INSTITUTE OF PHYSICS PUBLISHING SEMICONDUCTOR SCIENCE AND TECHNOLOGY
Semicond. Sci. Technol. **16** (2001) 831–835 PII: S0268-1242(01)24098-X

Thermodynamic analysis of the MBE growth of GaInAsN

V A Odnoblyudov, A Yu Egorov, A R Kovsh, A E Zhukov, N A Maleev, E S Semenova and V M Ustinov

Ioffe Physico-Technical Institute, 26 Polytekhnicheskaya Str., St Petersburg 194021, Russia

Received 12 April 2000
Published 30 August 2001
Online at stacks.iop.org/SST/16/831

Abstract
A thermodynamic approach to analysis of the growth of InGaAsN compounds by molecular beam epitaxy (MBE) is proposed. The developed thermodynamic model allows estimation of the mole fraction of nitrogen in the obtained alloys as a function of external growth parameters: element fluxes and growth temperature. The model predicts that the nitrogen incorporation is temperature-independent below 500 °C and markedly diminishes at higher growth temperatures. The incorporation of nitrogen is suppressed on raising the arsenic flux; the content of group III elements in the alloy affects the nitrogen incorporation only slightly. The results of simulation are compared with experimental data on MBE-grown InGaAsN alloys with small nitrogen content ($< 3\%$).

1. Introduction

InGaAsN has recently been proposed as a novel material for near-infrared lasers [1]. The merits of this material are due to the strong bowing in the bandgap of the GaAs–GaN alloy system, which enables the extension of the spectral range of light emitted from GaAs-based structures to 1.3 μm and longer. At the same time, the band-offsets between InGaAsN and GaAs exceed those in the commonly used InGaAsP system, which must markedly improve the high-temperature performance of 1.3 μm lasers. Combination with the presently available GaAs/AlAs distributed Bragg reflector (DBR) technology could also give novel vertical-cavity lasers for the long wavelength region.

Recently, MBE- and MOCVD-grown GaInAsN QW laser structures have shown rapid progress in laser characteristics [2–5]. The best results have been obtained with MBE. In spite of the rapid progress in material growth, little attention has been paid to theoretical modelling and interpretation of the growth of the nitride–arsenide compound. Kinetic models of the growth of GaInAsN quaternary alloys were developed in [6]. However, this approach failed to relate the growth parameters and the elemental composition of a growing film.

It has been shown previously that molecular beam epitaxy can be considered in the framework of a thermodynamic description under the assumption that an equilibrium is established between the gas and solid phases on the surface of a crystal at the substrate temperature [7, 8]. In the present study, we make a thermodynamic analysis of the growth of nitrogen-containing ternary and quaternary Ga(In)AsN compounds. The employed model predicts the mole fraction of nitrogen in the obtained alloys as a function of the external growth parameters (fluxes of group III and V elements and growth temperature).

2. Thermodynamic analysis

We use the thermodynamic model developed in [9] to analyse the MBE growth of quaternary (ternary) nitrogen-containing compounds. The mass action law describes the equilibrium between the gas and solid phases. The substrate temperature is taken to be the system temperature. The properties of quaternary compounds are described in terms of the regular solution model [10]. Nitrogen atoms are assumed to be the active species.

According to the regular solution model, the reaction in which the quaternary compound InGaAsN is formed:

$$x\mathrm{Ga} + (1-x)\mathrm{In} + \mathrm{yN} + 0.5(1-\mathrm{y})\mathrm{As}_2 \Leftrightarrow \mathrm{In}_{1-\mathrm{x}}\mathrm{Ga}_{\mathrm{x}}\mathrm{N}_{y}\mathrm{As}_{1-y} \quad (1)$$

can be written as four reactions yielding binary compounds:

$$\begin{aligned} \mathrm{Ga} + 0.5\mathrm{As}_2 &\Leftrightarrow \mathrm{GaAs} \\ \mathrm{In} + 0.5\mathrm{As}_2 &\Leftrightarrow \mathrm{InAs} \\ \mathrm{Ga} + \mathrm{N} &\Leftrightarrow \mathrm{GaN} \\ \mathrm{In} + \mathrm{N} &\Leftrightarrow \mathrm{InN}. \end{aligned} \tag{2}$$

