The role of gaseous species in group-III nitride growth

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Abstract

A quasi-thermodynamic model accounting for kinetics of molecular nitrogen evaporation is applied to simulate the growth of binary and ternary group-III nitrides using atomic group-III elements and molecular ammonia as the sources. The values of the molecular nitrogen evaporation coefficients from the surface of GaN and AlN necessary for the simulation are extracted from experiments on free evaporation of the crystals in vacuum, while for InN only estimates are available. The growth process of AlN and InN is studied by analyzing the composition of the desorbed vapor species that are thought to influence the native defect formation in group-III nitrides. Different channels of desorption from the surfaces of group-III nitrides (related either to group-III atoms or to their hydrides) are compared. Specific features of the growth processes under the metal-rich and N-rich conditions are analyzed. The developed approach is extended to study the growth of the ternary compounds GaInN and AlGaN. The growth rate of ternary compounds versus temperature shows a two-drop behavior corresponding to the rapid increase of the respective group-III atom desorption. The effect is accompanied by a corresponding stepwise change in the solid phase composition. Factors retarding the growth of ternary compounds — the miscibility gap related to internal strain accumulated in the solid phase due to the lattice mismatch of binary constituents, and the extra liquid phase formation during growth — are discussed with respect to GaInN.

1. Introduction

Group-III nitrides have attracted considerable interest in recent years due to their potential application to blue/green light emitters (including lasers), high-temperature electronic devices, and UV photodetectors [1]. During the early stage, high-quality epitaxial layers were obtained mainly by using the Metal Organic Chemical Vapor Deposition (MOCVD) technique [2][3][4]. Now, Molecular Beam Epitaxy (MBE) also plays an important role in growth of nitrides. This is due, in part, to the possibility of detailed studies of the growth process with standard MBE tools – Reflection High Energy Electron Diffraction (RHEED) and Desorption Mass Spectrometry (DMS) [5][6][7][8][9]. Additional progress has been achieved in the last few years by implementation in MBE of gaseous ammonia as the source of reactive nitrogen [10][11][12][13]. The ammonia source provides relatively high growth rates, comparable with those of MOCVD, and produces high-quality epitaxial layers [11][12][13][14] without having the effects of accelerated ions on material properties (as takes place in MBE based on plasma activated molecular nitrogen [15]). At the same time the use of an ammonia source results in more complicated heterogeneous chemical reactions occurring on the growing surface. This increases the difficulties of growth process control.

One of the essential features of group-III nitrides is the significant influence of surface kinetics on the incorporation and desorption of molecular nitrogen [16]. It was shown that both GaN and AlN exhibit very low (~10^{-15}—10^{-13}) evaporation/condensation coefficients for N_2 on semiconductor surfaces [17][18]. This effect results not only in negligible incorporation efficiency of molecular nitrogen into the crystals, but also in significant suppression of N_2

evaporation as compared to that occuring under real Knudsen conditions where the evaporation process is governed by thermodynamic properties of the material. Obviously, this kinetic effect enhances the thermal stability of GaN and AlN and is expected to hold also in the case of InN. However, no attempts to quantitatively estimate the value of the N_2 evaporation coefficient on the InN surface have been done to date.

Another specific feature related to the growth of group-III nitrides with an ammonia source is the important role of gaseous species. This problem includes many aspects. The first one is formation of adducts in MOCVD reactors [19] [20] which influences the transport of group-III species to the growing surface. The second is addressed to the process of ammonia cracking, which is of a catalytic character occurring on different materials with essentially distinct efficiencies [21] [22]. Finally, the influence of hydrogen on group-III nitride growth is of a great variety. It is learned that hydrogen can enhance liquid droplet formation [19], influence the growth rate of semiconductor [23], and change the solid composition of ternary compounds [24]. In addition, the observed difficulties in p-doping of group-III nitrides by Mg are commonly attributed to the effect of hydrogen formed during the growth process [1].

In this paper we report results of a theoretical study of group-III nitride growth using ammonia and atomic group-III elements as material sources. For this purpose a quasi-thermodynamic model developed in references [17] [25] is applied. We consider binary (AlN and InN) and ternary (AlGaN and GaInN) compounds paying main attention to the accurate treatment of the kinetic effects and detailed analysis of the role of gaseous components (first of all, ammonia and hydrogen) in the growth process. Finally, we discuss factors which retard the growth of nitrides — formation of extra liquid phase and spinodal decomposition of ternary compounds. The former factor is found to be especially essential for InN, and both of them are important for GaInN solid solutions.

2. Binary compounds

The first evidence of the kinetic limitation of molecular nitrogen evaporation from the surfaces of GaN and AlN was derived from the data on Langmuir evaporation of these materials [26] [27]. The measured total partial pressures of group-III atoms and N_2 appeared four to five orders of magnitude less than those predicted using the thermodynamic analysis. The comparison allowed one to extract the evaporation or condensation coefficients (assumed to be equal each other) of N_2 from the surfaces of GaN and AlN [17]. The small values of these coefficients ($\sim 10^{-15}$-10^{-13}) were attributed in references [17] [18] to a physisorption precursor trapping molecular nitrogen near the surface. Another possible explanation assumes that instead of a physisorption state there exists a configurational barrier (see Figure 1) which inhibits chemisorption of N_2 on the surface of the crystal. In both cases the kinetic barrier separating the adsorption layer on the crystalline surface from the gas phase should be large enough [16] to provide extremely low values of the evaporation coefficient.

