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Thermodynamic aspects of the GaN deposition from the gaseous phase

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Abstract

On the basis of the thorough thermodynamic analysis feasible conditions for the deposition of GaN epitaxial layers in the hydride and metalorganic systems were determined. The optimized thermodynamic data for solid GaN were used for the equilibrium calculations. Good agreement between the calculated and experimental results was achieved.

Keywords: Gallium nitride; VPE; MOCVD; Thermodynamic properties; Equilibrium calculations

1. Introduction

Gallium nitride, one of the less-common III–V semiconducting materials, has an energy gap of 3.4 eV at room temperature. Because of this large energy gap, GaN can be potentially used for visible-light optoelectronic devices [1-3]. Hydride [4-7] and metalorganic [8-14] systems were used for the preparation of GaN, $(Ga_{1-x}AI_x)N$ and $(Ga_{1-x}In_x)N$ epitaxial structures. The chemistry of vapour-phase processes leading to the deposition of GaN was not completely understood. Calculations of the equilibrium composition in the Ga–N–Cl–H and Ga–N– C–H systems were reported by Ban [15] and Chegnov [16]. Nevertheless there are some differences between the calculated and experimental results. The goal of this study was to determine on the basis of the thorough thermodynamic analysis feasible conditions for the deposition of GaN epitaxial layers in the Ga-N-Cl-H and Ga-N-C-H systems.

2. Calculation method and input thermodynamic data

In order to calculate the chemical equilibrium in the above-mentioned systems, 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. It is the modified RAND method using the calculation algorithm CHEMEQ described elsewhere [17].

The substances included in the equilibrium calculations and the sources of input thermodynamic data are summarized in Table 1. The ideal behaviour of the gaseous phase as well as the unit activity of all condensed substances were assumed. The solubility

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Table 1

Substances included into calculations and sources of thermodynamic data

Substance	Ref.
$\label{eq:Ga} \hline Ga(g), Ga(l), N(g), N_2(g), NH(g), NH_2(g), NH_3(g), \\ H(g), H_2(g), Cl(g), Cl_2(g), HCl(g), CH(g), \\ CH_2(g), CH_3(g), CH_4(g), C(s) \\ \hline \hline$	[19]
GaCl(g), GaCl ₂ (g), GaCl ₃ (g), Ga ₂ Cl ₂ (g), Ga ₂ Cl ₄ (g), Ga ₂ Cl ₆ (g)	[20,21]
$GaCH_3(g), Ga(CH_3)_2(g), Ga(CH_3)_3(g)$ GaH(g) GaN(s)	[22] [23] see text

of N_2 in liquid gallium is relatively small (approximately 5.8×10^{-3} at% at 1000 K [18]) and was not taken into account in the calculations. The thermodynamic data for solid GaN are presented in several tables. In all cases the values of the standard heat of formation $\Delta H_{\rm f}^0(298.15 \text{ K}) = -109.621 \text{ kJ/mol}$ [24], -110.5 kJ/mol [25], -109.620 kJ/mol [26] and -109.621 kJ/mol [27] are derived from calorimetric measurements of Hahn and Juza [28]. The value of the standard molar entropy $S_m^0(298.15 \text{ K}) =$ 29.706 J/K mol [26,27] as well as the coefficients of the temperature dependence of the molar heat capacity at constant standard pressure C_{pm}^{0} were estimated, where the standard pressure $p^{0} = 101325$ Pa. The reliability of these data was assessed on the basis of calculation of the N₂ decomposition pressure in the system $GaN(s)-Ga(l)-N_2(g)$. From the published thermodynamic data for GaN(s) [26,27], the temperature dependence of $p(N_2)$ was calculated in the following form

$$\log(p(N_2)/p^0) = 12.9992 - \frac{11952.971}{T}.$$
 (1)

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The decomposition temperature of solid GaN in the air $(p(N_2)/p^0 = 0.79)$ calculated from Eq. (1) is 912 K. This very low value is inconsistent with the experimental results of a number of papers dealing with GaN deposition in the 1050–1300 K tempera-