By definition, the sticking (incorporation) coefficient η of nitrogen is the ratio of the incorporated nitrogen flux to the external nitrogen flux supplied from the nitrogen source:

$$\eta = \frac{F_{\mathrm{N}}^0 - F_{\mathrm{N}}}{F_{\mathrm{N}}^0}. \tag{3}$$

Here, and below F_i^0 is the external flux of an element from the source, and F_i is the flux of the element re-evaporated from the substrate. The re-evaporated flux of a given element is assumed to be the flux corresponding to the equilibrium partial pressure over the surface. The difference between the external and re-evaporated fluxes is incorporated into the growing film. Thus, the mole fraction of nitrogen in the solid, y, is related to the arsenic and nitrogen fluxes by

$$\frac{y}{1-y} = \frac{F_{\mathrm{N}}^0 - F_{\mathrm{N}}}{2\left(F_{\mathrm{As2}}^0 - F_{\mathrm{As2}}\right)}. \tag{4}$$

With (3) and (4) combined, the sticking coefficient η can be written as:

$$\eta = \frac{2}{F_{\mathrm{N}}^0}\frac{y}{1-y}\left(F_{\mathrm{As2}}^0 - F_{\mathrm{As2}}\right). \tag{5}$$

Applied to the formation of binary compounds in the alloy, the mass action law establishes a relationship between the equilibrium partial pressures of the elements involved, the activity coefficients of the corresponding binaries and the equilibrium constants. In a manner similar to the approach developed in [8], the activity coefficients can be expressed in terms of the interaction parameters of the binary compounds and the mole fractions of the elements in the solid solutions.

The values of interaction parameters used in numerical calculations are listed in table 1. It should be noted that no published data are available for the parameters describing the GaN–InN interaction in the GaInN solid ternary alloy and the InAs–InN interaction in InAsN. To estimate these unknown parameters, we used the well-known fact that the interaction parameters for GaAs–GaP in GaAsP and InAs–InP in InAsP are equal [11]. In a similar manner, in our numerical calculation, the GaAs–GaN interaction parameter for the GaAsN ternary alloy (a_3) is supposed to be equal to the InAs–InN interaction parameter (a_4, see table 1). We also assume that the GaN–InN interaction parameter (a_1) is equal to that describing the GaP–InP interaction. It is worth mentioning that varying the values of a_1 and a_3 within $\pm 30\%$ has only a minor effect on the results of the numerical calculation (less than 1%).

The unknown equilibrium constants for GaN and InN were found using the known temperature dependences of the Gibbs free energy [13] of the corresponding reactions. The equilibrium constants for GaAs and InAs were taken from [7].

Table 1. Interaction parameters for binary compounds in ternary alloys.

	Interaction parameters (J mol^{-1})	Reference
GaN–InN (a_1)	1.44×10^4	By author
GaAs–InAs (a_2)	1.23×10^4	[11]
GaAs–GaN (a_3)	2.16×10^5	[12]
InAs–InN (a_4)	2.16×10^5	By author

This thermodynamic consideration enabled a study of how the nitrogen incorporation efficiency η depends on the set of growth parameters, including the substrate temperature T, the growth rate and the ratio of group V and III elements. This allowed us to predict the nitrogen content in the grown layers for all types of atomic nitrogen sources.

3. Experiment

To evaluate the applicability of the proposed thermodynamic model, we fabricated a set of nitrogen-containing heterostructures and then compared the experimental content of nitrogen with the predictions of the numerical calculation. The structures under investigation were grown in a Riber EpiNeat MBE machine.

The typical growth rates were 0.6–1.2 monolayer per second (ML s^{-1}). A growth rate of 1 ML s^{-1} corresponds to a supplied gallium flux of 6.2×10^{14} cm^{-2} s. The external arsenic flux was 2.5–3.5 times the external gallium and indium fluxes, as determined by reconstruction of a reflection high-energy electron diffraction (RHEED) pattern. The supplied atomic nitrogen flux was determined from the GaN growth rate under gallium-rich conditions, with complete nitrogen incorporation assumed in this case. The nitrogen content of the grown samples was found from x-ray diffraction (XRD) rocking curves taken around GaAs (004). The lattice constant of the cubic GaN was taken to be 0.451 nm.

