# A rate equation model for the growth of GaN on GaN(0001) by molecular beam epitaxy

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GaN(0001) films were grown by molecular beam epitaxy using ammonia and elemental Ga. The surface reactivity and growth kinetics of GaN(0001) were investigated as a function of growth parameters using desorption mass spectroscopy. Growth proceeds either by island nucleation or by step flow, depending on the steady state surface coverage of Ga. Three Ga adsorption states were found on the surface, one chemisorption and two weak states. One of the weak states corresponds to Ga adsorbed on a gallided surface, while the other corresponded to an intrinsic physisorption state on a hydrogen-passivated, nitrided surface. An abrupt growth mode transition between excess Ga and excess nitrogen was found as a function of growth parameters. The transition was modeled by rate equations based on growth at step edges and the three types of adsorption states. © 2000 American Institute of Physics. [S0021-8979(00)03802-0]

## I. INTRODUCTION

GaN is a direct, wide band gap semiconductor making it attractive for blue light-emitting diodes (LEDs) and lasers, as well as high temperature and power devices.<sup>1</sup> Since the mid 80's major efforts have been underway to produce high quality material using a variety of growth methods.<sup>2,3</sup> The growth has proven difficult. Among the multiple challenges in growing high quality material by molecular beam epitaxy (MBE) is the control of growth kinetics, which requires a good understanding of the processes taking place on the GaN surface.

A picture of GaN growth is beginning to emerge but there have been relatively few models proposed. Newman et al.4 and Averyanova et al.5 examined growth from thermodynamic points of view. These were concerned with the regimes where GaN could be grown and in particular the rate of decomposition of GaN. Both relied on an activation barrier to nitrogen desorption; Averyanova et al. showed that if an activation barrier were included then mass action could quantitatively be applied to control the decomposition rates of GaN. In the case of MBE, Crawford et al.<sup>6</sup> showed that weakly bound Ga on a Ga terminated GaN surface would inhibit growth and developed a simple rate equation to describe this. Tarsa et al.7 examined MBE growth on GaN(0001) and showed that under excess N conditions the surface morphology evolved according to kinetic roughening. More recently, Koleske et al.8 proposed a rate equation model, coupling the surface coverages of Ga and N, seeking to describe growth under a very wide range of conditions and techniques. However the rate equation model was only indirectly compared to the data in the sense that only various measures of material quality were examined, as opposed to coverages or rates. The work to be presented here examines

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a very well-defined growth regime, expanding the study of Crawford *et al.*, to model the MBE growth of GaN on GaN( $000\overline{1}$ ), with more specific mechanisms given. We have chosen a temperature regime where decomposition can be neglected and where, as much as possible, the morphology remains constant. Rates in the model are directly compared to desorption data.

Previously<sup>9</sup> we examined the structure and composition of the polar GaN{0001} surfaces. We showed that for the GaN(0001) polarity, the surface can be prepared with either of two terminations, by exposure to a flux of Ga or to a flux of NH<sub>3</sub>.<sup>9–11</sup> These two surfaces have different structures and reactivities. Which of these surfaces dominates during growth depends on the incident fluxes. We showed that under excess Ga conditions growth can be inhibited by weakly adsorbed Ga, and a very general kinetic model was developed. In this article we examine the detailed kinetics of growth under both excess Ga and NH<sub>3</sub> conditions.

In this work the adsorption of Ga on  $GaN(000\overline{1})$  was studied by exposing the surface to an incident Ga flux while measuring the desorbing Ga flux versus time. First we will examine the difference in adsorption of Ga on surfaces that have been exposed to Ga, termed gallided, and on surfaces that have been annealed in NH<sub>3</sub>, termed nitrided. We will show that a gallided surface adsorbs additional Ga only weakly, while a surface that has been nitrided has strong and weak adsorption states. On a nitrided surface, using a single chemisorption state and two different weak states, we will develop a rate equation model of the adsorption. Then we will examine GaN growth, during exposure to both NH<sub>3</sub> and Ga fluxes, expanding the model to show the observed crossover in growth regimes and measured growth rates.

## **II. EXPERIMENT**

In order to investigate surface processes we used desorption mass spectroscopy (DMS) to measure the flux of mol-

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ecules leaving the sample surface either on heating or in response to an incident flux.<sup>10-14</sup> Our DMS employs a quadrupole mass spectrometer aimed at the sample, which is collimated so as to restrict the sampled region to an area that is about 6 mm in diameter. Over this region, temperature variations were estimated to be less than about 1 °C, as determined from changes in the adsorption behavior measured by reflection high-energy electron diffraction (RHEED) over a similar area.<sup>10,11</sup> However, collimation reduced the signal relative to background and shot noise. Installation of a liquid nitrogen shroud around the ionizer reduced the NH<sub>3</sub> background, increasing the signal to noise ratio by more than one order of magnitude. Nonetheless, because the bulk GaN substrates available to us were less than 6 mm in diameter, all of the DMS measurements reported here were performed on GaN films grown on sapphire. All films were prepared with a GaN buffer which was found to give a  $GaN(000\overline{1})$ polarity.9,11

