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Thermodynamic aspects of the $Ga_{1-x}In_xN$ growth by MOCVD

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Abstract

On the basis of a thorough thermodynamic analysis in the Ga–In–N–C–H system, feasible technological conditions for deposition of the solid $Ga_{1-x}In_xN$ mixed nitride are discussed. The analysis was performed in the temperature range of 600–900°C at pressures of 1 and 0.1 atm for various input gaseous phase compositions. Liquid $Ga_{1-y}In_y$ alloy, solid $Ga_{1-x}In_xN$ mixed nitride and solid graphite were considered in equilibrium with the gaseous phase. It was shown that the $Ga_{1-x}In_xN$ composition varies greatly with input gas phase composition, temperature, total pressure and character of the carrier gas. Possible formation of the liquid phase as well as solid graphite was predicted for some deposition conditions. The calculated results are in qualitative agreement with published experimental observations. © 1998 Elsevier Science B.V.

Keywords: Gallium indium nitride; MOCVD; Thermodynamic modeling; Equilibrium calculations

1. Introduction

The group A^{III}-nitrides (AlN, GaN, InN) and their solid solutions have the direct transition type band structure with the energy band gap from 1.9 eV (InN) to 6.2 eV (AlN). Furthermore, they show excellent thermal properties and so are promising materials for the fabrication of light emitting diodes and lasers in the blue to ultraviolet regions as well as of high temperature electronic devices [1]. Recently high quality thin layers and structures of (Al, Ga)N, (Ga, In)N and (Al, Ga, In)N were grown by metalorganic chemical vapour deposition (MOCVD) [2–9].

To describe the deposition of $A^{III}B^V$ solid solutions by MOCVD the simple thermodynamic model is frequently applied and useful predictions of suitable growth conditions are achieved [10–12]. Under normal growth conditions the input vapour phase is highly supersaturated and the input V/III ratio is larger then unity. For the pseudobinary solid solutions of the $A_1^{III}A_2^{III}B^V$ type, where the mixing is restricted on the A^{III}-element sublattice only, the calculated distribution coefficient $k_i = x_{i(s)}/x^0_{i(g)}$ ($i = A_1$ or A_2, molar fractions are expressed to the sum of A^{III} elements) is unity in the temperature range 500–800°C. The composition of deposited layers shows that the agreement between the experimental results and the thermodynamic calculations is very good for pseudobinary phosphides, arsenides and antimonides. However, there are significant deviations between the experimental results and theoretically predicted composition of the $Ga_{1-x}In_xN$ at temperatures higher than 500°C. The thermodynamic

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analysis of this system has been reported by Koukitu et al. [13]. The $Ga_{1-y}In_y$ liquid phase was not taken into account and only six species were chosen as the necessary vapor species in their calculations. The mole fraction of decomposed NH_3 was introduced as the fitting parameter to obtain an agreement between the calculated composition of solid $Ga_{1-x}In_xN$ and the experimental data of Matsuoka et al. [4].

In this paper the results of the thorough thermodynamic analysis of the $Ga_{1-x}In_xN$ growth in the Ga–In–N–C–H system are reported. The number of substances included in the equilibrium calculations was extended in comparison with Koukitu et al. [13] and the possible formation of liquid phase was considered. No adjustable parameter was used in the calculations. Theoretical results are compared with experimental data [3–7].

2. Calculation method and input thermodynamic data

In order to calculate the chemical equilibrium in the abovementioned heterogeneous system a general method based on minimization of the total Gibbs energy of the system on a set of points satisfying the material balance conditions was used. The calculation algorithm and the computer program CHEMEQ were described elsewhere [14].

Substances included in the calculation and sources of the thermodynamic data [15–26] are summarized in Table 1. For the solid InN the values of standard heat of formation $\Delta H_f^o(298.15) = -125$ kJ/mol and standard molar entropy $S_m^o(298.15) = 50$ J/K mol were derived from experimental data [21–26]. The ideal behaviour of the gaseous phase was assumed. The Redlich–Kister equation [27]

$$\Delta G_m^E = x_1 x_2 [L_0 + L_1(x_1 - x_2)] \quad (1)$$

with parameters $L_0 = 4450.0 + 1.19185$ T (J/mol) and $L_1 = 0.25943$ T (J/mol) published by Anderson and Ansara [28] was used to describe the excess Gibbs energy (ΔG_m^E) of the liquid phase $Ga_{1-y}In_y$. The solubility of nitrogen in the liquid alloy was neglected. The solid $Ga_{1-x}In_xN$ was modeled as the pseudobinary solution of GaN and InN components. Non-ideal behaviour of this phase was described by the Redlich–Kister Eq. (1). Relevant interaction parameters $L_0 = 31500$ J/mol and $L_1 = 3400$ J/mol were estimated from the empirical correlation between known interaction parameters and nearest neighbour distance differences in sphalerite or wurtzite structure within a group of $A^{III}B^V$ pseudobinary solid solutions [29]. The values of these parameters are in good agreement with the data of Ho and Stringfellow [30] obtained by using a modified valence-force-field model. It is interesting to note that significant nonideality causes the solid phase miscibility gap. For the temperature of 800°C the composition of coexisting solid solutions $(Ga_{0.04}In_{0.96})N$ and $(Ga_{0.98}In_{0.02})N$ was predicted using accepted thermodynamic description of pseudobinary nitride [29].