4. Results and discussion

In this section the results of a thermodynamic simulation of the MBE growth of InGaAsN compounds are presented and compared with experimental data obtained under varied growth parameters.

4.1. Influence of growth temperature on the sticking coefficient of atomic nitrogen

The dependence of the sticking coefficient of nitrogen on the substrate temperature is presented in figure 1 for the case of GaAsN growth. The substrate temperature was varied in the range from 400 to 540 °C. The fluxes of the elements were 1.5×10^{15}, 1.2×10^{13} and 6.1×10^{14} cm^{-2} s^{-1} for As, N and Ga, respectively.

The nitrogen sticking coefficient remains constant ($\eta = 0.96$) at substrate temperatures of 400−475 °C. Raising the substrate temperature beyond this range suppresses the nitrogen incorporation, and the nitrogen sticking coefficient decreases. This leads to a decrease in the mole fraction of nitrogen in GaAsN at temperatures above 500 °C. The

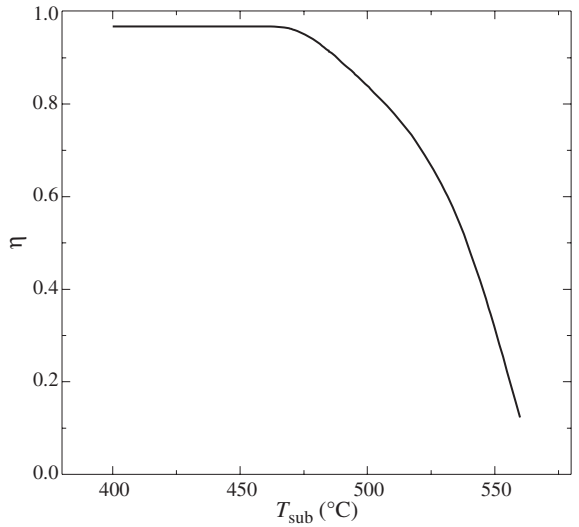

Figure 1. Nitrogen sticking coefficient η versus the substrate temperature T in GaAsN growth at $V = 1$ ML s^{-1}, $F^0_{As2} = 1.5 \times 10^{15}$ cm^{-2} s^{-1} and $F^0_N = 1.2 \times 10^{13}$ cm^{-2} s^{-1}.

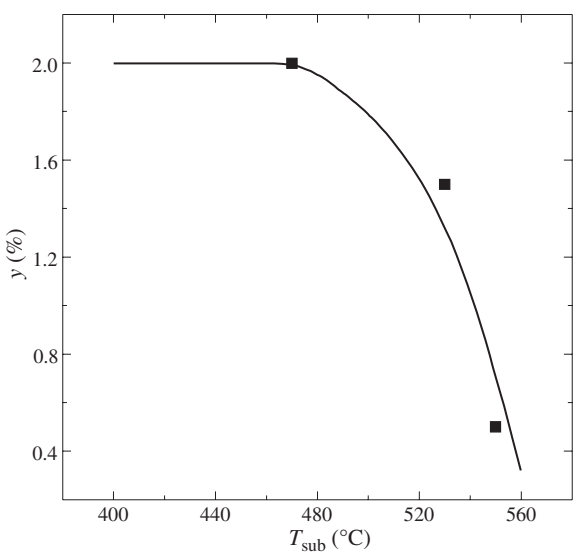

Figure 2. Temperature dependence of the nitrogen mole fraction y in GaAsN growth at $V = 1$ ML s^{-1}, $F^0_{As2} = 1.5 \times 10^{15}$ cm^{-2} s^{-1} and $F^0_N = 1.2 \times 10^{13}$ cm^{-2} s^{-1}.

