# Deviation from thermodynamic equilibrium at the initial stage of the GaN growth by metalorganic chemical vapor deposition (MOCVD)

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LT-MOCVD growth runs of GaN are conventionally used for the formation of the nucleation layers prior to epitaxial growth of GaN is substantially determined by the low temperature (LT) grown layers. Therefore, study of the LT runs is very important. One of the main concerns of the crystal growth is its “driving force” that is the affinity of the heterogeneous formation reaction of the GaN. The ratio between the affinity of the reaction and temperature in the energy units is the quantitative criterion of deviation from thermodynamic equilibrium whereby the ratio between the rates of the right and the back reactions can be estimated. LT-MOCVD of the GaN epilayers on both basal planes is presented. One and two variants of the GaN formation reactions on (0001) A and (0001) B planes, respectively, are described. Trimethylgallium and ammonia are considered as the precursors of the gallium and nitrogen, respectively. Decomposition of ammonia is presented as the catalitic reaction on the surface of the growing layer. The ratios between the affinity and temperature in the energy units are substantially larger than unity for crystallization processes on both planes. Thus, the considered formation reactions are far from thermodynamic equilibrium and, respectively, the rates of the back reactions are negligible small with comparison to the rates of the right reactions. Far from thermodynamic equilibrium growth conditions lead to formation of thermodynamically stable hexagonal and thermodynamically metastable cubic crystal modifications of GaN in the same growth process.

*Keywords*: MOCVD; Epitaxy; GaN; Adsorption process

## 1. Introduction

The GaN is a direct wide band gap semiconductor, making it attractive for blue light-emitting diodes and lasers, as well as for high temperature power devices. In the last years a great effort has been made on the semiconductor technology to produce high quality material using a variety of growth methods[1].

However there even exist multiple challenges in growing high quality material due to the existence of non well known phenomena involved in the control of the growth process[2]. GaN films are currently grown on sapphire (0001) substrates by a two-stage MOCVD process, wherein growth of GaN nucleation layers at a low temperature (400-600°C) is followed by growth of epitaxial GaN films at a high temperature (1000-1200°C) [3,4,5]. It has been demonstrated that the cubic GaN (c-GaN) and the hexagonal GaN (h-GaN) coexist in the nucleation layers. Upon annealing to a high temperatures prior to the second stage growth, GaN nucleation layer mostly transform into the h-GaN [5,6]. The resulting electrical, optical, and structural properties depend sensitively on the growth conditions under which the nucleation layer is processed [3].

For explaining those phenomena several thermodynamic and kinetic models have been proposed [7,8]. The models have not considered the peculiarities occurring on the surface, such as the adsorption of the different species involved in the epilayer GaN growth. In recent studies the surface adsorption phenomena taking place in the GaN(0001)A and GaN(0001)B substrate surfaces have been analyzed, revealing the importance of the physisorption and chemisorption processes [9,10]. On the GaN(0001)B two surface termination are observed, a gallided one and a nitrided surface; and for the GaN(0001)A surface only a gallided termination was detected [1]. The two crystal faces have different structure, composition and chemical behavior, these peculiarities impact directly on the GaN growth kinetics.

In this work we propose a model for describing the growth of GaN on GaN(0001)A and GaN(0001)B surfaces by low temperature MOCVD when ammonia and trimethylgallium are used like precursors. The approach recognizes the fact that the growth processes proceeds under non-equilibrium conditions. The growth process is described through a consistent set of chemical reactions. Such specific chemical reactions were identified from related studies involving conditions similar to those used for the growth of GaN by MOCVD.

The quantitative description is based on the analysis of the reaction affinities for the set of chemical reactions including the surface processes. The analysis considers the existence of chemical species identified in the adsorbed layer which limit the growth process. The ratio between the affinity of the reaction and temperature in the energy units is used as the quantitative criterion of deviation from thermodynamic equilibrium whereby the ratio between the rates of the right and back reactions can be estimated. The calculation of the affinities of the reactions was made using the thermodynamic data in the literature[11].

## 2. The model

Several studies have shown the differences between the adsorption processes when growing GaN epilayers on GaN(0001)A and GaN(0001)B substrates [1,9,10]. The termination bonds on both surfaces are different (figs. 1a y 1b) and can be distinguished by their behavior as physisorption or chemisorption states.

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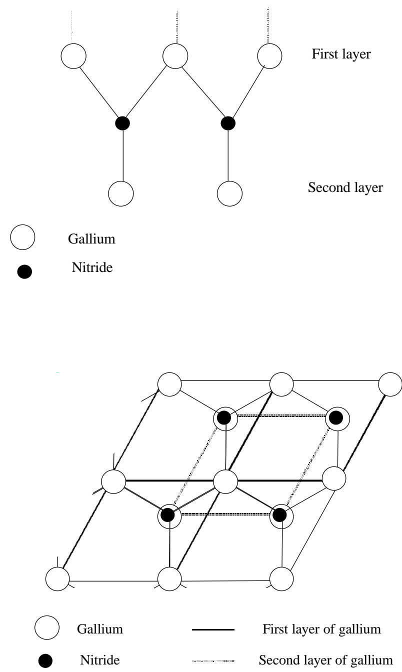



