Transition between the 1×1 and $(\sqrt{3} \times 2\sqrt{3})R30°$ surface structures of GaN in the vapor-phase environment

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Out-of-plane structures of the GaN(0001) surface in the metal-organic chemical vapor deposition (MOCVD) environment have been determined using *in situ* grazing-incidence x-ray scattering. We measured $11\bar{2}l$ crystal truncation rod intensities at a variety of temperatures and ammonia partial pressures on both sides of the 1×1 to $(\sqrt{3} \times 2\sqrt{3})R30°$ surface phase transition. The out-of-plane structure of the $(\sqrt{3} \times 2\sqrt{3})R30°$ phase appears to be nearly independent of temperature below the transition, while the structure of the 1×1 phase changes increasingly rapidly as the phase transition is approached from above. A model for the structure of the 1×1 phase with a partially-occupied top Ga layer agrees well with the data. The observed temperature dependence is consistent with a simple model of the equilibrium between the vapor phase and the surface coverage of Ga and N. In addition, we present results on the kinetics of reconstruction domain coarsening following a "quench" into the $(\sqrt{3} \times 2\sqrt{3})R30°$ phase field.

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A. Introduction

The use of GaN-based materials has allowed dramatic improvements to be made in optoelectronic devices such as blue lasers [1]. The production of these devices typically relies on epitaxial crystal growth using metal-organic chemical vapor deposition (MOCVD) [2]. Although the understanding of atomic-scale surface structure during MOCVD growth would greatly facilitate optimization of GaN-based devices, there are few probes of surface structure compatible with the near-atmospheric-pressure, high-temperature, reactive vapor-phase environment of this process. Our approach to this challenge has been to use x-ray scattering to conduct *in situ* measurements of GaN surface structure in the MOCVD environment [3].

In previous work [4], we presented grazing-incidence x-ray scattering results that characterize the in-plane surface structure of GaN(0001) in the MOCVD environment. We found that the surface equilibrium phase diagram as a function of temperature and ammonia partial pressure shows a transition between two phases with structures having 1×1 and $(\sqrt{3} \times 2\sqrt{3})R30°$ symmetries. We determined the in-plane structure of the $(\sqrt{3} \times 2\sqrt{3})R30°$ phase to be a novel "missing row" structure with 1/3 of the surface Ga atoms absent, as shown in Fig. 1. In this paper, we present further x-ray scattering results that characterize the out-of-plane surface structure of these surface phases. A model for the structure of the 1×1 phase with a partially-occupied top Ga layer agrees well with the data. The observed temperature dependence is consistent with a simple model of the interaction between the chemistry of the vapor phase and the surface structure. In addition, we present results on the kinetics of reconstruction domain coarsening following a "quench" into the $(\sqrt{3} \times 2\sqrt{3})R30°$ phase field. Related *in situ* x-ray scattering studies of growth on these surfaces have been published elsewhere [5].

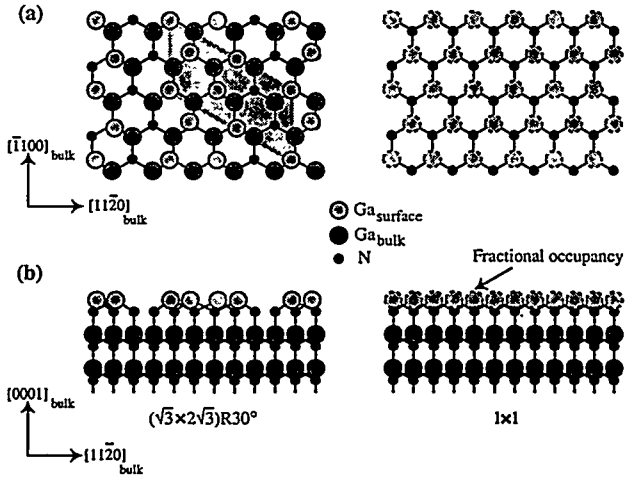

FIG. 1. (a) In-plane structure of the GaN(0001) $(\sqrt{3} \times 2\sqrt{3})$R30° and 1×1 phases, obtained previously [4]. In the 1×1 structure the top Ga-layer has fractional occupancy. (b) Schematic of the GaN(0001) structures normal to the surface.

