THERMODYNAMIC ANALYSIS OF THE DEPOSITION OF (Ga, Al)As EPITAXIAL LAYERS PREPARED BY THE MOCVD TECHNIQUE

Jindřich LEITNER[a], Petr VOŇKA[b], Jan MIKULEC[a], Josef STEJSKAL[c] and Přemysl KLÍMA[c]

[a] *Department of Materials for Electronics, Prague Institute of Chemical Technology, 166 28 Prague 6*
[b] *Department of Physical Chemistry, Prague Institute of Chemical Technology, 166 28 Prague 6*
[c] *A. S. Popov Research Institute of Radiocommunication, 142 21 Prague 4*

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Based on a detailed thermodynamic analysis of the Ga–Al–As–C–H system, starting conditions were determined under with the reaction of trimethylgallium, trimethylaluminium and arsine in hydrogen results in the formation of a single condensed phase, viz. solid (Ga, Al)As. At initial ratios $B^V/A^{III} < 1$, liquid Ga–Al–As and solid Al_4C_3 are also formed. At high initial concentrations of the A^{III}-element alkyl derivatives, solid graphite also emerges, particularly at elevated temperatures and reduced pressures. The calculated composition of the solid (Ga, Al)As is compared with experimental data.

Deposition of epitaxial layers and structures of $A^{III}B^V$ type semiconductors by reacting organometallic compounds (the MOCVD method) finds wide applications in the manufacture of microelectronic and optoelectronic components[1–3]. The layer growth is a complex heterogeneous process, whose course and result are simultaneously affected by thermodynamic, transport and kinetic factors. Although diffusion of the starting gaseous substances to the substrate surface or a chemical surface reaction are usually assumed to be the controlling phenomenon, thermodynamic aspects of the MOCVD process receive considerable attention as well[4–13].

Results of thermodynamic analysis of the Ga–Al–As–C–H system have been published by several authors. In addition to the calculations of the homogeneous gas-phase chemical equilibrium[10], results of calculations of the heterogeneous chemical equilibrium have also been published[7,12], a single condensed phase, viz. solid (Ga, Al)As, being included in the model. Actually, however, other condensed phases such as Ga–Al–As melt, solid Al_4Cl_3, graphite, and in general also solid arsenic, can emerge according to the starting conditions.

This paper presents a detailed thermodynamic analysis of the Ga–Al–As–C–H system. As in our preceding paper[13] dealing with the deposition of GaAs in the

Ga–As–C–H system, attention is paid to establishing conditions in which a single condensed phase, viz. solid (Ga, Al)As, is thermodynamically stable in the system. The effect of the starting conditions on the equilibrium composition of the solid (Ga, Al)As is also examined and the results are compared with experimental data.

METHOD OF CALCULATION, DESCRIPTION OF THE SYSTEM AND INPUT THERMODYNAMIC DATA

The chemical equilibrium in the system under study was calculated by using the general method based on a minimization of the total Gibbs energy of the system on a set of points satisfying the mass balance conditions[14]. This is a modification of the White–Johnson–Dantzig method, and the corresponding computer program is based on an algorithm described by Eriksson[15].

Ideal behaviour of the gas phase was invariably assumed, and the following gaseous substances were included: Ga, $Ga(CH_3)_3$, $GaCH_3$, GaH_3, GaH_2, GaH, Al, $Al(CH_3)_3$, $AlCH_3$, AlH_3, AlH_2, AlH, As_2, As_3, As_4, AsH_3, CH_3, C_2H_6, C_2H_4 and H_2; these were selected based on preliminary calculations and published data[10,12]. Four condensed phases were also taken into account: solid (Ga, Al)As, the Ga–Al–As melt, solid Al_4C_3 and solid carbon. Solid arsenic was not considered because within the temperature region studied, the vapour pressure of arsenic gas in contact with As(s) is always higher[16] than the partial pressure of arsenic formed by dissociation of AsH_3(g) in hydrogen.

