparently N-induced (3×3) reconstruction, the nature of which is as yet unknown. The formation of a cubic template manifests itself by the subsequent appearance of diffuse spots at the expected position for cubic GaN which elongate and transform to streaks within ≈ 100 Å of GaN deposition. A predominantly streaky RHEED pattern, along with a clear $2\times$ reconstruction along all major azimuths, is observed after about 500 Å of deposition. The measurements shown below are taken after 1000 Å of GaN growth, after which the surface is sufficiently smooth for accurate RHEED recordings.

Figure 1 displays x-ray reciprocal space maps[5] for two GaN layers grown (a) under N excess and (b) under near-stoichiometric conditions. Besides the (002) reflections of the GaAs substrate, the (002) reflections of zinc-blende GaN are visible in both scans. The additional diffraction feature detected for the sample in (a) arises from the $(10\bar{1}1)$ reflection of wurtzite GaN domains oriented such that [0001] $\|[111]B$. Note that the intensity of the wurtzite and the zinc-blende reflections in (a) are of comparable intensity. We point out that the commonly employed x-ray scans, regard-

 © 1995 The American Physical Society

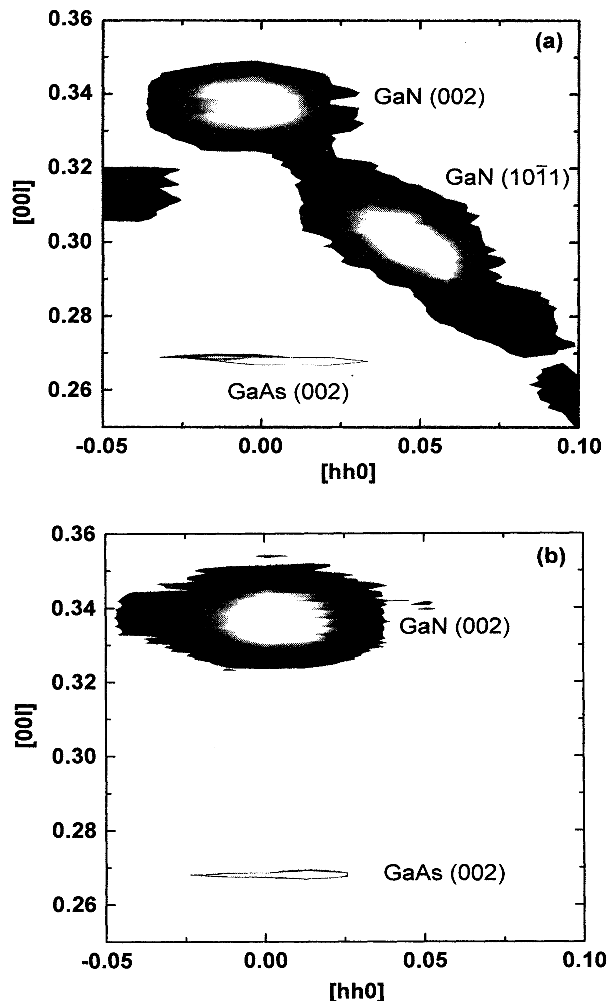

FIG. 1. X-ray reciprocal space maps of GaN layers on GaAs(001) grown under (a) N-excess and (b) stoichiometric conditions. The map is in units of $\lambda/2d$, where λ is the wavelength of the Cu $K\alpha_1$ line (1.5405 Å) and d is the lattice spacing in the given direction. Intensity increases from blue over red to yellow. The nature of each reflection is indicated in the figure.

less of being taken in the θ-2θ (i.e., along [001]) or the ω (i.e., along $[hh0]$) modes, are insufficient for detecting hexagonal grains other than oriented such that [0001]‖[001]. As already stressed by Lei, Ludwig, and Moustakas,[4] these simple scans may prove the existence of the cubic phase, but by no means the absence of hexagonal components. In addition to detailed x-ray measurements, such as carried out in the work of Lei, Ludwig, and Moustakas and here, other experimental techniques may serve as valuable and, perhaps, more convenient tools for detecting hexagonal components in supposedly cubic GaAs films.

