

EQUILIBRIUM GAS PHASE SPECIES FOR MOCVD OF $\text{Al}_x\text{Ga}_{1-x}\text{As}$

Max TIRTOWIDJOJO and Richard POLLARD

Department of Chemical Engineering, University of Houston, Houston, Texas 77004, USA

Thermochemical properties have been estimated for plausible gas phase intermediates in metalorganic chemical vapor deposition (MOCVD) of $\text{Al}_x\text{Ga}_{1-x}\text{As}$. These values have been used in thermodynamic calculations to assess the relative stability of the species for a wide range of operating conditions. The results indicate that polymers and adducts containing Ga and As are unimportant in the gas phase. The most stable intermediates for gallium are GaCH_3 and GaH_2 and, for aluminum, are AlH_3 , AlCH_3 , and AlH_2 . Equilibrium gas phase compositions are presented for different carrier gases and organometallic reactants.

1. Introduction

Metalorganic CVD is an important technique for epitaxial growth of compound semiconductors [1,2]. However, there are many conflicting viewpoints concerning the physical factors that control the behavior of MOCVD reactors. For example, the dominant species in the gas phase have not been identified for deposition of GaAs from $\text{Ga}(\text{CH}_3)_3$ (TMG) and AsH_3 . Some workers have suggested that polymers or adducts containing gallium and arsenic are formed [3,4] whereas others have postulated that TMG only decomposes at the substrate surface [5] or that gallium atoms [6,7] or radicals such as GaCH_3 or $\text{Ga}(\text{CH}_3)_2$ [8,9] are the major Ga-containing species. Arsine [6,7] and As_4 [10] have also been proposed as dominant gas phase molecules. In this paper, an equilibrium analysis is used to help determine which intermediate species could be important in MOCVD of $\text{Al}_x\text{Ga}_{1-x}\text{As}$. Thermochemical properties are calculated for a large number of plausible gas phase species and the information is used to predict equilibrium compositions for a wide range of pressures, temperatures, and initial gas compositions. We have attempted to consider all gas phase species that could conceivably exist in the reactor. With this approach, the results are as general as possible and are not biased by any previous opinions. The results indicate which species are most likely to form in the gas phase as a consequence of

decomposition of the reactants. The predicted order of importance of gaseous intermediates is essentially unchanged by the inclusion of heat, mass, and momentum transport in the analysis [11]. Therefore, the effects of changes in operating conditions on the relative stability of the intermediates presented here are also expected to be valid for MOCVD reactors that operate under completely mass-transport controlled conditions.

2. Analysis

Equilibrium gas phase compositions are determined for a large number of species that could be important in MOCVD of $\text{Al}_x\text{Ga}_{1-x}\text{As}$. These calculations are for a hypothetical gaseous system with constant mass and total pressure. The gas mixture is comprised of n species that contain m types of atoms. For each type of atom, an overall material balance is written in the form *

$$\sum_{i=1}^n \alpha_{ij} (p_i^0 - \eta p_i) = 0, \quad (1)$$

where α_{ij} is the number of atoms of type j in species i and η is the fractional change in the total number of moles in the gas phase. If the chemical reactions are fast and reversible, and if the gas

* Note list of symbols at the end of this paper.

mixture is ideal, the partial pressures p_i are related through equilibrium constants, according to

$$K_{pI} = \prod_i p_i^{-\nu_{iI}}. \quad (2)$$

Thermochemical property values needed to estimate the magnitudes of the equilibrium constants are only available for a few of the species. Values for the other species are estimated using statistical thermodynamics and bond dissociation enthalpies. Details of the calculations are presented in the appendix.

For the system considered, there are $n - m$ independent reactions and, consequently, $n - m$ equilibrium constants can be specified by eq. (2). These relations, Dalton's law, and the m independent conservation constraints given by eq. (1) are solved simultaneously to determine η and the n equilibrium partial pressures of the species for a specified pressure, temperature, and initial composition. The results are for equilibrium in the gas phase and, hence, they do not depend on the choice of reaction mechanism; any combination of $n - m$ reactions will yield the same results provided that they form an independent set [12]. For this reason, it is not meaningful to list one particular set of reactions.

3. Results and discussion

Equilibrium partial pressures for a typical initial mixture are presented in fig. 1 and table 1. The results indicate that, if equilibrium is attained, the major Ga-containing species are $GaCH_3$ and GaH_2 , with somewhat smaller quantities of GaH , Ga , and GaH_3 . The stability of GaH_3 falls as the temperature is increased since its formation reaction is exothermic. Conversely, Ga atoms become more important at high temperatures but, even at 1000 K, they represent less than 1% of the initial TMG. The dominant arsenic species is As_4 , although As_2 becomes significant at high temperatures because decomposition of As_4 is endothermic. For the temperature range of interest, the equilibrium partial pressure of AsH_3 is more than 300 times smaller than that of As_4 .

The results show that TMG and AsH_3 decom-

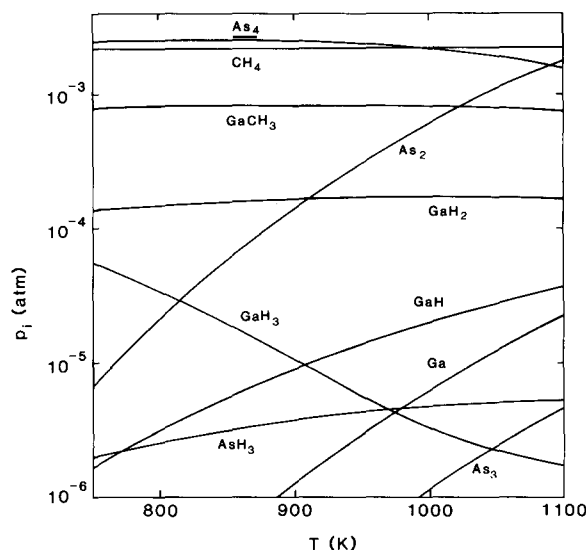


Fig. 1. Temperature dependence of equilibrium partial pressures in the gas phase for the TMG- AsH_3 - H_2 system. Results are calculated for a pressure of 1.0 atm and an initial composition of $p_{AsH_3}^0 = 0.01$ atm and $p_{AsH_3}^0/p_{TMG}^0 = 10$. Thermochemical property values for the 41 species treated in the calculations are presented in tables 2 and 3. Typical results for species with partial pressures below 10^{-6} atm. are presented in table 1. (The hydrogen partial pressure, which is close to unity, is not shown.)

pose independently in the gas phase; the partial pressures of the most stable adducts ($AsGaCH_3$ and $HAsGaCH_3$) are 11 orders of magnitude smaller than those for the major species, and polymers of the form $(GaAs)_n$ are even less stable.