Table 1
Substances included into calculations and sources of thermodynamic data

Substance	Ref.
Ga(g), In(g), N_2(g), H_2(g), NH_3(g), CH_4(g), C(s)	[15]
$GaCH_3$(g), $Ga(CH_3)_2$(g), $Ga(CH_3)_3$(g)	[16]
$InCH_3$(g), $In(CH_3)_2$(g), $In(CH_3)_3$(g)	[17]
GaH(g), InH(g)	[18]
Ga(l), In(l)	[19]
GaN(s)	[20]
InN(s)	[21–26]

3. Calculated results and discussion

The calculations of the equilibrium composition in the Ga–In–N–C–H system were carried out in the temperature range of 500–900°C, at relative pressures $p/p^0 = 1$ and 0.1 ($p^0 = 1$ atm), for various initial compositions of the gaseous phase. Trimethylgallium $(CH_3)_3Ga$ (TMGa), trimethylindium $(CH_3)_3In$ (TMIn), ammonia and hydrogen or nitrogen were considered as input gaseous species.

Fig. 1 shows the temperature dependence of the InN molar fraction, x_{InN} in $Ga_{1-x}In_xN$ solid solution. The equilibrium phase compositions are presented in Table 2. In the temperature range of 600–700°C only the solid mixed nitride exists in the equilibrium with the gaseous phase. The values of x_{InN} are independent on temperature, pressure and character of the carrier gas. If the temperature is

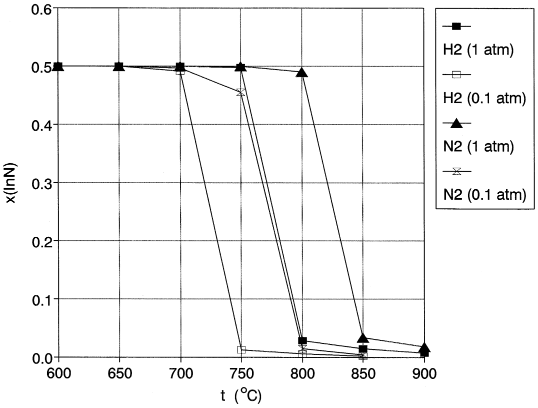

Fig. 1. Temperature dependence of indium content in the solid $Ga_{1-x}In_xN$ for various carrier gases and total pressures, $n^0(H_2)$ or $n^0(N_2) = 1$ mol, $n^0(NH_3) = 0.8$ mol, $n^0(TMGa) = 2 \times 10^{-5}$ mol, $n^0(TMIn) = 2 \times 10^{-5}$ mol, $NH_3/A^{III} = 20000$.

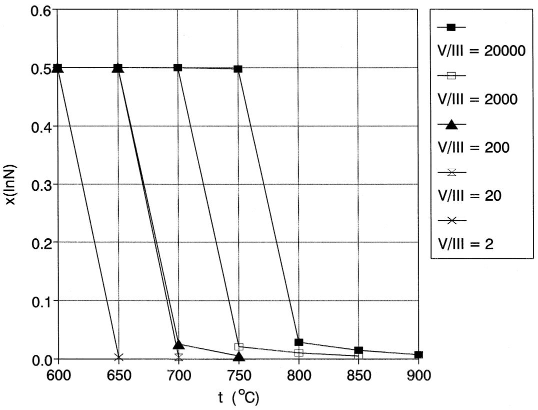

Fig. 2. Temperature dependence of indium content in the solid $Ga_{1-x}In_xN$ for the total pressure of 1 atm and various input NH_3/A^{III} ratios, $n^0(H_2) = 1$ mol, $n^0(TMGa) = 2 \times 10^{-5}$ mol, $n^0(TMIn) = 2 \times 10^{-5}$ mol.

raised to 700–900°C, the x_{InN} value decreases steeply and the formation of the $Ga_{1-y}In_y$ liquid phase was predicted by the calculation. A significant dependence of the x_{InN} values on pressure and character of the carrier gas is also evident. At the total pressure of 0.1 atm and the temperature of 850°C the indium rich liquid is not found to be due to the relatively low partial pressure of TMIn (1.11×10^{-6} atm) in comparison with saturated vapour pressure of indium (2.77×10^{-6} atm [31]) and only gallium rich nitride exists ($x_{GaN} \approx 0.99$). At the same pressure (0.1 atm) and the temperature of 900°C no condensed phases are formed. The system is homogeneous and major Ga, In and N gaseous species in equilibrium are Ga, GaH, $GaCH_3$, In, InH and N_2.