Indeed, SEM shows that the conucleation of cubic and hexagonal grains, triggered by a N excess during growth, leads to a severe roughening of the surface morphology. Sometimes, crystallites having the characteristic hexagonal *habitus* are found. Luminescence spectra of such films exhibit, besides lines in the region between 3.0 and 3.27 eV which we attribute to the cubic phase, an additional line at 3.47 eV which is close to the position of the hexagonal band gap. This line has been frequently observed for supposedly purely cubic GaAs films,[3] but in our experience its appearance correlates with the presence of a significant volume fraction of hexagonal components as also suspected by Ramírez-Flores *et al.*[7] In fact, Raman measurements of these GaN films exhibit, in addition to the cubic TO- and LO-phonon modes, a strong resonance at the position of the E_2 (high) phonon characteristic for the hexagonal modification. In contrast, Ga-rich conditions result in smooth films intersected by cubic crystallites, which nucleate inside Ga droplets via the vapor-liquid-solid mechanism.[8] The luminescence of these films is dominated by the shallow, probably excitonic transition at 3.27 eV related to the cubic phase. No higher energy line related to hexagonal grains is observed for such samples, and also no E_2 (high) phonon can be detected by Raman spectroscopy. However, high electron concentrations up to 8×10^{18} cm^{-3} are measured for all samples grown under Ga-rich conditions. The obvious conclusion we draw from these findings is that any deviation from stoichio-

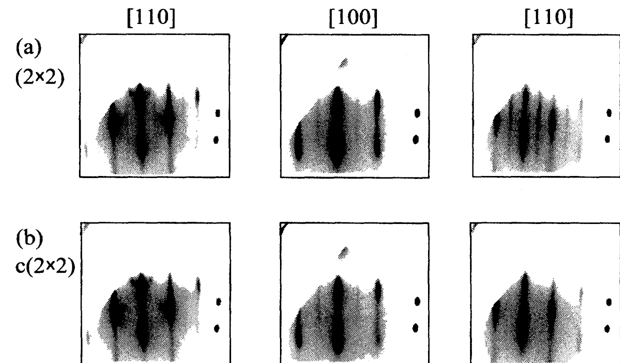

FIG. 2. RHEED patterns taken during growth along the [110], [100], and [$\bar{1}$10] azimuths for two different V/III ratios. The conditions employed in (a) correspond to a slight N excess, whereas (b) was recorded at near stoichiometry. The patterns in (a) constitute a (2×2) and those in (b) a $c(2\times2)$ reconstruction. The patterns are contrast inverted for better visibility. The two spots on the right-hand side of each pattern stem from light-emitting diodes signalizing the "open" state for both Ga and N shutters.

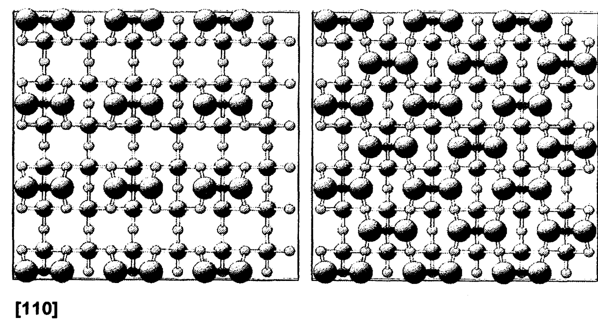

FIG. 3. Surface structure models for the experimentally observed (2×2) (left) and $c(2\times2)$ (right) reconstructions. N and Ga atoms in the second and third layers are represented by orange and blue spheres, and Ga surface dimers in the topmost layer are represented by oversized blue spheres connected by the dimer bond.

metric conditions deteriorates crystal quality in one way or another, and thus has to be avoided.

Figure 2 displays the RHEED patterns obtained along all major azimuths after ≈1000 Å of GaAs growth (a) under slight N excess and (b) near-stoichiometric conditions. All patterns only exhibit diffraction features of the cubic phase of the GaN film. Along the [110] azimuth, additional spots near the (004) reflection and diffuse streaks along the ⟨111⟩ directions are observed, which originate from twins and from a high density of stacking faults, respectively, both of which are formed on the two inclined $\{111\}B$ planes. The hexagonal grains revealed in Fig. 1(a) for the sample grown under N-rich conditions are, in general, undetectable by RHEED since the diffraction conditions are not satisfied for the RHEED geometry. The lattice constant of the cubic phase is determined to be (4.53 ± 0.01) Å by analyzing the separation of the transmission reflections, in agreement with the x-ray measurements of Powell *et al.*[3] Most important, however, is the appearance of (2×2) and $c(2\times 2)$ reconstructions in (a) and (b), respectively. Since surface reconstructions are, generally, related to specific stoichiometry ranges in the surface phase diagram,[9] this observation opens the way towards the *in situ* control of surface stoichiometry. In fact, as detailed below, clear surface phase transitions are observed depending on the relative amount of Ga and N impinging on the surface.