Table 1

Equilibrium partial pressures of minor species in the gas phase for the TMG- AsH_3 - H_2 system at $T = 1000$ K; operating conditions are as specified in fig. 1; species considered that have equilibrium partial pressures below 10^{-14} atm are (in order of decreasing importance): $AsCH_3$, $AsGaCH_3$, $HAsGaCH_3$, TMG, $As(CH_3)_2$, $HAs(CH_3)_2$, $AsGa(CH_3)H$, $As(CH_3)_3$, $AsGa(CH_3)_2$, $H_3AsGa(CH_3)_3$, C, $(GaAs)_{3,C}$, $(GaAs)_{5,C}$, $(GaAs)_{3,L}$, $(GaAs)_{5,L}$.

Species	p_i (atm)	Species	p_i (atm)
$HGaCH_3$	5×10^{-9}	As	3×10^{-10}
H	2×10^{-9}	CH_3	2×10^{-10}
AsH	1×10^{-9}	$Ga(CH_3)_2$	2×10^{-12}
C_2H_6	1×10^{-9}	$HGa(CH_3)_2$	3×10^{-13}
GaAs	1×10^{-9}	Ga_2H_6	1×10^{-13}
H_2GaCH_3	9×10^{-10}	H_2AsCH_3	1×10^{-13}
AsH_2	8×10^{-10}	$HAsCH_3$	8×10^{-14}
C_2H_4	4×10^{-10}		

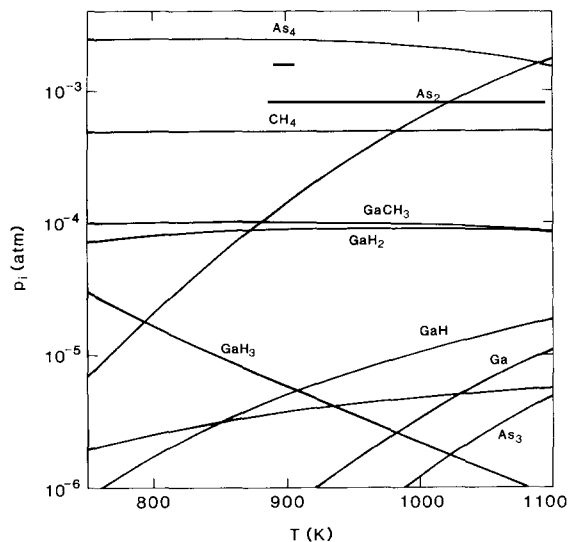


Fig. 2. Temperature dependence of equilibrium partial pressures for major gas phase species in the TMG-AsH₃-H₂ system. Conditions are as in fig. 1, except that p_{TMG}^0 is reduced to give $p_{AsH_3}^0/p_{TMG}^0 = 50$.

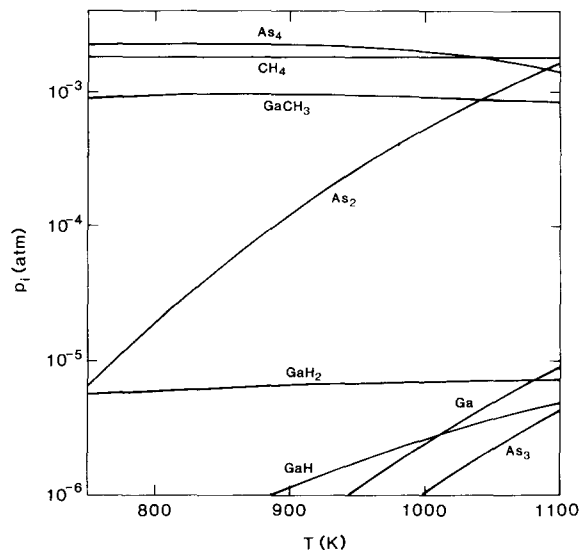


Fig. 3. Temperature dependence of equilibrium partial pressures for major gas phase species in the TMG-AsH₃-H₂ system. Conditions are as in fig. 1, except that $p_{H_2}^0$ is reduced to give a total system pressure of 0.1 atm.

Also, carbon atoms are unimportant in the gas phase. A similar distribution of species is predicted with a lower initial partial pressure of TMG. The major effect of such a change is to increase the stability of GaH₂ at the expense of GaCH₃ (see fig. 2). If the initial partial pressure of TMG is reduced further, GaH₂ becomes the dominant Ga-containing species at equilibrium. In contrast, fig. 3 indicates that a reduction in total pressure favors formation of GaCH₃. Under these conditions, the hydrides are less stable since the partial pressure of hydrogen has been reduced. This effect becomes accentuated when H₂ is replaced by He as the carrier gas. For the conditions in fig. 1, p_{GaH_2} is approximately 400 times smaller with He than with H₂, and the partial pressure of C₂H₄ at 1000 K rises over 3 orders of magnitude to 10⁻⁶ atm. In this case, p_{H_2} is 0.014 atm at equilibrium and p_{CH_3} increases to 10⁻⁹ atm.

Chemical equilibria have also been evaluated using Ga(C₂H₅)₃ (TEG) as a starting material. The calculations predict that the equilibrium gas phase compositions are essentially the same as those using TMG, except that the partial pressure of methane is doubled. For typical operating con-

ditions, none of the additional 15 species included (see table 2) have equilibrium partial pressures above 2×10^{-8} atm. The stablest one, GaC₂H₅, has a partial pressure of 1.3×10^{-8} atm for the conditions in table 1. The observation of ethylene in MOCVD processes using TEG [13,14] suggests that hydrogenation steps may be kinetically controlled under some circumstances.

