

# A kinetic Study of the MOCVD of GaN

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## ABSTRACT

Quantum chemistry investigations have been performed to study the gas phase chemistry active during the MOVPE of GaN when  $\text{Ga}(\text{CH}_3)_3$  and  $\text{NH}_3$ , diluted in a  $\text{H}_2$  carrier gas, are used as precursors. Optimized molecular geometries, energies, and transition state structures of gas phase species have been determined with density functional theory at the B3LYP/6-311+G(d,p) level. We found that the GaN gas phase chemistry is dominated by a radical chain mechanism, started by the  $\text{CH}_3\cdot$  groups originated by the gas phase and surface decomposition of  $\text{Ga}(\text{CH}_3)_3$ , and resulting in the fast formation of linear covalently bonded  $\text{R}(\text{GaN})_x$  adducts. These molecules can give fast cyclization reactions that lead to the formation of six membered cyclic species, which, similarly to benzene for combustion can be considered as the first GaN nuclei. The determined mechanism was then reduced through sensitivity analysis to a set of 15 reactions involving 15 species, which can be easily introduced in a suitable reactor model to simulate the global growth process. As a results of these simulations we found that the presence of  $\text{H}_2$  as a carrier gas can greatly enhance the rate of formation of gas phase particles as it is a major source of atomic hydrogen, promoter of gas phase reactivity.

**Keywords:** MOCVD, GaN, Semiconductor, Quantum Chemistry, Kinetic.

## 1 INTRODUCTION

The GaN electronic and optoelectronic industry has developed greatly in the last years and is still going through a fast expansion. Among the problems to overcome in order to produce GaN devices with improved properties two stand out: The low cost production of GaN substrates to replace sapphire, and the control of the formation of powders in the gas phase [1-3]. Development of a gas phase kinetic mechanism that might explain the mechanism of formation of GaN powders, determination of the main precursors to the deposition of GaN, and systematically investigation of the growth of GaN in a commercial reactor are the aims of this investigation. The mechanism here proposed differs from others previously used to describe the GaN gas phase chemistry, which are based on neutral-neutral reactions proceeding through methane elimination [4], in that the adduct formation is driven by a fast radical chain mechanism.

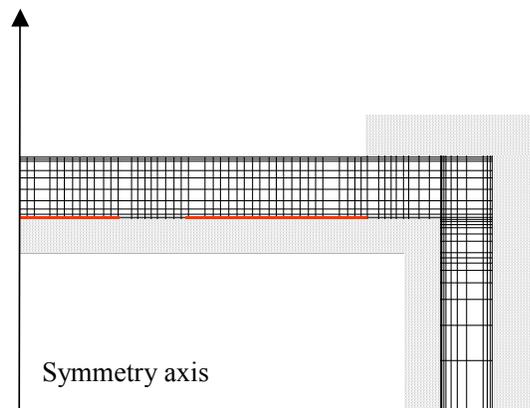
## 2 METHODS

The quantum chemistry method adopted to investigate GaN gas phase chemistry was density functional theory (DFT), which combines a good accuracy with a limited computational demand. The Becke 3 parameters and Lee Yang Parr functionals were adopted to evaluate the exchange and correlation energy [5]. The computational approach we adopted is the same described in our previous publications [6,7]. All calculations were performed with the Gaussian 98 suite of programs [8].

Among the different basis sets considered the best agreement between calculated and experimental bond energies was obtained with the all electron 6-311 basis set with added polarization functions (6-311G(d,p)). However similar results were produced with a much smaller basis set adopting the Dunning/Huzinaga valence double zeta basis set on the first row atoms and the Stuttgart/Dresden or Hay and Wadt effective core potential basis set on the others (briefly, SDD and LANL2DZ, respectively). Therefore the following strategy was adopted in the calculations: first structures and energies were determined adopting the SDD or LANL2DZ basis set, then the geometries so optimized were adopted as input for the calculations with the larger basis set. The geometry of each molecular structure was considered stable only after calculating vibrational frequencies and force constants and if no imaginary vibrational frequency were found. Transition state structures were located adopting the synchronous transit-guided quasi Newton method and were characterized by a single imaginary vibrational frequency.

Quantum chemistry has already been used by used by several groups to investigate the complicated GaN gas phase chemistry, and it has been shown that it can give rise to very unusual and complicated structures [9]. To determine the extent to which the gas phase chemistry is active in a commercial MOCVD reactor, as well as to test weather the kinetic mechanism we are proposing proceeds at a significant rate, deposition on heated substrates was simulated solving the associated 2D computational fluid dynamic problem. The gas phase species concentrations and the temperature profiles were determined through the solution of the mass, momentum and energy balance equations for an axial symmetric geometry and a diluted gas mixture. The geometry of the reactor used for the simulations is that of a commercial reactor and it is sketched, together with the FEM mesh, in Fig. 1a; while

operative conditions adopted in the simulations are standard operating parameters for a GaN deposition reactor and reported in Fig. 1b.