All measurements were performed by monitoring the Ga flux that desorbed from the sample surface. This flux was calibrated by comparing a known incident flux to the Ga signal measured by the quadrupole analyzer. First, the sample temperature was set to a point slightly above which liquid Ga condensed on the surface. At this temperature, and in the absence of an NH<sub>3</sub> flux, a steady state is reached in which the incident Ga flux equals the desorbed flux. The incident Ga flux was calibrated with GaAs RHEED intensity oscillations. Hence the measured analyzer signal could be set to correspond to the incident flux, without having to know either the solid angle subtended by the detector or the transmission function of the analyzer. With this method the measured DMS current was calibrated to better than 10%.<sup>10,11</sup>

#### **III. RESULTS**

The main types of data to be analyzed are shown in Fig. 1 for two different initial surface conditions. No NH<sub>3</sub> flux was incident on the surface in this case, and the Ga shutter sequence is indicated by two vertical dashed lines. At this sample temperature, the desorbing Ga flux matches the incident Ga flux at steady state, as indicated by a horizontal dashed line labeled  $F_{Ga}$ ; its absolute value was determined from GaAs RHEED intensity oscillations. When adding an NH<sub>3</sub> flux, a reduction in the desorbing Ga flux is observed and similar curves were obtained for different substrate temperatures and NH<sub>3</sub> fluxes. We will try to understand the adsorption behavior of Ga by analyzing these data and by fitting them to a rate equation model of the adsorption kinetics. We will first consider the data shown in Fig. 1 where there is no growth and then later extend the model to include an NH<sub>3</sub> flux.

The adsorption of Ga in Fig. 1 depends strongly on the initial preparation of the surface, as evident from very different transient responses to an incident Ga flux. To observe the behavior shown in Fig. 1(a), the surface was initially gallided by exposure to a Ga flux of 0.6 ML/s for 1 min in the absence of NH<sub>3</sub>. Upon initiation of the Ga flux, the Ga desorption signal rapidly rises until the desorbed flux equals the incident flux. By contrast, for Fig. 1(b), a nitrided surface



FIG. 1. Measured Ga desorption vs time for a (a) gallided surface and (b) nitrided surface. (c) Enlarged view of the initial desorption rise in panel (a). (d) Enlarged view of the initial desorption rise in panel (b), showing the knee in the data that we interpret as being due to desorption from a very weakly adsorbed state. For the data in each panel, the incident Ga flux,  $F_{\rm Ga}$  was 0.6 ML/s, and the substrate temperature was 765 °C.

was prepared by annealing in NH<sub>3</sub> at a BEP of  $1 \times 10^{-4}$  Torr for approximately 1 min. Then the NH<sub>3</sub> flux was switched off and the background NH3 removed. Upon opening the Ga shutter there is an initial signal rise to about 1/3 of the incident Ga flux, where it levels out. After a few seconds, though, the desorbing Ga flux rises again, eventually reaching steady state at a value equal to the incident Ga flux. If only one state on the surface were being filled by Ga, we would expect the desorbing flux to rise gradually without delay. Instead, the rapid increase to an intermediate value suggests that a fraction of the incident flux is desorbed very quickly, while the remainder gradually fills a site that has a slow desorption rate. This will be discussed further in Sec. IV. These measurements on both a gallided and an initially nitrided surface<sup>9-11</sup> should represent the limits of growth under high Ga/NH<sub>3</sub> and NH<sub>3</sub>/Ga flux ratios, respectively.

When exposing an initially nitrided surface [Fig. 1(b)] to a sufficient amount of Ga, some of the Ga is adsorbed resulting in the gallided surface [Fig. 1(a)]. On the gallided surface, however, there is no net adsorption above the condensation temperature.<sup>9</sup> More specifically, both surfaces in Fig. 1 were exposed to  $F_{Ga}\Delta t$  layers of Ga, where  $F_{Ga}$  is the incident Ga flux and  $\Delta t$  the exposure time between opening and closing the Ga shutter. The net amount of Ga adsorbed is the area between the line at  $F_{Ga}$  and the curve describing the measured desorbed Ga flux during exposure, less the area under the curve of the desorbed flux after exposure. For the gallided surface, the Ga adsorbed during Ga exposure equaled the amount desorbed after closing the shutter, i.e., the difference between the two areas was within the DMS measurement error of about 0.1 ML. By contrast, the nitrided surface retained a net amount, usually on the order of 0.5-1.0 ML. This net amount will be termed the uptake, and its value depended on sample history and the substrate temperature. The total amount of Ga uptake was always less than 1 ML, and after reaching steady-state Ga desorption, no additional Ga could be added. This suggests that the maximum coverage of strongly adsorbed Ga is unity and that if we define  $\theta_{s,o}$  as the initial coverage of strongly adsorbed Ga, then the Ga uptake is  $1 - \theta_{s,o}$ . In other words, the nitrided surface is reactive to Ga, with an initial Ga coverage, converting to an unreactive gallided surface once the chemisorption process is completed.