The temperature dependent evaporation coefficient of N_2 obtained from the experimental data is the key point of the quasi-thermodynamic approach proposed in [17] for analysis of the growth rate and the conditions of extra liquid phase appearance on the surface during growth of nitrides. This approach was originally developed for the simple case of a plasma activated nitrogen source where only a limited number of gaseous species take part in the growth process. Recently the approach was extended to the case of a multicomponent vapor phase specific to growth of GaN with ammonia as the nitrogen source [25]. The following assumptions form the basis of the model –

   A. All gaseous components (except molecular nitrogen) are in heterogeneous equilibrium with each other and obey standard mass action law equations connecting the partial pressures of the desorbed species.
   B. Interaction of molecular nitrogen with the surface of the nitride (A^3N where A^3 indicates the group-III element: Al, Ga or In) is kinetically limited. The kinetic effects are accounted for by introducing into the corresponding mass action law equation:

$$P_A \cdot P_{N_2}^{1/2} = \alpha^{1/2} \cdot K_{AN}(T) \tag{1}$$

   the temperature dependent evaporation coefficient α [17]. In Equation 1 P_v is the partial pressure of the v-th desorbed species; K_{AN} is the equilibrium constant for the formation reaction of solid A^3N from the gaseous species (it can be calculated using standard thermodynamic properties of the components [28]).
   C. The partial pressures of desorbed components are related to corresponding fluxes by the Hertz-Knudsen equation:

$$F_v = \beta_v \cdot P_v \quad , \quad \beta_v = \left(2\pi m_v kT\right)^{1/2} \tag{2}$$

where β_v is the Hertz-Knudsen factor with m_v and k being the mass of the molecule (atom) and the Boltzmann constant, respectively. Supplementing Equation 1 and the mass action law equations for the rest of the components with mass balance equations for group-III elements, nitrogen and hydrogen, one can obtain a closed system allowing determination of all of the partial pressures P_v and the growth rate of the crystal [25].

We should notice that kinetics of N_2 evaporation is exhibited not only in the decomposition reaction of A^3N related to Equation 1. Using the mass action equations written for the other heterogeneous reactions and assumption A, one can show that the evaporation coefficient α arises in every equation related to the interaction of N_2 with other gaseous species. This means that kinetics of N_2 evaporation results in a shift of the heterogeneous chemical equilibrium involving other components containing nitrogen. In particular, the kinetic limitation of N_2 evaporation must lead to a suppression of the heterogeneous cracking of NH_3 on the surface of GaN and AlN.

To employ this approach one should evaluate the evaporation coefficients involved in Equation 1. The temperature dependence of these coefficients can be fitted to the Arrhenius form $\alpha(T)=\alpha_0 \cdot \exp(-A/T)$. Using the experimental data of references [27][26] obtained on AlN and GaN and the refined data on free evaporation of GaN [29] measured directly in an MBE chamber, we have determined the parameters α_0 and A collected in Table 1. The data for InN included in Table 1 will be discussed later in Section 2.2.

2.1. Growth of AlN using ammonia source

Considering the growth of AlN with atomic Al and molecular NH_3 beams we take into account the following components which are thought to be *a priori* important: NH_3, Al, N_2, H_2, H, N, NH, NH_2, N_2H_4 and AlH (it has been shown for GaN as an example that the role of higher hydrides A^3H_2 and A^3H_3 is negligible as compared to A^3H due to the low pressure of hydrogen in the growth chamber [25]).

In Figure 2 the growth rate of AlN versus temperature calculated for different V/III ratios is plotted. We should notice that in the case of GaN only a small fraction of NH_3 (1/170 at the temperature of 760°C) arriving at the surface incorporates into the crystal [11][25]. In reference [9] this effect is attributed to blocking of NH_3 adsorption sites on the surface of the crystal by Ga atoms accumulated in the adsorption layer. By analogy, this effect is expected for AlN as well. However, no experimental information is available for AlN concerning NH_3 incorporation efficiency. Therefore, the V/III ratio indicated in Figure 2 takes into account only the reactive fraction of ammonia which chemically interacts with the surface of the crystal.

As seen from Figure 2, a remarkable drop of the growth rate occurs at temperatures as high as ~1400°C. This temperature is weakly dependent on V/III ratio or on which growth conditions (Al-limited or NH_3-limited) are realized. To investigate the behavior of the gas phase composition we calculate the dependence of the partial pressures of the desorbed species versus temperature for NH_3-limited (V/III=0.5) and Al-limited (V/III=2) growth conditions (Figure 3). One can see that the behavior of the hydrogen species (H_2 and H) is very similar in both cases. At the same time N_2 appears with a noticeable concentration only if V/III>1 (a rapid increase of N_2 partial pressure at high temperature observed in both cases is related to the start of the intense vaporization of AlN). At V/III<1 the amount of N_2 in the outgoing flux is negligibly small. Cracking of ammonia on the surface of AlN is also very different in the cases of NH_3-limited (complete cracking in the whole temperature range) and Al-limited (effective cracking only at T > 650°C) growth conditions. Both effects can influence the nitrogen vacancy formation which in many respects determines the electrical and optical properties of the grown crystal.