Inclusion of Al₂(CH₃)₆ in the initial gas mixture results in only minor changes in the equilibrium compositions for species that contain Ga or As (compare figs. 1 and 4). The major Al-containing species are AlH₃, AlCH₃, and AlH₂. The next most important species is AlH, but its equilibrium partial pressure is generally more than 500 times smaller than that for AlH₃. Aluminum atoms are significantly less stable than AlH, and Al₂(CH₃)₆ is the least stable compound for the temperature and composition range of interest.

Many of the thermochemical quantities used in the calculations have been estimated theoretically and it is important to assess the sensitivity of the model predictions to uncertainties in these property values. Errors in calculated values for S_{298}^0 and C_p are usually quite small [15,16], whereas

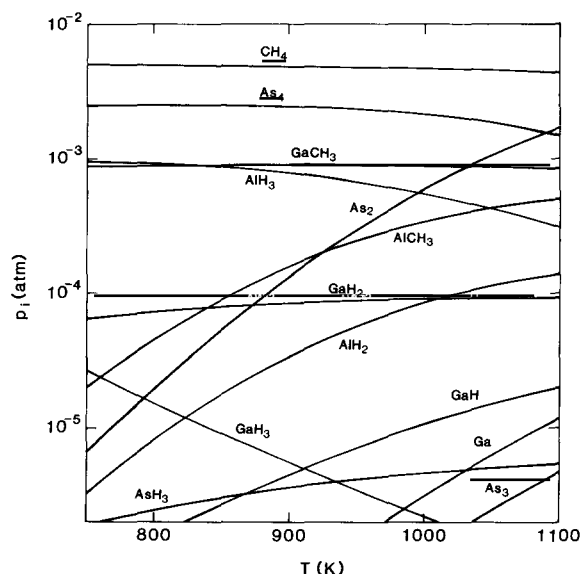


Fig. 4. Temperature dependence of equilibrium partial pressures for major gas phase species in the $\text{TMG-Al}_2(\text{CH}_3)_6\text{-AsH}_3\text{-H}_2$ system. Conditions are as in fig. 1, and $2p_{\text{Al}_2(\text{CH}_3)_6} = p_{\text{TMG}}$. A total of 57 species are included in the calculations. The minor species are (in order of decreasing importance): AlH , HAlCH_3 , Al , $\text{HAl}(\text{CH}_3)_2$, $\text{Al}(\text{CH}_3)_2$, Al_2H_6 , AsAlCH_3 , HASAlCH_3 , $\text{Al}(\text{CH}_3)_3$, H_2AlCH_3 , $\text{AsAl}(\text{CH}_3)_2$, AlAs , $\text{Al}_2(\text{CH}_3)_6$.

uncertainties in $\Delta H_{f,298}^\circ$ and $D^\circ[\text{Y-Z}]$ values are often considerably larger. For example, the values for $D^\circ[\text{HGa-H}]$ and $D^\circ[\text{H}_2\text{Ga-H}]$ are estimated by comparison with the corresponding quantities for BH_2 and BH_3 which, in turn, are determined from experimental $\Delta H_{f,298}^\circ$ values. The experimental standard heats of formation are also subject to errors. The combination of uncertainties suggests that $D^\circ[\text{HGa-H}]$ and $D^\circ[\text{H}_2\text{Ga-H}]$ can only be estimated to within approximately $\pm 25\%$. A 25% increase in $D^\circ[\text{HGa-H}]$ reduces calculated $\Delta H_{f,298}^\circ$ values for Ga_2H_6 , GaH_2 , and HGaCH_3 by 104%, 41%, and 14%, respectively. The major impact of these changes on the equilibrium gas phase compositions is to raise the stability of GaH_2 relative to that of GaCH_3 . For the conditions in fig. 1 and $T = 1000$ K, $p_{\text{GaH}_2}/p_{\text{GaCH}_3}$ is increased from 0.2 to 485. Also, p_{GaH_3} is increased seven fold, and both p_{Ga} and p_{GaH} are reduced by a factor of approximately 550. Despite these changes, polymers and adducts are not affected appreciably and can still be regarded as minor species.

It is conceivable that several $D^\circ[\text{Y-Z}]$ values in table 4 are inexact, and it is of interest to consider plausible changes in a set of $D^\circ[\text{Y-Z}]$ values that would tend to make a particular species as stable as possible. For example, the equilibrium partial pressure of gallium atoms can be raised 27% by reducing the values for $D^\circ[\text{HGa-H}]$ and $D^\circ[\text{H}_2\text{Ga-H}]$ in table 4 by 25%. The predicted Ga atom stability can be increased further if uncertainties in experimental $\Delta H_{f,298}^\circ$ and $D^\circ[\text{Y-Z}]$ values are also included. The ratio $p_{\text{Ga}}/p_{\text{GaCH}_3}$ is raised from 8×10^{-3} to 0.25 for the conditions in fig. 1 and $T = 1000$ K if $D^\circ[\text{Me}_2\text{Ga-Me}]$ and $D^\circ[\text{MeGa-Me}]$ are increased by 4.8 kJ/mol [17] and $\Delta H_{f,298}^\circ$ values for CH_3 , Ga, GaH , and TMG are changed by -4.8, -4.8, 9.6, and 9.6 kJ/mol, respectively, based on the spread of reported data. However, it should be emphasized that this increase in $p_{\text{Ga}}/p_{\text{GaCH}_3}$ would require a concerted set of errors in eight independent property values, each value being changed to the extremity of its expected range. Also, there is an equal possibility of the values being in error in the opposite direction and for $p_{\text{Ga}}/p_{\text{GaCH}_3}$ to be less than 8×10^{-3} , accordingly. Finally, it should be noted that if $D^\circ[\text{Me}_2\text{Ga-Me}]$ and $D^\circ[\text{MeGa-Me}]$ are taken to equal $\bar{D}^\circ[\text{Ga-Me}]$, the stability of Ga atoms is not increased significantly. Instead, GaH_2 becomes the dominant Ga-containing species.