 Table 2

 Experimental data for solid GaN used for optimization

Thermodynamic functions	Ref.
$\overline{C_{\rm pm}^0(T)}; T = 5-300 \text{ K}$	[36]
$S_{\rm m}^0(298.15 {\rm K})$	[36]
$H_{\rm m}^0(T) - H_{\rm m}^0(T); T = 812 - 1075 {\rm K}$	[37]
$\Delta H_{\rm f}^0(298.15 \text{ K})$	[28]
$2GaN(s) = Ga(l) + N_2(g)$	[29,31-35]
$p(\mathbf{N}_{2}) = f(T)$	[29,31-35]
$2GaN(s) = Ga(g) + N_2(g)$	[30]
p = f(T)	[30]

ture range [4-14] as well as with direct measurements of the N₂ decomposition pressure [29-35]. So some correction of thermodynamic data for solid GaN is necessary.

The optimization procedure OPTIM and selected experimental data summarized in Table 2 were used for evaluation of thermodynamic properties of GaN(s). First, the coefficients of a polynomial temperature dependence of C_{pm}^0 in the form $C_{pm}^0 = A +$ $BT + C/T^2$ were calculated using the least-squares analysis of the heat content data [37] with the boundary conditions H(T) - H(298.15) = 0 and C_{pm}^0 (298.15 K) = 34.9 J/K mol [36]. Comparison of calculated and experimental values of the heat content of solid GaN is shown in Fig. 1. Subsequently the value of $\Delta H_{\rm f}^0$ (298.15 K) was derived as a weighed mean of experimental data from Refs. [28,31,33-35]. Assessed value of $S_m^0(298.15 \text{ K})$ is based on the low temperature C_{pm}^0 measurements [36]. The optimized thermodynamic data for GaN(s) are presented in Table 3. The temperature dependence of the N₂ decomposition pressure calculated from these data has the following form

$$\log(p(N_2)/p^0) = 12.0695 - \frac{15956,901}{T}.$$
 (2)

The calculated decomposition temperature of 1311 K in the air is now in good agreement with experimental results [37]. Fig. 2 shows the calculated and

Table 3 Optimized thermodynamic data for solid GaN

1 2	
$\Delta H_{\rm f}^0({\rm GaN, s, 298.15 K}) = -150.0 {\rm kJ/mol}$	$S_{\rm m}^0({\rm GaN, s, 298.15 K}) = 36.5 {\rm J/K mol}$
C_{pm}^{0} (GaN, s) = 27.067 + 32.903 × 10 ⁻³ T - 1.757 × 1	$10^5/T^2$ J/K mol (298–1300 K)



Fig. 1. The heat content of solid gallium nitride; a comparison of the calculated temperature dependence using the optimized thermodynamic data for solid GaN with experimental values.

experimentally obtained temperature dependences of the nitrogen equilibrium dissociation pressure in the system $GaN(s)-Ga(l)-N_2(g)$. Such obtained optimized thermodynamic data for solid GaN were used for equilibrium calculations.

3. Calculated results and discussion

The calculations of equilibrium composition of the systems under investigation were carried out for the temperature range of 600–1300 K, at relative pressures $p/p^0 = 1$ and 0.01 for various initial com-



Fig. 2. Temperature dependence of the nitrogen equilibrium decomposition pressure.

positions of the gaseous phase. Gallium monochloride or trimethylgallium, ammonia and hydrogen were supposed in the initial gaseous mixture. The results of calculations are summarized in Table 4 and in Figs. 3 and 4. From the obtained results it follows that both hydride and metalorganic systems can be utilized for the deposition of GaN epitaxial layers. The deposition efficiency (amount of the solid GaN deposited) is higher in the metalorganic than in the hydride system. This conclusion is in qualitative agreement with the measured growth rate. At the atmospheric pressure and a temperature around 1300 K, the reduced growth rate (growth rate divided by the gallium flux to the deposition zone of reactor) is

Table 4

Equilibrium phase composition of the systems Ga-N-Cl-H and Ga-N-C-H (only condensed phases are mentioned)

