Comparison of trimethylgallium decomposition models for epitaxy growth analysis in MOVPE reactors

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Abstract. Numerical analysis of the trimethylgallium (TMGa) decomposition during epitaxy growth process was analysed. The main aim is to compare previously published trimethylgallium decomposition models. Hence, thermo-fluidic and species transport simulations of the MOVPE (metal-organic vapour phase epitaxy) reactor were performed. Study is focused on a simplified, but most crucial mechanism of epitaxy growth: chemical model of a TMGa decomposition. Analysis of species densities and pyrolysis speed for different approaches were beneficial to understand emerging phenomena during epitaxy growth and to choose most applicable method for future consideration. Analysis have been conducted with the aid of Ansys Fluent software. Numerical simulations depict extreme results, indicating that selecting correct model as a base for the growth process modelling is crucial.

1. Introduction
In order to satisfy a need for more precise and more compact electronic devices based on III-V group compounds[1-5], such as gallium nitride (GaN) and indium gallium nitride (InGaN), consistent and reliable method to create thin, uniform semiconductor layers is needed. One way to fulfil this demand is Metal-Organic Vapour Phase Epitaxy (MOVPE). This epitaxy growth technique is widely used to produce high quality layers and micro- and nano-scale 3D structures in optoelectronics and power electronics [1,3,5]. Although this process is used by a large number of researchers worldwide, its method of operation is highly complex, associated with transport of species, mass and heat, as well as chemical reactions, decomposition and deposition. Such complexity, combined with lack of proper in-situ measurements, leads to various issues during the process [3-8].

MOVPE uses metal-organic precursors, such as trimethylgallium (Ga(CH3)3) or triethylindium (In(C2H5)3), diluted in carrier gases as a source of gallium or indium injected into a reactor chamber. Due to chemical reactions occurring within the chamber between an inlet and a heated substrate, thin solid film deposition is carried out. To ensure, that layers obtained during this process have suitable quality and purity, detailed control of the growth process and accurate equipment are required. Previous studies [6-10] focus on numerical analyses of temperature and velocity as important factors in crystal growth investigations. One of the most crucial steps to achieve uniform and precise results with MOVPE thin film manufacturing is a metal-organic sources decomposition. Aim of the study is to investigate and compare different trimethylgallium models [11-13] and to reveal the most applicable one for epitaxy growth simulations.
2. Epitaxy growth model

Based on [10] suitable MOVPE reactor model has been prepared for further analysis of the epitaxy simulations. To analyse thermo-fluidic phenomena occurring within a reactor chamber, numerical simulations have been performed with the aid of ANSYS - finite volume method based software. Heat and mass transport in the investigated model are described by conservation of mass, momentum and energy equations:

- **Continuity equation:**
  \[
  \frac{\partial \rho}{\partial t} + \nabla \cdot (\rho \mathbf{V}) = 0
  \]

- **Momentum equation:**
  \[
  \rho \frac{D \mathbf{V}}{Dt} = \rho \mathbf{g} - \nabla p + \mu \nabla \mathbf{V} + \frac{1}{3} \mu \nabla (\nabla \cdot \mathbf{V})
  \]

- **Thermal energy equation:**
  \[
  \rho c_p \frac{DT}{Dt} = \nabla (k \nabla T) + \frac{\partial p}{\partial t} + q_v
  \]

where: \(\rho\) – denotes gas density \([\text{kg/m}^3]\), \(t\) – time \([\text{s}]\), \(\mathbf{V}\) – velocity vector \([\text{m/s}]\), \(\mathbf{g}\) – gravity vector \([\text{m/s}^2]\), \(p\) – pressure \([\text{Pa}]\), \(\mu\) – dynamic viscosity \([\text{kg/m/s}]\), \(k\) – thermal conductivity \([\text{W/m/K}]\), \(c_p\) – specific heat \([\text{J/kg·K}]\), \(T\) – temperature \([\text{K}]\), \(q_v\) – volumetric heat sources \([\text{W/m}^3]\).

While the chemical reaction rates are determined by:

- **Arrhenius equation**
  \[
  k = k_0 T^\beta \exp \left( \frac{-E_a}{RT} \right)
  \]

where: \(k_0\) – pre-exponential factor, \(\beta\) – temperature coefficient, \(E_a\) – activation Energy \([\text{kcal/mol}]\), \(R\) – gas constraint \([\text{J/mol·K}]\).

Numerical analysis is based on a 3D CAD representation of the reactor, simplified and conformed to simulations. The outline of the model cross-section is depicted in figure 1. MOVPE reactor construction consists of an inlet, a chamber with a heated susceptor (marked with a continuous red line) and an outlet.