The morphology of both gallided and nitrided  $GaN(000\overline{1})$  surfaces was examined by atomic force microscopy on bulk samples. Growth on these surfaces was described previously<sup>9</sup> and showed a range of features, depending on the growth parameters. Some samples exhibited macrosteps with large terraces. On these, two distinct morphologies were obtained, shown in Fig. 2. Figure 2(a) shows a sample that was annealed after growth for several minutes under NH<sub>3</sub> and then cooled, which resulted in terraces covered with irregularly shaped islands on the order of 500 Å and 2-5 Å in height. Figure 2(b) shows a sample that was cooled down at a a moderate rate of roughly 100° per min. Areas with similar islands are observed, but only in regions starting at a descending step edge. Apart from this island region, the rest of the surface is featureless. Finally, the sample shown in Fig. 2(c), was quenched after the Ga shutter was closed. This last sample was grown in a different MBE apparatus using similar growth conditions. As can be seen in this case, all terraces appeared featureless, except for a few atomic steps between the macrosteps. The width of the island regions originating from descending step edges depended on annealing time (or quenching rate) under NH<sub>3</sub>, while the remainder of the surface was unchanged. This last surface could equivalently be obtained by adding less than a monolayer of Ga to the surface shown in Fig. 2(a). Note that the initial surface of Fig. 1(a) corresponded to Fig. 2(c) and the initial surface of Fig. 1(b) corresponded to Fig. 2(a). Guided by these results, as well as the measurements presented in the preceding paragraph, we interpret the islands in the nitrided regions as an initial coverage of strongly bound Ga,  $\theta_{s,o}$ .

For some of the curves similar to Fig. 1(b), the initial knee showed a slight decrease between the first rise in the



FIG. 2. Three 1  $\mu$ m×1  $\mu$ m AFM scans of the GaN(0001) surface showing macrosteps and large, smooth terraces. These epitaxial films were grown on bulk GaN under conditions of excess Ga at a substrate temperature of 725 °C and then cooled at different rates under an NH<sub>3</sub> flux. (a) Annealed in NH<sub>3</sub> (nitrided) and then cooled, showing an island structure. (b) Cooled rapidly, showing some nitridation at the edges of macrosteps. (c) Quenched, showing a gallided surface with macrosteps separated by featureless terraces. Alternatively this could be prepared by adding Ga to (a) without NH<sub>3</sub> present (Ref. 9).

mass spectrometer signal and the final rise to steady state. However, the decrease was comparable to the noise in the data. In order to increase the signal to noise ratio, we repeated the experiment of Fig. 1(b) ten times under similar conditions, and averaged those curves. Figure 3 shows this average in the absence of NH<sub>3</sub>. After each measurement, the surface was annealed in NH<sub>3</sub> for 1 min at  $1 \times 10^{-4}$  Torr. As before, a nearly instantaneous increase in the desorbing Ga flux is observed upon opening the Ga shutter. After this initial rise, a small dip in the desorbing Ga signal is clearly seen. This is followed by the increase to steady state, where the desorbed flux equals the incident flux. As for the results in Fig. 1(a), a data average on the gallided surface does not show the knee in the DMS signal after opening the Ga shut-



FIG. 3. Average of 10 uptake curves from a nitrided surface in the absence of  $NH_3$  and a calculation from the model of Eqs. (1)–(3).

ter. Though averaging significantly increased the signal to noise ratio, we did not employ this technique for the rest of the uptake curves due to the long time required to acquire each data set.

The initial rise in the transient signal of Fig. 1(b) is fast, within the resolution of our DMS, which was limited by the 100 ms time constant of the signal preamplifier. This rise is fast enough to ask whether the incident Ga is reflected or first adsorbed and then quickly desorbed. Atoms trapped in an adsorption state, even briefly, are expected to lose all information associated with their angle of incidence. To resolve this issue we varied the angle between the sample and the incident beam by 30°, leaving the detector fixed. No angular dependence was found in the shape of the transient uptake data, indicating that this initial rise in the data of Fig. 1 is not due to a reflected signal, instead suggesting desorption from a weakly bound state. The nature of this state is suggested by noting that H<sub>2</sub> was desorbed from the surface during the duration of the knee.<sup>6</sup> Consequently, we associate the knee with Ga adsorption onto a hydrogen passivated, nitrided surface.