The standard molar Gibbs energies $G_i^0(T)$, summarized in Table I, were used as the input data for the individual substances. For the gaseous substances, the values were calculated from the standard molar heats of formation ΔH_f^0(298 K), standard molar entropies S^0(298 K) and temperature dependences of molar heat capacities $C_p = f(T)$ which, for the sake of internal consistency, were all taken from a single source[10]. The data for solid GaAs were calculated from the ΔH_f^0(GaAs, s, 298 K) and S^0(GaAs, s, 298 K) values[17] and from the $C_p = f(T)$ dependences taken from ref.[18]. The data for Ga(l), Al(l), As(s), AlAs(s), Al_4C_3(s) and C(s) were taken from ref.[18] as well. The temperature dependence of the molar Gibbs energy of melting of pure arsenic[19] was employed for the calculation of the standard molar Gibbs energy of liquid As.

The solid (Ga, Al)As solution was regarded as a pseudobinary solution of GaAs(s) and AlAs(s) which behaves nearly ideally[20]. The simple solution model[20] was used in describing the thermodydamic properties of the Ga–Al–As liquid phase. In this case, the activity coefficients γ_i of the components of the N-component solution obey the relation

$$RT \ln \gamma_i = \sum_{j=1}^{N} x_j [\Omega_{ij} - (1/2) \sum_{k=1}^{N} x_k \Omega_{kj}] , \quad (1)$$

where Ω_{ij} is the so-called interaction parameter of the i–j system ($\Omega_{ji} = \Omega_{ij}$, $\Omega_{ii} = 0$), which is indepedent of the solution composition but generally can depend on temperature. The following. interaction parameters were used[21]: $\Omega_{Ga-As} = 7\,782 - 25{\cdot}10T$, $\Omega_{Al-As} = -49\,387 - 5{\cdot}25T$ and $\Omega_{Ga-Al} = 1\,267$ (all in J mol^{-1}), as obtained by optimization analysis of published experimental data of the melt–solid equilibria in the Ga–As, Ga–Al and Ga–Al–As systems.

RESULTS OF CALCULATIONS AND DISCUSSION

The chemical equilibrium calculations in the Ga–Al–As–C–H system were performed for temperatures of 600 – 800°C (50°C intervals), relative pressures of 1, 0·1 and 0·01

and for different gas phase compositions. Trimethylgallium (TMGa) ($n^0_{TMGa} = 10^{-1}$ to 10^{-4} mol), trimethylaluminium (TMAl) ($n^0_{TMAl} = 10^{-1}$ to 10^{-4} mol), arsine ($n^0_{AsH_3} = 10^{-1}$ to 10^{-4} mol) and hydrogen ($n^0_{H_2} = 1 - n^0_{TMGa} - n^0_{TMAl} - n^0_{AsH_3}$ in all cases) were considered as the starting substances. For selected sets of starting conditions, Table II gives the equilibrium amounts of substance and compositions of the condensed phases that can form in the Ga–Al–As–C–H system. Figures 1 and 2 show the dependences of the equilibrium amounts of the aluminium-containing condensed phases and of the distribution of aluminium among them on the starting concentration of TMAl in the gas phase, both at 700°C. For this temperature, Fig. 3

TABLE I

Input standard molar Gibbs energies at various temperatures

Substance	$-G^0_i$, kJ mol^{-1}				
	600°C	650°C	700°C	750°C	800°C
Ga(g)	−113·324	−103·385	−93·387	−83·335	−73·231
$GaCH_3$(g)	170·773	187·117	203·680	220·453	237·431
$Ga(CH_3)_3$(g)	401·813	427·977	454·702	481·974	509·775
GaH(g)	−36·456	−24·909	−13·270	−1·544	10·265
GaH_2(g)	46·330	59·874	73·551	87·357	101·286
GaH_3(g)	93·485	106·125	118·835	131·604	144·422
Al(g)	−176·224	−166·836	−157·391	−147·894	−138·344
$AlCH_3$(g)	154·844	170·558	186·491	202·637	218·988
$Al(CH_3)_3$(g)	423·942	449·197	475·023	501·402	528·322
AlH(g)	−84·436	−73·338	−62·150	−50·874	−39·514
AlH_2(g)	38·475	51·934	65·536	79·276	93·147
AlH_3(g)	126·349	139·904	153·842	167·569	181·665
As_2(g)	33·732	47·704	61·778	75·946	90·206
As_3(g)	31·317	50·182	69·216	88·409	107·753
As_4(g)	154·476	174·610	194·968	215·538	236·310
AsH_3(g)	144·900	158·800	172·867	187·096	201·483
CH_4(g)	255·407	267·929	280·713	293·757	307·061
C_2H_6(g)	312·557	328·877	345·567	362·624	380·042
C_2H_4(g)	158·111	172·040	186·113	200·315	214·637
H_2(g)	124·884	133·108	141·426	149·834	158·331
Ga(l)	56·045	60·496	65·019	69·613	74·270
Al(l)	33·635	37·137	40·735	44·417	48·175
As(l)	35·771	40·078	44·468	48·937	53·476
GaAs(s)	157·879	163·912	170·084	176·389	182·816
AlAs(s)	192·188	197·811	203·573	209·455	215·468
Al_4C_3(s)	350·602	364·175	378·225	392·731	407·681
C(s)	9·774	10·887	12·057	13·281	14·559

