

Journal of Crystal Growth 144 (1994) 1-8

GROWTH

Thermodynamic aspects of the preparation of AlAs and $Ga_{1-x}Al_xAs$ epitaxial layers in hydride and chloride systems

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Received 20 February 1994; manuscript received in final form 1 August 1994

Abstract

On the basis of a thorough thermodynamic analysis of the Al-As-Cl-H and Al-Ga-As-Cl-H systems, feasible technological conditions for the deposition of the solid AlAs and $Ga_{1-x}Al_xAs$ in hydride or chloride transport systems were determined. Under these conditions, there is no undesirable predeposition of the solid phase, which complicates the use of the systems for the preparation of the layers and structures containing aluminium. The calculated results were compared with the experimentally obtained values available. Further, a thermodynamic analysis of the Ga-As-Cl-H system was made. It follows, from a comparison of the calculated results that the different behaviour of the systems given is predominantly related to the different thermodynamic stabilities of aluminium and gallium chlorides in the vapour phase.

1. Introduction

At present, the layered structures of Ga_{1-x} Al_xAs/GaAs are widely used mainly in optoelectronics (LEDs, QW lasers, integrated optoelectronical circuits) as well as in the microwave technology (HEMTs). The techniques mostly utilized for their preparation are the LPE, MOCVD and MBE methods. The hydride and chloride transport systems [1–4] were used for the preparation of the Ga_{1-x}Al_xAs/GaAs structures with some difficulties as well.

In the studies of the conditions suitable for

deposition of the pseudobinary solid solution of $Ga_{1-x}Al_xAs$ in the system of Al-Ga-As-Cl-H, noticeable attention was paid to deposition of pure AlAs in the subsystem of Al-As-Cl-H [4-10] and some difficulties have appeared. The first is more of technological nature and consists in the corrosion of quartz glass by the gaseous aluminium chlorides at common deposition temperatures with a consequent contamination of the layers with silicon [5]. This is relatively easy to be solved [4,6-10]. The second problem is connected with relatively high oversaturation of the gaseous phase, which leads to the predeposition of the solid AlAs on the reactor wall immediately after mixing of the gaseous aluminium chlorides with AsH_3 or $AsCl_3$ [4–8]. This predeposition also occurred in the case of $Ga_{1-r}Al_rAs$ growth [1–4].

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The goal of the study is to determine, on the basis of a detailed thermodynamic analysis, feasible conditions for the deposition of AlAs and $Ga_{1-x}Al_xAs$ layers in hydride or chloride transport systems, and further, to elucidate the different behaviour of the Al-As-Cl-H and Ga-As-Cl-H systems.

2. Calculation method, system description, and input thermodynamic data

In order to calculate the chemical equilibrium for 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 [11]. It is a modified RAND method using the calculation algorithm described previously [12].

Only one solid substance (AlAs or GaAs or pseudobinary solid solution $Ga_{1-x}Al_xAs$) was assumed in equilibrium with the gaseous phase. Solid or liquid elements of Al, Ga and As were not taken into account for the calculation because, from the thermodynamic point of view, their presence is impossible within the range of the reaction conditions studied. For the calculation

Table 1 Substances included into the equilibrium calculations and sources of the appropriate thermodynamic data

Substance	Ref.	Substance	Ref.	Substance	Ref.
Al(g)	[13]	AlHCl ₂ (g)	[13]	$As_4(g)$	[16]
AlH(g)	[13]	Ga(g)	[13]	AsH ₃ (g)	[17]
AlH ₂ (g)	[13]	GaH(g)	[13]	$H_2(g)$	[18]
AlH ₃ (g)	[13]	GaCl(g)	[14,15]	H(g)	[18]
AlCl(g)	[13]	GaCl ₂ (g)	[14,15]	$Cl_2(g)$	[18]
$AlCl_2(g)$	[13]	$GaCl_3(g)$	[14,15]	Cl(g)	[18]
$AlCl_{3}(g)$	[13]	$Ga_2Cl_2(g)$	[14]	HCl(g)	[18]
$Al_2Cl_6(g)$	[13]	$Ga_2Cl_4(g)$	[14]	AlAs(s)	[19]
AlHCl(g)	[13]	$Ga_2Cl_6(g)$	[14,15]	GaAs(s)	[20]
AlH ₂ Cl(g)	[13]	As ₂ (g)	[16]		