B. Experimental

These *in-situ* x-ray studies of the GaN surface structure were carried out at the BESSRC undulator beamline 12-ID-D at the Advanced Photon Source, as described previously [4]. We used a vertical-flow MOCVD chamber mounted on a "z-axis" surface diffractometer designed for grazing-incidence x-ray scattering [3]. To penetrate the 2-mm-thick quartz walls of the chamber, an x-ray energy of 24 keV was used. In order to maximize the scattering from the surface relative to the bulk, the incident angle was chosen to be near the critical angle (0.12 degrees). The width of the GaN bulk diffraction peaks indicated an in-plane crystal mosaic of 0.17 degrees. The polarity of the surface was confirmed to be GaN(0001) (i.e. Ga-face) by convergent-beam electron diffraction.

C. Out-of-Plane Structure

Because of the termination of the bulk crystal at the surface, streaks of scattering intensity extend from the Bragg peaks along the direction of the surface normal. These streaks, often called crystal truncation rods (CTRs) [6], are sensitive to the out-of-plane surface structure, including roughness, relaxation, and reconstructions [7]. We measured $11\bar{2}l$ CTR intensities at a variety of temperatures and ammonia partial pressures in both the 1×1 and $(\sqrt{3} \times 2\sqrt{3})R30°$ regions of the phase diagram, as shown in Fig. 2. A typical series of CTR scans at various temperatures for a fixed ammonia partial pressure are shown in Fig. 3. In general, at higher temperatures the CTR is more intense and has a minimum at a higher value of l, although at the highest temperature

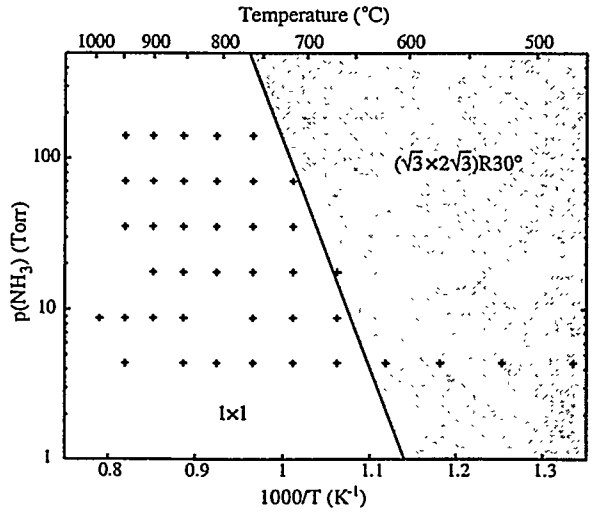

FIG. 2. Crosses show the $p(NH_3)$ and temperature conditions investigated, superimposed on the equilibrium surface phase diagram for GaN(0001) [4]. Shaded area is the $(\sqrt{3} \times 2\sqrt{3})R30°$ phase field.

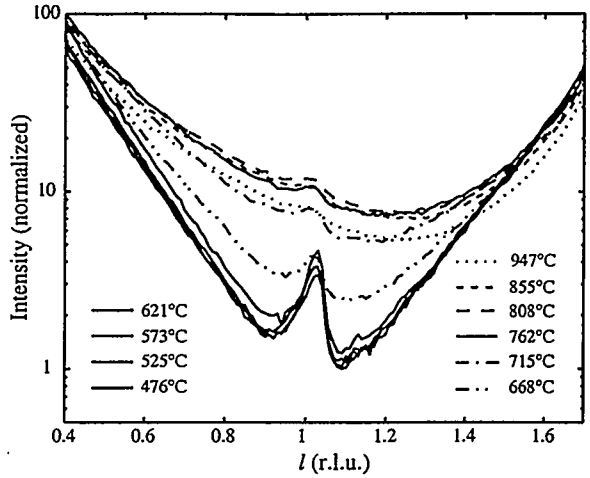

FIG. 3. Scans along the $11\bar{2}l$ CTR from $l = 0.4$ to 1.7, at various temperatures for fixed $p(NH_3) = 4.4$ Torr. The reciprocal lattice units used for l correspond to the room-temperature lattice constant of GaN, $c = 5.178$Å; thermal expansion is neglected. Each scan was aligned in h and k to the position of the CTR at that temperature, and backgrounds obtained at $\Delta h = 0.003$ have been subtracted. The measured intensity is normalized to the minimum of the scans taken below the phase transition.

the intensity begins to decrease. As the temperature is lowered, the intensity is reduced and the CTR becomes more symmetric as the minimum shifts from $l = 1.25$ towards $l = 1$. A narrow peak near $l = 1$ appears as the intensity of the CTR is reduced. At the four lowest temperatures, the curves overlap; the CTR becomes independent of temperature. The temperature below which the CTR does not change corresponds to the temperature at which the $(\sqrt{3} \times 2\sqrt{3})R30°$ reconstruction is formed for this ammonia partial pressure (~ 638°C).

