

# Kinetic modeling of microscopic processes during electron cyclotron resonance microwave plasma-assisted molecular beam epitaxial growth of GaN/GaAs-based heterostructures

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Microscopic growth processes associated with GaN/GaAs molecular beam epitaxy (MBE) are examined through the introduction of a first-order kinetic model. The model is applied to the electron cyclotron resonance microwave plasma-assisted MBE (ECR-MBE) growth of a set of  $\delta$ -GaN<sub>y</sub>As<sub>1-y</sub>/GaAs strained-layer superlattices that consist of nitrided GaAs monolayers separated by GaAs spacers, and that exhibit a strong decrease of  $y$  with increasing  $T$  over the range 540–580 °C. This  $y(T)$  dependence is quantitatively explained in terms of microscopic anion exchange, and thermally activated N surface-desorption and surface-segregation processes. N surface segregation is found to be significant during GaAs overgrowth of GaN<sub>y</sub>As<sub>1-y</sub> layers at typical GaN ECR-MBE growth temperatures, with an estimated activation energy  $E_s \sim 0.9$  eV. The observed  $y(T)$  dependence is shown to result from a combination of N surface segregation/desorption processes.

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The wide band-gap refractory semiconductor, GaN, related alloys, and heterostructures have recently come under active investigation due to their technological promise as light emitters in the blue to UV region.<sup>1–3</sup> While much recent GaN research has emphasized growth of device structures (blue LEDs and lasers) on various substrates,<sup>4–6</sup> comparatively little work has concentrated on the microscopic growth processes that are of significance, for example, in the electron cyclotron resonance plasma-assisted molecular beam epitaxial (ECR-MBE) growth of GaN-related heterostructures. Recently, we have shown<sup>7,8</sup> that it is possible to produce high quality, fully commensurate GaN<sub>y</sub>As<sub>1-y</sub>/GaAs strained-layer superlattices (SLS). Analysis of such structures through time-resolved reflection high energy electron diffraction (RHEED) and high-resolution x-ray diffraction (HRXRD) measurements recently revealed evidence of distinct thermally activated microscopic processes, but, in the absence of a quantitative model to consistently account for these separate RHEED and HRXRD observations, only tentative identification of processes, and at best, semiquantitative assessment of kinetics has been possible to date.<sup>8</sup>

In this letter, we examine the initial nitridation, N surface desorption, and N surface segregation processes observed in ECR-MBE-grown GaN<sub>y</sub>As<sub>1-y</sub>/GaAs heterostructures through the introduction of a quantitative model that is based on first-order kinetic theory. For the first time, the existence of a thermally activated N surface-segregation mechanism, which appears to be significant under typical

GaN/GaAs ECR-MBE growth conditions, is conclusively established and quantitatively assessed. Through application of our model to an unusually strong growth temperature dependence of  $y$  in GaN<sub>y</sub>As<sub>1-y</sub>/GaAs superlattices, the existence of a strong N-surface-segregation mechanism, which we suggested previously,<sup>8</sup> but could not conclusively establish in the absence of a suitable quantitative model (which is necessary to adequately describe the combined effects of concurrent, thermally activated N surface-segregation and surface-desorption processes) is now quantitatively confirmed. Numerical estimates of activation energies for the N surface segregation as well as surface desorption processes are given, within the context of first-order kinetics. Finally, the broader significance of a strong N surface-segregation effect to GaN/GaAs heteroepitaxy is discussed.

The samples and experimental details that are of relevance to the present work have been described in Ref. 8; for convenience, we briefly repeat the most pertinent details here. A set of 36-period “ $\delta$ -GaN<sub>y</sub>As<sub>1-y</sub>/GaAs” superlattices, each consisting nominally of GaN<sub>y</sub>As<sub>1-y</sub> monolayers (ML) separated by GaAs spacers, was grown on GaAs (100) as a function of substrate temperature (540–580 °C) in an ECR-MBE system. GaN<sub>y</sub>As<sub>1-y</sub> monolayers were produced through brief (4 s) N<sub>2</sub> plasma exposure of an As-stabilized GaAs surface, followed immediately by GaAs overgrowth at a fixed growth rate (0.75 ML/s), and an “As-soak” (30 s). The entire sample set was characterized through HRXRD, which confirmed commensurate growth, and from which N content ( $y$  in GaN<sub>y</sub>As<sub>1-y</sub> layers) was determined. The resultant compositional dependence on growth temperature,  $y(T)$ , from Ref. 8 is reproduced here in Fig. 1. For the purpose of the present work, the key finding is the unexpectedly abrupt