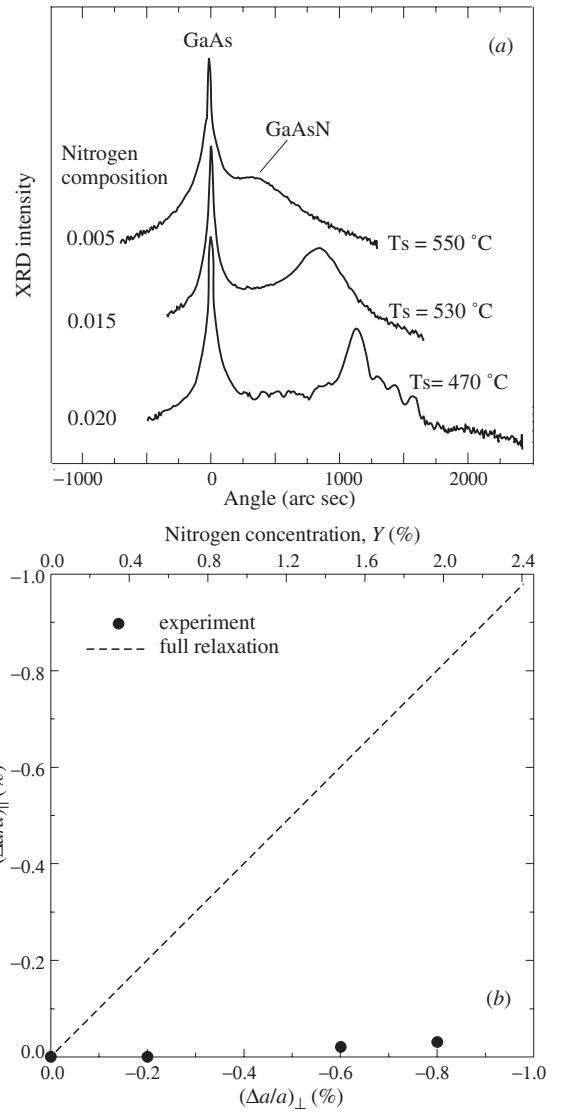

Figure 3. (*a*) X-ray diffraction rocking curves around (004) reflex for 0.2 μm thick GaAsN epilayers grown at different substrate temperatures. (*b*) Relationship between lattice mismatch in the growth direction, evaluated from asymmetric (224) and symmetric (004) x-ray diffraction measurements, $(\Delta a/a)_\perp$, and the in-plane mismatch $(\Delta a/a)_\parallel$ for bulk GaAsN layers.

temperature dependence of the mole fraction of nitrogen in GaAsN is shown in figure 2 (full curve).

The nitrogen mole fraction in the grown samples was estimated by the x-ray diffraction technique. Figure 3(*a*) shows 004-rocking curves of the samples grown at different substrate temperatures. The lattice mismatch in the growth direction, $(\Delta a/a)_\perp$, and the in-plane lattice mismatch $(\Delta a/a)_\parallel$ were calculated using asymmetric (224) reflection scans. Full circles in figure 3(*b*) represent the experimental values of the in-plane lattice mismatch $(\Delta a/a)_\parallel$ as a function of $(\Delta a/a)_\perp$. The dotted curve corresponds to the case of full strain relaxation. The experimental value of $(\Delta a/a)_\parallel$ remains small for the entire data set, indicating a pseudomorphic growth mode of GaAsN in the temperature interval under investigation.

The experimental dependence of the nitrogen content on the growth temperature is shown in figure 2 by solid squares. The accuracy of substrate temperature measurement was $\pm 5\,^\circ$C. It can be seen that the results of theoretical simulation, presented in figure 2, are in good agreement with the data obtained in a growth experiment.

4.2. Interaction of group V elements

The sticking coefficient of nitrogen was calculated for varied arsenic flux and constant fluxes of N and Ga and fixed growth temperature in order to investigate the influence of the interaction of group V elements on nitrogen incorporation. The results of calculation for two different substrate temperatures are shown in figure 4 by curves 1 ($T = 440\,^\circ$C) and 3 ($T = 490\,^\circ$C). The nitrogen sticking coefficient is plotted versus the ratio of fluxes of group V elements, (F^0_{As2}/F^0_N).