We first estimate the nature and the coverage of the species related to the reconstructions observed. Under a permanently supplied active N flux the (001) GaN surface is unreconstructed and exhibits the (1×1) bulk symmetry. An impinging Ga flux alone induces first (at 0.5 ML Ga coverage) a (2×2) reconstructed surface which is transformed at higher Ga coverage (1 ML) into a $c(2\times 2)$ reconstruction. In vacuum, the surface relaxes invariably towards the (2×2) reconstruction which is stable up to the highest temperatures used in this study (680 °C). We thus conclude that the (1×1) pattern corresponds to a N terminated surface whereas both the (2×2) and $c(2\times 2)$ patterns are related to Ga stabilized surfaces covered with 0.5 and 1.0 ML of Ga, respectively.

In Fig. 3 we display structural models of the (2×2) (a) and the $c(2\times 2)$ (b) reconstructions consistent with the experimentally determined Ga coverages as well as the reconstruction symmetries. The (2×2) reconstruction is thought to be formed by Ga dimer rows along the [110] direction which are separated by one missing dimer row. Further Ga deposition results in the filling of the missing dimer rows at the center positions of the four adjacent Ga dimers. At full monolayer coverage, this arrangement corresponds to the $c(2\times 2)$ reconstruction.

The different stability of the (2×2) and $c(2\times 2)$ reconstructions is an interesting point which deserves a brief comment. Both of these reconstructions are spanned up by chemically identical basic units, namely, the Ga dimers. Simple arguments considering the electronic[10] and mechanical[11] stability of the surface have, however, also difficulties in convincingly explaining this stability difference. While it is true that the (2×2) reconstructed surface is less polar than the $c(2\times 2)$ one ($-1e$ versus $+2e$ per unit mesh), and, additionally, that the (2×2)-related dimer bonds are less strained than those building up the $c(2\times 2)$ reconstruction, it is not clear how these qualitative differences actually are related to the surface energy. For a quantitative understanding of this phenomenon, *ab initio* total-energy calculations are needed. In the following, we will thus take the stability difference between (2×2) and $c(2\times 2)$ reconstructions as an empirical fact.

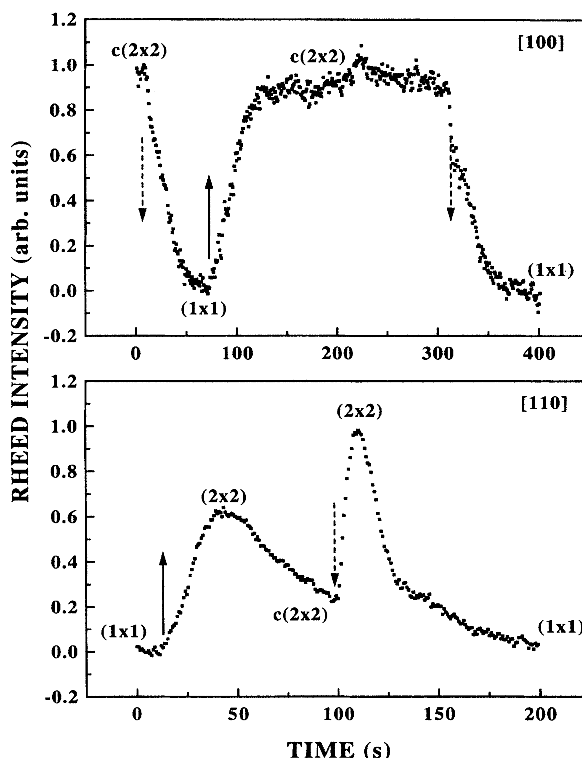

FIG. 4. Experimental RHEED intensity transients of the half-order reconstruction streak along [100] (a) and $[\bar{1}10]$ (b) for the dynamic (growing) surface. Both the impinging Ga and active N fluxes are ≈0.03 ML/s. Upward and downward arrows indicate opening and closing of the Ga shutter.

Having determined the nature of the reconstructions observed, it remains to understand their dynamics for being able to monitor the surface stoichiometry in real time during growth. In other words, we are seeking for transitions between the surface constituents of GaN at actual growth conditions. Figure 4 shows examples of such transients taken along [100] and [110]. The Ga flux used for these experiments was 0.03 ML/s, and substrate temperature was set to 620 °C. Transitions between the surface reconstructions take place when either N and/or Ga flux are impinging onto the growth front. The present example corresponds to a stable $c(2\times 2)$ reconstruction during growth without accumulation of liquid Ga on the surface. These were the conditions used for the growth of the GaN film whose reciprocal space maps [Fig. 1(b)] demonstrate it to be purely cubic. Monitoring the reconstruction intensity during growth thus provides a means for the determination and control of appropriate growth conditions.

