

Theoretical Model for Analysis and Optimization of Group III-Nitrides Growth by Molecular Beam Epitaxy

M. V. Averyanova

Russian Research Center "Applied Chemistry"

S. Yu. Karpov

Advanced Technology Center

Yu. N. Makarov

Lehrstuhl für Strömungsmechanik, University of Erlangen-Nürnberg

I. N. Przhevalskii

Russian Research Center "Applied Chemistry"

M. S. Ramm, R. A. Talalaev

Ioffe Physical-Technical Institute

This article was received on May 27, 1996 and accepted on October 31, 1996.

Abstract

A theoretical model which accounts for a physisorption precursor of molecular nitrogen is proposed for the analysis of group III-nitride growth by molecular beam epitaxy (MBE). The kinetics of nitrogen evaporation are found to be an essential factor influencing the MBE growth process of group III-nitrides. The high thermal stability of nitrides is explained to be related to the desorption kinetics resulting in a low value of the evaporation coefficient. The values of the evaporation coefficients as functions of temperature are extracted from the experimental Langmuir evaporation data of GaN and AlN. Using the revised thermodynamic properties of the group III-nitrides, and the obtained values of the evaporation coefficient, the process parameter dependent growth rate and transition to extra liquid phase formation during the GaN MBE are calculated. The theoretical results are compared to the available experimental data.

1. Introduction

Group III-nitrides are of great importance for green, blue and ultraviolet light emitting and laser diodes, as well as high power and high temperature electronic devices [1]. Progress in this field is closely related to success in growing epitaxial layers and heterostructures. For this purpose both metal-organic vapor phase epitaxy (MOVPE) and molecular beam epitaxy (MBE) are employed. Optimization of the growth process using these techniques is a key issue of many recent studies.

Numerous experiments have shown that the properties of group III-nitrides differ significantly from those of other III-V compounds. Molecular nitrogen interacts poorly with the surfaces of nitrides. As a result, an activation of nitrogen (by plasma or ionization assistance) is necessary for effective growth of nitrides at lower temperatures. The second peculiarity is the relatively high thermal stability of GaN and InN in the temperature range where these compounds dissociate into the liquid and vapor phases, in accordance with thermodynamic estimations [2][3]. The thermal stability results causes the fall in the GaN growth rate due to thermal desorption to occur at temperatures considerably higher than typical of GaAs and GaP [4]. Desorption is delayed despite of the higher volatility of nitrogen compared with other group V molecular species. Finally, group III-nitrides exhibit a drastic dependence of the nitrogen partial pressure on the orifice area in the case of vaporization from the Knudsen cell [5][6].

All these observations can be consistently explained by assuming the existence of a physisorption precursor at the surface of the nitrides which provides the low evaporation/condensation coefficient of N_2 . Using this assumption, we develop a quasi-thermodynamic approach which allows the trends in nitride MBE to be modeled, along with the prediction of the growth conditions where extra liquid phase appears on the surface.

2. Physisorption precursor of N_2

The physisorption precursor can be represented schematically (Figure 1) as a potential well separated from the crystal surface.

The main parameters of the precursor are the heights of the potential barriers that must be overcome by N_2 molecules to reach the surface (W_{in}) and to exit into the vacuum (W_{out}), and the relevant transition frequencies:

$$\nu_{in} = g_{in} \nu_{ph} \cdot \exp\left(-W_{in} / kT\right) \quad (1)$$

and

$$\nu_{out} = g_{out} \nu_{ph} \cdot \exp\left(-W_{out} / kT\right) \quad (2)$$

where ν_{ph} is the oscillation frequency of nitrogen in the physisorption precursor, and g_{in} and g_{out} are the state degeneracy factors corresponding to activated N_2 complex on the top of the respective potential barrier. We do not distinguish between the states of the atoms in the bulk of the crystal and the atoms chemisorbed in the adsorption layer. This simplification is workable if the exchange reaction between the crystal and adsorption layer is not the limiting step in the growth or evaporation of the material.