(a)  
**Operating Conditions**

Pressure	50 torr
T Susceptor	1000 °C
T Inlet	298 °C
NH <sub>3</sub> /H <sub>2</sub> ratio	0.5
Ga(CH <sub>3</sub> ) <sub>3</sub>	220 μmol/min
Total Inlet Flow	24 slm
Chamber Height	1.6 cm

(b)

### 3 RESULTS AND DISCUSSION

The gas phase kinetic scheme proposed here is the extension of an idea that we developed to describe the MOCVD of ZnSe to the GaN gas phase chemistry (6,7,10). Our hypothesis is that the driving force for the whole gas phase reactivity during the GaN MOCVD is given by CH<sub>3</sub> radicals that are desorbed from the surface as a result of the growth process or that are originated by the gas phase decomposition of Ga(CH<sub>3</sub>)<sub>3</sub>. These radicals can start a series of very fast reactions that give rise to a very rich gas phase chemistry. It is our opinion that this reaction pathway is active in many MOCVD systems, since the formation of hydrocarbon radicals in many cases follows the adsorption of the metal organic precursors on the growth surface.

The kinetic mechanism consists of elementary reactions which kinetics constants were either experimentally or theoretically determined. An extensive literature survey has been done and experimentally determined kinetic constants were adopted when data existed, which was the case for the decomposition of Ga(CH<sub>3</sub>)<sub>3</sub>. Kinetic constants of unknown reaction were determined using first principles calculations and transitions state theory. Since many kinetic parameters are not known, in particular for what concerns reactions between Ga species and NH<sub>x</sub> molecules, we investigated a

large number of reactions in order to identify the main kinetic pathway responsible for the formation of GaN adducts in the gas phase. For the sake of brevity we have named GaN cyclic adducts comprising x Ga atoms, y N atoms, and the H or CH<sub>3</sub> groups necessary to saturate all the dangling bonds, as Ga<sub>x</sub>N<sub>y</sub>.

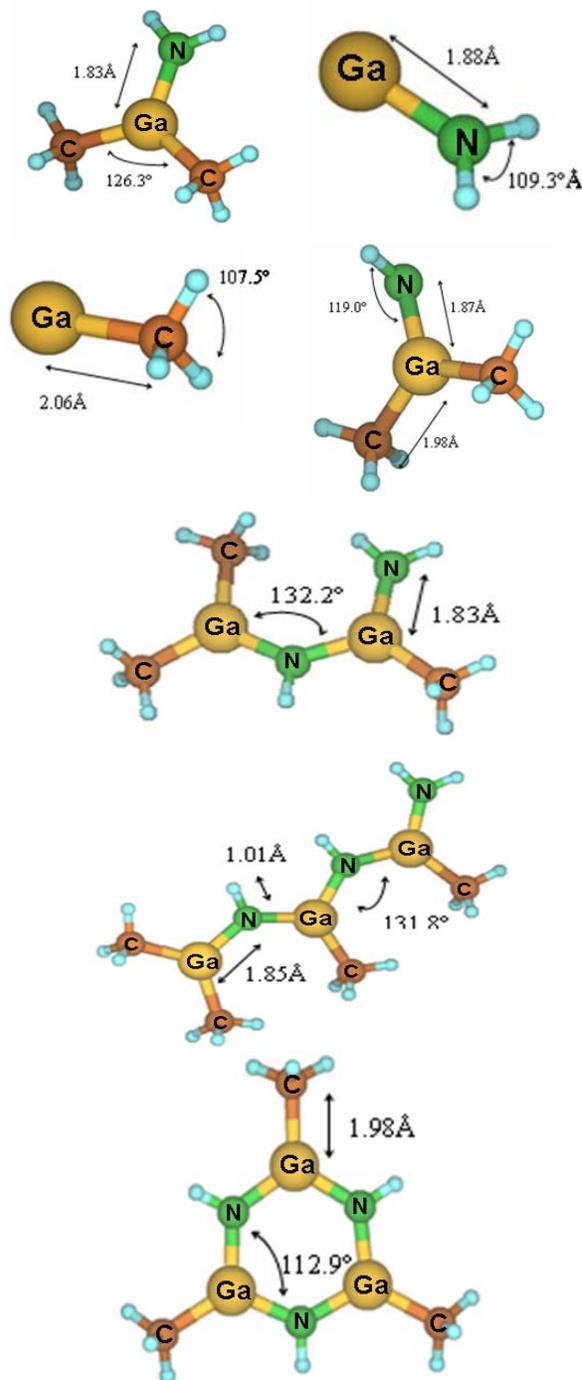


Fig. 2 Molecular structure of some GaN gas phase species: a) Ga(CH<sub>3</sub>)<sub>2</sub>NH<sub>2</sub>, b) GaNH<sub>2</sub>, c) GaCH<sub>3</sub>, d) (CH<sub>3</sub>)<sub>2</sub>GaNH, e) Ga<sub>2</sub>N<sub>2</sub>, f) Ga<sub>2</sub>N, g) cGa<sub>3</sub>N<sub>3</sub>.