Summarizing, we have presented an approach for the *in situ* control of surface stoichiometry for the synthesis of zinc-blende GaN on GaAs(001). Films grown under near-

stoichiometric conditions are, in fact, purely cubic *for all practical purposes*, in the sense that no traces of hexagonal components can be detected by any experimental technique employed here. As will be discussed in a forthcoming publication, such films are furthermore distinguished by a smooth surface morphology, a low background carrier concentration, and the absence of deep-level luminescence.

We are much indebted to Johann Menninger and Uwe Jahn for SEM and cathodoluminescence, Robert Klann, Jochen Müllhäuser, and Lutz Schrottke for photoluminescence, and Manfred Ramsteiner for Raman measurements. We acknowledge financial support of this work by the Bundesministerium für Bildung und Forschung der Bundesrepublik Deutschland (BMBF).

[*]Permanent address: Kyushu Institute of Technology, 1-1, Sensui-cho, Tobata-ku, Kita-kyushu 804, Japan.

[1]P. Lawaetz, Phys. Rev. B **5**, 4039 (1972).

[2]S. Strite and H. Morkoç, J. Vac. Sci. Technol. B **10**, 1237 (1992).

[3]M. J. Paisley, Z. Sitar, J. B. Posthill, and R. F. Davis, J. Vac. Sci. Technol. A **7**, 701 (1989); S. Strite, J. Ruan, Z. Li, A. Salvador, H. Chen, D. J. Smith, W. J. Choyke, and H. Morkoç, J. Vac. Sci. Technol. B **9**, 1924 (1991); T. Lei, T. D. Moustakas, R. J. Graham, Y. He, and S. J. Berkowitz, J. Appl. Phys. **71**, 4933 (1992); R. C. Powell, N.-E. Lee,Y.-W. Kim, and J. E. Greene, *ibid.* **73**, 189 (1993); H. Liu, A. C. Vrenkel, J. G. Kim, and R. M. Park, *ibid.* **74**, 6124 (1993); T. S. Cheng, L. C. Jenkins, S. E. Hooper, C. T. Foxon, J. W. Orton, and D. E. Lacklison, *ibid.* **66**, 1509 (1995).

[4]T. Lei, K. F. Ludwig, Jr., and T. D. Moustakas, J. Appl. Phys. **74**, 4430 (1993).

[5]At pressures p above 2×10^{-4} Torr, the mean free path gets of the order of the distance L between Ga source and substrate. The effective Ga flux j_{Ga} impinging onto the surface is thus reduced according to $j_{\mathrm{Ga}}=j^0_{\mathrm{Ga}}(1+\pi\sigma Lp/kT)^{-1}$, where j^0_{Ga} is the Ga flux in vacuum, σ is the molecular cross section, and kT is the thermal energy.

[6]The measurements are performed with a double-crystal diffractometer equipped with two asymmetrically cut, grooved silicon crystals in $(-n,+n)$ setting, and employing Cu $K\alpha_1$ radiation from a rotating-anode source.

[7]G. Ramírez-Flores, H. Navarro-Contreras, A. Lastras-Martínez, R. C. Powell, and J. Greene, Phys. Rev. B **50**, 8433 (1994).

[8]A. Tatarchenko, in *Handbook of Crystal Growth: Thin Films and Epitaxy*, edited by D. T. J. Hurle (North-Holland, Amsterdam, 1994), Vol. 2b, p. 1011.

[9]L. Däweritz and R. Hey, Surf. Sci. **236**, 15 (1990).

[10]W. A. Harrison, J. Vac. Sci. Technol. **16**, 1492 (1979).

[11]R. M. Martin, Phys. Rev. B **1**, 4005 (1970).