It is known that N_2 poorly chemisorbs on the surfaces of nitrides. This results from the small value of its condensation coefficient α_c considerably less than unity. Assuming second order dissociative chemisorption of N_2 on the surface, and considering the dynamics of its arrival and release from the physisorption precursor similarly to [7] [8], we can obtain the following expression for the condensation coefficient:

$$\alpha_c = \left[1 + \frac{g_{out}}{g_{in}} \exp\left(\frac{\Delta W}{kT}\right) \right]^{-1}, \quad \Delta W = W_{in} - W_{out} \quad (3)$$

Then the flux of the molecules incorporating into the crystal is equal to $\alpha_c \cdot F_{N_2}$, where F_{N_2} is the incident N_2 flux. This means that only a small part of the N_2 arriving at the surface is able to incorporate into the crystal while the rest of the molecules reflect from the surface without any chemical interaction. By similar consideration of the reverse transition of nitrogen atoms from the crystal (or chemisorption layer) to the molecular state in vacuum, one can find that the desorbed N_2 flux ($F_{N_2}^d$) is related to the desorbed flux established under thermodynamic equilibrium ($F_{N_2}^{eq}$) as:

$$F_{N_2}^d = \alpha_e \cdot F_{N_2}^{eq} \quad (4)$$

where α_e is the evaporation coefficient of N_2 . In our model of the physisorption state, the evaporation coefficient is found to be equal to the condensation coefficient ($\alpha_e = \alpha_c$). Thus the expression (4) shows that the physisorption precursor provides additional stability to the crystal by suppressing the desorption of N_2 .

Simulation of the growth process requires us to know the evaporation coefficients over a wide temperature range. To obtain them, we compare the pressures of the gaseous components measured under Langmuir evaporation of AlN and GaN [5] [9] to the pressures calculated for the case of congruent vaporization of the crystals. The standard thermodynamic properties used in the calculations are refined to account for new information on specific heat and

enthalpy of formation of the nitrides. The data obtained by such a way are then extrapolated using the Arrhenius function in accordance with Equation 4. As a result we obtain:

$$\begin{aligned} \alpha_e &= 2.29 \cdot 10^{-7} \cdot \exp\left(-\frac{18103}{T}\right) && \text{for GaN} \\ \alpha_e &= 7.14 \cdot 10^8 \cdot \exp\left(-\frac{61272}{T}\right) && \text{for AlN} \end{aligned} \quad (5)$$

The corresponding data for InN are unavailable due to the lack of experimental information of its Langmuir vaporization.

3. Model of nitrides growth by MBE

We consider nitride growth of certain nitrides using external fluxes of group-III atoms (F_{III}) and activated nitrogen (F_N). Both group III and activated nitrogen species (atomic nitrogen, N^+ ion, etc.) are assumed to have condensation coefficients near unity. In this case the elements, conservation on the growing surface can be written in the form:

$$F_{III} - F_{III}^d = \mathcal{N} \quad , \quad nF_N - 2F_{N_2}^d = \mathcal{N} \quad (6)$$

Here n is the number of atoms in the activated nitrogen complex, σ is the surface density of crystalline sites, and V is the growth rate measured in monolayers per second. According to the thermodynamic approach [10] these expressions have to be added by the mass action law equation:

$$P_{III} \cdot P_{N_2}^{1/2} = K_{III-N}^* \quad (7)$$

which follows from the assumption that heterogeneous 'vapor-solid' equilibrium is established between the desorbed species and the crystal. In Eq. (7), P_{III} and P_{N_2} denote the partial pressures of the desorbed

group III atoms and N_2 molecules, K_{III-N}^* is the equilibrium constant of nitride formation from the gaseous

components; K_{III-N}^* is proportional to $\exp\left[-\left(E_{III}^v + \frac{1}{2}E_{N_2}^v\right) / kT\right]$ (see figure 1). Taking into account

that partial pressures are related to desorbed fluxes by the Hertz-Knudsen equation: $F_v^d = \beta_v \cdot P_v$ (here

