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Thermodynamics of Gas-Phase Parasitic Reactions in AlGaN MOVPE Growth

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A thermodynamic analysis of the system Al–Ga–N–C–H was performed to explain the influence of gas-phase parasitic reactions on the growth of AlGaN by metalorganic vapour phase epitaxy (MOVPE). It is shown that the relatively high stability of trimeric amide $[DMAlNH_2]_3$ can lead to the Al depletion in the gas phase, and the Al/Ga ratio in the gas phase near the substrate is lower than the one in the initial gaseous mixture. Qualitative agreement was found between a number of experimental results and the thermodynamic prediction of the influence of pressure and the initial gas phase composition on the solid AlGaN composition.

1. Introduction A^{III} nitrides and their solid solutions are promising materials for advanced optoelectronic and microelectronic devices such as light-emitting diodes, lasers and high-temperature and high-power devices. Various methods are utilised for deposition of epitaxial layers and structures of these materials. Metalorganic vapour phase epitaxy (MOVPE) has some advantages over other techniques and it became the leading epitaxial technology in the last decade.

Quasi-thermodynamic [1, 2] as well as transport-kinetic [3] simulations of the AlGaN growth by MOVPE have been presented in literature and some conclusions have been drawn about the influence of growth conditions on the growth rate and composition of deposited layers. While adducts $TMA^{III}:NH_3$ (A^{III} = Al or Ga) and various dimeric and trimeric amides and imides were considered in the kinetic modelling of complex gas-phase reactions [3], only trimethyl precursors of A^{III} elements and gaseous A^{III} were taken into account in the thermodynamic calculations [1, 2]. Such a simple thermodynamic model gives some predictions, which are in contradiction with experimental observations as, for example, the influence of pressure on Al content in the solid AlGaN [4, 5].

It has been observed that gas-phase parasitic reactions among ammonia and TMA^{III} significantly influence the deposition process, especially in case of the aluminium. The goal of this work is the thermodynamic analysis of the gas-phase reactions including the formation of $TMA^{III}:NH_3$ adducts and trimeric amides $[DMA^{III}NH_2]_3$, which take part in the system Al–Ga–N–C–H relevant to the AlGaN growth by MOVPE.

2. Thermodynamic Calculations The non-stoichiometric method based on minimisation of the total Gibbs energy of the system on the set of points satisfying the material

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balance conditions [6] was used for the calculation of metastable gas-phase equilibrium composition of the above-mentioned system. 36 gaseous species were taken into account including the following A^{III} species: A^{III}, A^{III}_2, $A^{III}H$, $A^{III}H_2$, $A^{III}H_3$, $A^{III}CH_3$, $A^{III}(CH_3)_2$, $A^{III}(CH_3)_3$, $TMA^{III}:NH_3$, $[DMA^{III}NH_2]_3$ and $A^{III}N$. Thermodynamic data for all species were taken from literature [7–9]. These data were estimated in some cases and therefore the calculated results have to be treated as an estimation, too.

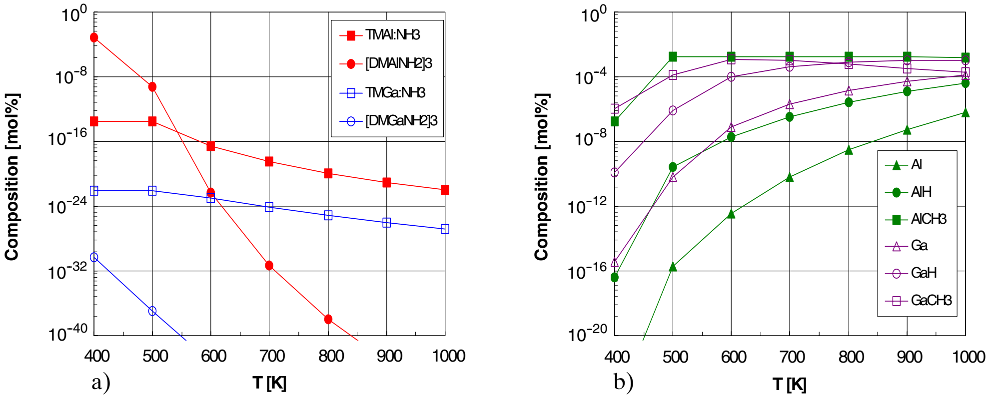
3. Results and Discussion The gas-phase composition (metastable in respect of condensed phases formation) was calculated in the temperature range of 400–1000 K at pressures p/p^0 from 0.01 to 1 ($p^0 = 101.325$ kPa) for various initial gaseous phase compositions. As the basis for the following discussion the results at the atmospheric pressure, $n^0(H_2) = 1$ mol, $n^0(NH_3) = 1$ mol, $n^0(TMAl) = n^0(TMGa) = 5 \times 10^{-5}$ mol (V/III = 10000, $x^0(TMAl) = x^0(TMGa) = 0.5$) are mentioned first.

Figure 1 shows the temperature dependencies of the equilibrium gas-phase concentrations of $TMA^{III}:NH_3$ and $[DMA^{III}NH_2]_3$ (Fig. 1a) and A^{III}, $A^{III}H$ and $A^{III}CH_3$ (Fig. 1b) under the above-mentioned conditions. While the trimeric $[DMA^{III}NH_2]_3$ is the dominant Al-containing specie at 400 K, gallium is predominantly presented in smaller molecules $GaCH_3$ and GaH.

As the trimeric aluminium amide has very low vapour pressure at this temperature, its condensation on the cold part of reactor is possible, which brings the depletion of Al in the gaseous phase. The stability of $[DMA^{III}NH_2]_3$ decreases with increasing temperature, and at 1000 K only the A^{III}, $A^{III}H$ and $A^{III}CH_3$ species are presented in considerable concentrations.