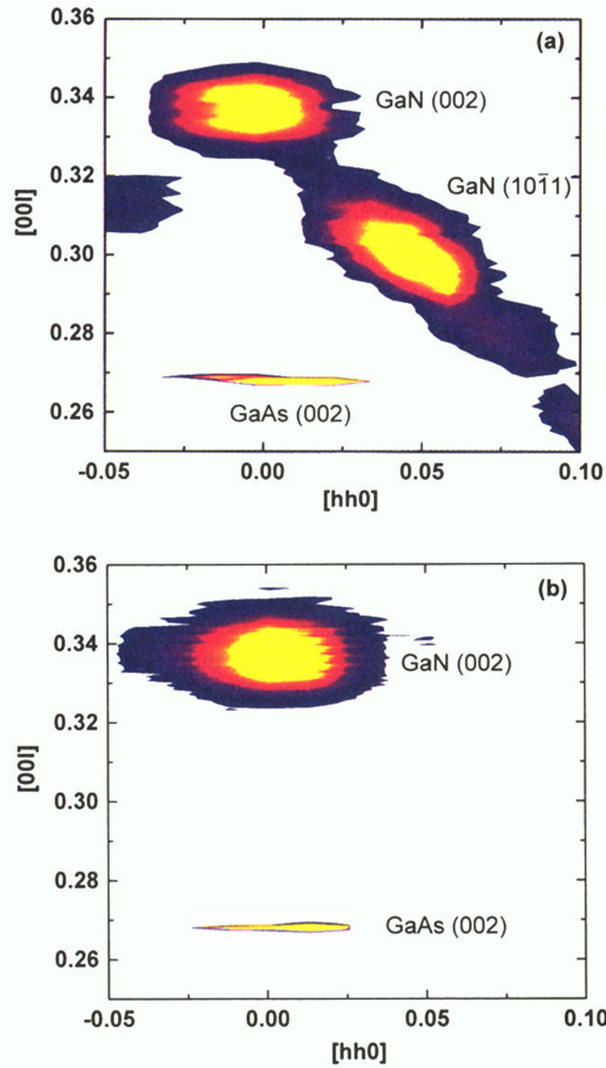

FIG. 1. X-ray reciprocal space maps of GaN layers on GaAs(001) grown under (a) N-excess and (b) stoichiometric conditions. The map is in units of $\lambda/2d$, where λ is the wavelength of the Cu $K\alpha_1$ line (1.5405 Å) and d is the lattice spacing in the given direction. Intensity increases from blue over red to yellow. The nature of each reflection is indicated in the figure.

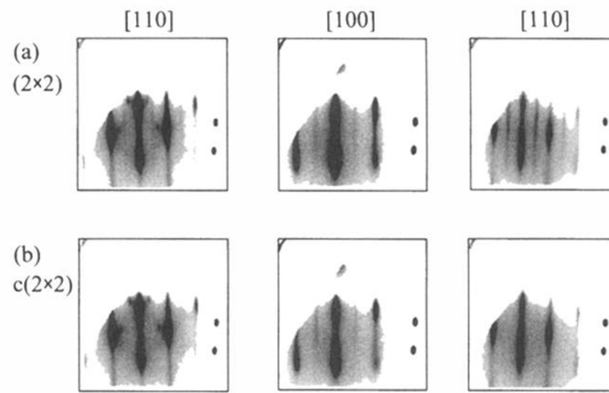

FIG. 2. RHEED patterns taken during growth along the [110], [100], and [$\bar{1}10$] azimuths for two different V/III ratios. The conditions employed in (a) correspond to a slight N excess, whereas (b) was recorded at near stoichiometry. The patterns in (a) constitute a (2×2) and those in (b) a $c(2\times2)$ reconstruction. The patterns are contrast inverted for better visibility. The two spots on the right-hand side of each pattern stem from light-emitting diodes signalizing the "open" state for both Ga and N shutters.

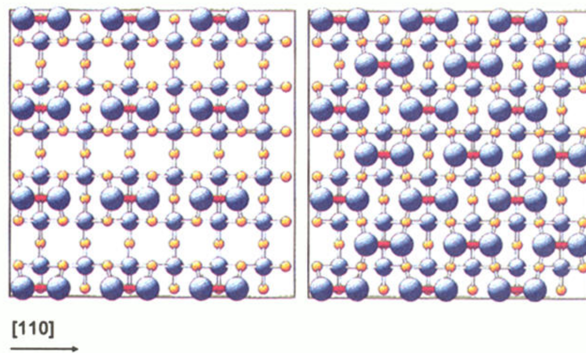

FIG. 3. Surface structure models for the experimentally observed (2×2) (left) and $c(2\times2)$ (right) reconstructions. N and Ga atoms in the second and third layers are represented by orange and blue spheres, and Ga surface dimers in the topmost layer are represented by oversized blue spheres connected by the dimer bond.