The results presented above suggest that gallium atoms are relatively unstable in the gas phase and that they are unlikely to be the dominant Ga-containing species. This is consistent with the reported inability to detect free gallium atoms in the gas phase [18].

A similar approach has been taken to assess whether or not adducts or polymers could be important in the gas phase, within the bounds of plausible uncertainties in property values. In this case, D° for coordination bonding is replaced by covalent bonding, which corresponds to a five-fold increase in Ga-As bond strength [19]. For the conditions in fig. 1, this change increases the equilibrium partial pressures for adducts by a factor of 5×10^8 although the stablest adduct, AsGaCH_3 , is still a relatively minor species, e.g. $p_{\text{AsGaCH}_3}/p_{\text{GaCH}_3}$ is 9×10^{-4} at 1000 K. Inclusion of experimental errors can raise p_{HASGaCH_3} above

p_{AsGaCH_3} but, even using extreme error values, $p_{HASGaCH_3}/p_{GaCH_3}$ is only 3×10^{-3} at 1000 K. Any attempt to increase adduct stability also increases $GaCH_3$ stability since their standard heats of formation are directly related.

The impact of covalent (cf. coordination) bonding is magnified in $(GaAs)_n$ polymers since several Ga–As bonds are involved. For cyclic $(GaAs)_5$, the change to covalent bonding increases the equilibrium partial pressure by 40 orders of magnitude, but it is still a minor species. Even with the inclusion of estimates for experimental uncertainties designed to make $GaCH_3$, GaH_2 , GaH , etc. as unstable as possible, $p_{(GaAs)_5,C}/p_{GaCH_3}$ is still less than 10^{-4} for the conditions in fig. 1 and $T = 1000$ K. This ratio does increase to 10^{-2} at 900 K but only for this extreme set of property values. In this case, $(GaAs)_{3,C}$ is slightly more stable than the two-ring compound at 1000 K, but it becomes less important below 940 K. Linear $(GaAs)_3$ and $(GaAs)_5$ polymers are predicted to be less stable than their cyclic counterparts since one less Ga–As bond is formed.

There are also uncertainties in bond dissociation enthalpies for aluminum compounds. Sets of experimental and calculated thermochemical quantities have been changed by amounts based on estimated uncertainties in an attempt to influence the relative stability of the Al-containing species. The calculations show that the polymers and adducts are always minor species and that Al and AlH do not become more stable than AlH_3 , even with extreme sets of property values.

4. Conclusions

An equilibrium analysis has been used to establish the relative importance of gas phase species that could be formed during deposition of $Al_xGa_{1-x}As$ from AsH_3 , $Al_2(CH_3)_6$, and TMG or TEG using H_2 or He as a carrier gas. Thermochemical property values are calculated for plausible gaseous intermediates and the results are used to determine equilibrium compositions for typical operating conditions. Despite uncertainties in several $\Delta H_{f,298}^\circ$ values, the thermodynamic study indicates that: (i) AsH_3 , $Al_2(CH_3)_6$, and TMG or

TEG do not interact significantly in the gas phase and polymers and adducts containing Ga and As or Al and As are unimportant; (ii) equilibrium partial pressures of carbon atoms and CH_3 radicals in the gas phase are small; (iii) the Ga-containing species with the highest equilibrium partial pressures are $GaCH_3$ and GaH_2 and the importance of $GaCH_3$ increases if the initial composition of TMG is increased, the partial pressure of H_2 is reduced, or He is used as the carrier gas; (iv) the dominant Al-containing species at equilibrium are AlH_3 , $AlCH_3$, and AlH_2 ; and (v) GaH , Ga , and GaH_3 are expected to be less stable than either $GaCH_3$ or GaH_2 but additional bond strength data are needed to predict accurate partial pressures for these intermediates.

Acknowledgment

This work was supported by the National Science Foundation (Grant No. CBT-845112).

Appendix. Thermochemical and physical properties

Values of S_{298}° and C_p for gas phase species are presented in table 2. References are included for experimental data. However, in many cases, data are not available and the quantities are calculated from statistical mechanical relations [15,16,25,26]. The translational entropy contribution is determined using the molecular weight and the electronic term is evaluated from the number of unpaired electrons. The entropy contribution from external rotation is estimated from the moment of inertia and the symmetry number. Moments of inertia are, in turn, calculated from a knowledge of bond angles and bond lengths [27]. The bond angles are assumed to correspond to those for covalent bonds except for $Al_2(CH_3)_6$, Al_2H_6 and Ga_2H_6 , and adducts, which are taken to have methyl bridge bonding [28], hydrogen bridge bonding [28], and coordination bonding [29], respectively. If an experimental bond length is not available, it is determined from covalent interatomic distances corrected for the electronegativity difference of the atom [27]. The reduced moment of inertia and the symmetry number are

Table 2

Standard entropies and heat capacities for gaseous species in MOCVD of $Al_xGa_{1-x}As$; methyl and ethyl groups are abbreviated as Me and Et, respectively