Figure 1. Outline of MOCVD vertical, rotating disc reactor.

The inlet system, situated at the top of the construction, injects carrier gas (H\(_2\)) with diluted metal-organics for GaN growth in form of trimethylgallium (TMGa, Ga Metal-Organic source). Precursors flow within reactor chamber towards the growth zone situated on the heated, rotating susceptor. Unnecessary gases and redundant reaction products are pumped out from the reactor through the outlet.
In the present study, simulations have been conducted for the following assumptions and boundary conditions:

- reference pressure in the reactor equals 0.25 bar;
- relative pressure at the outlet equals 0 bar;
- inlet temperature of the gases equals to 22.5 °C;
- to ensure proper temperature gradient, temperature of reactor walls is 50 °C (water cooled walls) and the heater temperature equals to 1050 °C (uniform temperature condition on the upper susceptor surface);
- rotational speed of the susceptor is set to 150 rpm;

Properties of gas-phase species used in simulations are gathered in Table 1. Data are given for standard conditions (25 °C and 1 bar) [11, 14].

| Molecular Weight [kg/kmol] | Standard State Enthalpy [J/kmol] | Standard State Entropy [J/kmol·K] | L-J Characteristic Length [Å] | L-J Energy Parameter [K] |
|---------------------------|---------------------------------|-----------------------------------|-----------------------------|------------------------|
| Hydrogen (H2)             | 2.02                            | -2.05·10⁴                         | 130502.5                    | 2.83                   | 59.7                   |
| trimethylgallium (TMGa)   | 114.83                          | -4.5·10⁷                         | 354572.1                    | 5.47                   | 378.2                  |
| dimethylgallium (DMGa)    | 99.79                           | 7.8·10⁷                          | 318939.8                    | 4.95                   | 373.9                  |
| monomethylgallium (MMGa)  | 84.76                           | 7.9·10⁷                          | 250917.7                    | 4.29                   | 389.6                  |
| Alkyl (CH₃)               | 15.03                           | 1.46·10⁸                         | 193751.5                    | 3.49                   | 123.3                  |

In order to analyse MOVPE growth process, various models can be used. Previous studies highlighted metal-organics decomposition, adducts creation, volumetric reactions and surface reactions as most important steps in the epitaxial growth. Various studies [6-13] present attempts to recreate the phenomena using different approaches and simplifications. Most of them covers both the upper route (adduct formation) and the lower route (metal-organic precursor decomposition), while some of them focuses on one route only.

Investigated and presented in the paper reaction model is based on the decomposition of the trimethylgallium (TMGa) into dimethylgallium (DMGa) and in the next step into monomethylgallium (MMGa) and alkyls (CH₃). In order to focus on metal-organic reactions and analyse it thoroughly, other chemistry paths are omitted. To compare various available models of the TMGa decomposition, reduced model of this phenomenon is used. It is based on two major reactions:

\[ \text{G1: } \text{Ga}(\text{CH}_3)_3 \rightarrow \text{Ga}(\text{CH}_3)_2 + \text{CH}_3 \]  \hspace{1cm} (5)
\[ \text{G2: } \text{Ga}(\text{CH}_3)_2 \rightarrow \text{Ga}(\text{CH}_3) + \text{CH}_3 \]  \hspace{1cm} (6)

G1 and G2 equations create a simplified trimethylgallium decomposition model, where TMGa is decomposed into DMGa and MMGa with CH₃ as a by-product. To integrate chemistry calculation to the analysis, reaction rate parameters are needed. By using Arrhenius equation (4), one can calculate
reaction speed and plot it as function of temperature. Such graph is presented in figure 2. Analysis containing chemical Model 1 [11], Model 2 [12] and Model 3 [13] was conducted to compare mass flow within the chamber and species distribution from the inlet to the susceptor. Reaction rate parameters of the models are shown in Table 2.

### Table 2. Calculated reaction rate parameters [11-13].

| Model | G1         | Activation Energy [kcal/mol] | Temperature coefficient [β] |
|-------|------------|-----------------------------|-----------------------------|
| Model 1 | 3.5·10^{15} | 2.49·10^{19} | 0 |
|       | 8.7·10^{7} | 1.48·10^{5} | 0 |
| Model 2 | 1.0·10^{47} | 3.22·10^{5} | -9.18 |
|       | 7.67·10^{43} | 1.42·10^{5} | -9.8 |
| Model 3 | 1.6·10^{17} | 2.5·10^{5} | 0 |
|       | 2.5·10^{15} | 1.49·10^{5} | 0 |