The pressure reduction leads to significant decrease of $[DMA^{III}NH_2]_3$ concentration in the gas phase due to enhancement of large molecules dissociation. While almost 100% of Al is presented in $[DMAlNH_2]_3$ at 400 K under the pressure $p/p^0 = 1$, only 2.2% under $p/p^0 = 0.01$.

The influence of V/III ratio variation in the range of 100–10000 on Al distribution between $[DMAlNH_2]_3$ and other gaseous species is insignificant due to the large excess of ammonia. Figure 2 shows the Al fraction presented in $[DMAlNH_2]_3$ in dependence of the



a) b)

Fig. 1 (online colour). a) Equilibrium gas-phase concentrations of $TMA^{III}:NH_3$ and $[DMA^{III}NH_2]_3$ as a function of temperature at $p/p^0 = 1$ (V/III = 10000); b) Equilibrium gas-phase concentrations of A^{III}, $A^{III}H$ and $A^{III}CH_3$ as a function of temperature at $p/p^0 = 1$ (V/III = 10000)

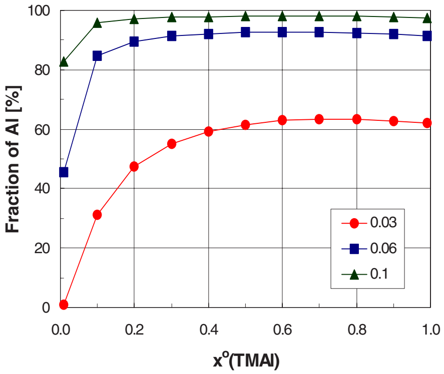


Fig. 2

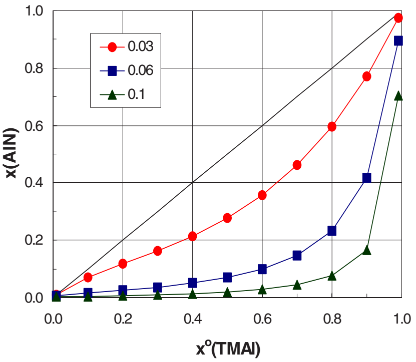


Fig. 3

Fig. 2 (online colour). Equilibrium Al fraction presented in $[\mathrm{DMAlNH_2}]_3$ in dependence on initial TMAl concentration at 400 K and $p/p^0 = 0.03$, 0.06 and 0.1 (V/III = 10000)

Fig. 3 (online colour). Solid AlGaN composition in dependence on initial TMAl concentration at 400 K and $p/p^0 = 0.03$, 0.06 and 0.1 (V/III = 10000)

initial TMAl concentration (relative to the sum of $\mathrm{TMA^{III}}$) at 400 K and $p/p^0 = 0.03$, 0.06 and 0.1. The fraction of Al bounded in trimeric amide initially increases with the increasing input TMAl concentration till the saturation is reached, which is shifted to the lower values of x^0(TMAl) as the pressure increases.

On the basis of the above-mentioned results it is possible to explain some phenomena observed during the AlGaN growth. We suppose, as it has been postulated in the frame of the reaction-transport model [3], that the trimers do not contribute to growth and mixing of the $\mathrm{TMA^{III}}$ and ammonia streams proceed in the cold part of reactor. Then the Al/Ga ratio in the gaseous phase near the susceptor is lower than the nominal one in the input gaseous mixture and the AlGaN layers with the lower Al content will be deposited. The higher the total pressure, the higher is Al depletion in the gas phase. If we roughly assume that the distribution coefficients of the both elements are equal to 1, the AlN mol fraction in solid AlGaN, x(AlN), can be calculated as follows:

$$x(\mathrm{AlN}) = x(\mathrm{Al,\,g}) = \frac{n^0(\mathrm{TMAl}) - 3n^{\mathrm{eq}}([\mathrm{DMAlNH_2}]_3)}{n^0(\mathrm{TMGa}) + n^0(\mathrm{TMAl}) - 3n^{\mathrm{eq}}([\mathrm{DMAlNH_2}]_3)}\,. \tag{1}$$

$x(\mathrm{Al,\,g})$ is molar fraction of Al in the gaseous phase near the substrate and $n^{\mathrm{eq}}([\mathrm{DMAlNH_2}]_3)$ is the calculated equilibrium amount of the trimer at a chosen temperature of mixing of the source gases. Figure 3 shows the calculated dependence of solid nitride composition on x^0(TMAl) for the mixing temperature of 400 K and pressures 0.03, 0.06 and 0.1. The apparent distribution coefficient of Al, k_{Al}, (calculated with respect to the input Al concentration in the gas phase) is lower than one now. These findings are in agreement with the experimental results [5, 10], while values k_{Al} equal to one [11] or slightly greater then one [12] were observed by some other investigators.

4. Conclusions The Lewis acid–base adduct $\mathrm{TMAl{:}NH_3}$ formation and the subsequent methane elimination leading to the trimeric amide $[\mathrm{DMAlNH_2}]_3$ is the dominant reaction pathway for Al-containing species at low temperatures and atmospheric pressure. In case of gallium, the breaking of Ga–C bonds and formation of $GaCH_3$ is predominant at the same conditions. Considering the readily condensation of trimeric amide complexes, these findings can explain the depletion of aluminium in the gaseous phase and the deterioration of the Al incorporation into the growing layers. The pressure reduction has the significant influence on the gas-phase reactions at low temperatures due to enhancement of large molecules dissociation.

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