shows the dependence of the equilibrium composition of solid (Ga, Al)As on the starting concentration of TMAl in the gas phase.

The following conclusions can be drawn from the results:

a) In conventional conditions of deposition of (Ga, Al)As epitaxial layers, i.e. $x^0_{TMAl} + x^0_{TMGa} = 10^{-4}$ to 10^{-3} and the starting ratio $B^V/A^{III} > 1$, the A^{III} elements are virtually quantitatively transferred from the gas phase to the solid (Ga, Al)As, which is the single thermodynamically stable condensed phase in the system at the temperatures and pressures considered. The amount of the separated (Ga, Al)As decreases very slightly with increasing temperature, decreasing pressure and de-

TABLE II

Calculated equilibrium amounts and composition of condensed phases in the Ga–Al–As–C–H system for selected sets of starting conditions ($n^0_{TMGa} = n^0_{TMAl}$ in all cases)

n^0_{TMAl} mmol	$n^0_{AsH_3}$ mmol	B^V/A^{III}	$n_{(l)}$ [a] mmol	$x_{Ga(l)}$	$x_{As(l)}.10^4$	$n_{(s)}$ [b] mmol	x_{AlAs}	n_C mmol	$n_{Al_4C_3}$ mmol
				$t = 600°C$, $p_{rel} = 1$					
0·05	1	10	0	0	0	0·1	0·50	0	0
0·05	0·1	1	0	0	0	0·1	0·50	0	0
50	100	1	0	0	0	100	0·50	0	0
50	10	0·1	48·4	0·99	1·35	9·99	0·83	0	10·4
				$t = 600°C$, $p_{rel} = 0·01$					
0·05	1	10	0	0	0	0·1	0·50	0	0
0·05	0·1	1	0	0	0	0·1	0·50	0	0
50	100	1	0	0	0	100	0·50	290	0
50	10	0·1	48·1	0·99	1·58	9·99	0·80	260	10·5
				$t = 800°C$, $p_{rel} = 1$					
0·05	1	10	0	0	0	0·1	0·50	0	0
0·05	0·1	1	0	0	0	0·0994	0·50	0	0
50	100	1	0	0	0	100	0·50	220	0
50	10	0·1	49·0	0·99	26·2	9·87	0·86	190	10·3
				$t = 800°C$, $p_{rel} = 0·01$					
0·05	1	10	0	0	0	0·0981	0·51	0	0
0·05	0·1	1	0·0097	0·99	67·2	0·0803	0·62	0	0
50	100	1	0·0312	0·99	88·0	99·9	0·50	300	0
50	10	0·1	49·1	0·99	26·2	9·87	0·86	270	10·3

[a] Equilibrium amount of the Ga–Al–As liquid phase; [b] equilibrium amount of solid (Ga,Al)As.

creasing aluminium content. The Al/Ga ratio in the solid corresponds exactly to the TMAl/TMGa ratio in the starting gas mixture and under the conditions studied, is virtually independent of the temperature and the total pressure in the system.

