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# Ga adsorbate on (0001) GaN: *In situ* characterization with quadrupole mass spectrometry and reflection high-energy electron diffraction

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We have investigated the adsorption and subsequent desorption of Ga on (0001) GaN using simultaneous line-of-sight quadrupole mass spectrometry (QMS) and reflection high-energy electron diffraction (RHEED). The *in situ* QMS and RHEED desorption transient measurements demonstrate the Ga flux dependent accumulation of the theoretically predicted laterally contracted Ga bilayer [J. E. Northrup *et al.*, Phys. Rev. B **61**, 9932 (2000)] under conditions similar to those used during GaN growth by rf-plasma molecular beam epitaxy. We correlated bioscillatory RHEED desorption transients [C. Adelman *et al.*, J. Appl. Phys. **91**, 9638 (2002)] to QMS-measured Ga-adsorbate coverage and found both to be consistent with layer-by-layer desorption of the Ga-adsorbate bilayer. The QMS-measured steady-state Ga-adlayer coverage exhibited a continuous increase from 0 to 2.4 ML (monolayer) with respect to impinging Ga flux at substrate temperatures of 640–700 °C. We observed an exponential dependence of the Ga flux corresponding to 1.0 ML Ga-adsorbate coverage on substrate temperature and we measured an apparent activation energy of  $2.43 \pm 0.11$  eV and an attempt prefactor of  $6.77 \times 10^{12}$  nm/min ( $4.36 \times 10^{11}$  Hz) for this transition.

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## I. INTRODUCTION

Recent improvements in GaN-based electronic<sup>1</sup> and optoelectronic devices<sup>2</sup> grown by rf-plasma assisted molecular beam epitaxy (PA-MBE) have demonstrated several important advantages as compared to chemical vapor deposition III-nitride growth technology. The key features of III-nitride growth by PA-MBE include complete composition control of the AlGa<sub>x</sub>N (Ref. 3) and InGa<sub>x</sub>N (Ref. 4) ternary alloys, abrupt *p*-type Mg doping profiles without postgrowth activation,<sup>5</sup> and heterostructure growth control on the monolayer scale<sup>6</sup> to take advantage of the spontaneous and piezoelectric polarization-induced electric fields<sup>7</sup> in device engineering. Further optimized GaN growth, resulting in smooth surfaces, low structural defect densities, and the elimination of morphological features, including pitting or metal droplets in PA-MBE, is desirable for improved device yield across full wafers.

Homoepitaxial GaN growth by PA-MBE has been characterized *ex situ* by atomic force microscopy, electron microscopy, x-ray diffraction, photoluminescence, and optical microscopy to establish a flux and substrate temperature diagram with three distinct regimes.<sup>8,9</sup> As the Ga flux is increased above stoichiometric conditions, the surface rough-

ness is observed to decrease until the Ga flux is sufficient for Ga droplet accumulation. Rough and faceted GaN growth, indicative of low adatom diffusion lengths, is observed when the N flux exceeds the Ga flux. Under Ga-droplet formation flux conditions, step-flow GaN morphology without pits is observed, indicative of high mobility adatoms. Under conditions where the Ga flux is intermediate to the Ga-droplet and N-rich regimes, GaN morphology ranges from rough to step flow with faceted pits. The pit formation is associated with threading dislocations and is the MBE analog of V defects commonly observed under low surface mobility conditions of metal-organic chemical vapor deposition of GaN.<sup>10,11</sup> Under typical PA-MBE GaN growth conditions, with substrate temperatures of 700–750 °C, optimized electrical and optical quality GaN has been obtained with excess Ga fluxes just below the Ga-droplet formation flux.<sup>12</sup> The critical excess Ga flux required for Ga-droplet formation during GaN growth was found to increase exponentially with substrate temperature with an activation energy of  $\sim 2.83$  eV, which is the same as the activation energy associated with the Ga partial pressure over liquid Ga.<sup>8</sup>

More recent morphological investigation of the GaN growth dependence on Ga flux has found that by varying the Ga flux from N-rich to Ga-droplet conditions the surface pit density decreases monotonously up to the Ga-droplet formation flux commensurate with increasing Ga-adsorbate

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coverage.<sup>13</sup> The PA-MBE GaN morphology is consistent with the continuously increasing adatom mobility with increasing Ga flux from stoichiometry up to the Ga-droplet formation flux.<sup>9</sup>

Neugebauer *et al.*<sup>14</sup> and Zywiets *et al.*<sup>15</sup> provided theoretical and experimental evidence that N-adatom mobility on the GaN growth surface may be directly mediated by the presence or the absence of Ga adsorbate on GaN. The two N-adatom limited diffusion cases that have been found are complete Ga-bilayer coverage [ $\sim 2.4$  ML (monolayer)] and the bare GaN (0001) surface. For complete bilayer coverage, the energy barrier for N diffusion was predicted to be as low as 0.5 eV, representing a significant decrease from the 1.4 eV energy barrier for N diffusion on the bare GaN (0001) surface. This theoretical prediction is consistent with the empirical GaN morphology of PA-MBE grown under N-rich and Ga-droplet conditions.<sup>8,9</sup>

