

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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(Received 5 September 1995; accepted for publication 4 January 1996)

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 δ -GaN_yAs_{1-y}/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_yAs_{1-y} 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.¹⁻³ While much recent GaN research has emphasized growth of device structures (blue LEDs and lasers) on various substrates,⁴⁻⁶ 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^{7,8} that it is possible to produce high quality, fully commensurate GaN_yAs_{1-y}/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.⁸

In this letter, we examine the initial nitridation, N surface desorption, and N surface segregation processes observed in ECR-MBE-grown GaN_yAs_{1-y}/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_yAs_{1-y}/GaAs superlattices, the existence of a strong N-surface-segregation mechanism, which we suggested previously,⁸ 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 “ δ -GaN_yAs_{1-y}/GaAs” superlattices, each consisting nominally of GaN_yAs_{1-y} 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_yAs_{1-y} monolayers were produced through brief (4 s) N₂ 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_yAs_{1-y} 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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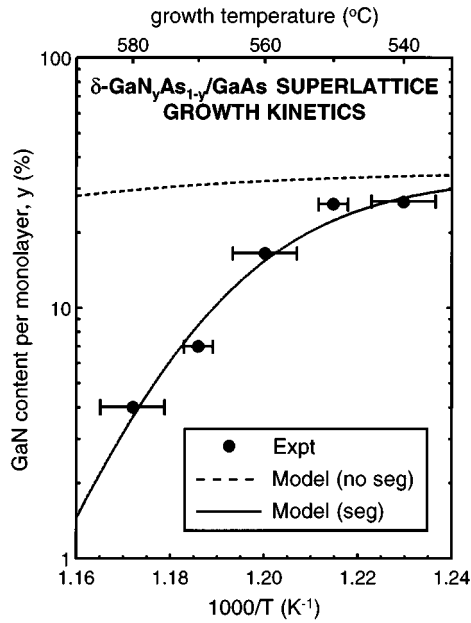


FIG. 1. Growth-kinetic models to explain the strong $y(T)$ dependence observed for ECR-MBE-growth $\delta\text{-Ga}_y\text{As}_{1-y}/\text{GaAs}$ strained-layer superlattices. Experimental data points are reproduced from Ref. 8. Dashed curve: model calculation neglecting N surface segregation [Eq. (2)]. 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;⁷ 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 (~ 2.1 eV).⁸

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 Φ ; to an overall “efficiency factor” s ;⁹ 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_{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.^{7,8} 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.⁸

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_{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.⁸ This is supported qualitatively by our experimental observation that GaN-related (3×3) 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 δ -GaN_yAs_{1-y}/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 τ_{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 τ_{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.¹⁰ 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.¹¹

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 δ -GaN_yAs_{1-y}/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.

This work was supported by the Office of Naval Research under Grant No. N00014-92-J-1845. Additionally, R.J.H. and M.L.O. wish to acknowledge the support of Air Force Office of Scientific Research under Contract Nos. F49620-93-1-0211 and F49620-93-10389, and the support of the Advanced Research Projects Agency, monitored through the Army Research Office under Contract No. DAAH04-94-G-0393.

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⁹The efficiency factor (defined here with units of area) corresponds to possible physical subprocesses such as adsorption, surface migration, dimerization and re-evaporation, chemical kinetics of As-N exchange, etc., and in general might depend on surface chemistry, strain, and temperature, but in our simplified model, is approximated as constant over the temperature and compositional ranges of interest.

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