b) At starting ratios $B^V/A^{III} < 1$, additional condensed phases containing the A^{III} elements, viz. liquid Ga–Al–As phase and solid Al_4C_3, are also formed. The composition of (Ga, Al)As then is shifted significantly in favour of the thermodynamically more stable AlAs and is affected appreciably by the formation of the above condensed phases. The aluminium content of (Ga, Al)As increases with decreasing temperature, increasing pressure, increasing starting concentration of TMAl, decreasing starting B^V/A^{III} ratio and decreasing total reactant concentration ($TMAl + TMGa + AsH_3$) in hydrogen. The amount of the liquid phase formed is virtually independent of temperature and increases with decreasing starting concentration of TMAl and, slightly, also with increasing pressure. Temperature, however, affects the composition of the melt, viz. so that the aluminium content increases with increasing temperature. The amount of Al_4C_3 is also virtually temperature-independent and increases with increasing starting concentration of TMAl and slightly also with increasing pressure.

c) Solid graphite can also be formed at higher starting concentrations of the A^{III}-element alkyl derivatives. The amount of carbon separated increases with increasing temperature, decreasing pressure and decreasing starting concentration of TMAl. If TMAl is initially present in a high concentration and the starting B^V/A^{III} ratio is lower than unity, graphite does not form and carbon separates from the gas phase in the form of Al_4C_3.

d) If all the four condensed phases exist in equilibrium with the gas phase, then – according to the Gibbs phase rule – the number of degrees of freedom of the system is zero, which is manifested by invariable composition of the solid (Ga, Al)As as well as the Ga–Al–As melt. The composition of the former is $x_{AlAs} = 0{\cdot}801$, 0·835 and 0·859 at 600, 700 and 800°C, respectively.

e) The presence of aluminium in the system has virtually no effect on the concentrations of the gaseous substances that do not contain this element. Because of the possibility of formation of the thermodynamically highly stable solid AlAs and Al_4C_3, gaseous aluminium compounds are very little stable and are contained in the gas phase in negligible quantities. The $AlCH_3$ radical is the relatively most stable, and the hydrides AlH_3 and AlH_2 follow. Since the thermodynamic data of the majority of the gaseous substances were initially only estimated, the calculated concentrations of the substances should be regarded as estimates, too.

The calculated equilibrium composition of solid (Ga, Al)As can be compared with data obtained experimentally during the growth of epitaxial layers under various deposition conditions. Experimental results are usually presented in a graphical form, as the x_{AlAs} vs $x^0_{Al(g)}$ plot or as the $x_{AlAs}/(1 - x_{AlAs})$ vs $x^0_{Al(g)}/(1 - x^0_{Al(g)})$

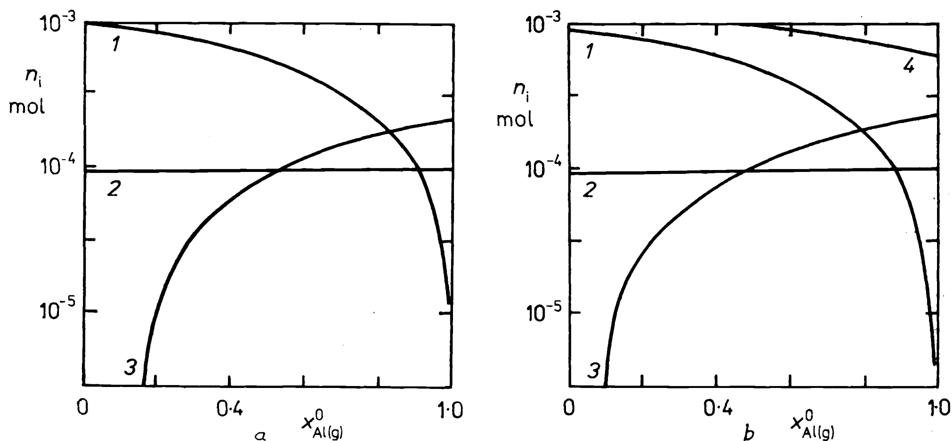

FIG. 1

Dependence of the equilibrium amounts of condensed phases in the Ga–Al–As–C–H system on the starting concentraton of TMAl in the gas phase. Temperature 700°C, relative pressure 1 (*a*) or 0·01 (*b*), $n^0_{AsH_3} = 1 \cdot 10^{-4}$ mol, $B^V/A^{III} = 0 \cdot 1$. Phase labelling: *1* Ga–Al–As(l), *2* (Ga,Al).As(s), *3* Al_4C_3(s), *4* C(s). $x^0_{Al(g)} = n^0_{TMAl}/(n^0_{TMAl} + m^0_{TMGa})$