$\beta_v = \left(2 \pi m_v kT\right)^{-1/2}$ is the Hertz-Knudsen factor for the v -th species, m_v is the mass of v -th component, and k is the Boltzmann constant), one can derive from Equation 7 an additional relationship valid for the desorbed fluxes F_{III}^d and F_N^d :

$$F_{III}^d \cdot \left(F_{N_2}^d\right)^{1/2} = K_{III-N} \quad , \quad K_{III-N} = \beta_{III} \beta_{N_2}^{1/2} \cdot K_{III-N}^* \quad (8)$$

In contrast to this thermodynamic consideration in the case of nitrides, however, a systematic shift from the equilibrium conditions arises due to the extremely low evaporation coefficient of N_2 (see Equation 4). This means that instead of the mass action law Equation 8, we should use the equation

$$F_{III}^d \cdot \left(F_{N_2}^d\right)^{1/2} = \alpha_e^{1/2} \cdot K_{III-N} \quad (9)$$

which accounts for the existence of the nitrogen physisorption precursor. Eqs. (6) and (9) form a closed equation system. Its solution allows the determination of the desorbed fluxes of all species, and the growth rate as function of temperature and incident fluxes.

4. Formation of the liquid phase during nitride growth

Prediction of liquid phase formation during nitride growth can be accomplished using the approach proposed in [11] in which a minimum incident group V molecular flux was predicted to be needed to provide the growth of a III-V compound under constant incident group III atomic flux growth without the appearance of an undesirable liquid phase on the surface. The main idea employed in [11] is to set the minimum group V incident flux to correspond to the three-phase ‘vapor-liquid-solid’ heterogeneous equilibrium. The value of minimum group V flux can be obtained from the numerical solution of the equations combining conservation of elements on the growth surface with the mass action equations.

Here we present the analytical expression for minimum active nitrogen flux F_N^{\min} providing for the growth of a nitride without appearance of liquid droplets on the growth surface. This expression can be obtained from the Eqs.

(6) and (9), and by taking the desorbed group-III flux F_{III}^d to be equal to the saturated vapor pressure over the

liquid phase: $\beta_{III} \cdot P_{III}^{sat}$ (detailed analysis of this follows in a separate paper). We find:

$$F_N^{\min} = n^{-1} \left[F_{III} - \beta_{III} P_{III}^{sat} + 2 \alpha_c \cdot \left(\frac{K_{III-N}}{\beta_{III} P_{III}^{sat}} \right)^2 \right] \quad (10)$$

Both the P_{III}^{sat} and K_{III-N} in Equation 10 can be calculated using the standard thermodynamic properties of nitrides and the relevant elements.

5. Results of calculations and comparison to experiment

To verify the proposed approach we compare theoretical results with the experimental data obtained for the MBE growth of GaN using activated nitrogen as a source.

Figure 2 shows the minimum nitrogen flux needed to avoid the appearance of the liquid phase during GaN growth as a function of inverse temperature. This curve represents a boundary between the area where epitaxial growth occurs without liquid droplets formation and the area where appearance of the extra liquid phase is expected. The dashed curve in figure 2 is calculated using pure thermodynamics [3] without accounting for the evaporation kinetics of N_2 . The solid curve in figure 2 is obtained using Equation 10. It is seen that the consideration of the physisorption precursor drastically shifts the position and shape of the calculated boundary of the liquid phase formation. In the case of pure thermodynamics, the liquid phase is expected to be formed under practically all common growth conditions. This prediction is not supported by experiment. The existence of the nitrogen precursor results in a temperature gap where the liquid phase is not formed, even at negligibly small incident nitrogen fluxes (a similar gap has been predicted earlier for AIAs and AIP [11]).

Detailed experimental data on liquid droplet formation while growing GaN were obtained from [12][13]. In these works, the incident Ga flux (i.e. growth rate) and temperature were varied while holding the incident nitrogen flux constant. The appearance of droplets was monitored during growth. Assuming the value of activated nitrogen flux to be equal to 0.15 ML/s, we calculate the critical growth rate separating the area of extra liquid phase formation which is plotted in figure 3. The solid and open circles in figure 3 denote the growth regimes with and without droplets, respectively. One can see that theory and experiment agree with one another.