Species	S_{298}° (J/mol·K)	C_p (J/mol·K) = $\alpha + \beta T + \gamma T^2 + \delta T^{-2}$				Refs.
		α	$10^3\beta$	$10^5\gamma$	$10^{-5}\delta$	
As	174.1	20.8	0.0	0.0	0.0	[20]
As ₂	239.3	37.2	0.2	0.0	-2.0	[20,21]
As ₃	310.1	62.1	0.2	0.0	-2.8	[20]
As ₄	313.8	82.9	0.1	0.0	-5.2	[20-22]
AsH	200.8	23.0	13.4	-0.4	2.0	
AsH ₂	185.8	24.3	34.3	-1.0	1.3	
AsH ₃	222.6	42.1	22.6	0.0	-9.2	[20,21,23]
AsMe ₃	343.1	55.7	219.3	-6.3	-15.9	
AsMe ₂	318.0	54.0	128.5	-3.4	-12.3	
AsMe	255.2	39.8	59.0	-1.6	-5.4	
HAsMe ₂	313.8	56.1	152.8	-4.1	-16.6	
HAsMe	263.6	54.4	154.8	-4.3	-15.9	
H ₂ AsMe	259.4	58.2	176.2	-4.9	-21.2	
C	158.0	20.8	0.0	0.0	0.0	[20-24]
CH ₃	193.0	23.0	49.2	0.0	-1.2	[20,23]
CH ₄	186.2	12.5	76.7	1.5	-1.8	[20,21]
C ₂ H ₄	219.3	25.4	98.6	-7.4	-2.7	[20,21]
C ₂ H ₅	242.7	11.1	132.9	-1.1	-3.7	[15]
C ₂ H ₆	229.5	12.8	154.2	-2.1	-4.4	[21]
H ₂	130.6	27.3	3.3	0.5	0.0	[20,21]
H	114.6	20.8	0.0	0.0	0.0	[20,21]
Ga	175.3	21.3	0.0	0.0	0.0	[20,22,23]
GaH	196.7	24.0	15.1	-0.5	1.0	[23]
GaH ₂	224.0	28.7	31.6	-1.0	-0.3	
GaH ₃	218.0	28.0	56.9	-6.2	-15.9	
Ga ₂ H ₆	276.2	69.5	128.0	-4.1	-27.6	
GaAs	252.9	37.2	0.2	0.0	-1.4	
(GaAs) _{3,L}	511.0	106.7	27.2	-1.4	0.0	
(GaAs) _{5,L}	774.0	240.3	50.6	-2.5	0.0	
(GaAs) _{3,C}	400.0	117.1	27.6	-1.2	0.0	
(GaAs) _{5,C}	522.0	202.7	51.9	-2.2	0.0	
GaMe ₃	351.5	74.5	195.0	-5.3	-16.7	
GaMe ₂	322.2	64.0	116.7	-3.1	-13.0	
GaMe	255.2	40.2	59.0	-1.6	-4.6	
HGaMe ₂	318.0	64.0	144.8	-3.9	-15.9	
AsGaMe	343.0	62.6	55.6	-1.4	-6.6	
HAsGaMe	351.5	63.2	78.7	-2.2	-7.0	
AsGaMeH	338.9	71.1	72.8	-1.9	-11.7	
H ₃ AsGaMe ₃	410.0	103.8	266.5	-7.5	-26.8	
GaEt ₃	451.9	87.5	409.6	-11.7	-40.2	
GaEt ₂	401.7	69.9	261.0	-7.5	-25.1	
GaEt	326.4	52.7	114.2	-3.3	-10.9	
HGaEt ₂	402.0	61.5	243.5	-6.7	-21.3	
HGaEt	334.7	60.7	133.8	-3.8	-14.6	
HGaMe	263.6	48.5	76.2	-2.1	-9.6	
H ₂ GaMe	259.4	56.9	93.7	-2.5	-14.6	
AsGaMe ₂	364.0	82.4	123.4	-3.2	-13.4	
H ₂ GaEt	334.7	68.6	151.9	-4.2	-18.4	
AsGaEt ₂	439.3	99.2	253.6	-7.1	-28.9	
AsGaEt	380.8	90.4	121.8	-3.4	-23.4	

Table 2 (continued)

Species	S_{298}° (J/mol·K)	$C_p(\text{J/mol}\cdot\text{K}) = \alpha + \beta T + \gamma T^2 + \delta T^{-2}$				Refs.
		α	$10^3\beta$	$10^5\gamma$	$10^{-5}\delta$	
HAsGaEt	389.1	37.2	243.1	-8.2	0.0	
H ₃ AsGaEt ₃	497.9	91.2	481.2	-13.8	-46.9	
MeGaEt ₂	426.8	86.2	330.1	-9.2	-37.2	
Me ₂ GaEt	389.1	72.2	272.4	-7.5	-28.0	
MeGaEt	359.8	63.6	191.2	-5.2	-20.0	
HMeGaEt	355.6	70.7	210.9	-5.9	-24.7	
Al	164.7	20.9	0.0	0.0	0.0	[20,23]
AlH	187.8	24.2	14.6	-0.5	1.0	[23]
AlH ₂	217.6	40.7	19.5	-0.6	-5.7	
AlH ₃	209.2	40.2	44.4	-1.3	-8.8	
Al ₂ H ₆	251.0	38.5	168.6	-5.4	-25.9	
AlAs	242.6	37.5	0.0	0.0	0.8	
AlMe ₃	334.7	62.8	209.2	-5.7	-19.7	
Al ₂ Me ₆	451.9	168.6	401.7	-11.0	-58.2	
AlMe ₂	309.6	61.5	117.6	-3.0	-15.1	
AlMe	242.7	39.7	60.3	-1.6	-5.3	
HAlMe ₂	301.3	57.7	156.1	-4.4	-19.6	
HAlMe	251.1	44.4	84.1	-2.4	-10.0	
H ₂ AlMe	246.9	49.0	108.0	-3.2	-15.1	
AsAlMe ₂	364.0	87.5	118.4	-3.1	-13.8	
AsAlMe	326.4	62.8	56.1	-1.5	-8.4	
HAsAlMe	334.7	64.0	81.6	-2.1	-12.1	

used to obtain the standard entropy for free internal rotation. The vibrational contributions to the entropy and heat capacity, S_{vib} and $C_{p,\text{vib}}$, are evaluated from the fundamental frequencies for stretching, bending, rocking, and wagging. Experimental frequencies have been measured spectroscopically for TMG, GaH₃, Ga(C₂H₅)₃, Al(CH₃)₃, AlH₃, AsH₃, and As(CH₃)₃ [30–37]. An average frequency representing each operation (e.g. bend, stretch, etc. for given bonds) [38] for these molecules is used to calculate $C_{p,\text{vib}}$ and S_{vib} for related species and intermediate species, based on the appropriate number of modes. For species with Ga–As bonding or coordination bonding, the fundamental frequencies are calculated using the reduced mass of the molecule, the bond length, and the number of outer shell electrons [39]. The corresponding bending and rocking frequencies are assumed to be equal to those for similar molecules with As replaced by C. For bridge bonding, the characteristic vibrational frequency is assumed to be the average between the bending and stretching frequencies for the

corresponding single covalent bond. It should be noted that the groups attached to a bond are assumed to rotate freely except for those at the C–C bond in TEG and its derivatives and those at C–As bonds in As(CH₃)₃. Experimental torsional data are available for C–As bonds [37] but, for TEG, the C–C bond torsion is taken to be the same as that for ethane [15]. The external rotation term for C_p is determined by the number of degrees of freedom and the influence of free internal rotation is calculated using the number of unrestricted rotational modes [15,16,25]. Fitted coefficients for the temperature dependence of C_p are given in table 2.