tions, ideal behaviour of the gaseous phase as well as of the $Ga_{1-x}Al_xAs$ solid solution was assumed. Substances included in the calculations and the sources of appropriate thermodynamic data are summarized in Table 1.

3. Calculated results and discussion

The calculations of the equilibrium composition were carried out for the temperature range of 800–1400 K, at pressures of 1 and 0.01 atm,



Fig. 1. Temperature dependence of equilibrium amount of the solid AlAs deposited in the Al-As-Cl-H system at different values of pressure and parameters A and B: (a) p = 1 atm, A = 10 and (b) B = 2 (dashed curves mean that the solid phase is not created in the whole temperature range of 100 K).

and for various initial compositions of the gaseous phase. The initial amounts of hydrogen $n^0(H_2) =$ 1 mol, and of the group III elements $n^0(A^{III}) =$ 10^{-3} mol ($A^{III} = AI$ or Ga) were constant for all the calculations. The As and Cl contents in the systems were characterized by the parameters $A = n^0(As)/n^0(A^{III})$ and $B = n^0(Cl)/n^0(A^{IIII})$. The values of the parameters were varied in the calculations within the range of 1 to 10 (for A) and 1 to 5 (for B). The aluminium content in the gaseous phase was expressed, owing to the total content of the A^{III} elements, as molar fraction $x_{Al(g)} = n^0(Al)/(n^0(Al) + n^0(Ga))$, which value was varied in the range of 0 to 1 for the calculations.

3.1. Al-As-Cl-H system

The temperature dependence of the equilibrium amount of solid AlAs in the Al-As-Cl-H system at different values of pressure and parameters A and B is plotted in Fig. 1. It is obvious that there are two possibilities of deposition for solid AlAs in the system of Al-As-Cl-H. At atmospheric pressure the initial composition is to be chosen to reach a relatively high value of the ratio B by supplying HCl to the mixing zone of the reactor. In this case it is suitable to maintain the deposition zone at higher temperature (T_d) than the source (or mixing) zone (temperature $T_{\rm c}$), and the transport of AlAs is driven in the direction of increasing temperature. Thus, e.g. for values of A = 10, B = 3.5, $T_s = 900$ K (the system is homogeneous at this temperature) and $T_d =$ 1100 K, a solid AlAs will be formed and the deposition efficiency defined as $\alpha(\%) = 100 \times$ $n(AIAs, s)/n^{0}(AI, g)$ will be approximately 12.5%. Deposition efficiency could, in this case, be increased by means of a certain increase of deposition temperature. For the above-mentioned conditions and deposition temperature of $T_d = 1200$ K, the efficiency would be 22.5%. Further temperature increase (see Fig. 1), however, does not lead to an increase of the AlAs amount deposited, and at a temperature of $T_d > 1300$ K, the deposition efficiency decreases considerably.

At low pressure of 0.01 atm (see Fig. 1b), the transport of the solid AlAs can be carried out in the direction of decreasing temperature. Thus,



Fig. 2. Comparison of the calculated amount of deposited solid AlAs and the experimentally found growth rates in the systems of $AlCl_3-As_4-H_2$ (curve a) and $AlCl_3-AsH_3-H_2$ (curve b) in dependence on temperature (for the calculation of curve b the gaseous As₂ and As₄ were not considered).

e.g. for the values of A = 10, B = 2, $T_s = 1200$ K (the system is homogeneous at this temperature) and $T_d = 1000$ K, solid AlAs will be formed and the efficiency will be approximately 51.7%. In this case a further decrease of deposition temperature leads to a decrease in deposition efficiency. The deposition under low pressure in hydride and chloride systems was successfully applied to the preparation of GaAs layers [21-24]. The temperature T_s in the source zone can be decreased through utilization of a lower value of the parameter A. The lower content of As in the gaseous phase can, however, result in worse quality of the AlAs layers deposited due to a formation of vacancies in the positions of the As atoms. In the extreme case (A < 1), even droplets of Al can be formed on the surface of the solid AlAs, which considerably affects the morphology of the growing layers.