Detailed measurements of the GaN growth rate versus temperature under nitrogen rich conditions have been carried out [4]. The authors used an ECR-plasma for nitrogen activation. Assuming the incident Ga flux is equal to that corresponding to the low-temperature growth rate of 0.2 $\mu\text{m/h}$, we calculated the growth rate at different V/III ratios over a wide temperature range (see figure 4). One can see that the theoretical curve reproduces as a whole the behavior of the growth rate, although it predicts a more steep drop of the growth rate with increasing temperature than that observed in the experiment.

6. Conclusion

In this work a quasi-thermodynamic model for the analysis of group III-nitride growth by MBE and the conditions of surface liquid phase formation are developed. In the model, the shift of heterogeneous equilibrium attributed to the evaporation kinetics of N₂ is taken into account. Reasonable agreement between the theory and experimental data obtained for MBE GaN growth supports the concept of a physisorption precursor which we propose to explain the MBE growth of nitrides. The model allows a straightforward generalization to the case of ternary nitrides.

Acknowledgments

This work was supported in part by Grant No 96-02-17203 from the Russian Foundation of Basic Research.

References

- [1] S Strite, ME Lin, H Morkoc, *Thin Sol. Films* **231**, 197-210 (1993).
- [2] N. Newman, J. Ross, M. Rubin, *Appl. Phys. Lett.* **62**, 1242-1244 (1993).
- [3] SYu Karpov, Yu N Makarov, M S Ramm, R A Talalaevin *Proc. of 6-th European Workshop on MOCVD and Related Growth Techniques, Gent, Belgium*, (1995) B9.
- [4] H Morkoc, A Botchkarev, A Salvador, et al., *J. Cryst. Growth* **150**, 887-891 (1995).
- [5] Z. A. Munir, A. W. Searcy, *J. Chem. Phys.* **42**, 4223 (1965).
- [6] SP Gordienko, BV Fenchka, *Russ. J. Phys. Chem.* **51**, 530-531 (1977).
- [7] JR Arthur, *Surf. Sci.* **43**, 449 (1974).
- [8] SYu Karpov, MI Maiorov, *Surf. Sci.* **344**, 11-22 (1995).
- [9] LH Dreger, VV Dadape, JL Margrave, *J. Phys. Chem.* **66**, 1556-1559 (1962).
- [10] JY Shen, C Chatillon, *J. Cryst. Growth* **106**, 553-565 (1990).
- [11] SYu Karpov, YuV Kovalchuk, VE Myachin, YuV Pogorelsky, *J. Cryst. Growth* **129**, 563-570 (1993).
- [12] SH Cho, H Sakamoto, K Akimoto, Y Okada, M Akimoto, *Jpn. J. Appl. Phys.* **34**, L236-L239 (1995).
- [13] C. R. Eddy, T. D. Moustakas, J. Scanlon, *J. Appl. Phys.* **73**, 448-455 (1993).