Static first principles total energy calculations by Northrup *et al.* have predicted the stability of several phases of Ga adsorbate on the Ga-polar (0001) GaN surface.<sup>16</sup> In the Ga-rich limit, the energetically favorable Ga-adsorbate structure was found to be a laterally contracted bilayer. The first Ga-adsorbate monolayer was found to be pseudomorphic (PM) to the (0001) GaN lattice with an areal density of  $1.14 \times 10^{15} \text{ cm}^{-2}$ , in terms of (0001) GaN density. The second Ga-adsorbate monolayer was found to prefer a lateral contraction (LC) toward the bulk Ga nearest neighbor distance, with a GaN-equivalent coverage of  $\sim 1.4$  ML. Additional Ga monolayers were found to be less energetically favorable than the bilayer, a result that is consistent with the experimental conclusion that sufficient Ga fluxes result in liquid Ga-droplet formation beyond the bilayer completion.<sup>17</sup>

Analysis of GaN (0001) surfaces after PA-MBE growth under excess Ga conditions via scanning tunneling electron microscopy (STM), low energy electron diffraction (LEED), and Auger electron spectroscopy (AES) has been consistent with the laterally contracted bilayer model predicted by theory.<sup>18</sup> Observation of  $1 \times 1$  STM corrugation patterns consistent with the underlying GaN wurtzite (WZ) bond length, 3.19 Å, may be assigned to the PM Ga adlayer which retains the hexagonal structure of the GaN (0001) surface. The diffraction satellite rings in the vicinity of the (0,1) LEED intensity maxima were assigned to an incommensurate adlayer that was laterally contracted toward the bulk Ga-Ga bond length of 2.7 Å. Finally, the AES measurements indicated the presence of 2–3 ML Ga adsorbate on the pseudo- $1 \times 1$  GaN (0001) surface. An analysis of several measurements of the Ga/GaN (0001) pseudo- $1 \times 1$  surface was consistent with an incommensurate fluid Ga adlayer above 350 °C.

The correlation between GaN surface PA-MBE growth morphology and excess adsorbed Ga on the GaN surface has motivated further detailed investigation of the structure and dynamics of adsorbed Ga phases on GaN in the absence of N flux. In Fig. 1(a), we show a Ga/GaN adsorption diagram, which is equivalent to the GaN growth diagram in the limit of zero N flux. Following previous work,<sup>19</sup> we note the important distinction between the GaN growth diagram<sup>8</sup> that is strictly valid only in the presence of N flux, and the Ga/GaN adsorption diagram in the absence of N flux. However, based

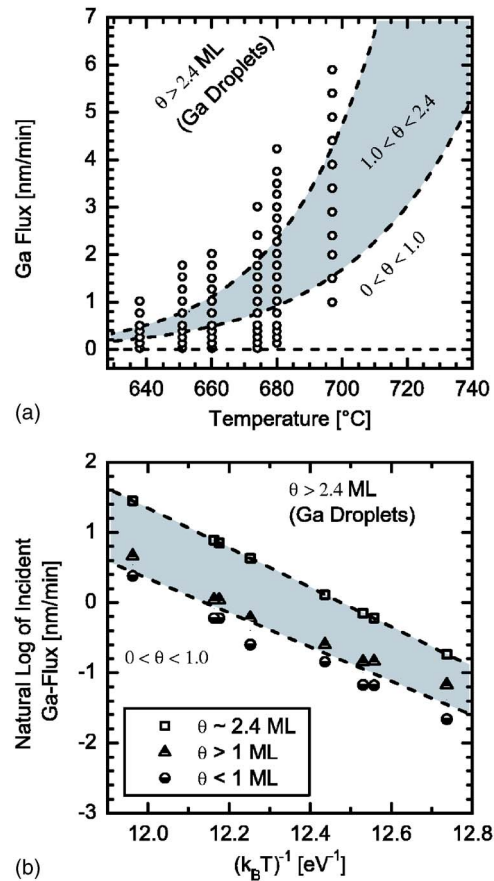


FIG. 1. (a) The “Ga/GaN (0001) adsorption diagram” correlates the exponential Ga-flux dependence of Ga-adsorbate coverage and Ga droplet formation on substrate temperature. The activation energy for 1 ML Ga-adsorbate was determined from *in situ* temperature dependent measurements, as shown in (b). The Ga fluxes and substrate temperatures used for 90 s adsorption in this work are indicated as open circles. (b) Arrhenius plot for the determination of single exponential activation energies and atomic attempt frequencies for critical fluxes to realize 1.0 and 2.4 ML gallium adsorbate coverage. For the critical flux to form 1.0 ML Ga on GaN after 90 s Ga adsorption, we measured an activation energy of  $2.43 \pm 0.11$  eV and a prefactor of  $6.77 \times 10^{12}$  nm/min. The activation energy and atomic attempt prefactor for the critical flux for 2.4 ML gallium coverage and droplet formation were previously reported in the context of GaN growth (e.g., see Ref. 8).

upon the invariance of the activation energies for the temperature dependence of the droplet formation flux on excess Ga flux in GaN growth and for bulk Ga vapor pressure,<sup>8</sup> it is reasonable to perform Ga-adsorption experiments and compare the results to the GaN growth diagram. Investigation of the temperature and flux dependences of Ga-adsorbate coverage on (0001) GaN is pursued in this work to improve control and understanding of the growth of GaN under Ga-rich conditions.