A specific feature of AlN growth under NH_3-limited conditions (V/III=0.5) is the high partial pressure of the desorbing Al. This results additionally in the generation of AlH, especially at low temperatures, although the partial pressure of the latter component is not yet sufficient to form the dominant desorption channel. The partial pressures of other species (N, NH, NH_2, N_2H_4) are negligibly small in the both cases of NH_3-limited and Al-limited growth condition.

2.2. Kinetics of InN evaporation

Up to now there has been limited information available on the kinetics of InN vaporization in vacuum. Therefore in this work we make an attempt to estimate the value of the N_2 evaporation coefficient from the surface of InN using indirect observations. For this purpose we use the fact that InN is thermally stable at room temperature and surely decomposes into the liquid and gas phases even at 400°C [30]. According to the analysis carried out in reference [18], the value of the evaporation coefficient at the congruent evaporation temperature of InN, T_c (this temperature separates the ranges of crystal stability and crystal decomposition), is related to this temperature through the expression

$$\alpha\left(T_c\right) = \left(\frac{m_N}{2m_{In}}\right)^{1/2} \cdot \frac{\left[P_{In}^l\left(T_c\right)\right]^3}{K_{InN}\left(T_c\right)} \tag{3}$$

where m_N and m_{In} are the molecular masses of elements, $P_{In}^l(T)$ is the saturated vapor pressure of In over the liquid phase, and $K_{InN}(T)$ is the equilibrium constant of the formation reaction of InN from the gaseous components. Assuming as a first approximation that $T_c \cong 350°C$, we can obtain a value of $\alpha(T_c)$ being nearly equal to ~1×10^{-14} at this temperature. Next, we assume that the activation energy E_a of the N_2 evaporation coefficient from the surface of InN is equal either to the value following from the data on InN evaporation[31], or to that specific for GaN [a]. The resulting parameters, α_0 and $A = E_a / k$, corresponding to these assumptions are indicated in Table 1 as the cases I and II, respectively. [b].

First of all we calculate the boundary of extra liquid phase formation on the surface of the crystal for the simplest case of InN growth using atomic In and activated N_2 (Figure 4). In the calculations we employ an analytical expression [17] :

$$F_N^{\min} = F_{In} - \beta_{In} P_{In}^l + 2\alpha \cdot \left(\frac{K_{InN}}{\beta_{In} P_{In}^l}\right)^2 \tag{4}$$

for the minimum active nitrogen flux, $F_N^{\min}$, necessary to suppress the liquid phase appearance. One can see that cases I and II differ remarkably from each other: in case I, growth of InN without liquid droplets formation is limited by temperatures of 470-480°C, while in case II, temperatures as high as 580-590°C are achievable for single crystal growth. In our opinion measurement of the temperature for appearance of liquid droplets on the surface of InN would be a good test for the proper choice of the activation energy of the N_2 evaporation coefficient. We would like to notice that the extra liquid phase diagram calculated for InN (Figure 4) is qualitatively different from those obtained for GaN and AlN [17]. An extremely small value of the evaporation coefficient results, in the case of GaN or AlN, in the appearance of a temperature gap where the liquid phase can not be formed on the surface under steady-state growth conditions. In contrast, in the case of InN this effect (kinetic by nature) is not exhibited. We attribute this distinction to a difference in the thermodynamic properties (first of all, enthalpies of formation) of binary nitrides.

Figure 5 shows the growth rate of InN versus temperature predicted for two accepted values of the evaporation coefficient of N_2, with NH_3 used as the source of active nitrogen. As in the case of AlN, we take into account the following set of the gaseous components: NH_3, In, N_2, H_2, H, N, NH, NH_2, N_2H_4, InN, InH_2 and InH_3 . It is seen that both curves predict an abrupt drop of the growth rate occurring, however, at different temperatures which are dependent on the chosen extrapolation of the evaporation coefficient. In contrast to AlN, there is only a limited number of desorbed gaseous components (see Figure 6). In fact, only In, N_2 and H_2 present in noticable amounts among the outgoing fluxes. At the same time the general behavior of these vapor species is similar to that observed on AlN in both the In-limited and NH_3-limited growth conditions. Since almost complete cracking of ammonia occurs

on the surface of InN in the whole temperature range, the determination of the conditions for extra liquid phase formation during growth of InN can be carried out on the basis of the phase diagram plotted in Figure 4. Using this diagram we estimate the maximum growth temperature of InN (V/III=2) achievable without formation of liquid droplets on the surface. It is equal to 455°C for the case I and to 540°C for the case II. In both cases growth under NH_3-limited conditions is predicted to result in the appearance of extra liquid phase on the surface. The latter contrasts with the case of GaN where growth under NH_3-limited conditions was routinely employed in experiments [23] [29].

