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Step bunching on the vicinal GaN(0001) surface

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Nominally 2° vicinal GaN(0001) surfaces exhibit monolayer-height steps at 990 °C in the metal-organic chemical vapor deposition environment. Real-time x-ray scattering observations at 715–990 °C indicate that there is a tendency for step bunching during growth. Below 850 °C, step bunches nucleated during growth remain and coarsen after growth, while above 850 °C, the surface reverts to monolayer-height steps after growth. Surfaces vicinal toward the $\{1\bar{1}00\}$ and the $\{11\bar{2}0\}$ planes exhibit similar behavior. We suggest a simple equilibrium surface orientational phase diagram for vicinal GaN(0001) that is consistent with these observations.

Device-quality gallium nitride films are typically grown by metal-organic chemical vapor deposition (MOCVD) at high temperature[1] under step-flow conditions.[2] In this growth regime, deposited species are more likely to diffuse to and attach at existing surface steps than to form additional steps by nucleating new islands.[3] The surface morphology thus evolves primarily by the motion of existing steps and the surface remains relatively smooth. While the effects of MOCVD parameters such as temperature and V/III ratio on the quality of GaN films have been studied extensively,[1] the influence of the misorientation from the low index (0001) facet has received less attention.[4,5] Increasing the vicinal angle reduces the step spacing and hence is expected to lower the temperature required for step-flow growth. However, both theory and experiments on other materials have shown that growth on vicinal surfaces can lead to kinetic instabilities in the form of step bunching[6–8] and wavy steps.[9] Moreover, the equilibrium morphology of a vicinal surface may consist of two phases, a low index facet mixed with step bunches.[3] Indeed, a previous study of 10-μm-thick GaN films grown by MOCVD on vicinal sapphire substrates found surface morphologies consisting of step bunches and large step-free regions.[4] Our goal is to understand both the equilibrium structure of vicinal GaN(0001) and whether step bunching instabilities occur during growth. In this paper, we report an *in situ*, real-time x-ray scattering investigation of the evolution of surface morphology on nominally 2° vicinal GaN(0001) surfaces during MOCVD and subsequent annealing.

The x-ray scattering experiments were performed at the BESSRC beamline 12-ID-D at the Advanced Photon Source using a system designed for real-time measurements during MOCVD.[2,10] The x rays are incident near the critical angle (0.12° for 24 keV x rays) to enhance the signal from the surface region of the sample. Trimethylgallium (TMG) and NH_3 were used as the precursors with N_2 as the carrier gas. All experiments described here were performed at an NH_3 flow rate of 1.2 standard liters per minute (slpm), a total flow of 5.25 slpm, and a total pressure of 200 Torr. Sample temperatures, accurate to ±5 °C, were calibrated using substrate thermal expansion.[2] In addition to the x-ray experiments, laser reflectivity was used to measure growth and evaporation rates of GaN as a function of temperature.

Vicinal GaN surfaces were prepared by depositing 3-μm-thick GaN films in a separate chamber[11] by atmospheric pressure MOCVD on nominally 2° vicinal $Al_2O_3(0001)$ substrates. The GaN films were found to have an out-of-plane 0002 rocking curve full width at half maximum (FWHM) of 0.061° and an in-plane $11\bar{2}0$ FWHM of 0.10°. For the experiments described below, the in-plane mosaic limits the lateral resolution of the measurement. Samples with surface normals tilted towards both the GaN *A* plane $\{11\bar{2}0\}$ and the *M* plane $\{\bar{1}100\}$ were investigated. Although step morphologies have been found to depend upon orientation,[12,13] in this study we did not find any significant difference in the step bunching behavior between the two orientations.

Images of steps on nominally singular GaN(0001) substrates[12] often show a twilled structure caused by a direction-dependent pairing of adjacent monolayer-height steps (1 ML$\equiv \frac{1}{2}c = 2.59$ Å). This structure could arise because adjacent steps on the (0001) plane of wurtzite GaN have different bonding geometries,[12–14] and hence, different free energies. Thus, three simple possibilities exist for the equilibrium surface structure of 2° vicinal GaN: large (0001) facets separated by step bunches, uniformly spaced monolayer-height steps, or uniformly spaced double-height steps. Figure 1 shows how these three surface structures would affect surface-sensitive features in the x-ray scattering pattern known as crystal truncation rods (CTR's).[15] The CTR's from large (0001) facets are oriented exactly along the *L* direction and connect Bragg peaks. The CTR's from a surface with uniformly spaced steps (or double steps), however, are tilted away from the *L* direction at the vicinal angle. The separation of the CTR's is inversely related to the step (or double step) spacing, and the sharpness of the peaks reflects the uniformity of the spacing.[16] To measure step mor-