Adelmann *et al.* explored the correspondence of Ga-adsorbate coverage to the impinging Ga flux at substrate temperatures of 700–740 °C, using reflection high-energy electron diffraction (RHEED).<sup>19,20</sup> Adsorption and subsequent desorption of the Ga-adsorbate on (0001) GaN were investigated by monitoring the intensity of the RHEED specular spot (00) along the  $[11\bar{2}0]$  azimuth. The Ga-adsorbate coverage was observed to depend on the impinging Ga flux, based on the dependence of the desorption time

on adsorption time. It was shown that near the critical Ga flux to form droplets, the specular intensity exhibited two complete oscillations during adsorption and during desorption, consistent with the layer-by-layer growth and desorption of an adsorbate bilayer. A signature of Ga-droplet formation was observed by monitoring the RHEED desorption transient duration after Ga shutter closure. When Ga droplets had formed on the GaN surface during Ga adsorption, the onset of the RHEED intensity oscillations was preceded by a delay that increased monotonously with increasing Ga flux or adsorption time. When the impinging flux was below the critical flux for Ga-droplet formation, desorption time saturation was observed, consistent with steady-state Ga-adsorbate coverage. At fixed temperatures, the dependence of desorption time on the impinging Ga flux exhibited a flux-invariant region for a range of Ga fluxes just below and up to the critical flux to form Ga droplets. The flux-invariant duration regime measured by RHEED specular intensity was attributed to the completion of the laterally contracted bilayer over a range of Ga fluxes.

Another more quantitative technique that has been implemented in the investigation of the Ga adsorbate on GaN is a line-of-sight quadrupole mass spectrometry (QMS).<sup>17</sup> The QMS technique measures the temporal desorption of Ga from the wafer surface, providing a direct measure of mean Ga adatom lifetime and adlayer coverage. Previous QMS measurements have shown that the two-dimensional Ga-adsorbate coverage on (0001) GaN saturates at  $\sim 2.4$  ML at temperatures of interest for MBE, and that additional Ga coverage may be accommodated in macroscopic Ga droplets, in agreement with the theoretically predicted Ga bilayer structure. Desorption activation energies derived from temperature dependent adatom lifetime measurements for both the PM (4.9 eV) and LC (3.7 eV) monolayers of the Ga adsorbate were used in a macroscopic rate equation analysis to model the QMS-measured desorption Ga-flux transients. The QMS-measured Ga-adsorbate coverage was found to increase continuously with increasing impinging Ga flux both in the absence of N flux and during GaN growth, in contrast to the RHEED experiments which were interpreted to reveal a regime of constant Ga coverage independent of adsorption flux.

In this work, we present the results of simultaneous RHEED and QMS *in situ* experiments of Ga-adsorbate desorption from (0001) GaN to investigate the correspondence of the information provided by both *in situ* MBE techniques. Both techniques have practical advantages in routine use to monitor the N and Ga fluxes and substrate temperature. Large sample size, similar to full wafers (50.8 mm diameter) used in this work, is required for the QMS signal detection in our MBE system, whereas small samples as small as  $\sim 2$  mm diameter provide sufficient contrast for use in RHEED experiments. Our experiments have been motivated both to realize a fundamental understanding of the kinetics of the Ga adsorbate on (0001) GaN, and with the more practical goal of developing reliable growth control techniques for samples of various sizes.

## II. EXPERIMENTS

The Ga adsorption experiments were performed on (0001) GaN with simultaneous QMS and RHEED in a Varian GEN II MBE system equipped with standard Ga effusion cells and a VEECO Unibulb rf-plasma N source. All experiments were performed on 2 inch (Lumilog) wafers of 2  $\mu\text{m}$  metal-organic chemical vapor deposition (MOCVD)-grown (0001) GaN on sapphire. Electron beam evaporation was used to deposit 0.5  $\mu\text{m}$  titanium films on the backside of the sapphire substrates to facilitate radiative heating. The substrates were degreased with solvents and outgassed in vacuum prior to introduction into the growth chamber. Prior to adsorption experiments,  $\sim 200$  nm thick GaN buffers were grown under Ga droplet conditions to realize smooth GaN surfaces and avoid surface contamination.<sup>21</sup> After GaN buffer growth, the desorption of Ga-adsorbate bilayer and droplets was monitored by QMS. Fluxes are expressed in (0001) GaN growth rate units, as measured by cross section transmission electron microscopy of Ga-limited and N-limited GaN films. For convenience of conversion to a.u., we note that in WZ GaN along [0001], 2.59  $\text{\AA}$  is the height of 1 ML.

A quadrupole mass spectrometer (Stanford Research Systems AMU-200) installed in a source port of the GEN II was used for QMS measurements. An aperture was placed between the substrate and the ionization grid to reduce the line-of-sight acceptance angle of the detector to exclude Ga atoms that do not originate on the wafer surface. The linear proportionality constant of the response of the QMS detector was measured by exposure of a sapphire wafer at  $\sim 850$   $^{\circ}\text{C}$  to impinging Ga fluxes (1–30 nm/min) well below the critical flux for Ga-droplet accumulation ( $\sim 430$  nm/min). Under these conditions, steady-state conservation of Ga flux allows a direct correlation from the QMS-measured <sup>69</sup>Ga partial pressure to total desorption Ga flux in GaN-equivalent growth rate units.