3. Ternary compounds

To simulate the growth process of ternary $A_x^3 B_{1-x}^3 N$ compounds we first of all, have to estimate the kinetics of molecular nitrogen evaporation from the growing surface. We assume that kinetic effects in the case of ternary compounds can be accounted for by introducing the temperature dependent evaporation coefficient with the parameters A and $\ln\alpha_0$ linearly dependent on the solid phase composition x. As before we use assumptions A-C (see Section 2) to obtain the closed system of equations with respect to the partial pressures of desorbed gaseous species, growth rate and composition of the ternary compound. For the simple case of MBE using activated N_2 as the nitrogen source this system of equations has the form

$$F_A - \beta_A P_A = \omega V_g \cdot x$$

$$F_B - \beta_B P_B = \omega V_g \cdot (1-x)$$

$$F_N - 2\beta_{N_2} P_{N_2} = \omega V_g \tag{5}$$

$$P_A \cdot P_{N_2}^{1/2} = \alpha^{1/2} \cdot \gamma_{AN} K_{AN} \cdot x$$

$$P_B \cdot P_{N_2}^{1/2} = \alpha^{1/2} \cdot \gamma_{BN} K_{BN} \cdot (1-x)$$

Here $\omega(x) = N_A \cdot [x\rho_{AN}/M_{AN} + (1-x)\rho_{BN}/M_{BN}]$, N_A is Avogadro's number, ρ_{AN} and ρ_{BN} are densities, and M_{AN} and M_{BN} are the molecular weights of binary compounds A^3N and B^3N, respectively. F_A, F_B and F_N are the incident fluxes of group-III atoms and activated nitrogen, V_g is the growth rate, and K_{AN} and K_{BN} are the equilibrium constants of the formation reactions of A^3N and B^3N from the gaseous components. The activity coefficients γ_{AN} and γ_{BN} of binary constituents can be calculated using the regular solution approximation

$$\gamma_{AN} = \exp\left[\frac{W}{RT}(1-x)^2\right] \quad , \quad \gamma_{BN} = \exp\left[\frac{W}{RT}x^2\right] \tag{6}$$

where W is the interaction energy of the binary constituents A^3N and B^3N in the ternary compound (actually W is the enthalpy of mixing of the binary constituents in the solid phase arising from the microscopic distortion of the crystalline lattice due to difference in the bond lengths). Combining Equation 5 and Equation 6 one can calculate the dependence of the growth rate V_g, the solid phase composition x and the partial pressures P_v of the desorbed components on the growth process parameters: temperature and incident fluxes F_A, F_B and F_N. Obviously, these calculations are valid for relaxed epitaxial layers [c].

Extension of this model to a multicomponent vapor phase requires the addition to the mass balance equations (the

first three equations in system Equation 6) of the terms accounting for the extra vapor components and the inclusion of additional relationships between the partial pressures corresponding to heterogeneous equilibrium of the gaseous species into the mass action law equations (the last two equations in the system Equation 6). Just such a procedure has been recently applied to analysis of GaN growth using atomic gallium and molecular ammonia beams [25].

Figure 7 and Figure 8 show the growth rate and solid phase composition versus temperature calculated for AlGaN and GaInN ternary compounds, respectively. To obtain these curves we use the interaction energy W=4800 J/mol for AlGaN and W=25700 J/mol for GaInN estimated by the Valence Force Field model [35]. The main peculiarity of the growth of ternary compounds is the two-stage decrease of the growth rate accompanied by a change in the solid phase composition. The effect is related to the start of intense desorption of different group-III atoms from the crystalline surface. One more feature following from the curves plotted in Figure 7 and Figure 8 is a deviation of the low-temperature solid phase composition from the value determined by the ratio of incident fluxes of different group-III atoms $F_A/(F_A+F_B)$ when growth is performed under NH_3-limited conditions. This effect is more pronounced for GaInN than for AlGaN and is related to predominant incorporation of the low-volatility species into the crystal.

The ternary GaInN compounds have a very large interaction energy W=25700 J/mol that is evidence of unfavorable mixing of GaN and InN in the solid phase due crystalline lattice distortion. This strain is caused by considerable mismatch of the lattice constants of GaN and InN. As a result, the GaInN solid solution exhibits a tendency towards spinodal decomposition [36] [37] or, equivalently, towards formation of a miscibility gap. Dashed and dash-dotted lines in Figure 8 present the spinodal and binodal curves calculated for GaInN ternary compounds using the regular solution approximation. Below the binodal curve the ternary compound tends to decompose into two other ternaries having the concentrations different from the initial one. This process requires overcoming a kinetic barrier related to the formation of the nuclei of new solid phases. Below the spinodal curve the height of this barrier approaches zero, and the GaInN ternary compound becomes thoroughly unstable. It is seen from Figure 8 that only ternary compounds with InN content less than 5% can be grown in the area of crystal stability, and those with InN content less than 15% can be obtained in the area of metastability of the solid phase (the area between the binodal and spinodal curves). To reach higher InN concentration either one has to use a higher growth temperature, or one has to employ strained GaInN layers (it is already mentioned that macroscopic elastic strain accumulated in the coherently grown film can suppress spinodal decomposition of the compound). The former way faces difficulties due to liquid droplet formation at high temperatures. The later one seems quite reasonable although it only allows growth of thin epilayers with thicknesses less than the critical one beyond which the relaxation of the elastic strain starts. Qualitatively similar conclusions can be made also for AlInN ternary compounds having even greater enthalpy of mixing than GaInN.

4. Conclusion

In this paper we apply the quasi-thermodynamic model to analyze the MBE growth process of binary and ternary group-III nitride compounds using ammonia as the reactive nitrogen source. Only the kinetics of molecular nitrogen evaporation from the surface of nitrides is accounted for in the model affecting all the chemical reactions with N_2 involved. The evaporation coefficients of molecular nitrogen from GaN and AlN surfaces are determined using the experimental data on Langmuir evaporation of these materials, while for InN, indirect estimations are done. According to experimental observations, only a fraction (~1/170 at 760°C on GaN) of the incident ammonia adsorbs on the growing surface of the crystal due to the effect of adsorption site blocking by accumulated gallium [9]. There is no similar information available for the other group-III nitrides, AlN and InN. Hence all V/III ratios referred to in our paper should be addressed to this reactive fraction of NH_3.