The theoretical relationship between the x_{InN} and the temperature for the NH_3/A^{III} ratio of 20–20000 and hydrogen as the carrier gas is shown in Fig. 2. The relevant phase compositions are demonstrated in Table 3. It is obvious from the calculations that the $(Ga_{1-x}In_x)N$ solid solution and the $Ga_{1-y}In_y$ liquid alloy coexist in equilibrium at the temperature of 800°C even if the NH_3/A^{III} ratio is as high as 20000. The lower the NH_3/A^{III} ratio is the lower the temperature when the liquid phase can be formed. The substitution of hydrogen with nitrogen as the

Table 2
Condensed phases in equilibrium with the gaseous phase for various carrier gases and total pressures, $n^0(H_2)$ or $n^0(N_2) = 1$ mol, $n^0(NH_3) = 0.8$ mol, $n^0(TMGa) = 2 \times 10^{-5}$ mol, $n^0(TMIn) = 2 \times 10^{-5}$ mol, $NH_3/A^{III} = 20000$ (L: liquid $Ga_{1-y}In_y$ alloy, S: solid $Ga_{1-x}In_xN$ solution)

Temperature (°C)	H_2, 1 atm	H_2, 0.1 atm	N_2, 1 atm	N_2, 0.1 atm
600	S	S	S	S
650	S	S	S	S
700	S	S	S	S
750	S	L, S	S	S
800	L, S	L, S	S	L, S
850	L, S	S	L, S	S
900	L, S		L, S	

Table 3
Condensed phases in equilibrium with the gaseous phase for the total pressure of 1 atm and various input NH_3/A^{III} ratios, $n^0(H_2) = 1$ mol, $n^0(TMGa) = 2 \times 10^{-5}$ mol, $n^0(TMIn) = 2 \times 10^{-5}$ mol (L: liquid $Ga_{1-y}In_y$ alloy, S: solid $Ga_{1-x}In_xN$ solution)

Temperature (°C)	NH_3/A^{III}			
	20	200	2000	20000
600	S	S	S	S
650	S	S	S	S
700	L, S	L, S	S	S
750	L	L, S	L, S	S
800	L	L	L, S	L, S
850	L	L	L, S	L, S
900	L	L	L	L, S

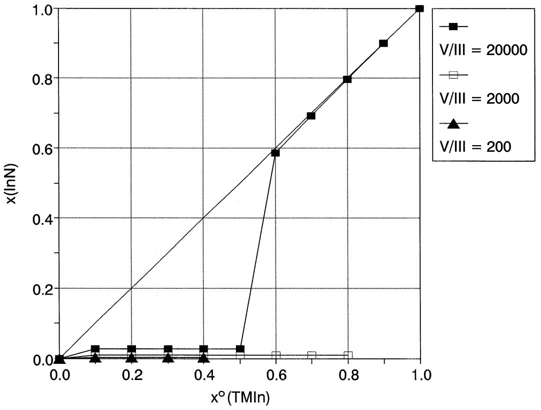

Fig. 3. Dependence of indium content in the solid $Ga_{1-x}In_xN$ on input concentration of TMIn in the gaseous phase for the temperature of 800°C, total pressure of 1 atm, and various input NH_3/A^{III} ratios, $n^0(H_2) = 1$ mol, $n^0(TMGa) + n^0(TMIn) = 4 \times 10^{-5}$ mol.

carrier gas increases the stability of the solid nitride and the liquid phase does not occur. The reduction of total pressure has the opposite influence.

The dependence of the x_{InN} on the input TMIn molar fraction x^0_{TMIn} $[x^0_{TMIn} = n^0_{TMIn}/(n^0_{TMIn} + n^0_{TMGa})]$ at the temperature of 800°C and the NH_3/A^{III} ratio of 200–20000 for hydrogen as the carrier gas is shown in Fig. 3. The equilibrium phase compositions are presented in Table 4. It is seen that for the high input TMIn concentration in the gaseous phase and the NH_3/A^{III} ratio up to 2000 the liquid alloy is created. The gallium rich $(Ga_{1-x}In_x)$N solid solution is the only stable condensed phase at $NH_3/A^{III} =$ 20000 and the high input TMIn concentration. The calculated distribution coefficient of indium, $k_{In} = x_{InN}/x^0_{TMIn}$ depends on the input NH_3/A^{III} ratio and it decreases from 0.02 to 0.005 as the x^0_{TMIn} increases from 0.1 to 0.4 at $NH_3/A^{III} = 200$, from 0.1 to 0.013 as the x^0_{TMIn} increases from 0.1 to 0.8 at $NH_3/A^{III} = 2000$ and from 0.28 to 0.056 as the x^0_{TMIn} increases from 0.1 to 0.5 at $NH_3/A^{III} = 20000$. The value of k_{In} strongly depends on the character of the carrier gas, too. When the nitrogen is used k_{In} is unity for the x^0_{TMIn} values ranged from 0 to 1 and the formation of mixed solid nitride only is predicted from calculations.