When there were both Ga and NH<sub>3</sub> incident on the sample surface, growth occurred. Depending on the NH<sub>3</sub>/Ga flux ratio, different uptake curves were obtained. A sequence of these desorption curves for increasing NH<sub>3</sub>/Ga flux ratios is shown in Fig. 4. Figure 4(a) shows a measurement of the Ga desorption flux at a low NH<sub>3</sub>/Ga flux ratio. The desorption behavior is similar to that in Fig. 1(b), but in this case the desorbing, steady state Ga flux is reduced, corresponding to the growth rate. In Figs. 4(b) and 4(c), the NH<sub>3</sub> flux is successively increased. The curves showed the same general features. In these two, the steady state flux was also reduced due to growth and the knee in the DMS signal remained approximately at the same level. The main difference is the duration of the knee, which increases with the NH<sub>3</sub> flux. Finally, in Fig. 4(d), at an NH<sub>3</sub> BEP of  $4 \times 10^{-6}$  Torr, the second rise in Ga desorption is completely absent. This last



FIG. 4. Measured Ga desorption vs time during growth. The incident Ga flux was 0.6 ML/s, the incident NH<sub>3</sub> BEP was (a) 0.5, (b) 2.5, (c) 3.0, and (d)  $4.0 \times 10^{-6}$  Torr. The substrate temperature was 750 °C.

curve shows that there is a maximum in the growth rate, with some Ga desorbing even under excess NH<sub>3</sub> conditions.

When increasing the NH<sub>3</sub>/Ga flux ratio, the duration of the knee versus NH<sub>3</sub> flux increases slowly until at a specific flux, the duration of the knee shows an abrupt increase. Past this point, as in Fig. 4(d), the desorbed Ga flux remains at the first, intermediate value. In this latter case, Ga is apparently continually adsorbing into the strongly bound site. The strong sites are never completely filled. This surface should be similar to the starting surface for Fig. 1(b) where a knee in the DMS signal is observed, i.e., it is an excess NH<sub>3</sub> growth regime. In the former case, the strongly bound sites are completely filled, forcing additional Ga to go into weakly adsorbed sites. Hence the DMS signal goes through the knee and reaches a steady state. In steady state the surface should be similar to Fig. 1(a) where only the weak adsorption is seen in the DMS signal, i.e., an excess Ga growth regime. This abrupt crossover suggests that two distinctly different growth modes are observed by DMS and that this feature can be used to determine whether the growth is excess Ga or excess NH<sub>3</sub>. The measured crossover for a fixed Ga flux as a function of ammonia flux and substrate temperature is indicated as the solid points in Fig. 5, which shows that either increasing the NH<sub>3</sub> flux or the substrate temperature leads to a change in growth mode. This transition is very sharp; in Fig. 4, for example, it was difficult to find a curve intermediate between those shown in parts (c) and (d). Any model of the growth must include this sharp transition.

The abrupt change between growth regimes is also seen in measurements of the steady state growth rate. Note that since there is no Ga accumulation at these temperatures and Ga flux, the instantaneous growth rate is given by the incident Ga flux minus the desorbing Ga flux.<sup>10,11</sup> Figure 6(a) shows the steady state growth rates measured as a function of temperature for several NH<sub>3</sub> fluxes at a fixed Ga flux. For these data, the NH<sub>3</sub> flux was fixed; the temperature was varied and the difference between the incident Ga flux and the



FIG. 5. Regime crossover. The solid points correspond to the temperature and flux at which the uptake curves of Fig. 4 ceased to exhibit a knee in the data. The curves are fits with different power law growth models of Eq. (4).

measured, steady-state Ga DMS signal determined. The dashed lines are to guide the eye between the data points, which are the filled symbols. The most noteworthy feature was that the growth rate abruptly increased at about the same temperature as the crossover between growth regimes in Fig. 5. In Fig. 6(a) the points on either side of the transition are separated by the line breaks, which are in turn connected by dotted lines. For low NH<sub>3</sub>/Ga flux ratios, as in Figs. 4(a) and 4(b), the steady state growth rate is only a small fraction of the incident Ga flux. This is a relatively unreactive steady state surface. On the other hand, for high NH<sub>3</sub>/Ga flux ratios, as in Fig. 4(d), a second rise in Ga desorption is never observed. This last curve is characteristic of the saturated growth rate in the upper curves of Fig. 6(a). The absence of the second rise in Ga adsorption and the abrupt increase in growth rate suggest that the surface is being continuously nitrided, never reaching the gallided state.