The small peak at $l = 1$ in the CTR would be a forbidden reflection for a perfect hexagonal crystal. By changing the incident angle (and thereby changing the penetration depth), we found that this peak does not originate from the surface, but instead from the bulk of the sample. We believe that this peak originates from defects in the bulk of the sample such as threading screw dislocations which destroy the exact ordering of adjacent GaN (0002) layers needed to cancel the scattering amplitude at the $11\bar{2}1$ position. (Note that any cubic component in the film arising from basal plane stacking faults, which have been observed in the nucleation layer [8], would not generate peaks at this position.) For purposes of extracting the surface structure, we have ignored this peak.

By masking out the data in the region of the $11\bar{2}1$ peak ($l = 0.92$ to 1.09) and fitting the remaining data to a polynomial function, we were able to extract the position and the intensity of the minimum in the CTR for all T and $p(NH_3)$ conditions investigated. These are shown in Fig. 4(a) and (b), plotted as a function of the temperature above the phase boundary of the 1×1 to

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$(\sqrt{3}\times 2\sqrt{3})R30°$ transition. The transition temperature T_{tr} as a function of $p(NH_3)$ was calculated from the relationship $p(NH_3)$(Torr)=exp(-3.00eV/kT_{tr}+39.69), which was obtained from the in-plane scattering data [4]. All of the points fall onto the same master curves, indicating that, to a good approximation, the dependences of the structure on temperature and ammonia partial pressure can be described by a single functional dependence on $T - T_{tr}$. The out-of-plane structure of the $(\sqrt{3}\times 2\sqrt{3})R30°$ phase appears to be nearly independent of temperature below the transition, while the structure of the 1×1 phase changes increasingly rapidly as the phase transition is approached from above.

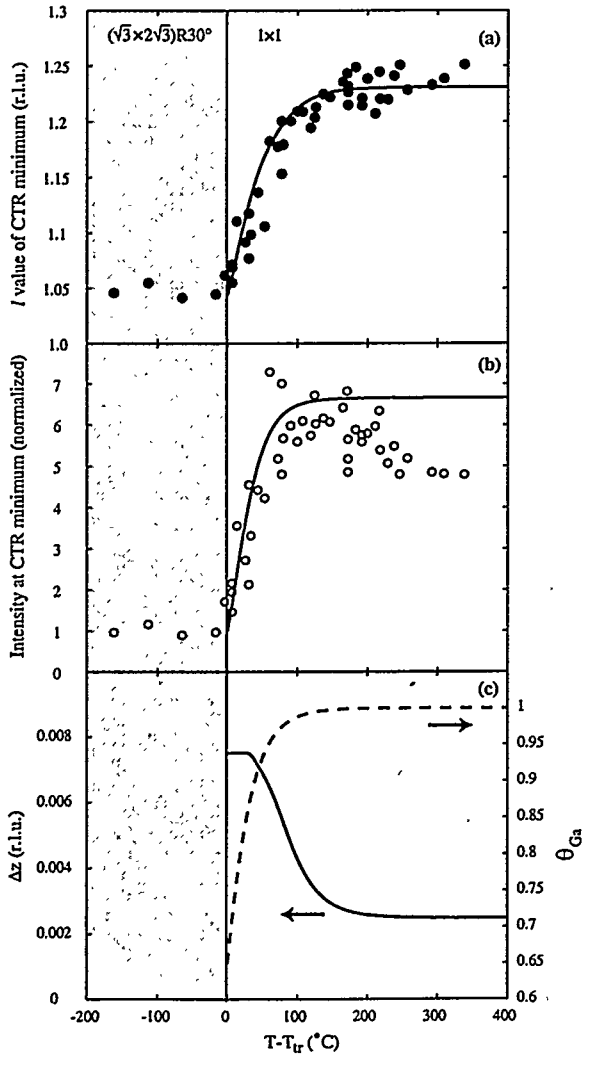

FIG. 4. (a) Position and (b) intensity of the minimum in the $11\bar{2}l$ CTR near $l = 1$, as a function of the temperature above the phase boundary of the 1×1 and $(\sqrt{3} \times 2\sqrt{3})R30°$ transition. Solid lines corresponds to the calculated position and intensity of the minimum based on the parameters shown in (c). (c) Expansion of the top Ga layer and its fractional occupancy as a function of temperature determined from equation (4).