Only growth of AlN under Al-limited growth conditions and temperature T<650°C is accompanied by incomplete cracking of the reactive part of ammonia on the surface of the crystal. In all other cases the main species desorbing from the growing surface are the group-III atoms, molecular nitrogen and hydrogen. This justifies the assumption that incomplete reactivity of NH_3 does not influence the heterogeneous quasi-equilibrium between gaseous species.

The partial pressure of the desorbed nitrogen changes significantly under transition from the metal-limited to NH_3-limited growth conditions. This can influence the process of nitrogen vacancy formation in the growing crystal.

The extra liquid phase diagram of InN differs qualitatively from those of GaN and AlN, and has the form typical for the most of other III-V compounds. As a result only InN among all binary nitrides is predicted to exhibit the limitation of high-temperature growth due to liquid droplet appearance. Correct determination of the maximum achievable growth temperature requires additional experimental information on free evaporation of InN and on temperature range of its stability.

The growth rate of ternary AlGaN and GaInN compounds versus temperature is predicted to reveal the two-drop

behavior corresponding to a fast increase of subsequent group-III atom desorption. This effect is accompanied by a relevant stepwise change in the composition of the solid phase. Two factors retard the growth process of GaInN, miscibility gap formation and liquid droplet appearance on the surface of the crystal. They boound the possible "growth window» of GaInN at low and high temperatures, respectively. However, it should be noticed that we can not make a definitive conclusion of whether this "window» exists at all in the case of the relaxed epitaxial layers because the N_2 evaporation coefficient from InN surface accepted for our analysis is based on estimates. As before, to finally clarify this question, new, reliable data on InN evaporation would be very helpful.

Acknowledgments

Footnotes

[a]An analogy for this choice is provided by similarity of the sticking coefficients of arsenic tetramers on GaAs and InAs surfaces — both of them are found to be close to each other (0.50 and 0.58 respectively) and weakly dependent on temperature in a wide range (see reference [32])

[b]In principle, Ref. [31] contains the experimental information allowing extraction of the value of the N_2 evaporation coefficient from the surface of InN. However, our attempt to apply this evaporation coefficient to examination of InN growth and In droplet formation on the surface meets some inconsistency with the experimental data. First, the theory predicts a high thermal stability for InN in vacuum (an absence of decomposition into liquid and gas phases) at any temperature, contrary to experimental observation of Ref. [30]. Second, the calculated growth rates of ternary compounds GaInN differs significantly from that measured in Ref. [33], even under a very wide variation of the growth parameters. The origin of this inconsistency may be attributed to a possible occurrence of decomposition of InN into the liquid and vapor phases during the experiments of Ref. [31] which are not revealed, for example, by simultaneous measurement of In and N_2 partial pressures. In this case data [31] on nitrogen pressure do not provide any information on the evaporation coefficient on InN surface. That is why in this work we provide two different estimates for the N_2 evaporation coefficient: one based on the activation energy reported in [31] and the other based on an activation energy obtained by analogy with GaN.

[c]In the case of strained epitaxial layers coherently grown on the substrate one should also take into account the influence of the macroscopic strain on thermodynamic properties of the ternary compound. This leads not only to the shift of thermodynamic equilibrium but also to an essential modification of the activity coefficients of the binary constituents in the ternary compound [34] allowing for their mixing in the solid phase. As a result, a significant difference between the behavior of strained and relaxed epilayers is expected. In particular, the strain effects can remarkably suppress the natural tendency of GaInN and AlInN solid solutions towards spinodal decomposition and liquid phase formation on the surface during growth.

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Table 1

Parameters of temperature dependent N_2 evaporation/condensation coefficients on the surface of binary group-III nitrides, fitted to the Arrhenius form. In the case of InN - I corresponds to the activation energy of evaporation coefficient derived from the experimental data of Ref. [31], II corresponds to the activation energy accepted in this work (it is equal to that of GaN).