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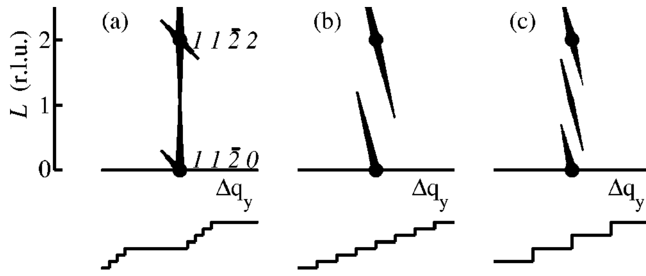

FIG. 1. Schematic of the crystal truncation rods from surfaces with (a) large (0001) facets; (b) monolayer-height steps; and (c) double-height steps. The index L is in reciprocal lattice units (r.l.u.).

phology, we recorded scans through the $11\bar{2}L$ CTR perpendicular to the step direction at fixed L, i.e., in the $11\bar{2}0$ and the $\bar{1}100$ reciprocal-space directions for surfaces vicinal toward the A plane and the M plane, respectively. For simplicity we will refer to both as ''transverse'' scans.

Figure 2(a) shows transverse scans through the $11\bar{2}L$ CTR at different L values measured *in situ* on a sample annealing at 990 °C. The split peak structure in the scans at $L=0.9$ and 1.1 indicates that the CTR's from the $11\bar{2}0$ and $11\bar{2}2$ bulk peaks do not coincide. Figure 2(b) shows the location of the main CTR peaks in the transverse scans at different L. The small central peak remains at $\Delta q_y=0$ independent of L. The CTR profiles show that, at 990 °C, this surface consists primarily of monolayer-height steps with a

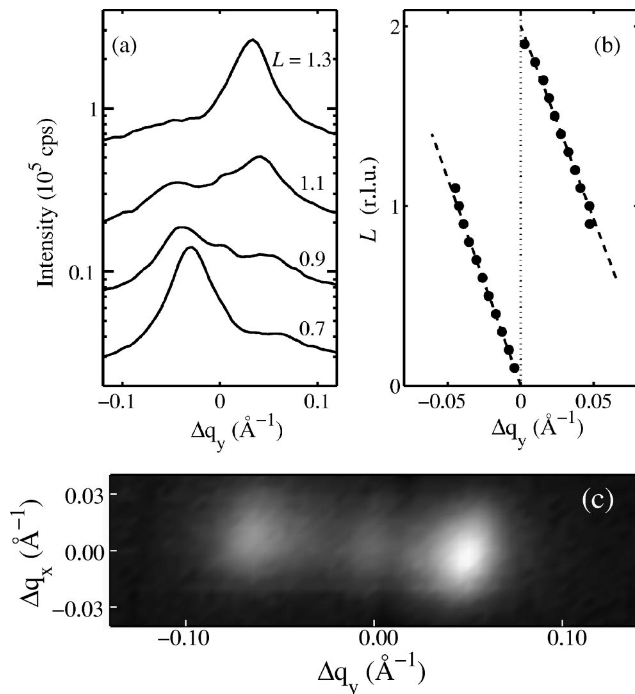

FIG. 2. (a) Transverse scans through the $11\bar{2}L$ CTR at different L from a GaN surface vicinal toward the M plane, annealed at 990 °C. The curves are offset by factors of 3 for clarity. The units of intensity are counts per second (cps) scaled to 100 mA of storage ring current. (b) The location of peaks in transverse scans between $L=0$ and $L=2$. (c) Intensity in the $L=1.1$ plane around the $11\bar{2}L$ position. The directions q_x and q_y are along $\bar{1}100$ and $11\bar{2}0$, respectively.

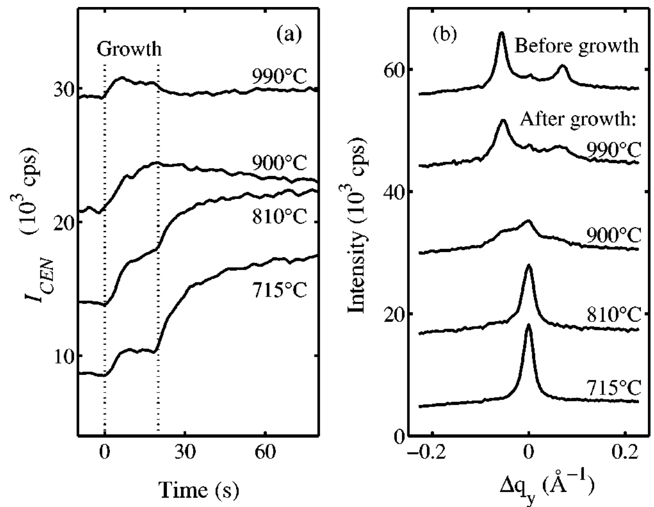

FIG. 3. (a) The evolution of intensity at the $11\bar{2}L$ position, $L=0.9$, and (b) transverse scans through this position before growth (typical) and five minutes after growth at different temperatures. In each case, 13 ML was deposited in 20 s, on a sample vicinal toward the M plane. The curves are offset by 6000 cps in (a) and 12000 cps in (b) for clarity. Similar behavior was observed on GaN(0001) vicinal towards the A plane.