**Figure 2.** Reaction rate in correlation with temperature for models 1-3.

### 3. Results and discussion

To compare trimethylgallium decomposition models, primary numerical simulations of the reactor are needed. To obtain temperature and velocity distribution required as a base for chemical analysis, basic thermo-kinetic analysis has been conducted. Figure 3 presents exemplary results of temperature gradient within reactor chamber collected for inlet gases composition of 0.00091% for trimethylgallium, 0.21% for ammonia and 0.78909% for hydrogen and reference pressure of 0.25 bar. Presented gradient is suitable for MOVPE growth, providing proper temperature profile within the reactor chamber for chemical reactions to occur. Thermal conditions between inlet and substrate surface assure proper TMGa decomposition.
With complete thermo-kinetic analysis, chemical model containing reactions described by Eq. (5) and Eq. (6) are introduced. Figure 4 shows mass fracture gradient of the trimethylgallium within reactor chamber for Model 2. Significant decrease of this species can be noticed in close proximity to the susceptor surface. This phenomenon is associated with the first reaction (see Eq. (5)), where trimethylgallium is decomposed into dimethylgallium and CH$_3$. Significant amount of trimethylgallium is pumped out from the reaction, what can be seen while analysing the outlet area. High loss of TMGa that runs towards the outlet causes lower amount of reagents in Eq. (5), which have a significant impact on further chemical reactions.

To examine TMGa mass fraction within the reactor chamber more thoroughly, mass fraction along an inlet-substrate line (see figure 4) was plotted in figure 5. Quantity of the reagents is similar for models
1 and 2, where half of the initial fraction is still not discomposed and reaches the substrate. This trend will be problematic in further growth analysis, where ideally, all of the TMGa should decompose into DMGa or MMGa, similarly to model 2. This phenomenon may be an indication, that reaction rates for models 1 and 2 are too low and trimethylgallium is not decomposed fast enough before reaching the surface.

**Figure 5.** Trimethylgallium mass fraction distribution along the inlet-substrate line.

Comparison of dimethylgallium mass fraction distribution along the inlet-substrate line presented in figure 6 shows significant amount of DMGa created in the middle of the chamber in model 2, where for models 1 and 3, mass fraction is less than $10^{-3}$. The difference is caused by higher reaction rate for model 2. As in the case of trimethylgallium mass fraction depicted in figure 3, similarities between models 1 and 3 can be seen.

**Figure 6.** Dimethylgallium mass fraction distribution along the inlet-substrate line.
Analysis of monomethylgallium, as a final product of the model and a source of Ga atoms deposited during GaN film growth, is the most important for further chemistry process. Distribution of MMGa along the inlet-substrate line illustrated in figure 7 shows high value of mass fraction reaching $1.6 \cdot 10^{-2}$ obtained for model 2 and much lower values for model 1 and 3. By analysing exclusively MMGa amount as a source of Ga for epitaxy growth on substrate, chemical reactions are much faster in model 2 and they generate much more products in comparison to models 1 and 3.

![Figure 7](image_url)  
**Figure 7.** Monomethylgallium mass fraction distribution along the inlet-substrate line.

To analyse amount of monomethylgallium reaching the substrate surface, its mass fraction is plotted along substrate diameter in figure 8. Acceptable uniformity of the mass fraction can be seen for all models in the centre area of the substrate. Decrease on the edges is caused mostly by additional, increased flow near the outlet. This phenomenon is problematic and will lead to lowered uniformity at the edges of the sample.

![Figure 8](image_url)  
**Figure 8.** Monomethylgallium mass fraction distribution along substrate diameter.
4. Conclusion
The paper presents comparison of three different numerical models of volumetric chemical reactions successfully used in several studies [3,6,11-13] covering analysis of GaN growth in MOCVD reactors. We have focused on metal-organic decomposition (lower route) only, as being claimed [11] as the main path for Ga atoms for thin film deposition. In all the cases, the same thermo-kinetic model [10] is used as a basis for the chemical simulations. With detailed information on TMGa and its product distributions, GaN epitaxy growth model can be improved.

The conducted investigation shows that chemical path and species quantity within reactor chamber were comparable for models 1 and 3 due to similarities in reaction rate parameters. It is worth to pay attention that the use of model 1 results in higher amount of TMGa and MMGa in the close proximity of the growth area, while more DMGa instead of MMGa is obtained for model 3. Model 2 presents elevated reaction speeds in comparison to other considered models, what corresponds to lack of TMGa in the growth area and higher amount of DMGa and MMGa. To confirm superiority of any of the studied approaches for accurate epitaxy growth predictions, further experimental research is required. With appropriate numerical analysis verification, one can deduce proper TMGa decomposition model, suitable for a chosen application.

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