Material	α_0	A,K
AlN	2.60×10^8	64746
GaN	2.81×10^4	23650
InN(I)	1.0×10^{15}	41403
InN(II)	1.0	23650
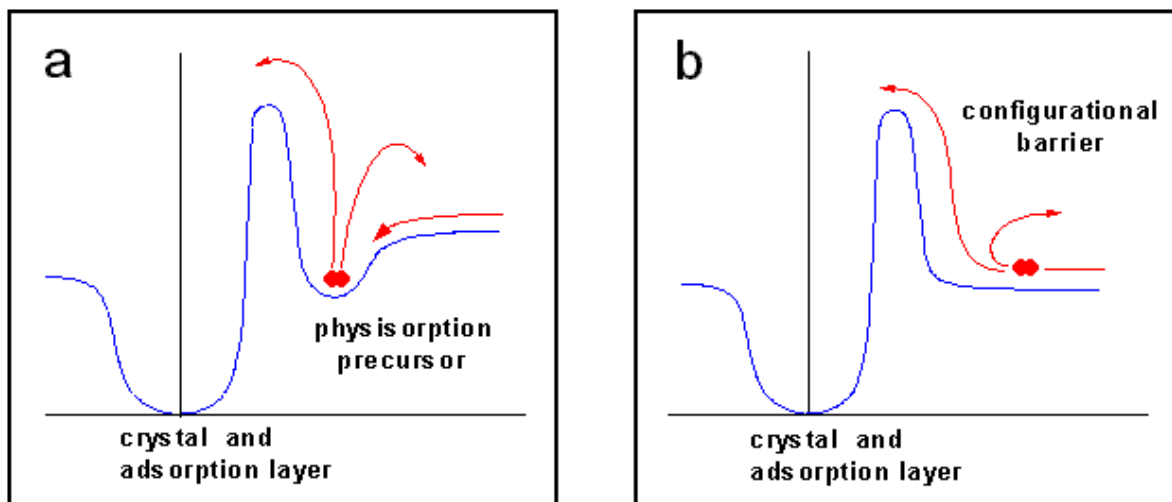
Figure 1. Two ways for getting low values of the evaporation/condensation coefficients – (a) due to a physisorption precursor of molecular nitrogen, and (b) due to a configurational barrier between adsorption layer and gas phase.
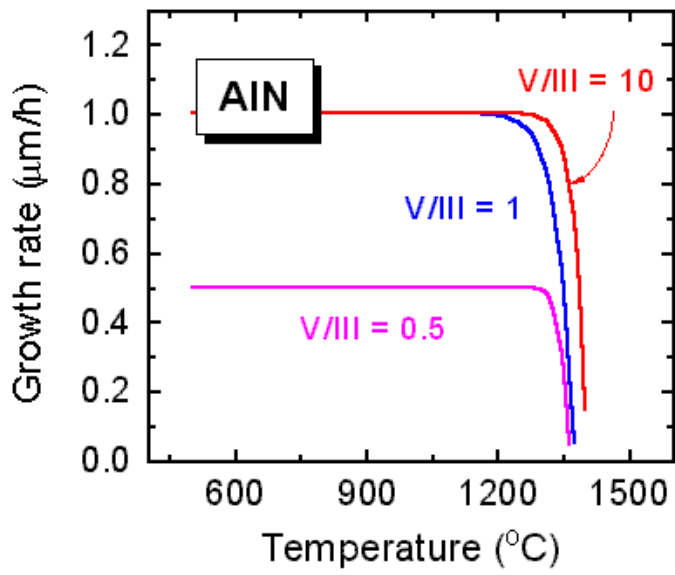
Figure 2. Growth rate of AlN versus temperature calculated for different V/III ratios, equal to 0.5, 1 and 10. The incident aluminum flux is equal to 1.115 ML/s.
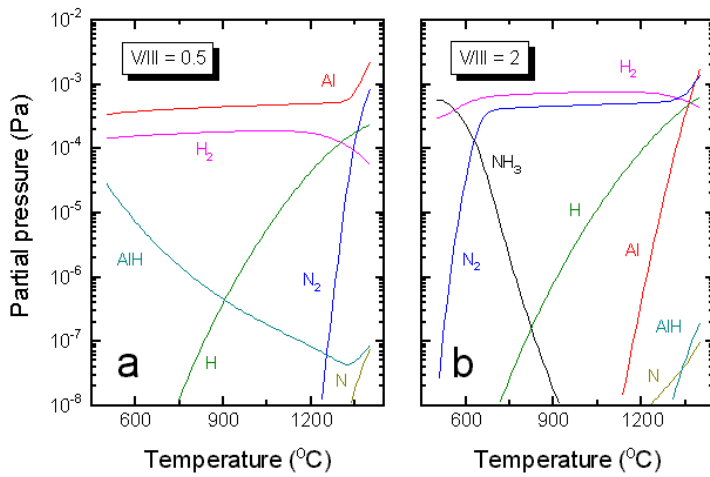