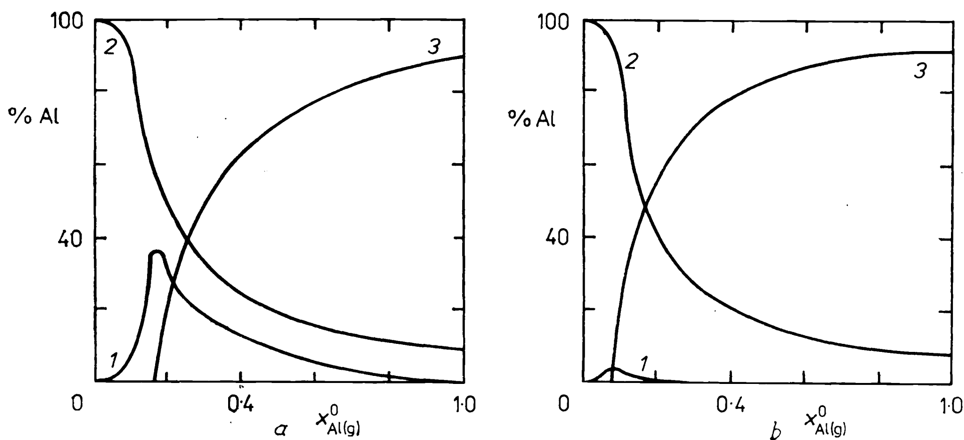

FIG. 2

Dependence of aluminium distribution among the condensed phases on the starting concentration of TMAl in the gas phase. Temperature 700°C, relative pressure 1 (*a*) or 0·01 (*b*), $n^0_{AsH_3} = 1 \cdot 10^{-4}$ mol, $B^V/A^{III} = 0 \cdot 1$. Phase labelling: *1* Ga–Al–As(l), *2* (Ga,Al)As(s), *3* Al_4C_3(s), *4* C(s). $x^0_{Al(g)} = n^0_{TMAl}/(n^0_{TMAl} + n^0_{TMGa})$

plot, where $x^0_{\mathrm{Al(g)}}$ is the starting concentration of aluminium in the gas phase relative to the total concentration of the A^{III} elements. The so-called distribution coefficients then are defined as

$$k_{\mathrm{Al}} = x_{\mathrm{AlAs}}/x^0_{\mathrm{Al(g)}} \quad (2)$$

or

$$\alpha_{\mathrm{Al}} = [x_{\mathrm{AlAs}}/(1 - x_{\mathrm{AlAs}})]/[x^0_{\mathrm{Al(g)}}/(1 - x^0_{\mathrm{Al(g)}})]\,; \quad (3)$$

they can generally depend on temperature and on the starting aluminium concentration in the gas phase.

For starting ratios $B^V/A^{III} > 1$, as usual in the deposition of epitaxial layers, the two distribution coefficients obtained from equilibrium calculations are equal to unity across the entire region of starting conditions studied. The k_{Al} values derived from published experimental data are given in Table III for a comparison. This table demonstrates that the experimental values of the distribution coefficient of aluminium are largely slightly higher than the calculated values. This can be explained in terms of a partial or total dimerization of TMAl in the gas phase[28], the actual starting aluminium concentration (relative to the overall concentration of A^{III} elements) being

$$x^0_{\mathrm{Al(g)}} = (1 + \beta)\, x^0_{\mathrm{TMAl}}/[(1 + \beta)\, x^0_{\mathrm{TMAl}} + x^0_{\mathrm{TMGa}}]\,, \quad (4)$$