In order to understand the structural changes underlying these changes in the CTR shape and intensity, we have made calculations of the $11\bar{2}l$ CTR intensity based on a model of the GaN(0001) surface. The reflection amplitude for the CTR of a perfectly-terminated GaN(0001) surface is given by [6]

$$r_0 = \frac{4\pi i R}{Aq} F_{GaN}(1 - \exp[2\pi i l])^{-1}, \qquad (1)$$

where R is the Thomson electron radius, A is the in-plane unit cell area (8.79Å^2 for GaN), q is the length of the scattering vector, F_{GaN} is the structure factor of a unit cell, and absorption has been neglected. The reflection amplitude for a crystal where the structure factor of the outermost unit cells F_{top} differs from that of the bulk is given by

$$r = r_0 \exp[2\pi i l] + \frac{4\pi i R}{Aq} F_{top}. \qquad (2)$$

The unit cell structure factor for the 1×1 structure shown in Fig. 1, where the outermost Ga layer has a fractional occupancy of θ_{Ga} and this layer is displaced uniformly by Δz along the surface normal, is given by

$$\begin{aligned} F_{top} = {} & f_N(\exp[2\pi i \frac{5}{8} l] + \exp[2\pi i (\frac{1}{3}h + \frac{2}{3}k + \frac{1}{8}l)]) + \\ & f_{Ga}(\exp[2\pi i (\frac{1}{3}h + \frac{2}{3}k + \frac{1}{2}l)] + \\ & \theta_{Ga} \exp[-2\pi i \Delta z]) \end{aligned} \qquad (3)$$

Note that for $\theta_{Ga} = 1$ and $\Delta z = 0$ this is identical to the structure factor of a bulk unit cell. The measured intensity of the CTR is given by $|r|^2$ multiplied by polarization and geometrical correction terms. We have calculated $11\bar{2}l$ CTR intensities for surfaces with a variety of different terminations. For a Ga-terminated surface, the CTR intensity is very sensitive to both the fractional occupancy θ_{Ga} and relaxation Δz of the top layer. In contrast, because of the lower density, the intensity from an N-terminated surface is affected much less by both occupancy and relaxation. The large observed CTR intensity changes are therefore consistent with that of a Ga-terminated surface, which agrees with our conclusion based on the in-plane reconstruction data [4]. A decrease in the occupancy in the top Ga layer causes a decrease in the CTR intensity, whereas a change in the surface relaxation predominantly shifts the position of the CTR minimum.

To make this model quantitative, we have used an expression for θ_{Ga} as a function of temperature obtained from a simple description of the equilibrium between the vapor phase and the surface coverage of Ga and N. At these temperatures N is much more volatile than Ga [9], so the adsorption and desorption of N determines the surface stoichiometry. Assuming that the N activity in

the vapor phase is given by $p(NH_3)$, one can express the ratio of N to Ga coverage as

$$\frac{1-\theta_{Ga}}{\theta_{Ga}} = \frac{1-\theta_{Ga}^{tr}}{\theta_{Ga}^{tr}} \frac{p(NH_3)}{p(NH_3)^{tr}} = \frac{1-\theta_{Ga}^{tr}}{\theta_{Ga}^{tr}} \exp\left(\frac{-3.00\text{eV}}{kT}\frac{T-T_{tr}}{T_{tr}}\right), \quad (4)$$

where it has been assumed that the Ga occupancy at the transition, θ_{Ga}^{tr}, is a fixed value, and the relationship between the ammonia partial pressure at the transition $p(NH_3)^{tr}$ and temperature measured in previous work [4] has been used. One can see that the Ga occupancy decreases as temperature decreases, and the relationship between θ_{Ga} and $T - T_{tr}$ is relatively independent of $p(NH_3)$ for a range of temperatures near T_{tr}, in agreement with the behavior of the data.