The QMS-measured temporal desorption Ga flux was integrated to determine the Ga-adsorbate steady-state coverage. The substrate temperature was measured *in situ* by pyrometer, but the temperatures we report were determined by comparing maximum steady-state Ga desorption rates to the Ga/GaN adsorption diagram (Fig. 1). This method provided a precise self-consistent correlation of substrate temperature to (critical) Ga droplet Ga flux, based upon previous *ex situ* measurements that were in agreement with the bulk Ga partial pressure.<sup>8</sup> At steady state, the critical flux to form droplets at fixed temperature is the same as the maximum Ga desorption rate from the wafer surface. When the impinging Ga flux, or excess Ga flux in the case of GaN growth, was in excess of the maximum Ga desorption rate, Ga-droplet accumulation occurred. Consequently, when the impinging Ga flux was incrementally increased up to and beyond the critical flux for droplet formation at fixed substrate temperature, we observed an increase in the maximum Ga desorption rate up to the critical (Ga-droplet formation) flux, followed by a saturation of the maximum rate of Ga desorption independent of further increases in Ga flux. By averaging the maximum Ga steady-state desorption rate from several adsorption



experiments, it was possible to determine the self-consistent substrate temperature with standard variation  $\pm 1$  °C via flux calibration and the response calibration of the QMS detector.

We monitored the integrated intensity of the RHEED specular spot (00) along the  $[11\bar{2}0]$  azimuth to characterize the structural organization of the Ga adsorbate. We used a 7 keV beam energy, a 2.7 mA filament current, and an  $\sim 1^\circ$ – $2^\circ$  incident angle. The time resolution of the charge-coupled device (CCD) detection system (k-Space Associates) was less than 0.5 s. We defined the RHEED desorption duration as the elapsed time after closing the Ga shutter to the time at which the derivative of the specular intensity reached zero. For comparison to RHEED desorption time, the QMS desorption duration was defined as the time elapsed after closing the Ga shutter for the desorbing Ga flux to decrease below 0.2 nm/min, the minimum detectable desorption flux.

### A. Ga adsorption: Variable adsorption time

We investigated Ga adsorption with variable adsorption time from 10 to 600 s, with impinging Ga fluxes of 0.8 and 3 nm/min and substrate temperature of  $678 \pm 1$  °C. The adsorbed Ga coverage was determined from the QMS measurements. The Ga-desorption duration was measured from the RHEED specular intensity oscillations. Variable adsorption time experiments were designed to confirm the presence of steady-state Ga-adsorbate coverage on (0001) GaN, previously observed by monitoring the dependence of RHEED desorption time on adsorption time.<sup>19</sup>

### B. Ga adsorption: Variable impinging Ga flux

In the second series of adsorption experiments, the impinging flux was varied incrementally (0.25–1.0 nm/min steps) to sample the Ga/GaN adsorption diagram [Fig. 1(a)] at selected substrate temperatures. For all fluxes and temperatures, the adsorption duration was held constant at 90 s for consistency with previous reports.<sup>19</sup> Variable Ga-flux experiments were performed at six substrate temperatures, from 638 to 697 °C as depicted by open circles in Fig. 1, to characterize the effect of temperature on the transition fluxes. We used substrate temperatures below 700 °C to minimize the contribution of GaN thermal decomposition to the Ga flux desorbing from the wafer.<sup>22</sup> The total adsorbed Ga coverage resulting from each impinging flux was determined by direct integration of the desorption Ga flux measured by QMS. The desorption duration was defined, as described above, for the fixed Ga-flux experiments for both QMS and RHEED data. Variable impinging flux experiments were performed to realize different initial Ga-adlayer coverages for comparison of adlayer morphology (characterized by RHEED) and coverage (measured by QMS) over a range of substrate temperatures.

## III. RESULTS

### A. Dynamic stability of Ga-adlayer coverage with impinging Ga flux

The QMS-measured Ga-adsorbate coverage and RHEED desorption duration are shown as a function of adsorption

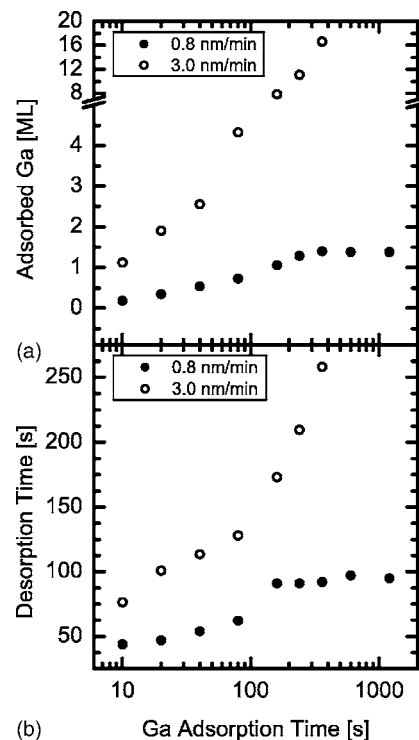


FIG. 2. Ga adsorption with variable adsorption time for impinging fluxes above (3.0 nm/min) and below (0.8 nm/min) the droplet formation flux at a substrate temperature of 678 °C. (a) QMS-measured total adsorbate coverage as a function of adsorption time. (b) RHEED measured desorption time evolution as a function of adsorption time.