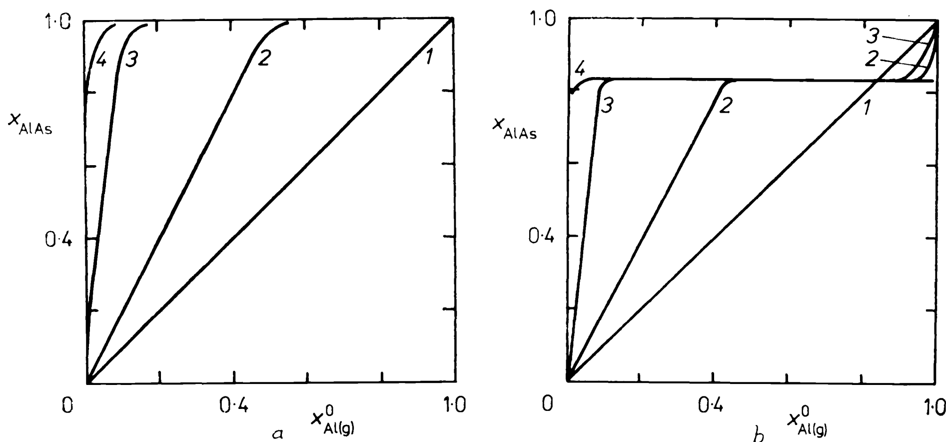

FIG. 3

Dependence of the equilibrium composition of solid (Ga,Al)As on the starting concentration of TMAl in the gas phase. Temperature 700°C, relative pressure 1 (*a*) or 0·01 (*b*), $n^0_{\mathrm{TMAl}} + n^0_{\mathrm{TMGa}} = 1 \,.\, 10^{-3}$ mol, B^V/A^{III}: *1* 1, *2* 0·5, *3* 0·1, *4* 0·01. $x^0_{\mathrm{Al(g)}} = n^0_{\mathrm{TMAl}}/(n^0_{\mathrm{TMAl}} + n^0_{\mathrm{TMGa}})$

where β is the TMAl dimerization degree, dependent on the deposition conditions. The dimerization degree can attain values from zero, when all TMAl is present in the monomeric form, to unity, when all TMAl is present in the dimeric form. If $\beta > 0$, the starting aluminium concentration in the gas phase is higher than the concentration corresponding to the occurrence of gaseous TMAl in the monomeric form solely. Thus, the aluminium distribution coefficient values determined assuming partial or total dimerization of TMAl will be slightly lower than the corresponding values given in Table III. Alternatively, the higher experimental k_{Al} values can be accounted for by transport and kinetic phenomena, which can affect appreciably the course and result of the deposition process.

CONCLUSIONS

Based on a detailed thermodynamic analysis of the Ga–Al–As–C–H system, starting conditions were established leading to the formation of solid (Ga, Al)As as a single condensed phase. These conditions, particularly the starting composition of the gas phase, agree with the conventional conditions of deposition of (Ga, Al)As layers by the MOCVD technique, which assure a good morphology of the layers. For the comparison of the calculated and experimental aluminium distribution coefficient values it can be deduced that transport phenomena as well as kinetic phenomena (homogeneous in the gas phase and heterogeneous at the substrate surface) should

TABLE III

Values of the distribution coefficient of aluminium k_{Al} derived from experimental data for various conditions of deposition of solid (Ga,Al)As. Starting substances: TMAl, TMGa, AsH_3 and H_2, starting B^V/A^{III} ratio was invariably higher than unity

Relative pressure	Temperature °C	x_{AlAs}	k_{Al}	Ref.
1	680–720	0·1–0·7	1·0	22
1	680–730	0·2–0·8	1·0	23
1	780	0 –0·3	1·1–1·6[a]	24
0·13	650–750	0·1–0·6	1·3[b]	25
0·02	650–750	0·1–0·8	1·3[b]	26
1	650	0 –0·2	1·1[c]	27
1	750	0 –0·8	1·5[b]	27

[a] Dependent on the total gas flow rate through the reactor; [b] determined from the plot for the value of $x^0_{TMAl}/(x^0_{TMAl} + x^0_{TMGa}) = 0·5$; [c] determined from the plot for the value $x^0_{TMAl}/(x^0_{TMAl} + x^0_{TMGa}) = 0·2$.

be taken into account to achieve a better agreement; actually, these phenomena can affect quite appreciably the result of the deposition process.

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