Figure 4(c) shows a plot of θ_{Ga} versus $T - T_{tr}$ chosen from this model, using $\theta_{Ga}^{tr} = 0.65$ and $p(NH_3) = 4.4$ Torr. Values of surface relaxation Δz were obtained as a function of θ_{Ga} so that the calculated position and intensity of the CTR minimum tracked those of the data. These values are also plotted in Fig. 4(c). Figure 5 shows CTR profiles calculated using these θ_{Ga} and Δz values, for various temperatures above T_{tr}. One can see that the changes in the observed CTR profiles can be qualitatively reproduced by the model. The calculated position and intensity of the CTR minimum as a function of $T-T_{tr}$ are plotted with all of the measured values in Fig. 4(a) and (b). The predicted size of change in the intensity agrees well with the data. We believe that the decrease in intensity observed at high temperature is due to Debye-Waller effects not included in the model. The value for Ga occupancy at the transition, $\theta_{Ga}^{tr} = 0.65$, agrees with the value of 2/3 found for the $(\sqrt{3}\times 2\sqrt{3})R30°$ structure [4], and the small values of relaxation Δz obtained are also physically reasonable. The model predicts that the top Ga layer is slightly relaxed outward at full coverage well above T_{tr}, and that the outward relaxation increases at lower coverages near T_{tr}. The model tends to overestimate the rate of change of the intensity of the CTR minimum near T_{tr}, which may reflect oversimplification of the relationship used for the temperature dependence of θ_{Ga}, equation (4). We do not expect quantitative agreement of the calculated and measured CTRs in Figures 5 and 3 because our calculation of the CTR intensity does not include surface roughness, which has the effect of lowering the intensity near the anti-Bragg condition ($l = 1$).

An assumption in this model for the 1×1 structure is that the in-plane coordinates of the top-layer Ga atoms remain at their bulk values. In contrast, for the $(\sqrt{3}\times 2\sqrt{3})R30°$ phase, we have found that the top layer Ga are displaced slightly in-plane, forming a herring-bone pattern of dimer rows [4]. Such in-plane displacements affect not only the in-plane scattering, but also the shape of the CTR in the out-of-plane direction, and hence the

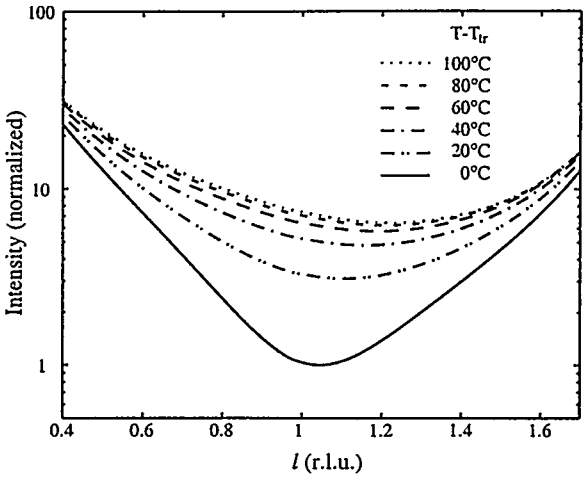

FIG. 5. Intensities of the $11\bar{2}l$ CTR for the 1×1 phase calculated from equation 2. Values for the top Ga layer expansion Δz and its fractional occupancy θ_{Ga} are shown in Fig 4(c). The intensity is normalized to the minimum intensity in order for direct comparison with the measured data shown in Fig. 3.

values of Δz and θ_{Ga} that best fit the data. In particular, to obtain agreement between the calculated and observed position of the CTR minimum for the $(\sqrt{3}\times 2\sqrt{3})R30°$ structure at $\theta_{Ga} = 2/3$ requires a value of relaxation $\Delta z = 0.030$, which is significantly larger than the value $\Delta z = 0.007$ obtained for the 1×1 structure using bulk in-plane positions. The continuous variation of the shape of the CTR observed as the boundary between the 1×1 and $(\sqrt{3}\times 2\sqrt{3})R30°$ phases is crossed provides evidence that the structural change is continuous. This implies that dimerization is occurring in the 1×1 phase near T_{tr}, although the dimers have not arranged into a reconstruction with long-range order. Since this in-plane relaxation is not part of the model for the 1×1 phase, one must use caution in applying this model near T_{tr}.