# **IV. DISCUSSION**

In order to develop a kinetic growth model, we first examine the dramatically different desorption curves shown in Fig. 1. Ga adsorbed onto the gallided surface is seen to be only weakly adsorbed, rapidly leaving the surface after the Ga shutter is closed. We showed previously that this process is well described by the equilibrium between liquid Ga and its vapor; hence the desorption rate can be described as  $\theta_w/\tau$ , where  $\tau$  is obtained from tabulated equilibrium vapor pressure data.<sup>15</sup> Note that for the Ga fluxes used in these experiments, the substrate temperatures were always higher than the temperature at which liquid Ga would condense on the sample surface. Hence the adsorption of Ga on the gallided surface will be described by a rate equation with first order desorption kinetics.

To account for the initial knee in the data of Figs. 1(b) and 3 on the nitrided surface and the lack of one on the gallided surface, we need to assume that the adsorption process depends upon the Ga coverage. We assume that on the nitrided portions of the surface, Ga first adsorbs into a physisorbed, precursor state. Part of this physisorbed Ga quickly desorbs and part becomes chemisorbed. This initial phys-



FIG. 6. (a) Steady state growth rate as a function of temperature for several NH<sub>3</sub> fluxes. The dashed lines are to guide the eye. The breaks correspond to the growth mode transition, as determined from the shape of the measured Ga DMS signal. (b) Calculation of the growth rate from the model in Eqs. (1)–(4). In both panels,  $T_c$  is the measured temperature at which Ga condenses on GaN(0001) in the absence of an NH<sub>3</sub> flux (Ref. 10).

isorption could occur if the measured hydrogen coverage passivates the nitrided surface, inhibiting chemisorption. For the chemisorption process to occur, the adsorbed hydrogen must be released. On gallided portions of the surface we assume only weak Ga adsorption. This Ga can either desorb or diffuse to chemisorption sites on the nitrided parts of the surface.<sup>16</sup> These relatively simple assumptions are sufficient to describe the data.

These two different reaction paths explained above are illustrated in Fig. 7. The left side of the illustration represents a GaN film, with a gallided top half and a nitrided bottom half. The gallided half shows a layer of chemisorbed Ga, while the bottom half is the hydrogen-passivated, nitrided surface. On the right side, potential wells representing the general reaction path are plotted for these two surfaces. On the gallided surface in Fig. 7(b), Ga can adsorb into a single, weak well, and then can either desorb or diffuse to a nitrided region, as indicated by the arrows. On the nitrided surface in Fig. 7(a), two potential wells are shown. The outer shallow well permits physisorption of Ga, which is either desorbed or chemisorbed into the deeper well. Once chemisorption occurs, the potential picture changes to the top half of the illustration. With the nature of the adsorption depending on the presence or absence of chemisorbed Ga, the differences



FIG. 7. Sketch of the reaction paths, depending on whether Ga is incident on (a) a nitrided surface or (b) a gallided surface. (c) The upper part shows a coverage of chemisorbed Ga,  $\theta_s$  in strong sites and the lower part shows a nitrided region with no strong sites. The coverage of weakly adsorbed Ga on chemisorbed Ga is  $\theta_w$ .

in the types of adsorption here are similar to the distinction made in physisorption between extrinsic and intrinsic sites.<sup>17</sup>

This model is described explicitly by the following rate equations:

$$\frac{d\theta_s}{dt} = (1 - \theta_s)\alpha F_{\rm Ga} + \theta_w (1 - \theta_s)k, \tag{1}$$

$$\frac{d\theta_w}{dt} = \theta_s F_{\rm Ga} - \theta_w / \tau - \theta_w (1 - \theta_s) k, \qquad (2)$$

$$F_{\rm d} = (1 - \alpha) F_{\rm Ga}(1 - \theta_s) + \theta_w / \tau, \qquad (3)$$

where  $\theta_s$  is the coverage of chemisorbed Ga, and  $\theta_w$  is the coverage of weakly adsorbed Ga on top of chemisorbed Ga, with a residence time of  $\tau$ . The fraction of incident Ga that adsorbs into chemisorption sites from the intrinsic physisorption state is described by  $\alpha$ . The first two equations describe the relative rates at which the chemisorbing and weakly adsorbed states are filled. No equation is given for the population of the intrinsic physisorption state, which is sufficiently described by  $\alpha$  due to their short residence time. The third equation is the desorbed Ga flux as measured by DMS.

Equation (1) contains the strongest assumptions. As illustrated in Fig. 7 two states are considered on the nitrided surface. Since the surface is passivated with hydrogen, incident Ga first adsorbs into the fast, intrinsic physisorption state. Part of the Ga then desorbs, and the remaining fraction,  $\alpha$ , chemisorbs into the deep well while releasing H<sub>2</sub>. The number of precursor sites is assumed to equal the number of empty chemisorption sites,  $1 - \theta_s$ . The first term in Eq. (1) covers this chemisorption process, which is proportional to the incident Ga flux, the number of unfilled chemisorption sites, and the fraction of Ga atoms chemisorbing from the fast intrinsic precursor state. The second term describes the filling of empty chemisorption sites from weakly adsorbed Ga on gallided parts of the surface (the filled chemisorption sites). To fit the data in Figs. 1(b) and 3, this equation must be coupled with the time variation of the weakly adsorbed Ga.