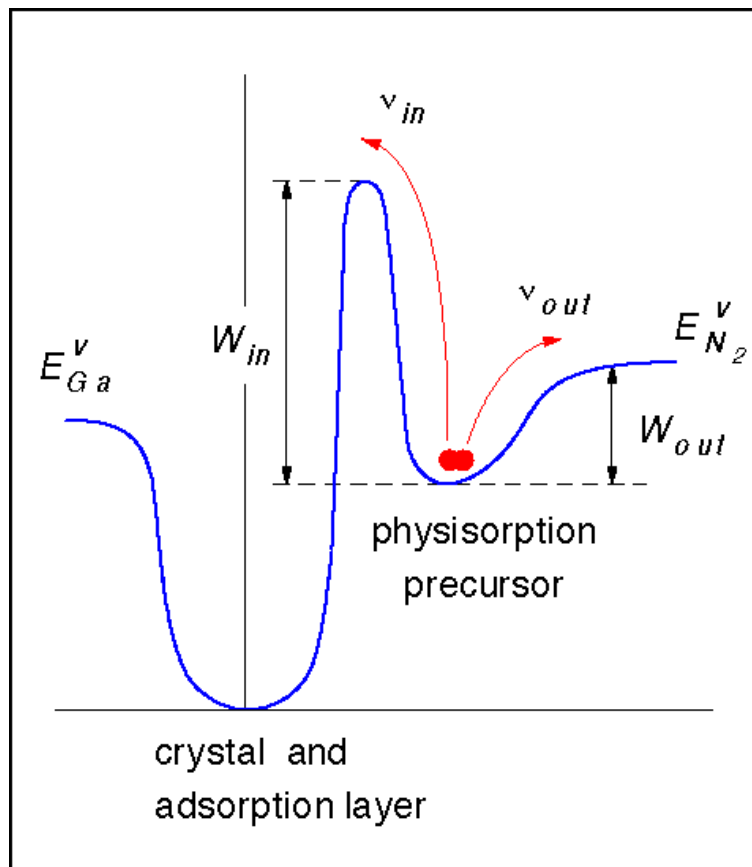


Figure 1. The configuration diagram for the physisorption precursor of N_2 . E_{Ga}^v and $E_{N_2}^v$ are the vacuum energy levels of the gaseous Ga and N_2 , respectively.

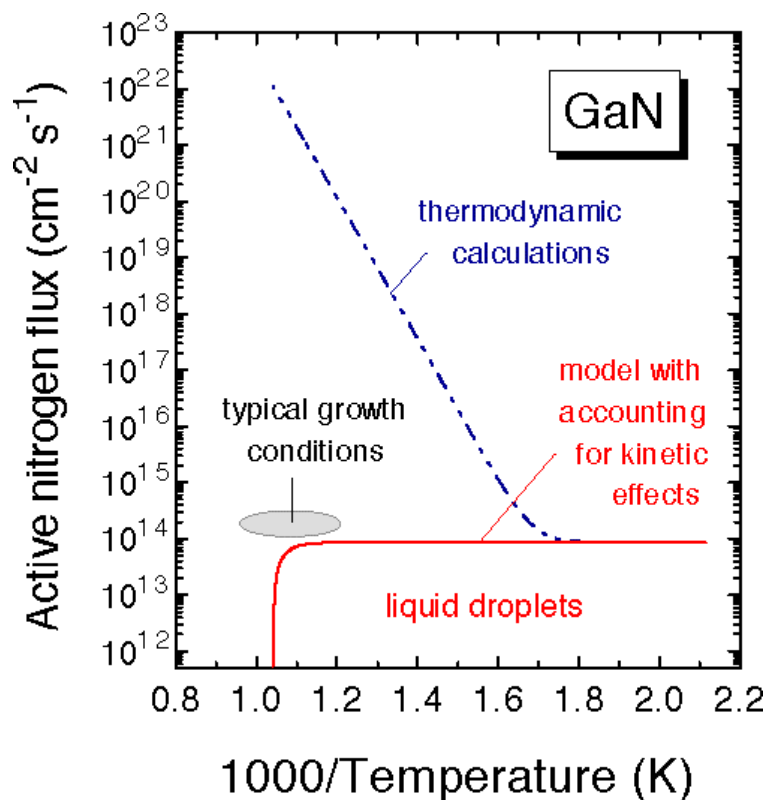


Figure 2. Boundary of liquid phase formation for GaN calculated at a Ga flux of 0.15 ML/s. The dashed-dotted line shows results obtained via a pure thermodynamic approach [3]. The solid line is obtained by the model proposed in this work (the high-temperature branch of this curve is not plotted since it lies above 2000°C). The shaded area indicates typical conditions of GaN growth by plasma enhanced and ion assisted MBE.