time for two impinging Ga fluxes in Fig. 2. From the Ga/GaN adsorption diagram (Fig. 1), at the substrate temperature of 678 °C, the critical Ga flux for Ga droplet formation is 2.2 nm/min. For a subcritical impinging Ga flux of 0.8 nm/min, the Ga-adsorbate coverage [Fig. 2(a)] saturated at  $1.4 \pm 0.01$  ML beyond 360 s of adsorption. This result provides an independent confirmation that stable steady-state Ga coverages exist, corresponding to Ga fluxes that are less than the critical Ga-droplet flux.<sup>19</sup> The total desorption time [Fig. 2(b)] determined from the RHEED specular intensity oscillations also showed an invariant adsorption time regime for 0.8 nm/min impinging flux, but the onset of the saturation occurred at 160 s of adsorption. We note that the RHEED spot size is  $\sim 1$  mm  $\times$  100  $\mu$ m, while the QMS measures the desorbing flux from the full 50.8 mm diam wafer. Due to the nonuniformity of the impinging flux, we speculate that the onset of steady-state coverage occurred inhomogeneously across the entire wafer.

With a supercritical impinging Ga flux of 3.0 nm/min, as shown in Fig. 2, neither the coverage or desorption time saturated, rather the adsorbed Ga coverage and desorption time increased monotonically with adsorption time. These Ga coverage and desorption time behavior are attributed to the completion of the Ga bilayer followed by accumulation of Ga in droplets, which is identical to the analysis of previous RHEED experiments<sup>19</sup> and QMS experiments.<sup>17</sup>

The results of this experiment are consistent with previous reports<sup>17,19</sup> and establish the foundation for variable Ga-flux experiments over a range of temperatures. We have observed this dichotomy of coverage stability for subcritical

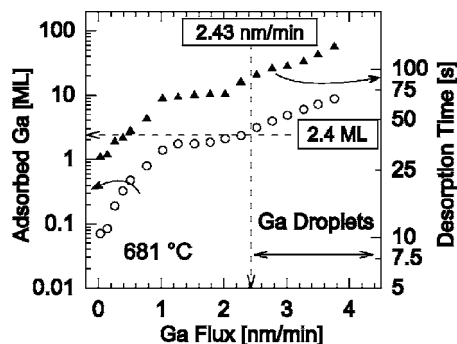


FIG. 3. Evolution of adsorbate Ga coverage and desorption time as a function of impinging Ga flux after 90 s adsorption at a substrate temperature of 681 °C. The droplet transition flux from the Ga/GaN(0001) growth diagram of 2.43 nm/min and the adsorbate coverage of 2.4 ML are indicated in relation to the measured adsorbed coverage.

and supercritical Ga fluxes at all temperatures presented in this work, in accordance with the Ga/GaN adsorption diagram [Fig. 1(a)].

### B. Ga-adsorbate coverage and desorption time evolution with impinging Ga flux

Figure 3 shows the dependence of the QMS-measured Ga-adsorbate coverage and QMS-measured desorption time on the impinging Ga flux at a substrate temperature of 681 °C. As shown in Fig. 3, the Ga-adsorbate coverage increased continuously with impinging Ga flux. From the Ga/GaN adsorption diagram [Fig. 1(a)], at 681 °C substrate temperature the critical Ga flux for Ga droplets formation is 2.43 nm/min. When the impinging Ga flux was subcritical (below 2.43 nm/min), the Ga-adsorbate coverage was between 0 and 2.4 ML. For supercritical Ga fluxes, the Ga coverage increased monotonically from 2.4 to 10 ML.

The duration of the desorption process increased over the same range of impinging Ga flux and resultant Ga-adsorbate coverages, with two subtle exceptions in the form of an abrupt increase and a flux-invariant plateau (Fig. 3). The Ga-adsorbate desorption time increased monotonically to 51 s as the adsorbed coverage reached 0.8 ML. Then, for a modest increase in coverage to 1.02 ML, the desorption time abruptly increased to 67 s. As the initial adsorbed coverage was subsequently increased further from 1.02 to 2.02 ML, the desorption time was nearly insensitive to the impinging flux, with a gradual increase to 71 s. Therefore, the PM monolayer accounted for approximately 94% of the total desorption time for the full 2.4 ML bilayer. We speculate that despite the larger coverage (1.4 ML) of the LC monolayer, the higher mean adatom desorption rate and the rapid transfer of adatoms from the LC to PM monolayer due to the energy minimization give rise to the negligibly small increase in total desorption time from the coverage range of 1.0–2.4 ML.