Dependence of the calculated equilibrium amount of the solid AlAs in the systems of $AlCl_3-As_4-H_2$ and $AlCl_3-AsH_3-H_2$ on temperature is plotted in Fig. 2. Curve b was calculated under the assumption that the only gaseous substance containing As was AsH_3 (As₂ and As₄



Fig. 3. (a) Comparison of the equilibrium amounts of solid AlAs in the Al-As-Cl-H system and solid GaAs in the Ga-As-Cl-H system in dependence on temperature. Curve a: p = 1 atm, A = 10, B = 1; curve b: p = 1 atm, A = 10, B = 3; curve c: p = 0.01 atm, A = 1, B = 1 (dashed curves mean that the solid phase is not created in the whole temperature range of 100 K). (b) Comparison of equilibrium concentrations (mole fractions) of gaseous Al and Ga chlorides in the Al-As-Cl-H and Ga-As-Cl-H systems in dependence on temperature, p = 1 atm, A = 10, B = 3.

were not taken into account for the calculations). This approach, which was also used by Kobayashi et al. [10], fits better to the course of the deposition in the reactor with a cold wall when a direct

reaction between AsH_3 and $AlCl_3$ is likely to occur on the surface of the substrate. Because As_2 and As_4 are the dominant As bearing components of the gaseous phase, omitting of them



Fig. 4. Temperature dependence of equilibrium amount (a) and composition (b) of solid $Ga_{1-x}Al_xAs$ for various values of B; p = 1 atm, $x_{Al(g)} = 0.5$ (dashed curves mean that the solid phase is not created in the whole temperature range of 100 K).

leads during the calculations to higher values of the AlAs amount deposited. Experimental data of AlAs layer growth rates [10] are given in Fig. 2 too. It is clear that the experimentally found increase of deposition rate within the range of higher temperatures is adequate for the increase of the calculated equilibrium amount of AlAs deposited as the result of the decreased stability of the gaseous AlCl₃.

3.2. Ga-As-Cl-H system

The results of equilibrium calculations for the Ga-As-Cl-H system were published by a number of authors, e.g. Refs. [23-29]. In this study we used newly published values of the thermodynamic data for the gaseous chlorides of gallium [14,15] as well as for the solid GaAs [20]. The differences between the systems of Ga-As-Cl-H and of Al-As-Cl-H (see Fig. 3) is connected with different thermodynamic stabilities of the gaseous gallium and aluminium chlorides. In the low temperature region, the concentration of AlCl₃ is greater than that of GaCl and thus a higher amount of the solid GaAs is created in the system of Ga-As-Cl-H compared to the amount of AlAs in the system of Al-As-Cl-H. At higher temperature the concentration of GaCl is, on the contrary, greater than that of the Al chlorides and thus the amount of GaAs deposited is lower than that of the AlAs in this temperature range.

3.3. Al-Ga-As-Cl-H system

The dependence of the equilibrium amount and the composition of solid $Ga_{1-x}Al_xAs$ on temperature at atmospheric pressure is illustrated in Fig. 4. The temperature dependence is somewhat complex because of different thermodynamic stabilities of the gaseous chlorides of aluminium and gallium. At relatively high values of the parameter *B* the homogeneous gaseous phase is thermodynamically stable at higher temperatures. The oversaturation can be attained by the gaseous phase cooling down, resulting in the formation of the solid phase; however, it is obvious from Fig. 4b that under these conditions practically pure GaAs is deposited. The decrease of the overall pressure in the system down to the value of 0.01 atm has a significant influence on the course of the dependence investigated. The pressure decrease leads to a substantial decrease of thermodynamic stability of the solid arsenides, especially at higher temperature. Cooling down of the gaseous phase to temperatures between 800 and 1000 K leads to the formation of solid $Ga_{1-x}Al_xAs$ having variable content of aluminium within $x_{AlAs} = 0.003-0.95$.