Figure 3. Partial pressures of desorbed components during growth of AlN under (a) NH$_3$-limited conditions, and (b) Al-limited conditions. The incident aluminum flux is equal to 1.115 ML/s.
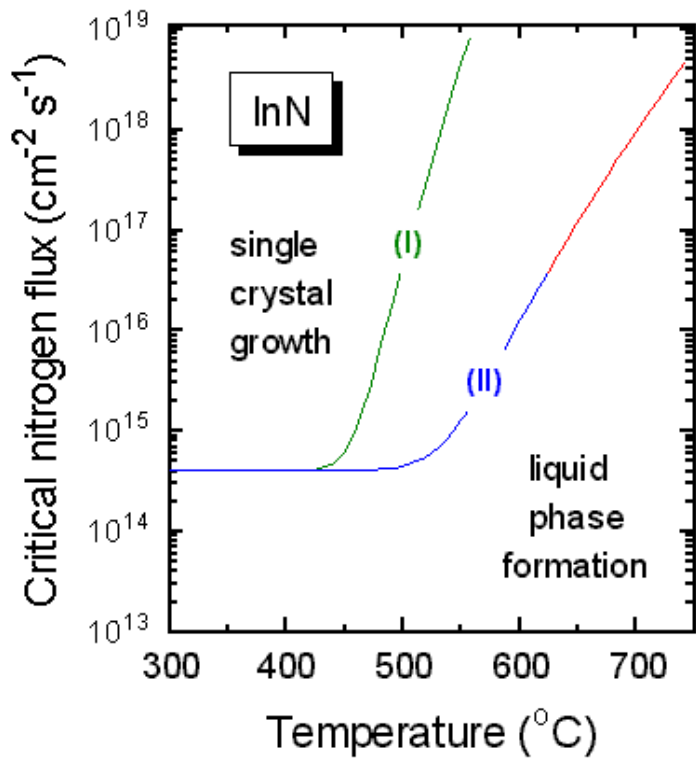
Figure 4. Boundary of liquid phase formation on the surface of InN calculated for incident In flux of 0.5 ML/s. Indices (I) and (II) in the figure denote the curves calculated for two activation energies of N_2 evaporation coefficient collected in Table 1: I — activation energy derived from experimental data of Ref. [31], II — activation energy accepted in this work which is equal to that of GaN. Change of the color from blue to red (curve II) indicates transition from growth to evaporation of the crystal. Curve I corresponds entirely to growth of the crystal.
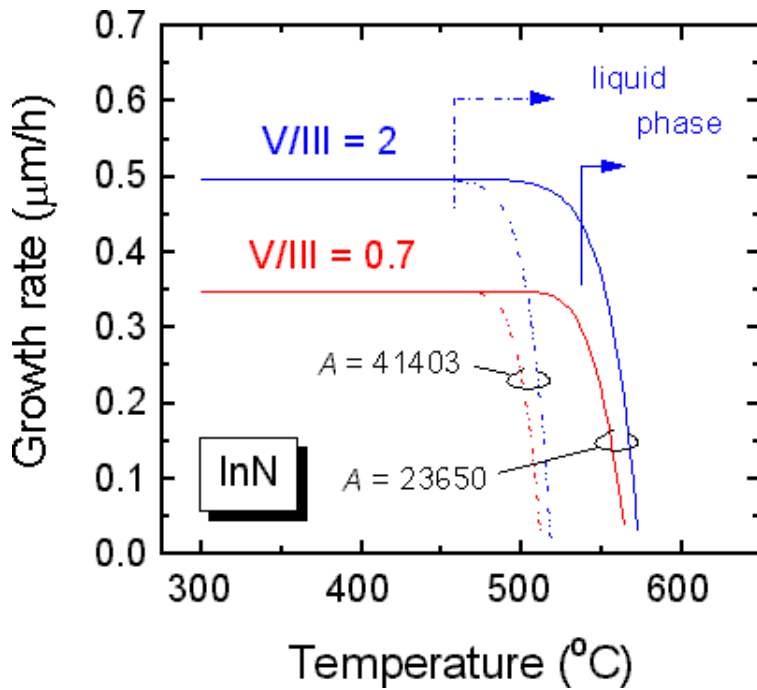
Figure 5. Growth rate of InN versus temperature calculated for In-limited (V/III = 2.0) and NH_3-limited (V/III = 0.7) conditions; the incident In flux is equal to 0.5 ML/s. Solid and dash-dotted curves correspond to different approximations of N_2 evaporation coefficient (see text). Vertical lines with arrows indicate for V/III = 2.0 the maximum temperature achievable without liquid droplets appearance on the surface. For both curves corresponding to V/III = 0.7 the liquid droplets are predicted to form during growth.
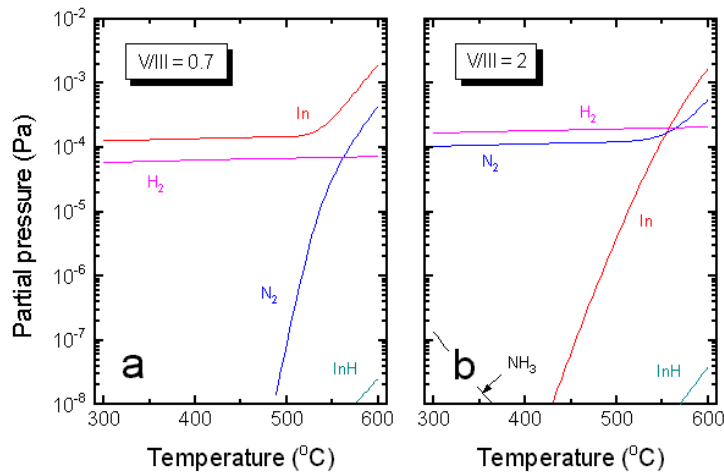
Figure 6. Partial pressures of desorbed components during growth of InN under (a) NH$_3$-limited conditions, and (b) In-limited conditions. The incident indium flux is equal to 0.5 ML/s.
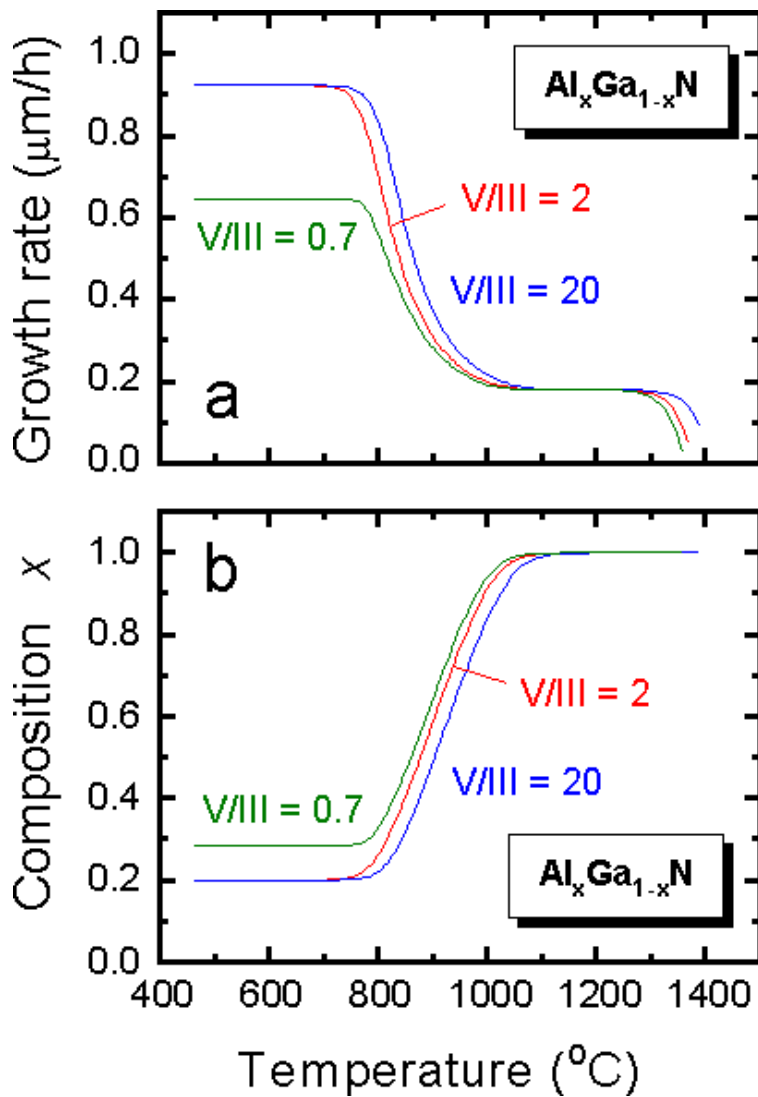