Our calculations show that methyl radicals generated through surface reactions diffuse in the gas phase and react both with the carrier gas and NH<sub>3</sub> to give reactive H and NH<sub>2</sub> radical species. Reactions of NH<sub>2</sub>, H and CH<sub>3</sub> with Ga(CH<sub>3</sub>)<sub>3</sub> and GaCH<sub>3</sub> are barrierless and thus proceed very fast resulting in the formation of Ga(CH<sub>3</sub>)<sub>2</sub>NH<sub>2</sub>, GaNH<sub>2</sub> and a GaNH reactive radical. These species can start a radical chain mechanism that proceeds through the abstraction of H atoms from R-NH<sub>2</sub> groups to generate new radical R-NH· species. Through fast barrierless reactions, R-NH· species react with neutral GaN gas phase compounds producing larger GaN gas phase adducts and methyl radicals that close the radical chain (examples of some of these species are

reported in Fig.2). Kinetic constants for the radical chain mechanism so determined are reported in Table I.

The surface kinetic mechanism has been kept as simple as possible, being the main aim of this work to investigate the gas phase chemistry. Thus it was assumed that the growth was determined by the irreversible adsorption of the principle gas phase species on the surface. In particular we introduced in the kinetic mechanism the surface reactions reported in Table II.

Table I. Gas phase kinetic mechanism. In reactions 11 and 14, n is either 0 or 1 depending on the overall stoichiometry. Kinetic constants expressed as  $k = A \cdot \exp(-Ea/RT)$  and reported in units consistent with kcal, mol, cm, s.

	Reaction	logA	$\alpha$	$E_a$
1	$\text{CH}_3 + \text{CH}_3 \rightarrow \text{C}_2\text{H}_6$	13.54	0.0	0.0
2	$\text{CH}_3 + \text{NH}_3 \leftrightarrow \text{NH}_2 + \text{CH}_4$	3.40	2.86	14.6
3	$\text{Ga}(\text{CH}_3)_3 \rightarrow \text{GaCH}_3 + 2\text{CH}_3$	15.54	0.0	59.5
4	$\text{GaCH}_3 + \text{NH}_3 \rightarrow \text{GaNh}_2 + \text{CH}_4$	9.33	1.0	18.5
5	$\text{GaCH}_3 + \text{NH}_2 \rightarrow \text{GaNh}_2 + \text{CH}_3$	11.59	0.5	0
6	$\text{Ga}(\text{CH}_3)_3 + \text{NH}_2 \rightarrow \text{Ga}(\text{CH}_3)_2\text{NH}_2 + \text{CH}_3$	12.28	0.5	0
7	$\text{Ga}(\text{CH}_3)_2\text{NH}_2 \rightarrow \text{GaNh}_2 + 2\text{CH}_3$	15.54	0.0	59.5
8	$\text{Ga}(\text{CH}_3)_2\text{NH}_2 + \text{NH}_2 \rightarrow \text{CH}_3\text{Ga}(\text{NH}_2)_2 + \text{CH}_3$	12.29	0.5	0
9	$\text{CH}_3\text{Ga}(\text{NH}_2)_2 + \text{CH}_3 \rightarrow \text{CH}_3\text{GaNh}_2\text{NH} + \text{CH}_4$	11.59	1.0	9.0
10	$\text{CH}_3\text{Ga}(\text{NH}_2)_2 + \text{NH}_2 \rightarrow \text{CH}_3\text{GaNh}_2\text{NH} + \text{NH}_3$	10.34	1.0	4.3
11	$\text{CH}_3\text{GaNh}_2\text{NH} + \text{GaNh}_2 / \text{Ga}(\text{CH}_3)_2\text{NH}_2 / \text{CH}_3\text{Ga}(\text{NH}_2)_2 \rightarrow \text{Ga}_2\text{N}_2 + n\text{CH}_3$	12.23	0.5	0
12	$\text{Ga}_2\text{N}_2 + \text{CH}_3 \rightarrow \text{Ga}_2\text{N}_2\cdot + \text{CH}_4$	11.59	1.0	9.0
13	$\text{Ga}_2\text{N}_2 + \text{NH}_2 \rightarrow \text{Ga}_2\text{N}_2\cdot + \text{NH}_3$	10.34	1.0	4.3
14	$\text{Ga}_2\text{N}_2\cdot + \text{GaNh}_2 / \text{Ga}(\text{CH}_3)_2\text{NH}_2 / \text{CH}_3\text{Ga}(\text{NH}_2)_2 \rightarrow \text{Ga}_3\text{N}_3 + n\text{CH}_3$	12.44	0.5	0
15	$\text{Ga}_3\text{N}_3 \rightarrow c\text{Ga}_3\text{N}_3 + \text{CH}_3$	9.16	1.0	20.0

Table II. Surface mechanism. For adsorption reaction is reported the sticking coefficient.