The second equation, Eq. (2), contains three terms describing the rate at which the population of weakly adsorbed Ga on gallided regions changes. The first term simply states that incident Ga adsorbs on top of filled chemisorption sites. No physisorbed intermediary is required for this process, and we do not consider multilayer adsorption, i.e., no accumulation of liquid Ga. The second term states that weakly adsorbed Ga desorbs at a rate proportional to its coverage. The last term describes the depletion of weakly adsorbed Ga due to diffusion to empty chemisorption sites, which balances the last term in Eq. (1), and is indicated by *k* in Fig. 7. There is no transfer from chemisorbed Ga,  $\theta_s$ , to weakly adsorbed Ga,  $\theta_w$ . This second equation, with  $\theta_s=1$ , fits the data in Fig. 1(a). For the residence time,  $\tau$ , we use  $\tau$  $= \tau_0 \exp(E_0/kT)$  where  $\tau_0=4.88 \times 10^{-14}$  s and  $E_0=2.70$ eV.<sup>11,15</sup> This equation is mainly a statement that the weakly adsorbed state obeys first order desorption and zeroth order adsorption kinetics.

Equation (3) is only necessary to compute the desorbing flux to compare to the measured data. The first term covers physisorbed Ga desorbed from the fast intrinsic precursor state, proportional to the sites available for chemisorption. The second term accounts for the physisorbed Ga that desorbs from the weakly adsorbed state.

To test this model we first performed a fit to the averaged uptake curve of Fig. 3. Both the original data and the computed curve are shown. This particular curve was measured at a substrate temperature of 756 °C and a Ga flux of 0.61 ML/s. For this curve, following the procedure described in Sec. III, we measured 0.77 ML of net Ga adsorption; hence to integrate Eqs. (1) and (2), we used the initial conditions  $\theta_{s,o} = 0.23$  ML and  $\theta_w(0) = 0$ . The best fit was achieved with  $\alpha = 0.45$  and a surface diffusion flux, *k*, of 35 ML/s. As can be seen, all of the details of the measured data are reproduced by the model.

The requirements on the fitting parameters are strict. The total Ga uptake fixes the fraction of initially filled chemisorption sites. Given  $\theta_{s,o}$ ,  $\alpha$  is determined by the initial signal rise just after opening the Ga shutter, since from Eq. (3),  $F_{\rm d}(0) = (1 - \alpha)(1 - \theta_{s,o})F_{\rm Ga}$ . The only fitting parameter is the temperature dependent surface diffusion parameter, k, which mainly determines the magnitude of the drop in the Ga desorption signal between the first and second rise. The higher this diffusion flux, the deeper the drop. Ga atoms will tend to diffuse to nitrided parts of the surface before a significant coverage of weakly adsorbed Ga can buildup on gallided parts of the surface, which is the cause of the second rise in the desorption signal. By comparing to measurements at different substrate temperatures, we obtain an activation energy for surface diffusion of  $1.5\pm1$  eV with a preexponential of  $1.2 \times 10^7$  ML/s.

Note that RHEED intensity oscillations are only observed under excess  $NH_3$  conditions on this polarity, and as shown in Fig. 2(c), on a gallided surface no islands are observed. These suggest that the diffusion described by k is dominated by the gallided portions of the surface. Further, we expect that under conditions of excess  $NH_3$ , growth is by island nucleation, while under excess Ga, growth is dominated by step flow.

Using the parameters determined by fitting to the data obtained without  $NH_3$ , we now expand the model to include a simultaneous  $NH_3$  flux. When opening the Ga shutter in the presence of  $NH_3$ , we expect that adsorption into chemisorp-



FIG. 8. Simulation of the uptake curves of Fig. 4 vs  $NH_3$  flux and T using Eqs. (2)–(4).

tion sites [galliding the surface as in Fig. 2(c)] competes against renitridation. Our atomic force microscopy (AFM) measurements indicate that nitridation only occurs at step edges of gallided parts of the surface;<sup>9</sup> hence we only have to modify the equation for the time behavior of the chemisorbing Ga as

$$\frac{d\theta_s}{dt} = (1 - \theta_s) \alpha F_{\text{Ga}} + (1 - \theta_s) \theta_w k$$
$$- (\theta_s - \theta_{s,o})^x (1 - \theta_s)^x F_N - f F_N (\theta_s - \theta_{s,o}) \kappa,$$
(4)