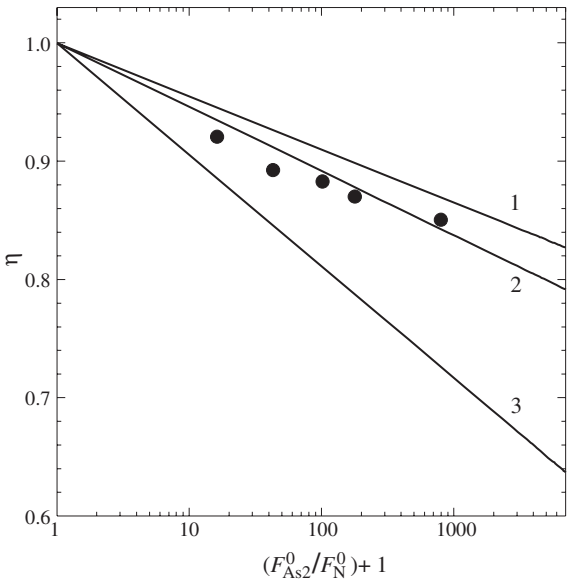

Figure 4. Calculated sticking coefficient of nitrogen, η, for GaAsN growth with varied flux of As and constant fluxes of N ($F^0_N = 1.2 \times 10^{13}$ cm^{-2} s^{-1}) and Ga ($V = 1$ ML s^{-1}) and fixed growth temperatures: curve 1, $T = 440\,^\circ$C and curve 3, $T = 490\,^\circ$C. Experimental data for $T = 440\,^\circ$C are shown by symbols and fitting-curve 2.

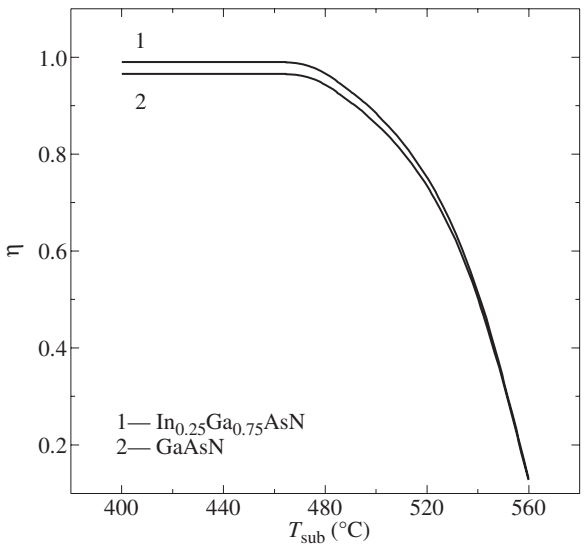

Figure 5. Sticking coefficient of nitrogen, η, versus the growth temperature T at $V = 1$ ML s^{-1}, $F^0_{As2} = 1.5 \times 10^{15}$ cm^{-2} s^{-1} and $F^0_N = 1.2 \times 10^{13}$ cm^{-2} s^{-1}. Curve 1, $In_{0.25}Ga_{0.75}AsN$ growth and curve 2, GaAsN growth.

Experimental data on growth of GaAsN alloys at a substrate temperature of 440 °C [14] are shown in figure 4 by symbols. It can be seen that the sticking coefficient of nitrogen decreases with increasing F^0_{As2}/F^0_N ratio, i.e., increasing As flux. The maximum possible sticking coefficient of nitrogen is achieved in the case of GaN growth under Ga-rich conditions at zero As-flux. The presented dependences can be fitted by the function

$$\eta = 1 + \xi \ln\left(\frac{F^0_{As2}}{F^0_N} + 1\right). \qquad (6)$$

Here ξ is the fitting parameter determining the slope of the $\eta(T)$ dependence. It was estimated to be 2.35×10^{-2} for the experimental data (curve 2) and 1.95×10^{-2} for the dependence simulated for a growth temperature of 440 °C. The difference between the estimated and experimental values of the interaction factor is only 15%, which corresponds to a difference between the experimental and theoretical values of the sticking coefficient of about 4%. A stronger dependence of η on As flux is observed for a higher substrate temperature of 490 °C ($\xi = 4.1 \times 10^{-2}$). This temperature corresponds to the range of growth temperatures in which the nitrogen incorporation is suppressed (see figure 1). Thus, ξ is the factor describing the interaction between arsenic and nitrogen in the formation of ternary compounds. Its decrease with increasing temperature reflects the preferable re-evaporation of nitrogen atoms from the growth surface.

It should be mentioned that the above dependence of the nitrogen sticking coefficient on the ratio of group V element fluxes was calculated with varied arsenic flux and nitrogen flux kept constant. The calculated nitrogen sticking coefficient remains practically unchanged when the incident nitrogen flux is varied within about 50% if the ratio of the fluxes of group V elements, F^0_{As2}/F^0_N, is kept constant. However, a stronger increase in the nitrogen flux leads to a noticeable decrease in the sticking coefficient. Thus, the nitrogen content does not grow linearly with the nitrogen flux, but tends to a constant value at high nitrogen fluxes (mole fraction of nitrogen exceeding 5%).