Standard heats of formation for the gas phase species are listed in table 3. Values not reported in the literature are calculated using bond dissociation enthalpies [27,54,55]. Table 4 gives published and calculated values for $D^\circ[Y-Z]$. The thermochemical data in tables 2 and 3 are used to calculate the equilibrium constant for a given reaction using Van 't Hoff's equation [64].

Table 3
Standard heats of formation for gaseous species in MOCVD of $\text{Al}_x\text{Ga}_{1-x}\text{As}$

Species	$\Delta H_{f,298}^\circ$ (kJ/mol)	Refs.	Species	$\Delta H_{f,298}^\circ$ (kJ/mol)	Refs.
As	301.9	[20,40]	H_2GaMe	60.0	
As_2	188.3	[20–23,41,42]	AsGaMe_2	325.0	
As_3	261.4	[20,41]	AsGaMe	334.0	
As_4	148.5	[20–23,41,42]	HAsGaMe	280.0	
AsH	247.0		AsGaMeH	375.0	
AsH_2	169.0	[41]	$\text{H}_3\text{AsGaMe}_3$	–18.8	
AsH_3	66.5	[20,23,41]	GaEt_3	–68.2	[49,50]
AsMe_3	11.7	[43,44]	GaEt_2	18.0	
AsMe_2	136.8		GaEt	71.0	
AsMe	236.8		HGaeEt_2	–9.2	
HAsMe_2	72.4		HGaeEt	91.6	
HAsMe	170.3		H_2GaEt	50.2	
H_2AsMe	96.2		AsGaEt_2	278.2	
C	716.7	[20–24]	AsGaEt	331.0	
CH_3	139.8	[15,20,23,45]	HAsGaEt	276.6	
CH_4	–74.8	[20,21,23,43]	$\text{H}_3\text{AsGaEt}_3$	–44.0	
C_2H_4	52.3	[20,21,23,46]	MeGaEt_2	–29.3	
C_2H_5	108.0	[15,23,45]	Me_2GaEt	–21.0	
C_2H_6	–84.7	[21,23,46]	MeGaEt	57.0	
H_2	0.0	[20,21,23]	HMeGaEt	16.0	
H	218.0	[20,47]	Al	327.6	[20,23,47,51]
Ga	274.1	[20,22,23,41]	AlH	259.4	[23,48]
GaH	219.2	[23,48]	AlH_2	167.8	
GaH_2	164.0		AlH_3	75.3	[52]
GaH_3	108.0		Al_2H_6	85.4	
Ga_2H_6	126.0		AlAs	429.3	
GaAs	353.6	[40]	AlMe_3	–81.2	[15,21,23,43,53]
$(\text{GaAs})_{3,\text{L}}$	1025.0		Al_2Me_6	–244.8	[15,23]
$(\text{GaAs})_{5,\text{L}}$	1680.0		AlMe_2	51.0	
$(\text{GaAs})_{3,\text{C}}$	983.0		AlMe	79.0	
$(\text{GaAs})_{5,\text{C}}$	1431.0		HAlMe	109.0	
GaMe_3	–43.5	[23,43,49]	H_2AlMe	24.0	
GaMe_2	65.7		AsAlMe_2	253.0	
GaMe	74.1		AsAlMe	280.0	
HGaeMe_2	10.0		HAsAlMe	226.0	
HGaeMe	116.0		HAlMe_2	–26.9	[53]

List of symbols

C_p	Molar heat capacity (J/mol · K)	m	Total number of different types of constituent atoms in the system
$D^\circ[\text{Y}–\text{Z}]$	Bond dissociation enthalpy of bond Y–Z (kJ/mol)	n	Total number of gaseous species in the system
$\bar{D}[\text{Y}–\text{Z}]$	Average bond dissociation enthalpy of bond Y–Z (kJ/mol)	p_i	Partial pressure of species i (atm)
$\Delta H_{f,298}^\circ$	Standard enthalpy of formation at 298 K (kJ/mol)	R	Universal gas constant (8.3143 J/mol · K)
$K_{p,l}$	Pressure-independent equilibrium constant for reaction l	S_{298}°	Standard entropy at 298 K (J/mol · K)
		T	Temperature (K)
		TEG	Triethyl gallium, $\text{Ga}(\text{C}_2\text{H}_5)_3$
		TMG	Trimethyl gallium, $\text{Ga}(\text{CH}_3)_3$

x	Mole fraction of AlAs in solid $Al_xGa_{1-x}As$	Subscripts n, C Cyclic polymer with n GaAs units n, L Linear polymer with n GaAs units vib Vibrational contribution
α_{ij}	Number of atoms of type j in species i	Superscript 0 Initial
η	Fractional change in the total number of moles in the gas phase	
ν_{il}	Stoichiometric coefficient for species i in reaction l (positive for reactants)	

References

- [1] H.M. Manasevit and W.I. Simpson, J. Electrochem. Soc. 116 (1969) 1725.