fairly uniform spacing. The direction of the main CTR's indicates that the surface is tilted 2.2° away from the GaN(0001) plane. The small peak at the center indicates that a small fraction of the surface consists of (0001) facets. Figure 2(c) shows a two-dimensional representation of the intensity distribution at $L=1.1$ around the $11\bar{2}L$ position. The location of the peaks indicates that the surface normal is essentially tilted toward the M plane (azimuth is $\approx 4°$ away from the M plane). A similar study of GaN(0001) vicinal toward the A plane also showed monolayer-height steps at 990 °C.

Vicinal GaN(0001) surfaces annealed at 990 °C were used as the starting surfaces for growth experiments. Figure 3 shows the evolution of the intensity I_{CEN} at the $11\bar{2}$ 0.9 position during and after deposition of 13 ML, as well as transverse scans through this position before and five minutes after deposition. At the temperatures (715–990 °C) investigated here, a split peak structure characteristic of monolayer-height steps was observed before growth. At 990 °C, the central intensity I_{CEN} initially increases during growth, but immediately decreases after growth is halted. The split CTR peaks are weaker and broader following growth. Thus, at 990 °C, the monolayer-height step structure is maintained but the terrace width distribution becomes broader during growth. At 900 °C, I_{CEN} rises continuously during growth, and a peak appears at the central position. This indicates that (0001) facets separated by step bunches have formed during growth. However, I_{CEN} decreases upon stopping growth showing that the step bunches begin to dissociate, and suggesting that the equilibrium morphology at 900 °C is a surface with monolayer-height steps. At 820 and 715 °C, the central intensity I_{CEN} rises during growth, again indicating a tendency for step bunching. Interestingly, at these lower temperatures I_{CEN} continues to rise even after growth, and the split CTR peaks disappear almost completely. This suggests that the step bunches nucleated during

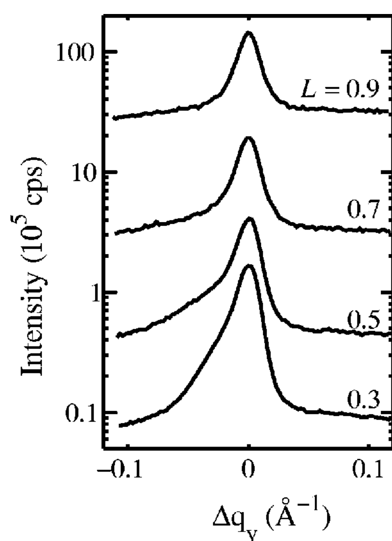

FIG. 4. Transverse scans through $11\bar{2}L$ at various L after deposition of 13 ML in 20 s at 715 °C on a GaN(0001) surface vicinal toward the M plane. The scans were taken 5–20 min after growth, and are offset by factors of 10 for clarity.

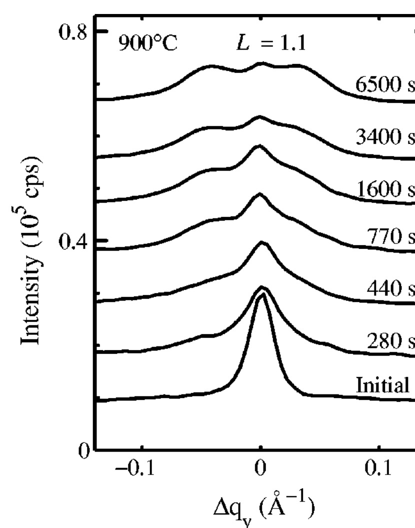

FIG. 5. Transverse scans at $L = 1.1$ during the evolution at 990 °C of a GaN(0001) surface vicinal towards the A plane. The starting step bunched surface was prepared by 13 ML deposition at 715 °C. The times after reaching 900 °C are indicated, and the curves are offset by 10^4 cps for clarity.

growth are stable, and that following growth these bunches undergo a domain coarsening process, leading to large step-free regions on the surface.