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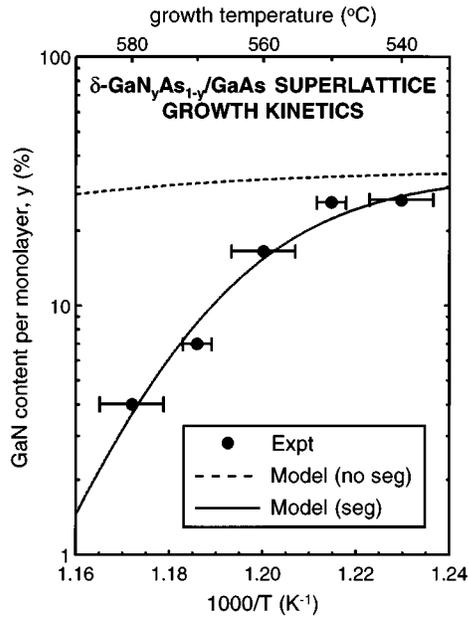


FIG. 1. Growth-kinetic models to explain the strong  $y(T)$  dependence observed for ECR-MBE-growth  $\delta\text{-Ga}_y\text{As}_{1-y}/\text{GaAs}$  strained-layer superlattices. Experimental data points are reproduced from Ref. 8. Dashed curve: model calculation neglecting N surface segregation [Eq. (2)]. Solid curve: model calculation including segregation [Eq. (4)].

drop in  $y$  with increasing growth temperature.

We now wish to understand the physical origin of this  $y(T)$  dependence. For this purpose, we devise an analytical model, based on first-order-kinetics arguments, which explicitly incorporates the distinct phases of our particular SLS growth sequence (nitridation/overgrowth/soak) as described above. First, let us consider the nitridation phase. The essential physical processes that describe the net rate of surface nitridation have been previously identified;<sup>7</sup> they are (i) N-for-As surface anion exchange (N gain), and (ii) surface N desorption (N loss). Mathematically, these processes can be modeled (up to terms linear in N concentration) as

$$\frac{dy}{dt} = s\Phi(1-y) - \frac{y}{\tau_d}. \quad (1)$$

In this equation, the term  $-y/\tau_d$  corresponds to N loss due to surface desorption and is described kinetically in terms of a thermally activated rate constant,  $\tau_d^{-1} = \tau_{0d}^{-1} \times \exp(-E_d/kT)$ , with activation energy  $E_d$ . We have directly observed such a process through RHEED observation of nitrided GaAs surfaces at elevated temperatures, and have previously reported estimates for  $E_d$  ( $\sim 2.1$  eV).<sup>8</sup>

The N gain term [first term on the right hand side of Eq. (1)] represents the N buildup on the As-stabilized GaAs surface due to anion exchange. This process is modeled (again up to terms linear in  $y$ ) as being proportional to the incident physically activated N flux  $\Phi$ ; to an overall “efficiency factor”  $s$ ;<sup>9</sup> and, to the fraction of available (As) surface sites,  $(1-y)$ . Defining an “effective dosing rate”  $r \equiv s\Phi$ , the solution to Eq. (1) for an initially N-free surface can be written as

$$y(t_{\text{exp}}) = y_{ss} [1 - \exp(-t_{\text{exp}}/\tau)], \quad (2)$$

where  $y_{ss} \equiv r\tau$  and  $\tau \equiv (\tau_d^{-1} + r)^{-1}$ , and  $t_{\text{exp}}$  is the nitrogen plasma exposure time. Equation (2) models the essential ni-

tridation kinetics without undue mathematical complexity, but ignores the subsequent stages of growth of our superlattices. A comparison of the dashed curve with experimental data points in Fig. 1 graphically illustrates the seriousness of this omission. The dashed curve is a plot of Eq. (2), taking  $t_{\text{exp}} = 4$  s, and making use of the RHEED-based experimental desorption parameters,  $E_d = 2.1$  eV, and  $\tau_d = 7$  s at  $592$  °C.<sup>7,8</sup> Additionally, the dosing rate  $r$  is estimated to be approximately 0.1 Hz from experimental  $y$  values at  $550$  °C for 4 and 6 s nitridations.<sup>8</sup>

Upon inspection of Fig. 1 it is evident that the processes of anion exchange and N desorption alone are insufficient to account for the strong falloff of  $y$  with increasing growth temperature in our  $\delta\text{-Ga}_y\text{As}_{1-y}/\text{GaAs}$  superlattices. The weak falloff of the model (dashed) curve with increasing  $T$  results from the negligible N desorption, which would be expected in the short time over which an initially nitrided surface remains exposed; i.e.,  $(t_{\text{exp}} + t_{\text{ML}}) \leq \tau_d$ , where  $t_{\text{ML}}$  is the monolayer deposition time of the GaAs overlayer. Since surface desorption is the only observed N loss mechanism in our samples, the effective time over which N persists on the (moving) growth surface must be substantially larger than  $\sim (t_{\text{exp}} + t_{\text{ML}})$ . To explain this, we hypothesize that thermally activated N surface segregation, with rate  $\tau_s^{-1} = \tau_{0s}^{-1} \exp(-E_s/kT)$ , is occurring during GaAs overgrowth.<sup>8</sup> This is supported qualitatively by our experimental observation that GaN-related  $(3 \times 3)$  RHEED surface reconstructions persist longer at higher substrate temperatures during GaAs overgrowth.