The equilibrium composition of the solid $Ga_{1-x}Al_xAs$ was compared with the values calculated by Bachem and Heyen [1] and, moreover, with the available experimental results [1–4]. Restrained to just the dominant components of the gaseous phase, the composition of the solid solution of $Ga_{1-x}Al_xAs$ is determined by the value of the standard Gibbs energy ΔG_r° of the reaction

$$GaAs(s) + AlCl_3(g) + H_2(g)$$

= AlAs(s) + GaCl(g) + 2 HCl(g).

The value of $\Delta G^{\circ}_{r} = 145.7$ kJ at a temperature of 1000 K follows from the data of Bachem and Heyen [1], and 135.7 kJ from our selected data. This difference is the cause that the composition of the solid Ga_{1-x}Al_xAs calculated by Bachem and Heyen is quite different from our results.

The dependence of the AlAs content in the solid phase on deposition temperature is plotted and compared with the experimental values [1] in Fig. 5. The temperature of the source (T_s) in which the gaseous Al and Ga chlorides are formed by the reaction of the Al-Ga melt with the gaseous HCl is the parameter here. The input thermodynamic data for the liquid Al and Ga were taken from the JANAF Tables [18] for the calculations of the gaseous phase equilibrium composition in the source. In order to describe the non-ideal behaviour of the melt, the Redlich-Kister equation was employed and the appropriate constants were taken from the paper of Watson [30]. Relatively good quantitative accordance between the calculated and experimentally found composition of the solid $Ga_{1-r}Al_rAs$ for deposition temperatures above 1000 K was obtained.

The calculated content of aluminium in the solid phase shows higher values when compared with the experimental data published by Deschler et al. [2] (see Fig. 6). The absolute difference of the value of x_{AlAs} is equal to 0.15–0.20. The dependence of x_{AlAs} on p^0 (AsH3) calculated by Deschler et al. [2] on the basis of the diffusion model is also plotted in Fig. 6. In this case the calculation gives a lower Al content in the solid phase; however, the quantitative agreement is better – the absolute difference of the value of x_{AlAs} is in the range from 0.05 to 0.10.

The values of x_{AlAs} calculated by us are, on the contrary, considerably lower when plotted against the experimental data published by Yamaguchi et al. [4]. At atmospheric pressure, deposition temperature of 873 K and gaseous phase initial composition of $n^0(AlCl_3) = 5.7 \times 10^{-5}$ mol, $n^0(GaCl_3) = 3.4 \times 10^{-6}$ mol, $n^0(AsH_3) = 3.7 \times$ 10^{-4} mol, $n^0(H_2) = 3.33 \times 10^{-3}$ mol and $n^0(He)$



Fig. 5. Comparison of calculated and experimentally found [1] composition of solid Ga_{1-x}Al_xAs in dependence on deposition temperature; p = 1 atm; source zone: 150 ml/min HCl/H₂, p^{0} (HCl) = 3×10^{-2} bar, $T_{s} = 1023$, 1053 and 1083 K; deposition zone: 150 ml/min AsH₃/H₂, p^{0} (AsH₃) = 4×10^{-2} bar, +750 ml/min H₂.



Fig. 6. Comparison of calculated and experimentally found [2] composition of solid Ga_{1-x}Al_xAs in dependence on initial partial pressure of AsH₃; p = 1 atm, $T_s = 1015$ K, $T_d = 1046$ K; source zone: 150 ml/min HCl/H₂, p^0 (HCl) = 2×10⁻² bar; deposition zone: 450 ml/min AsH₃/H₂ + 150 ml/min H₂.