where  $F_N$  is the NH<sub>3</sub> flux, proportional the ion gauge current, f is the efficiency at which NH<sub>3</sub> reacts with chemisorbed Ga at step edges, and  $\kappa = 1 - \theta_w$  is a factor inhibiting growth if there is appreciable Ga in weakly adsorbing sites.<sup>6,11</sup> Further, we require that  $\theta_{s,o} \leq \theta_s \leq 1$ , as expected by the assumptions of the model. In the third term, we assume that nitridation occurs at the island step edges, with x = 1/2 to account for the available step perimeter. This term contains both step edges around islands of strongly adsorbed Ga and the perimeter of holes, i.e.,  $\sqrt{1 - \theta_s}$ , as well. The fourth term corresponds to growth at step edges under excess Ga conditions. Results of these calculations are shown in Fig. 8 versus NH<sub>3</sub> flux and versus substrate temperature. The main result is that this model qualitatively fits the data and that there is a very sharp crossover as a function of both temperature and  $NH_3$  flux. For the calculation of Fig. 8 a step edge related growth efficiency of 0.1 was used, affecting the crossover only slightly. This illustrates that the crossover is relatively independent of the density of step edges on the gallided surface.

The growth rate was calculated versus substrate temperature for several NH<sub>3</sub> fluxes, as shown in Fig. 6(b), and should be compared to the measurement of Fig. 6(a). The calculation shows that under excess Ga, the growth rate increases with temperature and then rises abruptly as it crosses into the excess NH<sub>3</sub> regime. The abrupt crossover between excess Ga and NH<sub>3</sub> regimes is indicated by the dotted lines. Note that in the excess Ga regime, the growth rate goes to zero near the condensation temperature. And, like the measurement in Fig. 6(a), in the excess NH<sub>3</sub> regime, the growth rate decreases slightly with increasing temperature. In the calculation this decrease results from a reduction in  $\theta_s$  and hence an increase in the desorption of Ga from the fast, physisorption state. Qualitatively the calculation reproduces the experiment.

For the integration of the rate equations, shown in Figs. 8 and Fig. 6(b), we needed to know the initial Ga population of the chemisorbed sites,  $\theta_{s,o}$ . As discussed in Sec. III,  $\theta_{s,o}$  was never measured to be zero even after annealing in NH<sub>3</sub>. Further, it decreased slightly as the substrate temperature was increased. A measurement of the temperature dependence was complicated because at the higher temperatures, during the time it would take to remove the NH<sub>3</sub> from the growth chamber, a portion of the nitrided surface converted to gallided.<sup>9,18</sup> The progress of this conversion process was monitored by RHEED and a correction made. We estimated that  $\theta_{s,o}(T)$  is roughly given by  $\theta_{s,o}(T) = 2.62 - 0.00235$  T (ML), with T in K.<sup>18</sup>

As a measure of how well the model fits the data, Fig. 5 compares the modeled regime crossover to the measured crossover. It shows the crossover from step flow to island nucleation as a function of substrate temperature and NH<sub>3</sub> flux. The data was obtained for several NH<sub>3</sub> fluxes from data series as in Fig. 4. The model equations were then used to fit the experimental data, for several values of x: 1/2, 1, and 2. For all three parameters, the unknown ion gauge proportionality factor for  $F_N$  was adjusted to fit the experimental data for an NH<sub>3</sub> flux of  $2.5 \times 10^{-6}$  Torr. The best fit was obtained for x=2, though a value of x=1/2 is justified in terms of representing island perimeter. This may be a limitation of the rate equation method, though all values give a sharp crossover.

The form of the growth terms included in the rate equations determined the extent to which the abrupt crossover seen in the data could be modeled. For example, if we replaced the growth terms in Eq. (4) by only a term that is proportional to both  $F_N$  and  $\theta_s$ , as one would have if growth on gallided terraces dominated, then an abrupt crossover is not seen. Neglect of such a term is consistent with our experimental results, including the absence of RHEED intensity oscillations for growth under excess Ga conditions and the lack of islands in the AFM<sup>9</sup> measurements on gallided portions of the surface.

#### V. CONCLUSION

The growth of GaN on GaN( $000\overline{1}$ ) could be modeled by a set of rate equations with the following main assumptions: (1) Ga could adsorb into either of two weakly adsorbed states, (2) Ga from these weakly adsorbed states could, in turn, either chemisorb or desorb, (3) NH<sub>3</sub> only incorporated N at step edges, (4) Ga was more mobile on a Ga covered surface than on a nitrided surface. With these assumptions the main features of the measured desorption data could be described under conditions where there was either an incident Ga flux and no NH<sub>3</sub> flux or where there were both Ga and NH<sub>3</sub> fluxes incident on the sample.