4.3. Interaction of nitrogen with group III elements

The incorporation of nitrogen in ternary GaAsN and quaternary InGaAsN epilayers was calculated for constant fluxes of group V elements and varied growth temperature. The same growth rate, i.e., the same total flux of group III elements (Ga + In), was used in both cases. In the case of InGaAsN growth, 25% of the gallium flux was replaced with that of indium. The temperature dependence of the sticking coefficient of nitrogen as a function of the growth temperature is shown in figure 5 for both cases (curve 1, $In_{0.25}Ga_{0.75}AsN$; curve 2, GaAsN). It can be seen that the replacement of a quarter of the Ga flux with In leads to an insignificant increase in the nitrogen sticking coefficient (by about 3% at the substrate temperatures used). Thus, we can conclude that the replacement of Ga with In affects the sticking coefficient only slightly in the investigated range of substrate temperatures.

4.4. Influence of growth rate on the mole fraction of nitrogen in InGaAsN

The dependences of the nitrogen content y of the alloy on the growth rate V, calculated for growth GaAsN (curve 1) and $In_{0.25}Ga_{0.75}AsN$ (curve 2), are shown in figure 6. Curve 3 represents a direct proportionality between the nitrogen content and the ratio of the external flux of atomic nitrogen to the total external flux of group III elements. This curve corresponds to nitrogen incorporation with 100% sticking coefficient and y directly proportional to $1/V$ in the entire range of growth rates considered. The experimental data for GaAsN growth are presented in the same figure by symbols.

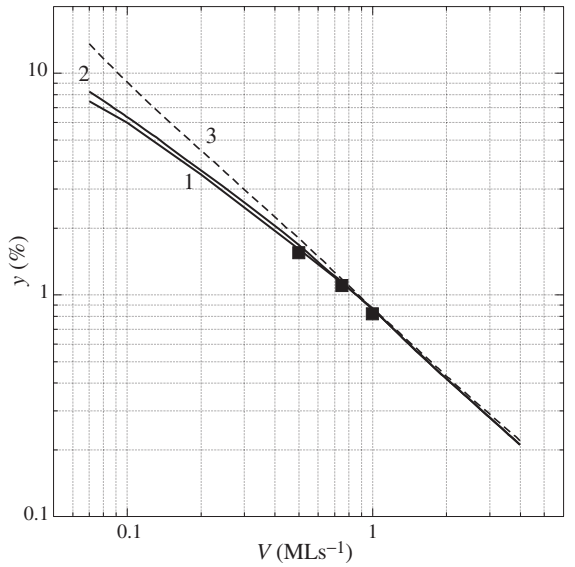

Figure 6. Calculated dependences of the content of nitrogen in the alloy, y, versus growth rate V for growth of GaAsN (curve 1) and $In_{0.25}Ga_{0.75}AsN$ (curve 2) at fixed $T = 450\,^{\circ}C$, $F^0_{As2} = 1.5 \times 10^{15}$ cm^{-2} s^{-1} and $F^0_N = 1.2 \times 10^{13}$ cm^{-2} s^{-1}. Curve 3 is for y varying in direct proportion to the ratio of the external flux of atomic nitrogen, F^0_N, to the total external flux of group III elements (this ratio is equivalent to V).

It can be seen that curves 1 and 2 are parallel to curve 3 at high growth rates. This means that in this range of growth rates the mole fraction of nitrogen is directly proportional to the ratio of nitrogen to Ga(+In) fluxes. At smaller growth rates, $y(V)$ deviates from the inversely proportional dependence, demonstrating lower nitrogen sticking coefficients, which must be a consequence of the increasing competition between nitrogen and arsenic. This dependence tends to 100% nitrogen content (GaN growth) with the growth rate approaching zero. Again, we come to a conclusion that the replacement of a part of Ga flux with In at the same total growth rate does not lead to any significant change in the nitrogen fraction.