Reaction	logA	$\alpha$	$E_a$
$\text{Ga}(\text{CH}_3)_3 + \$ \rightarrow \text{GaCH}_3^* + 2\text{CH}_3$	1.00	0.0	0.0
$\text{GaCH}_3 + \$ \rightarrow \text{GaCH}_3^*$	1.00	0.0	0.0
$\text{GaNh}_2 + \$ \rightarrow \text{GaNh}_2^*$	1.00	0.0	0.0
$\text{GaNh} + \$ \rightarrow \text{GaNh}^*$	1.00	0.0	0.0
$\text{GaCH}_3^* \rightarrow \text{GaCH}_3 + \$$	14.00	0.0	55000.0
$\text{GaNh}_2^* \rightarrow \text{GaN} + \$ + \text{H}_2$	14.00	0.0	44000.0
$\text{GaNh}^* \rightarrow \text{GaN} + \$ + \frac{1}{2}\text{H}_2$	14.00	0.0	44000.0

This mechanism can be easily inserted in a CVD fluid dynamic model to solve the equations of conservation of mass, energy, and momentum. For this purpose we used a two-dimensional CFD FEM model to investigate the formation of nuclei in a typical MOCVD reactor used to grow GaN. We assumed that the gas phase is composed mainly of  $\text{NH}_3$  and  $\text{H}_2$ , with a mole fraction of  $\text{Ga}(\text{CH}_3)_3$  of about  $10^{-3}$ , and that the deposition takes place on two 2" substrates, one positioned at the center of the susceptor and the other on the side. It was assumed that the growth is determined by the irreversible adsorption of the most abundant GaN gas phase species ( $\text{Ga}(\text{CH}_3)_{3-x}(\text{NH}_2)_x$ ,  $\text{GaNH}_2$ ), using a collisional rate with a unary sticking coefficient. We found that  $\text{GaNH}_2$  contributes more than 50% to the overall film growth rate. The computed temperature, flow fields,  $\text{Ga}(\text{CH}_3)_3$ ,  $\text{GaNH}_2$ , and nuclei concentrations for a typical deposition temperature of 1273 K (1000°C) are reported in Fig. 5. As can be observed,  $\text{GaNH}_2$  is rapidly produced upon the entrance in the reactor, as soon as the temperatures rises above 700 K, which corresponds to the decomposition of  $\text{Ga}(\text{CH}_3)_3$ , then it is rapidly consumed when it approaches the surface. The formation of gas phase nuclei begins in the thin layer where the concentration of  $\text{Ga}(\text{CH}_3)_{3-x}(\text{NH}_2)_x$  and  $\text{NH}_2$  radicals is particularly high, and increases in the part of the reactor where a small recirculation is present. This is due to two effects: the larger residence time of gases in reactors "dead" zones and the fact that we did not include surface reactions on the reactor walls, while it is likely that GaN can be deposited there at significant rate during the growth process. The oscillation of the  $\text{GaNH}_2$  gas phase concentration is due to the fact that, as mentioned, the deposition takes place on 2 different substrates and no deposition is allowed to occur on the susceptor.

As a final remark, it is interesting to observe that our model provides a simple mechanistic explanation of the reason why powders are usually observed in a region that is 6-8 mm distant from the deposition surface (1). This is in fact the part of the reactor where radicals, produced by surface reactions and by the decomposition of the  $\text{Ga}(\text{CH}_3)_3$ , meet the  $\text{Ga}(\text{CH}_3)_{3-x}(\text{NH}_2)_x$  species produced in the upper part of the reactor. This boosts the radical chain mechanism and determines the fast formation of GaN nuclei, and thus of powders. In regions closer to or farther from the substrate, the concentration of  $\text{Ga}(\text{CH}_3)_{3-x}(\text{NH}_2)_x$  and of radicals, respectively, is smaller and thus the formation of powders proceeds more slowly.

#### 4 CONCLUSION

In summary, we have presented a computational investigation of the gas phase chemistry active during the MOCVD of GaN. Our calculations suggest that the process is dominated by a radical chain mechanism, which we condensed in a simple set of reactions that can be inserted in a CFD model and used to predict the rate of

formation of gas phase nuclei as a function of the reactor operating conditions.

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