Let us consider explicitly the fractional loss of N from one period of a superlattice during overgrowth. In our model, we shall assume that (1) segregation is allowed only from the current first subsurface to the current surface layer; (2) desorption is allowed from all currently exposed surfaces, i.e., from the current surface and current partially exposed first subsurface layers; and (3) the segregation and desorption processes are statistically independent. It is convenient to define a relative GaN mole fraction  $S_n$  in monolayer  $n$  where, by definition, the content of the nitrided layer at the end of the nitridation step is normalized to  $S_0(t=0) \equiv 1$ . Under these conditions, the N content of monolayers  $n$  and  $n+1$  are related through

$$S_{n+1}(0) = [S_n(0) - S_n(t_{\text{ML}})] \frac{\tau_d}{\tau_{\text{tot}}}, \quad (3)$$

where  $\tau_{\text{tot}} \equiv \tau_s + \tau_d$ . Also, over the time interval  $0 \leq t \leq t_{\text{ML}}$ ,  $S_n(t)$  decays exponentially as  $\exp(-t/\tau_{\parallel})$ , where  $\tau_{\parallel}^{-1} \equiv (\tau_s^{-1} + \tau_d^{-1})$ . Using this expression in Eq. (3), it is straightforward to show that, in order to consistently incorporate N surface segregation into our model, Eq. (2) must be replaced by

$$y(t_{\text{exp}}) = y_{ss} \left[ 1 - \exp\left(\frac{-t_{\text{exp}}}{\tau}\right) \right] \left( \frac{\tau_{\text{tot}}}{\tau_d + \tau_s e^{t_{\text{ML}}/\tau_{\parallel}}} \right), \quad (4)$$

where the bracketed factor on the right is merely a dimensionless “correction factor” to Eq. (2) in the range 0 to 1, which physically represents the fraction of the initial N dose that is retained within each (nominally identical) period of the superlattice. Thus, Eq. (4), rather than Eq. (2) above, is

needed to quantitatively describe the nitridation/overgrowth/soak sequence of our  $\delta$ -GaN<sub>y</sub>As<sub>1-y</sub>/GaAs superlattices, in terms of microscopic anion exchange, desorption, and segregation processes.

With N surface segregation now properly included in our model, Eq. (4) is plotted as the solid curve in Fig. 1. This curve has been calculated through use of the identical dosing ( $r$ ) and desorption ( $E_d$  and  $\tau_{0d}$ ) parameter values that were used above to obtain the dashed curve while, at the same time, performing a nonlinear least-squares fit to the experimental data points shown in the figure through adjustment of the two segregation parameters  $E_s$  and  $\tau_{0s}$ . The surface-segregation activation energy that results from this procedure is estimated to be  $0.9 \text{ eV} \pm 30\%$ . From the figure it is seen that, with N surface segregation now included in our model, very good quantitative agreement with the experimental data is obtained, thereby tending to confirm our N surface-segregation hypothesis.

Our results imply that a compositional-profile smearing of N along the growth direction should be expected as a natural consequence of the segregation process. Preliminary cross-sectional scanning tunneling microscopy images of one of our superlattices confirm this.<sup>10</sup> Such direct-imaging techniques might provide a means for direct determination of the quantity  $E_s$ , since our model predicts the manner in which the spatial extent of profile smearing should increase with increasing growth temperature. Such profile-smearing effects would tend to limit heterojunction abruptness of nitride/arsenide heterostructures (assuming that a given GaN/GaAs-based heterostructure can be stabilized in the first place); however, such smearing effects might possibly be controlled through some of the MBE techniques that have been successfully applied to the problem of dopant-profile smearing in MBE-grown Si.<sup>11</sup>

In summary, we have developed a kinetic model to help identify and quantitatively assess some of the microscopic processes that are observed in ECR-MBE-grown GaN/GaAs-based heterostructures. Separate experimental observations

of anion exchange, N surface desorption, and an unusually strong decrease in N content with increasing growth temperature for the case of ECR-MBE-grown, coherently strained  $\delta$ -GaN<sub>y</sub>As<sub>1-y</sub>/GaAs superlattices, are all quantitatively explained in terms of this single, kinetic model. In particular, the strong  $y(T)$  dependence is quantitatively understood for the first time in terms of combined, thermally activated, N surface-segregation/surface-desorption processes. The N surface-segregation process appears to be significant under typical GaN/GaAs ECR-MBE growth conditions. Finally, our model enables for the first time a numerical estimate of the kinetic parameters that are associated with the N surface-segregation process.

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