For all substrate temperatures, we observed qualitatively similar evolution of Ga-adsorbate coverage and desorption time with impinging Ga flux, as shown in Fig. 4. The transition flux for bilayer completion and droplet formation increased exponentially with substrate temperature [Fig. 4(a)], as expected from the Ga/GaN adsorption diagram. As the

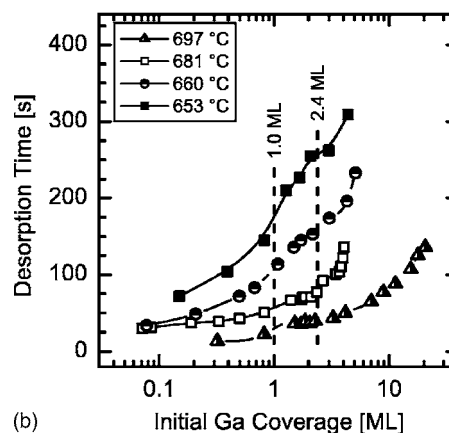
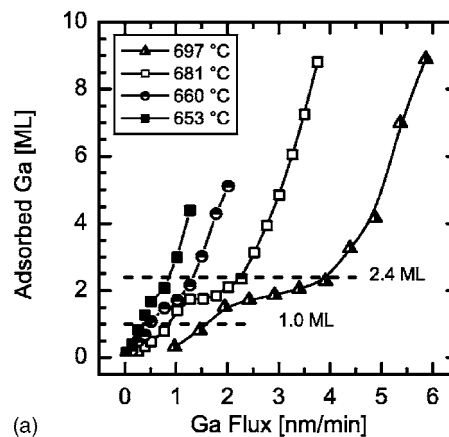


FIG. 4. (a) Dependence of the QMS-measured adsorbate Ga coverage on the impinging Ga flux for the substrate temperatures in the range of 653–697 °C. (b) Dependence of the Ga-adsorbate desorption time on the initial Ga-adsorbate coverage over the same range of substrate temperatures.

substrate temperature was increased, the desorption time decreased with respect to the initial coverage, and the flux-invariant desorption time plateau became more pronounced [Fig. 4(b)]. For example, the flux-invariant desorption time increased only a few seconds over the entire range of coverage at 697 °C, appearing to be nearly invariant with respect to the impinging flux. By comparison of desorption time to the QMS-measured initial coverage, our experiments demonstrate that the flux-invariant desorption time plateaus correspond to a region of gradually increasing Ga-adsorbate coverage. We propose that the abrupt increase in desorption time is a direct result of coverage sensitivity to adsorption flux in the vicinity of the completion of 1.0 ML total coverage. The subsequent slow increase of desorption time with increasing coverage is attributed to the difference in desorption rates between the 2 ML of the bilayer structure.<sup>17</sup> Desorption time as a function of Ga-adsorbate coverage is dominated by the first (PM) monolayer, due to the higher mean adatom lifetime of Ga atoms which are strongly bound to the underlying GaN.<sup>17</sup>

### C. Ga-adsorbate morphology and coverage

We assessed the correlation between the RHEED transient oscillations and the Ga-adsorbate coverage measured by QMS for the variable impinging Ga-flux experiments (Fig. 5). Zeros in the first derivative of the RHEED intensity,

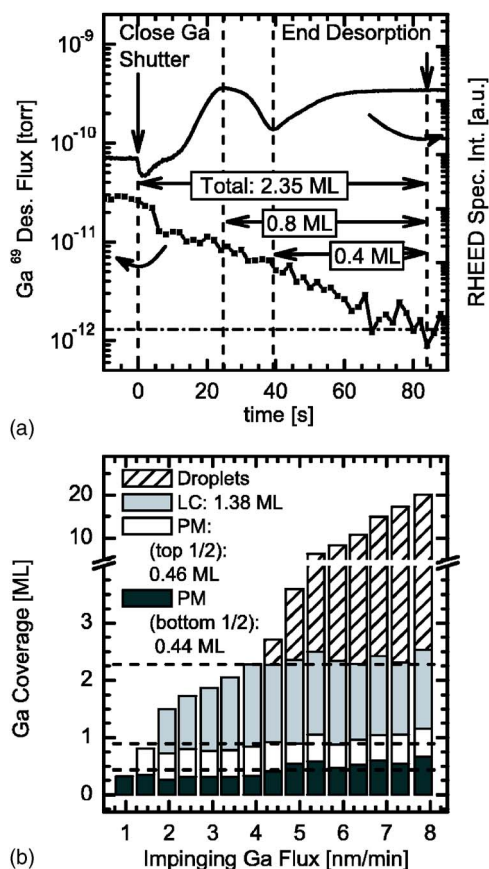


FIG. 5. (a) An example of RHEED delineated QMS integration experiment with 2.35 ML total adsorbed coverage after 90 s Ga adsorption with 2.2 nm/min impinging flux and a substrate temperature of 681 °C. (b) Correlation between laterally contracted (LC) and pseudomorphic (PM) monolayer intervals indicated by RHEED specular intensity extrema along  $[11\bar{2}0]$  azimuths and desorbed Ga-adsorbate coverage, obtained via integration of Ga-flux desorption transient intervals. The histogram plot indicates the breakdown of Ga-adsorbate coverage between the monolayer intervals as the incident Ga flux was increased from 1 to 8 nm/min with 697 °C substrate temperature.