D. Dynamics of Reconstruction Formation

We observed the kinetics of formation of the $(\sqrt{3}\times 2\sqrt{3})$R30° phase by monitoring the 20_{surf} $(\frac{1}{3}\frac{1}{3}\frac{2}{3}0_{bulk})$ reconstruction peak following a "quench" across the phase boundary produced by rapidly changing the ammonia partial pressure from 35 to 140 Torr at a temperature of 715°C. As shown in Fig. 6(a), a peak appeared and grew in intensity as a function of time. The decreasing width of the peak reflects the increasing domain size of the reconstruction. In such a domain coarsening process, the peak width W and domain size L are expected to follow a power law in time [10],

$$W^{-1} \propto L \propto (t - t_0)^n. \quad (5)$$

Figure 6(b) shows that peak width as a function of time does indeed follow a power law, with an exponent

$n = 1/4$. In a second experiment, the phase boundary was crossed by quenching the temperature from 760 to 715 °C at $p(NH)_3 = 140$ Torr. A similar time dependence of the reconstruction peak was observed which again followed equation (5) with $n = 1/4$. Although such power-law behavior is expected for a coarsening process, the observed value of the exponent is unanticipated. From dynamic scaling theory [11], one expects $n = 1/2$ for this class of system (non-conserved scalar order parameter with a few ground states). The observed value of n less than 1/2 may be an example of a transient regime or of pinning effects due to the multiple ground states which have been observed in some simulations [12]. One may also speculate that anisotropy in the domain structure could produce a different coarsening mechanism (e.g. coalescence of stripes by wall meandering [13]) which would obey a power law with $n = 1/4$. The observation of this unusual coarsening exponent indicates that the behavior of the $(\sqrt{3} \times 2\sqrt{3})$R30° phase may still hold some surprises for future studies.

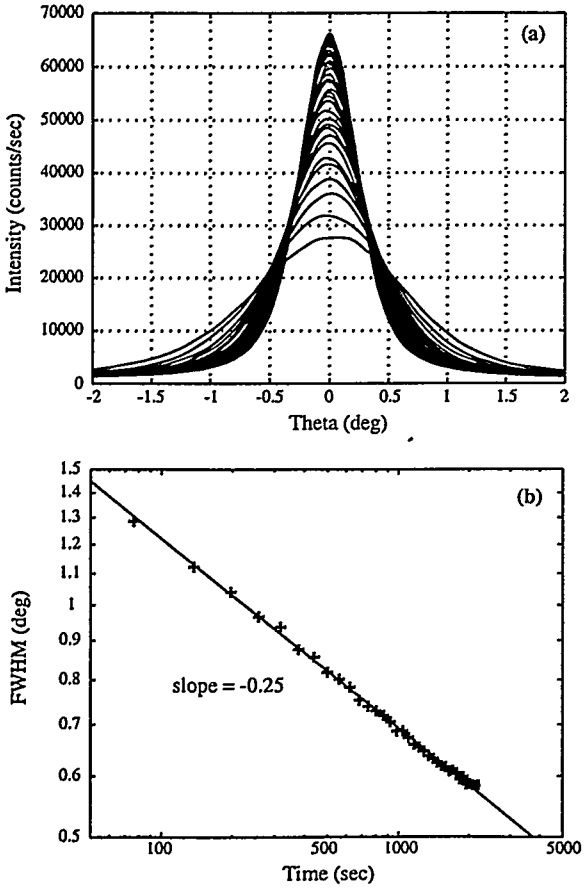

FIG. 6. (a) Theta rocking curves through the 20_{surf} reconstruction peak as a function of time after increasing the ammonia partial pressure and crossing the phase boundary at 715°. (b) Peak widths of the rocking curves are shown with the best power law fit.

E. Discussion and Conclusions

These results provide an example of an equilibrium response of a surface structure due to interaction with the vapor phase environment. As such, they demonstrate the power of x-ray scattering as a penetrating, *in situ* probe of surface structure for a broad class of problems. Such studies can provide unique direct information about the vapor/surface interaction and vapor-phase chemistry. To date, models of vapor-phase growth [9] have often relied on information obtained from studies in vacuum.

This study provides the first information about the atomic structure of the technologically-important high temperature 1×1 phase of GaN(0001) in the MOCVD environment. The results are consistent with a fairly simple description. At high temperature, the surface is terminated by a complete Ga layer with little relaxation. The Ga occupancy decreases with decreasing temperature, following a simple law based on a 3.0 eV activation energy for N desorption. When θ_{Ga} reaches a value of 2/3, the top Ga layer orders in-plane to form the $(\sqrt{3}\times 2\sqrt{3})R30°$ structure.

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