Figure 7. Growth rate (a) and solid phase composition (b) of ternary Al$_x$Ga$_{1-x}$N compound versus temperature.
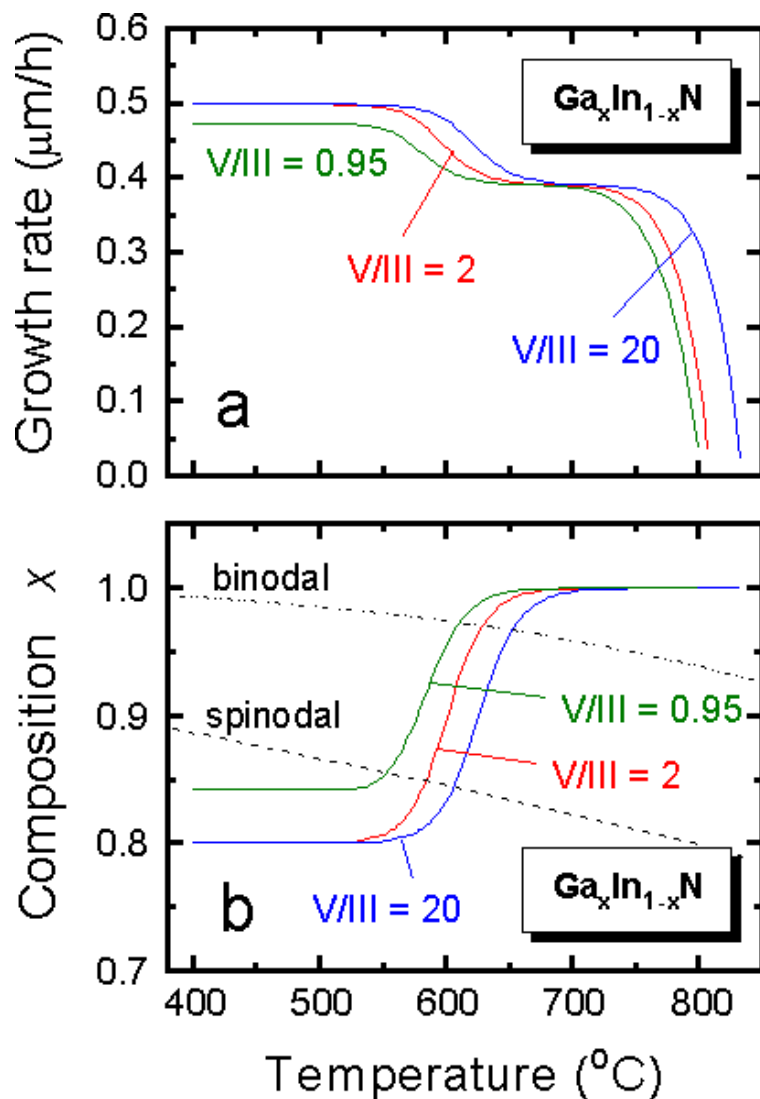
Figure 8. Growth rate (a) and solid phase composition (b) of ternary $Ga_xIn_{1-x}N$ compound versus temperature. All the curve are calculated for the case II corresponding to extrapolation of the N_2 evaporation coefficient from the surface of InN with $A = 23650$.

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