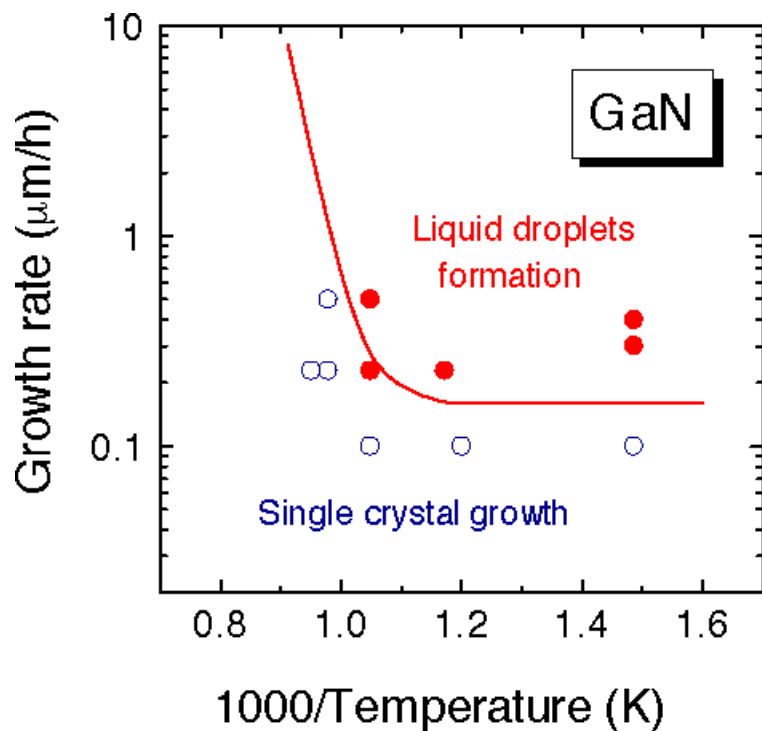


Figure 3. Critical growth rate resulting in liquid phase appearance. The solid circles represent data points at which GaN growth with droplets was observed, and the open circles are data points at which the growth was without droplets [12][13]. The solid curve shows the results of our calculations assuming an incident nitrogen flux of 0.15 ML/s.

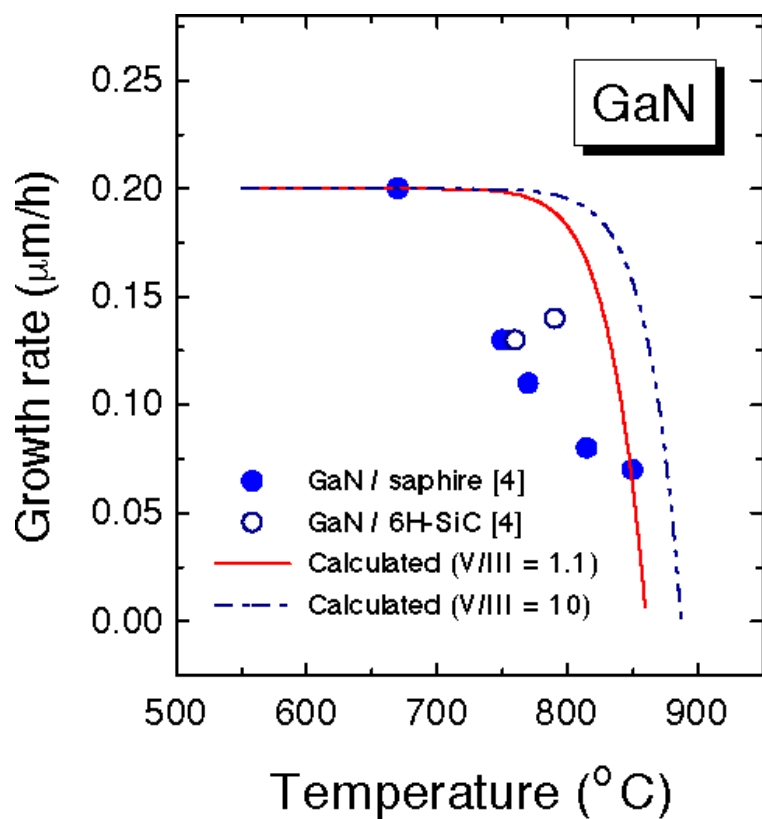


Figure 4. Growth rate of GaN vs temperature calculated for different V/III ratios. The incident Ga flux corresponds to the low temperature growth rate of 0.2 $\mu\text{m/h}$. The experimental points are taken from Ref. [4].

© 1996-1997 The Materials Research Society