Table 4

Bond dissociation enthalpies used to estimate standard heats of formation for intermediate species

Bond Y–Z	$D^\circ[Y-Z]$ kJ/mol	Ref./Method	Bond Y–Z	$D^\circ[Y-Z]$ kJ/mol	Ref./Method
Me ₂ Ga–Me	249.0	[56]	EtGa : As	41.8	D(Ga : As)
MeGa–Me	148.2	[56]	Et ₂ Ga–Et	194.6	[14]
Me ₂ Ga–H	273.6	C(Me, H)	EtGa–Et	160.3	[14]
MeGa–H	177.0	C(Me, H)	Et ₂ Ga–H	245.6	C(Et, H)
HMeGa–H	273.6	C(Me, H)	EtGa–H	197.1	C(Et, H)
HGa–H	273.6	R ₁ (B)	HEtGa–H	259.4	C(Et, H)
H ₂ Ga–H	273.6	R ₁ (B)	Et ₂ Ga : As	41.8	D(Ga : As)
Ga–H	273.6	[48,57,58]	H ₂ As : GaEt ₃	41.8	D(Ga : As)
Ga \wedge H	159.0	R ₂ (Al)	Al \wedge H	171.6	[28]
Me ₂ Ga : As	41.8	D(Ga : As)	Me ₂ Al–Me	272.0	[61]
MeGa : As	41.8	D(Ga : As)	MeAl–Me	167.4	R ₃ (Ga)
HMeGa : As	41.8	D(Ga : As)	Me ₂ Al–H	295.8	C(Me, H)
Ga–As	209.6	[19]	MeAl–H	188.3	C(Me, H)
As–H	272.0	[46]	HMeAl–H	302.9	C(Me, H)
H ₃ As : GaMe ₃	41.8	D(Ga : As)	HMeAl–Me	275.7	C(Me, H)
Me ₂ As–Me	262.8	[59]	HA1–H	309.6	R ₄ (B)
MeAs–Me	239.7	C(Me, H)	Al–As	199.2	[62]
Me ₂ As–H	282.4	[60]	Me ₂ Al : As	100.4	D(Al : As)
MeAs–H	284.5	C(Me, H)	MeAl : As	100.4	D(Al : As)
HMeAs–H	292.1	C(Me, H)	MeAl : AsH	100.4	D(Al : As)
HAs : GaMe	41.8	D(Ga : As)	Me ₃ Ga : AsMe ₃	41.8	[29]
MeEtGa–H	259.8	C(Me, Et)	Me ₃ Ga : SMe ₂	33.5	[29]
MeGa–Et	124.7	C(Me, Et)	Me ₃ Al : SMe ₂	79.5	[29]
Me ₂ Ga–Et	194.6	C(Me, Et)	GaAs : GaAs	41.8	D(Ga : As)
EtGa : AsH	41.8	D(Ga : As)	Me ₃ Al : AsMe ₃	100.4	R ₅ (Ga)
HEtGa : As	41.8	D(Ga : As)			

Symbols –, \wedge and : indicate covalent, hydrogen bridge, and coordination bonding, respectively.

Also, $\Psi(\xi) = D_2/(3\bar{D} - D_1 - D_2)$, where D_k and \bar{D} represent $D^\circ[H_{k-1}\xi-H]$ and $\bar{D}[\xi-H]$.

Key to methods:

R₁(B) sets $\Psi(\text{Ga}) = \Psi(\text{B})$ and extrapolates D_3/\bar{D} versus $\Delta H_{f,298}^\circ$ for B and Al [63] to obtain D_3/\bar{D} for Ga;

R₂(Al) equates $D^\circ[\xi \wedge H]/\bar{D}[\xi-H]$ for $\xi = \text{Ga}$ to that for $\xi = \text{Al}$;

R₃(B) equates $D^\circ[\text{Me}\xi-\text{Me}]/\bar{D}[\xi-\text{Me}]$ for $\xi = \text{Al}$ to that for $\xi = \text{B}$;

R₄(B) sets $\Psi(\text{Al}) = \Psi(\text{B})$;

R₅(Ga) equates $D^\circ[\text{Me}_3\xi:\text{AsMe}_3]/D^\circ[\text{Me}_3\xi:\text{SMe}_2]$ for $\xi = \text{Al}$ to that for $\xi = \text{Ga}$;

C(α , β) uses constrained optimization based on trends in $D^\circ[\tau\xi-\alpha]$ values for sets of compounds with related groups τ and with $\xi-\alpha$ bonds replaced by $\xi-\beta$ bonds;

D(Y : Z) equates $D^\circ[Y : Z]$ with $\bar{D}[Y : Z]$.