5. Conclusion

In this study, the growth of ternary and quaternary compounds was subjected to a thermodynamic analysis. The thermodynamic consideration made it possible to predict the nitrogen concentration in the GaAsN and InGaAsN layers as a function of the external growth parameters (substrate temperature, growth rate and external arsenic flux). The influence of these parameters on the nitrogen incorporation coefficient was investigated.

The model predicts that, in the case of GaAsN growth, the dependence of the nitrogen sticking coefficient on the substrate temperature shows a range of constant values very close to unity, which corresponds to complete nitrogen incorporation into a growing film. At substrate temperatures of 480−550 °C, a strong decrease in η with increasing T is observed. The dependences of the nitrogen mole fraction and the nitrogen sticking coefficient on the substrate temperature are much the same, with the theoretical predictions confirmed by the experimental data with very high precision, exceeding that of substrate temperature measurement. The dependence of the nitrogen fraction in the GaAsN and in the InGaAsN layers on the growth rate was investigated. At high growth rates ($V > 1$ ML s^{-1}), the nitrogen sticking coefficient is close to unity and nitrogen can be considered a dopant, i.e., y is directly proportional to $1/V$. At lower growth rates the nitrogen sticking coefficient becomes less than unity and the $y(V)$ dependence deviates from inverse proportionality. This should be taken into account in growth of In(Ga)AsN quantum dots because of the typically small V. The nitrogen sticking coefficient depends on the ratio of fluxes of group V elements, being independent of the absolute values of these parameters in the range of typical atomic nitrogen fluxes. A good agreement of the theoretical predictions with the experimental data was demonstrated. In addition, it was shown that the nitrogen sticking coefficient is determined by the total flux of group III elements, i.e., adding indium at fixed total growth rate does not significantly change the nitrogen incorporation into the growing film.

The proposed thermodynamic analysis can be applied to all kinds of nitrogen sources and to the case of gas-source MBE.

Acknowledgments

This work was supported by the Nato Science for Peace program (grant SfP-972484), CRDF (grant RE1-2221) and the Program of the Ministry of Science of the Russian Federation 'Physics of Solid-State Nanostructures' (grant 99-2034). One of the authors (V A O) was partly supported in this study by the Leonhard Euler Stipendium.

References

[1] Kondow M, Kitatani T, Nakatsuka S, Larson M C, Nakahara K, Yazawa Y and Uomi K 1999 *IEEE J. Sel. Topics Quantum Electron.* **3** 719
[2] Hohnsdorf F, Koch J, Leu S, Stolz W, Borchert B and Druminski M 1999 *Electron. Lett.* **35** 571
[3] Livshits D, Egorov A Yu and Riechert H 2000 *Electron. Lett.* **36** 1381
[4] Egorov A Yu, Bernklau D, Livshits D, Ustinov V, Alferov Zh I and Riechert H 1999 *Inst. Phys. Conf. Ser.* **166** p 359
[5] Ustinov V M and Zhukov A E 2000 *Semicond. Sci. Technol.* **15** R41
[6] Pan Z, Li L H, Zhang W, Lin Y W and Wu R H 2000 *Appl. Phys. Lett.* **77** 214
[7] Kop'ev P S and Ledentsov N N 1988 *Semiconductors* **22** 1729
[8] Egorov A Yu, Kovsh A R, Zhukov A E, Ustinov V M and Kop'ev P S 1997 *Semiconductors* **31** 1153
[9] Odnoblyudov V A, Kovsh A R, Zhukov A E, Maleev N A, Semenova E S and UstinovV M 2001 *Semiconductors* at press
[10] Jordan A S and Ilegems M 1975 *J. Phys. Chem. Sol.* **36** 329
[11] Panish M B and Ilegems M 1972 *Prog. Sol. St. Chem.* **7** 39
[12] Qiu Y, Nikishin S A, Temkin H, Elyukhin V A and Kudriavtsev Yu A 1997 *Appl. Phys. Lett.* **70** 2831
[13] Koukitu A and Seki H 1997 *Jpn. J. Appl. Phys.* **36** L750
[14] Egorov A Yu, Bernklau D, Borchert B, Illek S, Livshits D, Rucki A, Schuster M, Kaschner A, Hoffmann A, Dumitras Gh, Amann M C and Riechert H 2000 *Proc. 11th Int. Conf. on Molecular Beam Epitaxy (MBE-XI) (Beijing, September 2000)* No 3 p 1