Figure 4 shows transverse scans at different L values taken 5–20 min after deposition of 13 ML at 715 °C. A sharp peak is observed at $\Delta q_y = 0$ at all L values indicating that a typical step bunch consists of more than two or three steps. [A surface with double-height steps, for example, would have yielded a split peak in the transverse scan at $L = 0.5$ as shown in Fig. 1(c).] The transverse scans in Fig. 4 are asymmetric, especially at $L = 0.5$ and 0.3. Fitting each of the observed line shapes with two peaks suggests that the shoulder may be a vestige of the original CTR from the monolayer-height stepped surface. We did not observe a truncation rod corresponding to the step bunches as shown schematically in Fig. 1(a), indicating that the step bunches do not form a well-defined facet. Disordered step bunches were also observed in a study of GaN deposited by molecular beam epitaxy on a vicinal surface.[17]

In Fig. 3(a), I_{CEN} decreases after growth at 900 °C and above, indicating that monolayer-height steps may be the equilibrium surface morphology at these temperatures. To further test this idea, we explored the high temperature annealing of a faceted surface prepared by growth at low temperature. Figure 5 shows a series of transverse scans at 900 °C from a step bunched surface prepared by deposition at 715 °C. We see that the surface gradually reverts to one that is mostly covered by a uniform density of monolayer-height steps, supporting the hypothesis that this is the equilibrium state at 900 °C. Thus, for vicinal GaN(0001) under MOCVD conditions, we propose a surface orientational phase diagram of the form shown in Fig. 6, with a two-phase field consisting of (0001) facets plus regions with a high density of steps (step bunches) at low temperatures, and a single phase consisting of a uniform density of monolayer-height steps at high temperatures.[3,18] The phase with monolayer-height steps has a higher configurational entropy associated with the wandering of steps compared to the step-bunched morphology and is therefore stabilized at higher temperature. Our results suggest that the temperature below which the 2° vicinal GaN(0001) surface is facetted at equilibrium lies between 810 and 900 °C.

An alternative explanation for the observation of monolayer-height steps at high temperature is that they are stabilized by evaporation. To investigate this possibility, we measured GaN evaporation rates by laser reflectivity[10] at 1000–1060 °C. By extrapolating these high temperatures results, the GaN evaporation rate at 900 °C is estimated to be very small (≈0.003 Å/s). Therefore, we believe that the changes in the surface morphology during annealing at high temperature occur largely through surface diffusion driven by surface free energy reduction, and are not driven by evaporation.

The central intensity I_{CEN} rises during growth at all temperatures (715–990 °C), suggesting that growth favors step bunching. This is a kinetic effect and the instability is caused by the preferential attachment of atoms deposited on a ter-

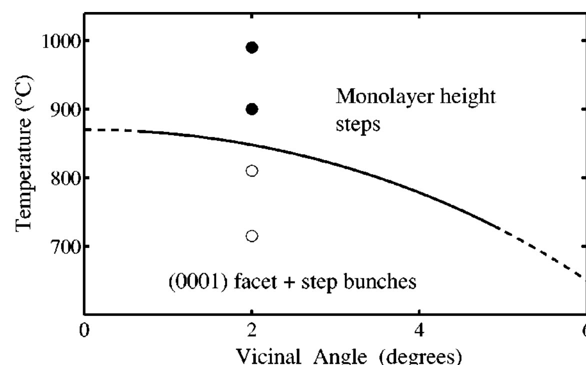

FIG. 6. Proposed equilibrium surface orientational phase diagram for the vicinal GaN(0001) surface, with monolayer-height steps at high temperature and a coexistence region of step bunches plus (0001) facets at low temperature.

race to the lower step.[6] One possible origin of this effect is a smaller activation barrier for attachment to a step from the upper side than the corresponding barrier to move to another site on the upper terrace, i.e., opposite to the ''normal'' Ehrlich-Schwoebel barrier.[6] Alternately, pinning of steps leading to bowed morphologies can cause step bunching.[19] Although we were unsuccessful in imaging the step bunch morphologies produced in this study using atomic force microscopy, other studies have found bowed steps suggesting that step pinning by dislocations plays an important role.[4,20] We note that the as-received vicinal GaN surfaces (3 μm GaN films grown on sapphire above 1000 °C) already had a monolayer-height step structure, in contrast to the step bunched structure found in previous work[4] for 10 μm films grown at 1025 °C. This difference may arise due to a lower density of step pinning sites for the films used here.

Step bunching was not observed when surfaces with monolayer-height steps prepared at high temperature (990 °C) were simply cooled to 810 and 715 °C. This indicates that, without growth, a very long time may be needed at these temperatures to nucleate a critical size step bunch required for the bunching transition to proceed; the monolayer-height step phase is thus metastable rather than unstable with respect to faceting for a 2° vicinal surface. Similar metastability has been observed for Si-induced faceting of GaAs(001) surfaces.[8]

In conclusion, nominally 2° vicinal GaN(0001) surfaces exhibit monolayer-height steps after annealing at 990 °C. Real-time x-ray scattering observations at 715–990 °C indicate that there is a tendency for step bunching during growth. Below 850 °C, step bunches nucleated during growth continue to coarsen after growth, while above 850 °C, the surface reverts to monolayer-height steps after growth. GaN(0001) surfaces vicinal toward both the *M* plane and the *A* plane show similar behavior.

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