- [2] G.B. Stringfellow, *Ann. Rev. Mater. Sci.* 8 (1978) 73.
- [3] I.A. Frolov, P.B. Boldyrevskii, B.L. Druz' and E.B. Sokolov, *Neorg. Mater.* 13 (1977) 773.
- [4] T. Soga, Y. Takahashi, S. Sakai and M. Umeno, *J. Crystal Growth* 68 (1984) 169.
- [5] M. Mizuta, T. Iwamoto, F. Moriyama, S. Kawata and H. Kukimoto, *J. Crystal Growth* 68 (1984) 142.
- [6] M.R. Leys and H. Veenliet, *J. Crystal Growth* 55 (1981) 145.
- [7] J. Nishizawa and T. Kurabayashi, *J. Electrochem. Soc.* 130 (1983) 413.
- [8] D.H. Reep and S.K. Ghandhi, *J. Electrochem. Soc.* 130 (1983) 675.
- [9] R.J. Field and S.K. Ghandhi, *J. Crystal Growth* 69 (1984) 581.
- [10] W.H. Petzke, V. Gottschalch and E. Butter, *Kristall Tech.* 9 (1974) 763.
- [11] M. Tirtowidjojo and R. Pollard, to be published.
- [12] J.M. Smith and H.C. Van Ness, *Introduction to Chemical Engineering Thermodynamics*, 3rd ed. (McGraw-Hill, New York, 1975).
- [13] F. Maury, M. Combes and G. Constant in: *Proc. EURO CVD IV*, Eindhoven, 1983, Eds. J. Bloem, B. Verspui and L.R. Wolf.
- [14] M.C. Paputa and S.J.W. Price, *Can. J. Chem.* 57 (1979) 3178.
- [15] S.W. Benson, *Thermochemical Kinetics*, 2nd ed. (Wiley, New York, 1976).
- [16] G.J. Janz, *Thermodynamic Properties of Organic Compounds*, revised ed. (Academic Press, New York, 1967).
- [17] G.P. Smith and R. Patrick, *Intern. J. Chem. Kinetics* 15 (1983) 167.
- [18] J. Haigh and S.O. Brian in: *Proc. EURO CVD IV*, Eindhoven, 1983, Eds. J. Bloem, B. Verspui and L.R. Wolf.
- [19] G. De Maria, L. Malaspina and V. Piacente, *J. Chem. Phys.* 52 (1970) 1019.
- [20] I. Barin, O. Knacke and O. Kubachewski, *Thermochemical Properties of Inorganic Substances* (Springer, Berlin, 1977).
- [21] H.H. Landolt and R. Börnstein, *Zahlenwerte und Funktionen aus Physik, Chemie, Astronomie, Geophysik, Technik*, Vol. II, No. 4 (Springer, Berlin, 1961).
- [22] D.R. Stull and G.C. Sinke, *Thermodynamic Properties of Elements* (Am. Chem. Soc., Washington, DC, 1965).
- [23] D.D. Wagman, W.H. Evans, V.B. Parker, I. Halow, S.M. Bailey and R.H. Schumm, *NBS Technical Note* 270-3 (1968).
- [24] M.W. Chase, Jr., J.L. Curnutt, J.R. Downey, Jr., R.A. McDonald, A.N. Syverud and E.A. Valenzuela, *J. Phys. Chem. Ref. Data*, 11 (1982) 695.
- [25] H.E. O'Neal and S.W. Benson, in: *Free Radicals*, Vol. II, Ed. J.K. Kochi (Wiley, New York, 1973).
- [26] R.E. Sonntag and G.J. Van Wylen, *Fundamentals of Statistical Thermodynamics* (Wiley, New York, 1965).
- [27] L. Pauling, *The Chemical Bond* (Cornell University Press, Ithaca, NY, 1967).
- [28] K. Wade, *J. Chem. Educ.* 49 (1972) 502.
- [29] G.E. Coates, *J. Chem. Soc.* (1951) 2003.
- [30] G.E. Coates and A.J. Downs, *J. Chem. Soc.* (1964) 3353.
- [31] J.D. Odom, K.K. Chatterjee and J.R. Durig, *J. Phys. Chem.* 84 (1980) 1843.
- [32] A.P. Kurbakova, L.A. Leimes, V.T. Aleksanyan, L.M. Golubinskaya, E.N. Zorina and V.I. Bregadze, *Zh. Strukt. Khim.* 15 (1974) 1083.
- [33] R.J. O'Brien and G.A. Ozin, *J. Chem. Soc.* (1971) 1136.
- [34] N.E. Maztek, *US Patent* 3,883,644.
- [35] R.N. Dixon and H.M. Lambertson, *J. Mol. Spectrosc.* 25 (1968) 12.
- [36] K.L. Yin and K.N. Rao, *J. Mol. Spectrosc.* 29 (1969) 486.
- [37] H. Rojhtalab and J.W. Nibler, *Spectrochim. Acta* 32A (1976) 947.
- [38] C.J. Dobratz, *Ind. Eng. Chem.* 33 (1941) 759.
- [39] K.M. Guggenheimer, *Disc. Faraday Soc.* 9 (1950) 221.
- [40] P. Klima, J. Silhavy, V. Rerabek, I. Braun, C. Cerny, P. Vonka and R. Holub, *J. Crystal Growth* 32 (1976) 279.
- [41] SGTE (Scientific Group Thermodata Europe), cited in: J.L. Gentner, C. Bernard and R. Cadoret, *J. Crystal Growth* 56 (1982) 332.
- [42] J.R. Arthur, *J. Phys. Chem. Solids* 28 (1967) 2257.
- [43] J.D. Cox and G. Pilcher, *Thermochemistry of Organic and Organometallic Compounds* (Academic Press, New York, 1970).
- [44] L.H. Long and J.F. Sackman, *Trans. Faraday Soc.* 52 (1956) 1201.
- [45] D.M. Golden and S.W. Benson, *Chem. Rev.* 69 (1969) 125.
- [46] R.C. Weast and M.J. Astle, Eds., *CRC Handbook of Chemistry and Physics*, 60th ed. (CRC Press, Boca Raton, FL, 1979).
- [47] Codata, *J. Chem. Thermodyn.* 8 (1976) 603.
- [48] W.M. Muller, J.P. Blackledge and G.G. Libowitz, *Metal Hydrides* (Academic Press, New York, 1968).
- [49] J.B. Pedley and J. Rylance, *Sussex-NPL Computer Analysed Thermochemical Data* (University of Sussex, Brighton, 1977).
- [50] I.B. Rabinovitch, G.M. Kol'yakova and E.N. Zorina, *Dokl. Akad. Nauk SSSR* 209 (1973) 616.
- [51] B. Stone and D. Hill, *Phys. Rev. Letters* 4 (1960) 282.
- [52] G.T. Armstrong, H.W. Wooley, W.H. Evans and L.A. Krieger, *NBS Report* 6484 (1959).
- [53] M.B. Smith, *J. Organometallic Chem.* 79 (1974) 171.
- [54] T.L. Cottrell, *The Strengths of Chemical Bonds* (Academic Press, London, 1954).
- [55] W.E. Dasent, *Nonexistent Compounds* (Dekker, New York, 1965).
- [56] M.G. Jacko and S.J.W. Price, *Can. J. Chem.* 41 (1963) 1560.
- [57] A. Kant and K.A. Moon, *High Temp. Sci.* 14 (1981) 23.
- [58] A.G. Gaydon, *Dissociation Energies* (Chapman and Hall, London, 1968).
- [59] S.J.W. Price and J.P. Richard, *Can. J. Chem.* 48 (1970) 3209.
- [60] D.C. McKean, I. Torto and A.R. Morrison, *J. Phys. Chem.* 86 (1982) 307.
- [61] C.H. Bamford and C.F.H. Tipper, Eds., *Comprehensive Chemical Kinetics*, Vol. 4 (Elsevier, Amsterdam, 1972).
- [62] V. Piacente, *J. Chem. Phys.* 70 (1979) 5911.
- [63] F.R. Hartley and S. Patai, *The Chemistry of the Metal-Carbon Bond*, Vol. 1 (Wiley, New York, 1982).
- [64] K. Denbigh, *The Principles of Chemical Equilibrium*, 4th ed. (Cambridge University Press, Cambridge, 1983).