= 6.56×10^{-3} mol, the aluminium content in the layers prepared was $x_{AIAs} = 0.7$ [4], while the equilibrium composition calculated was $x_{AIAs} = 0.03$.

From a comparison of the calculated and the experimentally found compositions of the solid $Ga_{1-x}Al_xAs$ it follows that the agreement of these results is qualitative only. As given previously, all the experimental results discussed here were obtained under the conditions that the formation of the solid phase occurred immediately after the gaseous chlorides of Al and Ga were mixed with AsH₃ (or with As₂ + As₄), i.e. before reaching the substrate. The predeposition of the solid phase can affect both *B* and $x_{Al(g)}$ considerably in the vicinity of the substrate. An increase of *B* results in a decrease of the value of x_{AlAs} , and an increase of the value of x_{AlAs} . Under the condi-

tions utilized in the deposition of $Ga_{1-ix}Al_xAs$ layers by Deschler et al. [2] (see Fig. 6), the calculated equilibrium composition of the solid phase ($x_{AlAs} = 0.47 - 0.58$) does not differ much from the experimentally used value of $x_{Al(g)} = 0.6$. Therefore, mainly the first factor is important for the resulting compositions of the epitaxial layers. Under the conditions for the deposition of $Ga_{1-x}Al_xAs$ used by Yamaguchi et al. [4], the value of $x_{Al(g)}$ is 0.94 and the calculated equilibrium composition of the solid phase is $x_{AlAs} =$ 0.03. It is likely that in this case, the predeposition significantly increases the value of $x_{Al(g)}$ near the substrate, and especially the second factor is the important one for the resulting composition of the epitaxial layers.

Another factor which can considerably affect the accordance between the calculated and experimentally obtained x_{AlAs} values is the influence of transport and kinetic phenomena which are not taken into account in the equilibrium model. The difference between the equilibrium and experimentally obtained compositions of the solid phase would be the higher, the higher would be the difference between diffusion coefficients of the dominant gaseous compounds of the A^{III} elements, i.e. AlCl₃ and GaCl, for deposition of $Ga_{1-x}Al_xAs$, or InCl and GaCl in the case of the deposition of $Ga_{1-x}In_xAs$. The values for binary diffusion coefficients of AlCl₃, GaCl and InCl in hydrogen were estimated by the Fuller semiempiric equation [31]. The values of diffusion volumes for Al, Ga and In were determined from the values of diffusion coefficients of trimethyland triethyl-derivatives of these elements calculated from the data published by Holstein [32]. The ratios of the appropriate diffusion coefficient values are $D(AlCl_3)/D(GaCl) = 0.77$ and D(In-Cl)/D(GaCl) = 0.92. It is obvious that the diffusion of the reactants to the substrate surface will affect the solid phase composition (and therefore the departure from equilibrium composition) in the case of the deposition of $Ga_{1-r}Al_rAs$ being more considerable than for $Ga_{1-x}In_xAs$. The results calculated on the basis of the diffusion model [2] (see Fig. 6) indicate that the experimentally obtained values of the solid phase composition can be better reproduced.

4. Conclusions

It follows from the results of the thermodynamic analysis of the Al-As-Cl-H and Al-Ga-As-Cl-H systems that hydride or chloride transport systems can be utilized for the deposition of epitaxial layers of AlAs or $Ga_{1-x}Al_xAs$ having variable aluminium content in the range of x_{AlAs} = 0-1 at decreased pressure (0.01 atm) and at a suitably chosen initial composition of the gaseous phase (B = 2). Undesirable predeposition of the solid phase on the reactor wall does not occur under these conditions. The oversaturation of the originally homogeneous gaseous phase can be attained by its cooling down from the temperature of the source zone of ca. 1100 to 1200 K to the temperature of the deposition zone of ca. 800 to 900 K.

Acknowledgment

This work was partly supported by the Grant Agency of the Czech Republic through Grant No. 106/93/0298.

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