corresponding to local extrema in the RHEED oscillation intensity, were used to delineate specific integration limits of the QMS signal. Under the assumption that the Ga bilayer adatoms adsorb and desorb via a sequential layer-by-layer process, the maxima in the RHEED intensity correspond to planar surfaces of completed monolayers. However, interpretation of the origin of the RHEED contrast may also depend on the GaN surface roughness evolution, substrate vicinality, azimuthal beam orientation, multiple (dynamic) scattering effects, disorder of individual monolayers, and the electron beam conditions.<sup>23</sup>

An example of simultaneous RHEED intensity oscillations and QMS desorption Ga-flux data is shown in Fig. 5(a), for an initial Ga coverage of 2.35 ML at a substrate temperature of 681 °C. The RHEED-delineated Ga-adsorbate coverage dependence measured by QMS on impinging Ga flux at a substrate temperature of 697 °C is shown in Fig. 5(b). The consistency between RHEED intensity oscillations and the QMS-measured coverage evolution shows that both types of measurements are in agreement with the predicted laterally

contracted Ga bilayer. These results confirm that the RHEED contrast is dominated by Ga-adlayer structure desorption by a sequential layer-by-layer process.

#### D. Activation energy for completion of 1.0 ML

As shown in Fig. 1(a), for 90 s adsorption, the Ga flux corresponding to 1.0 ML total Ga-adsorbate coverage increased exponentially with temperature, and was lower than the critical flux for 2.4 ML completion and subsequent Ga-droplet formation. Following the approach used to determine the activation energy for Ga droplets formation in GaN growth by PA-MBE,<sup>8</sup> we determined a thermal activation energy of  $2.43 \pm 0.11$  eV and an attempt frequency prefactor of  $6.77 \times 10^{12}$  nm/min ( $4.36 \times 10^{11}$  Hz) for the completion of 1.0 ML total adsorbate coverage. For each of the substrate temperatures of the variable Ga-flux adsorption experiments, we found the nearest fluxes above and below 1.0 ML coverage and interpolated to estimate the critical transition flux. An Arrhenius plot, shown in Fig. 1(b), demonstrates the single exponential behavior of both the 1.0 and 2.4 ML transition fluxes and the corresponding linear fits to extract the activation energies and attempt frequency prefactors. The temperature and flux dependent 1.0 ML formation flux was then superimposed on the Ga/GaN adsorption diagram. According to our measurements of Ga-adsorbate coverage corresponding uniquely to subcritical adsorption flux, a transition flux for any arbitrary coverage below 2.4 ML may be defined. We draw attention to the 1.0 ML coverage transition flux as a result of separate GaN growth experiments. The preliminary growth mode results have indicated that 1.0 ML coverage may mediate a transition in GaN growth mode. These results will be presented separately after further *in situ* QMS and RHEED experiments during GaN growth by PA-MBE.

#### IV. DISCUSSION AND CONCLUSIONS

The experimental results show the complementary nature of the information provided by the RHEED oscillations and the Ga-adlayer coverage measured by QMS. We have confirmed that steady-state Ga-adlayer coverages may be established below the critical impinging Ga flux necessary to form Ga droplets. The steady-state coverage dependence on adsorption time was directly observed by QMS and was consistent with the dependence of desorption time measured by QMS or RHEED. In principle, the correlation of desorption time with QMS-measured adlayer coverage, demonstrated at the substrate temperature of 678 °C in this work, could be used to estimate the Ga-adsorbate coverage at any substrate temperature. Below the critical Ga flux for Ga-droplet formation, the steady-state Ga-adlayer coverages increased continuously with impinging Ga flux. As demonstrated for the Ga-adsorbate coverage of 1.0 ML, the critical Ga flux corresponding to a specific Ga-adsorbate coverage up to 2.4 ML increased exponentially with substrate temperature. We have shown that each half period of RHEED specular reflection oscillation is associated with the corresponding (bottom) PM and (top) LC monolayers. This result confirms that the



RHEED specular intensity transients observed during adsorption and subsequent desorption are primarily due to the Ga-adsorbate bilayer.

We have argued that the discontinuous dependence of transient desorption time on increasing Ga flux is consistent with the continuously increasing Ga-adsorbate coverage due to the different desorption rates that have been measured for each monolayer.<sup>17</sup> Previous analyses of desorption time from RHEED specular reflection intensity transient oscillations have led to the conclusion that a 2.4 ML (complete bilayer) coverage may be established over a range of impinging Ga fluxes,<sup>20</sup> indicating a first order surface phase transition<sup>24</sup> between the Ga-adsorbate PM (1.0 ML) and LC (2.4 ML total Ga coverage) Ga-adsorbate phases. However, the QMS-measured Ga-adsorbate coverage has been found to increase monotonically with respect to impinging Ga flux from 0 to 2.4 ML, indicative of a continuous transition from 1.0 to 2.4 ML Ga-adsorbate coverage.<sup>13,17,25</sup> We propose that the large difference in adlayer desorption rates may be responsible for an error in coverage assessment exclusively based upon analysis of RHEED transients.