Input gaseous phase composition ¹	<i>p</i> / <i>p</i> ⁰	Temperature (K)							
		600	700	800	900	1000	1100	1200	1300
System Ga-N-Cl-H									
Ga: $1E - 3$, N: $1E - 2$	1	GaN	GaN	GaN	GaN	GaN	GaN	Ga	-
	0.01	GaN	GaN	GaN	GaN	-	_		-
Ga: 1E - 2, N: $1E - 3$	1	GaN, Ga	GaN	GaN	GaN	GaN	Ga	Ga	Ga
	0.01	GaN	GaN	GaN	GaN	Ga		-	-
Ga: 1E – 2, N: 1E – 1	1	GaN	GaN	GaN	GaN	GaN	GaN	Ga	Ga
	0.01	GaN	GaN	GaN	GaN	GaN	-		
System Ga-N-C-H									
Ga: 1E – 3, N: 1E – 2	1	GaN	GaN	GaN	GaN	GaN	GaN	Ga	Ga
	0.01	GaN	GaN	GaN	GaN	Ga, C	Ga, C	Ga, C	С
Ga: 1E – 2, N: 1E – 3	1	GaN, Ga	GaN, Ga	GaN, Ga	GaN, Ga	GaN, Ga	Ga	Ga, C	Ga, C
	0.01	GaN, Ga	GaN, Ga	GaN, Ga, C	GaN, Ga, C	Ga, C	Ga, C	Ga, C	Ga, C
Ga: 1E – 2, N: 1E – 1	1	GaN	GaN	GaN	GaN	GaN	GaN	Ga, C	Ga, C
	0.01	GaN	GaN	GaN, C	GaN, C	GaN, C	Ga, C	Ga, C	Ga, C

¹ Ga = n^0 (GaCl) or n^0 (Ga(CH₃)₃), N = n^0 (NH₃), n^0 (H₂) = 1 mol.



Fig. 3. Temperature dependence of the equilibrium amount of solid GaN formed in the Ga-N-Cl-H and Ga-N-C-H systems: n^{0} (GaCl) or n^{0} (Ga(CH₃)₃) = 10⁻³ mol, n^{0} (NH₃) = 10⁻² mol, n^{0} (H₂) = 1 mol.



Fig. 4. Temperature dependence of the equilibrium amount of gaseous gallium containing substances in the system Ga-N-Cl-H (a) and Ga-N-C-H (b): $n^0(GaCl)$ or $n^0(Ga(CH_3)_3) = 10^{-3}$ mol, $n^0(NH_3) = 10^{-2}$ mol, $n^0(H_2) = 1$ mol.

of the order of $10^2\ \mu m/mol$ Ga for the hydride system [6,7] and $10^3 \,\mu$ m/mol Ga for the metalorganic system [9]. The reduction of overall pressure to the value of 0.01 has a significant influence on the amount of GaN deposited. For the deposition of GaN(s) only, excess of N₂ in the gaseous phase must be realized $(n^0(NH_3)/n^0(GaCl))$ or $n^0(NH_3)/n^0(GaCl)$ $n^{0}(Ga(CH_{3})_{3}) > 1)$; otherwise liquid gallium can be formed. In the Ga-N-C-H system, solid graphite can also be formed especially at high initial trimethvlgallium concentration, high temperature and reduced total pressure. The difference between the hydride and metalorganic systems is connected especially with different thermodynamic stabilities of gallium containing species in the gaseous phase. The equilibrium concentration of GaCl in the system Ga-N-Cl-H is by several orders of magnitude higher than the concentration of GaCH₃ in the Ga-N-C-H system at comparable conditions.

4. Conclusions

From the results of the thermodynamic analysis of the Ga–N–Cl–H and Ga–N–C–H systems it follows that both systems can be utilized for the deposition of epitaxial layers of GaN from the gaseous phase. Our results, applying optimized thermodynamic data for solid GaN are in good agreement with experimental findings. Large discrepancies between the previously calculated [15,16] and experimental results can be explained by the inaccurate thermodynamic data for solid GaN.

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