In the case of Ga adsorption without an NH<sub>3</sub> flux incident on the sample, the DMS measurements depended on sample history. For  $GaN(000\overline{1})$  annealed in NH<sub>3</sub> there was a knee in the Ga DMS data that was understood as a competition between desorption from a weak precursor state and chemisorption into a strongly bound state. The surface before and after Ga adsorption was examined with AFM, and distinctly different morphologies were found. The surface annealed in NH<sub>3</sub> had an island morphology; after Ga adsorption the surface was featureless. We found that annealing a surface in NH<sub>3</sub> could never completely nitride the surface, with between 0.1 and 0.25 ML of strongly adsorbed, non-nitrided Ga remaining. Further, during adsorption of Ga onto a nitrided surface, fitting the rate equations showed that only about half of the incident flux could be used to fill strongly bound, chemisorbed states.

Fitting the measured DMS data during growth was more difficult since it had to account for the abrupt change in growth mode, from island nucleation to step flow, while still using the parameters determined from the adsorption experiments without  $NH_3$ . Further, we observed that on gallided surfaces nitridation began at step edges. Hence we needed to build in that  $NH_3$  only reacted at step edges, either those at islands or step edges due to the local miscut. We found terms that could be added to the rate equations, corresponding to growth at step edges, that gave good agreement with the abrupt crossover between excess Ga and excess N growth conditions. Also, the growth rates as a function of substrate temperature and of fluxes gave qualitative agreement with the model.

Two small issues in the comparison with model and experiment were noted. First, the exact temperature of the crossover between step flow and island nucleation predicted by the rate equation model, in which terms first order in island perimeter were included, decreased slightly more quickly with increasing temperature than that measured. Second, the actual growth rate would depend on the defect density present, which could change versus time. Nonetheless, the important result is that the rate equation model presented here shows what processes need to be emphasized in a more complete simulation and that the step edges play a key role.

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- <sup>1</sup>S. N. Mohammad, A. A. Salvador, and H. D. Morkoç, Proc. IEEE **83**, 1306 (1995).
- <sup>2</sup>S. Strite, M. E. Lin, and H. Morkoç, Thin Solid Films 231, 197 (1993).
- <sup>3</sup>R. F. Davis, J. Cryst. Growth **147**, 161 (1994).
- <sup>4</sup>N. Newman, J. Ross, and M. Rubin, Appl. Phys. Lett. **62**, 1242 (1993).
- <sup>5</sup>M. V. Averyanova, S. Karpov, N. Makarov Yu, I. N. Przhevalskii, M. S. Ramm, and R. A. Talalaev, MRS Internet J. Nitride Semicond. Res. **1**, 31 (1996).
- <sup>6</sup>D. Crawford, R. Held, A. M. Johnston, A. M. Dabiran, and P. I. Cohen, MRS Internet J. Nitride Semicond. Res. 1, 12 (1996).
- <sup>7</sup> E. J. Tarsa, B. Heying, X. H. Wu, P. Fini, S. P. DenBaars, and J. S. Speck, J. Appl. Phys. **82**, 5472 (1997).
- <sup>8</sup>D. D. Koleske, A. E. Wickenden, R. L. Henry, W. J. DeSisto, and R. J. Gorman, J. Appl. Phys. **84**, 1998 (1998).
- <sup>9</sup>R. Held, G. Nowak, B. Ishaug, S. M. Seutter, A. Parkhomovsky, A. M. Dabiran, P. I. Cohen, I. Grzegory, and S. Porowski, J. Appl. Phys. 85, 7697 (1999).
- <sup>10</sup> R. Held, D. E. Crawford, A. M. Johnston, A. M. Dabiran, and P. I. Cohen, J. Electron. Mater. **26**, 272 (1997).
- <sup>11</sup> R. Held, D. E. Crawford, A. M. Johnston, A. M. Dabiran, and P. I. Cohen, Surf. Rev. Lett. 5, 913 (1998).
- <sup>12</sup>J. R. Arthur, Surf. Sci. 43, 449 (1974).
- <sup>13</sup>J. Y. Tsao, T. M. Brennan, and B. E. Hammons, Appl. Phys. Lett. 53, 288 (1988).
- <sup>14</sup>C. R. Jones, T. Lei, R. Kaspi, and K. R. Evans, Mater. Res. Soc. Symp. Proc. **395**, 141 (1996).
- <sup>15</sup> CRC Handbook of Chemistry and Physics, 71st ed., edited by D. R. Lide (Chemical Rubber, Boca Raton, FL, 1990), pp. 5–70.
- <sup>16</sup>The rate for Ga diffusing from a weakly adsorbed sited on a gallide region to a chemisorbed site on a nitrided region implicitly includes the requirement for H to be desorbed.
- <sup>17</sup>G. Attard and C. Barnes, *Surfaces* (Oxford University Press, Oxford, 1998), p. 11.
- <sup>18</sup>R. Held, Ph.D. dissertation, University of Minnesota, 1999 (unpublished).