### A. Relevance for GaN growth

These results are relevant in a detailed description of the evolution of Ga-adsorbate coverage and resultant GaN growth mode in the intermediate regime, where the excess Ga fluxes are intermediate to stoichiometric and Ga-droplet conditions, of the PA-MBE GaN growth diagram, in accordance with previous studies.<sup>8,12,13,20</sup> The existence of a continuous increase<sup>24</sup> in Ga-adsorbate surface coverage with increasing Ga flux does not exclude the possibility of a PA-MBE GaN “growth window” under excess Ga growth conditions, in which fluctuations from nominal temperature and flux values do not adversely affect growth morphology. However, we propose that several of the important details of the diffusion pathways for the Ga/GaN (0001) growth surface and excess constituent vapor pressures, as manifested in growth experiments<sup>13</sup> and theoretical investigation,<sup>14</sup> are different than in the case of previously characterized materials<sup>26</sup> grown by MBE.

In MBE, the expression *growth window* is typically used to refer to a regime in which the growth mode and surface structure are insensitive to variations in flux and substrate temperature. Although molecular beam epitaxy cannot be explained in simple terms, thermodynamics provides a useful frame of reference for predicting stable surface phases.<sup>27</sup> In the most common applications, epitaxial growth of GaAs (001) occurs at substrate temperatures and excess As flux such that the As-rich  $2 \times 4$  reconstruction is observed.<sup>28</sup> The  $2 \times 4$  reconstruction occurs over a range of As coverage from 0.31 to 0.53 ML equivalent coverage, and a continuous increase in As coverage occurs with increasing As flux up to  $\sim 0.5$  ML when the  $c(4 \times 4)$  reconstruction is observed.<sup>29,30</sup> In typical GaAs MBE growth at substrate temperatures of 500–650 °C, typical As fluxes are several orders of magnitude smaller than the As flux required to form As precipitates.<sup>27</sup> In addition, impinging As<sub>2</sub> molecules have a sticking coefficient of  $\sim 1$  on exposed Ga adatoms on GaAs,

but the sticking coefficient is negligible for As<sub>2</sub> molecules impinging on the complete ( $2 \times 4$ ) reconstruction, providing a mechanism for self-limited As coverage at normal substrate temperatures during GaAs growth.<sup>31</sup>

The continuous morphology evolution of GaN commensurate with Ga flux variation and Ga-adsorbate coverage may be related to some of the important differences in surface kinetic mechanisms in comparison of GaAs (001) and GaN (0001) surfaces. Under As-rich  $2 \times 4$  GaAs (001) growth, Ga adatom surface diffusion has an apparent measured<sup>32</sup> and theoretical<sup>33</sup> activation energy of 1.3–1.5 eV. The As<sub>2</sub> molecules have been observed to diffuse with lower activation energy<sup>31</sup> of 0.25 eV, but the As<sub>2</sub> dissociation activation energy required for incorporation<sup>34</sup> is around 1.4 eV. In the case of GaN, as demonstrated by the two limiting cases of zero Ga-adsorbate coverage and full bilayer plus droplets, two different surface diffusion pathways have been proposed.<sup>14,15</sup> The lowest known activation energy barrier for N diffusion exists inside the bilayer, between the PM and LC monolayers. We speculate that the rapid Ga-adsorbate domain diffusion that has been observed by STM measurements<sup>18</sup> may lead to an averaging effect of diffusion mediation corresponding to Ga-adsorbate coverage of less than 2.4 ML. Domains of the LC phase that rapidly diffuse on top of the PM adlayer on the GaN growth surface could give rise to locally modulated surface diffusivity during growth. Under the assumption that LC domains may diffuse much more rapidly than N adatoms, this effect could give rise to a composite N-adatom surface diffusion that corresponds to LC occupation when the total surface coverage is between 1.0 and 2.4 ML. This proposed mechanism is consistent with the Ga-adsorbate coverage results presented here that show that coverage may increase systematically with impinging Ga flux, thereby increasing the local N diffusion length on the growth surface. It is also possible that further theoretical investigation of the Ga adlayer may find that intermediate barrier diffusion pathways exist, for example, on or through the PM monolayer.

Our previous experiments and current investigation of the Ga adsorbate are consistent with the absence of an intermediate GaN growth regime where the surface morphology may be invariant with respect to small variations in flux. However, with accurate flux calibration and QMS and RHEED *in situ* monitoring techniques, we note several routes for improved uniformity of growth of GaN by PA-MBE. With precision flux control, Ga-droplet density and surface pit density may be simultaneously minimized.<sup>13</sup> As mentioned in the discussion of experimental techniques, we propose that the most direct method for monitoring flux ratios and growth temperature is the QMS measurement of steady-state desorption Ga-flux during growth. Another route that has been demonstrated is the intentional modulation of the Ga flux, making use of two Ga effusion cells with Ga flux above and below the droplet formation flux, to achieve a net flux that is just below the droplet formation flux to obtain smooth GaN surfaces without droplets.<sup>35</sup> Finally, we suggest that it may be possible to grow under conditions of complete bilayer coverage and unstable droplet size. Classical nucleation and growth theory predict a balance between surface



energy and volume energy that results in a minimum (critical) nucleus volume, whereas droplets of supercritical volume may decrease their free energy with further volume increase.<sup>36</sup> Theoretical consideration of critical Ga-droplet volume and kinetic stability with respect to Ga vapor and substrate temperature could form the basis for GaN growth approaches that maximize adatom diffusion and minimize Ga-droplet formation.

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