Table 4
Condensed phases in equilibrium with the gaseous phase for the temperature of 800°C, total pressure of 1 atm, various input TMIn concentrations in the gaseous phase and various input NH_3/A^{III} ratios, $n^0(H_2) = 1$ mol, $n^0(TMGa) + n^0(TMIn) = 4 \times 10^{-5}$ mol (L: liquid $Ga_{1-y}In_y$ alloy, S: solid $Ga_{1-x}In_xN$ solution)

x^0_{TMIn}	NH_3/A^{III}			
	20	200	2000	20000
0	L	S	S	S
0.1	L	L, S	L, S	L, S
0.2	L	L, S	L, S	L, S
0.3	L	L, S	L, S	L, S
0.4	L	L, S	L, S	L, S
0.5	L	L	L, S	L, S
0.6	L	L	L, S	S
0.7	L	L	L, S	S
0.8	L	L	L, S	S
0.9	L	L	L	S
1	L	L	L	S

The formation of solid graphite was predicted only for low total pressure (0.1 atm), low input NH_3/A^{III} ratio using nitrogen as the carrier gas.

On the basis of the above presented results of the thermodynamic analysis it is possible to assume that the efficiency of the In incorporation into the solid $Ga_{1-x}In_xN$ is mainly influenced by the low thermodynamic stability of InN at temperatures higher than 700°C. The decomposition pressure of N_2 reaches 1 atm at the temperature of 888°C for InN but 1052°C for GaN. From the results of the equilibrium calculations it follows that difficulties in growing high-quality solid $Ga_{1-x}In_xN$ with sufficiently high indium content at temperatures higher than 700°C can be overcome by using nitrogen as the carrier gas and higher pressure (1 atm) at the adequate input concentration of TMIn ($x^0_{TMIn} > 0.5$). Utilization of hydrogen as the carrier gas and low operating pressure can result in the $Ga_{1-y}In_y$ liquid phase formation in the equilibrium system and these conditions are not suitable for layer growth. Indeed, an appearance of the droplets of liquid phase during the $Ga_{1-x}In_xN$ growth was proved in some experiments [4,7]. In a qualitative agreement with our calculated results are experimental data of Yashimoto et al. [3,4] (N_2 carrier gas, 0.1 atm total pressure) as well as Nakamura et al. [5,6] (H_2 carrier gas, 1 atm total pressure) who found strong decrease of indium content in the solid nitride as the temperature increases.

It should be mentioned that the results of the calculations depend significantly on the values of the used input thermodynamic data. There are some discrepancies in the published thermodynamic data for solid GaN and InN and further experimental information and assessment are needed to select the most consistent and reliable data set.

Another explanation for this poor agreement between our thermodynamic prediction and the experimental results is the principal influence of transport and kinetic factors on the deposition process. Koukitu et al. [13] found much better agreement introducing an adjustable parameter, which accounts for a kinetically limited NH_3 decomposition. Moreover, in their calculations the presence of the $Ga_{1-y}In_y$ liquid phase are not taken into account and nitrogen was considered as the inert gas. It is possible that, from the equilibrium point of view, these restrictions can better characterize the real course of layer growth.

4. Conclusions

From the results of the thermodynamic analysis it follows that the MOCVD method can be utilized for the deposition of the solid $Ga_{1-x}In_xN$ mixed nitride having a variable indium content in the range of $x_{InN} = 0–1$. It is necessary to apply (i) high input NH_3/A^{III} ratio (≈ 20000), (ii) nitrogen as the carrier gas, (iii) sufficiently high total pressure ($p = 1$ atm) and (iv) suitable input $n^0_{TMIn}/(n^0_{TMIn} + n^0_{TMGa})$ ratio to grow high-quality $Ga_{1-x}In_xN$ layers with a sufficiently high indium content at temperature of 800°C. In other cases the liquid $Ga_{1-y}In_y$ alloy can be simultaneously formed under equilibrium conditions. The presence of small droplets of liquid was confirmed experimentally as well as the steep decrease of the indium incorporation efficiency with increasing temperature.

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