**Figure 1a.** Atomic structure (top and side view) for the (0001)A Ga-terminated surface.

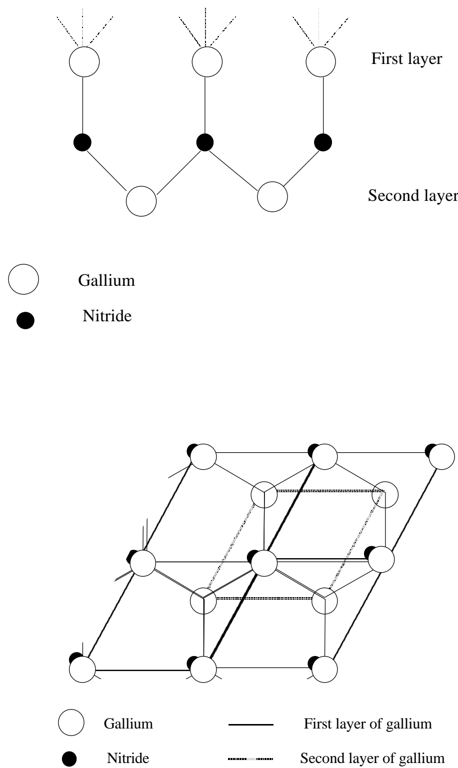



**Figure 1b.** Atomic structure (top and side view) for the (0001)B Ga-terminated surface.

Reflection High Energy Electron Difraction (RHEED) measurements of GaN surfaces exposed to Ga and $NH_3$ fluxes shown that two different surface terminations could be maintained on the GaN(0001)B surface, one of which is a stable gallided surface, while the other is a nitrided one. If the nitrided GaN(0001)B surface is heated in vacuum it returns to the gallided surface[1].

Otherwise for the GaN(0001)A only a gallided state was identified regardless of the sample history[10], that is the Ga atoms adsorb weakly after exposure to Ga or NH3 only (fig 2), and after a vacuum annealing. For both orientations the Ga adatoms have a significantly lower diffusion barrier that N adatoms; therefore the Ga adatoms were more mobile that N adatoms at typical growth temperatures. Considering the Ga bulk melts already slightly above room temperature, the Ga-Ga bonds are weakly and the Ga adatoms behave almost like liquid film on the surface[9].

The Ga adsorption on the nitrided GaN(0001)B surfaces presents some differences in comparison with gallided one. On the nitrided surface the Ga atoms adsorbs strongly, whereas on the gallided one the Ga adsorbs weakly. The last condition can be reproduced if the nitrided surface is annealed in vacuum, this says that the nature of the adsorption sites on GaN(0001)B depends on how the surface was prepared.

Desorption Mass Spectroscopy (DMS) studies of GaN(0001)B with synchronized pulses of Ga and ammonia shown important results. There were detected three adsorption states on the surface, one chemisorbed and two physisorbed states[1]. When the surface is exposed to a Ga flux, appear the Ga on Ga physisorbed state. If the surface is initially nitrided and subsequently exposed to a gallium flux, the desorption spectra shown in the first seconds a knee of adsorption, afterwards the adsorption decrease, and finally a stable state of Ga desorption rate is reached. Furthermore while the knee prevails, during the first seconds a desorption flux of H2 is observed. The knee is associated with Ga adsorption onto a hydrogen passivated nitrided surface[12].

When both the Ga and $NH_3$ fluxes arrives at the surface, growth occur, depending on the $NH_3$/Ga flux ratio. For a fixed Ga flux, as the flux of ammonia is increased the steady state for the gallium desorption level decreases, this mean that the Ga adsorbed increases for larger fluxes of ammonia, increasing the growth rate. For a specific value of the $NH_3$ flux the knee disappears, in this case the absence of the knee in Ga adsorption coincides with the increase in growth rate, suggesting the surface is being continuously nitrided. In this condition the stable gallided state is not reached.

During the GaN growth it is assumed that on the nitrided surface portions, Ga first adsorbs into a physisorbed precursor state. Part of this physisorbed Ga quickly desorbs and part becomes chemisorbed, for the chemisorption process to occur, the adsorbed hydrogen must be released (fig. 3). Then we can identify on the gallided portions of the surface only weak Ga adsorption. These gallium species can either desorb or diffuse to chemisorption sites on the nitrided parts on the surface.

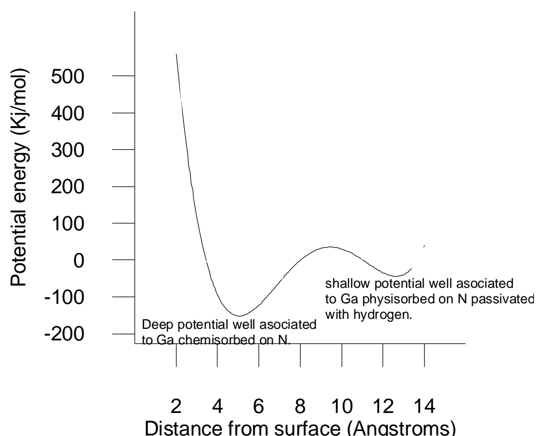



**Figure 3.** Sketch of the potential wells for the physisorbed and chemisorbed states of Ga incident on a nitrided surface, and the behavior of the gallium atoms on this surface.

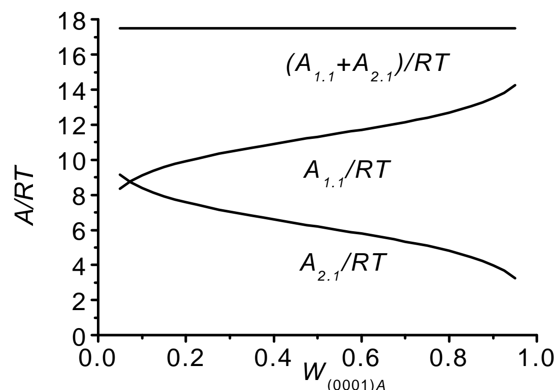



**Figure 4.** Ratios between the thermodynamic affinities of the heterogeneous reactions on the (0001)A plane and temperature in the energy units

The nitrided regions have an hydrogen coverage passivating the nitrided surface, the Ga first is physisorbed on the NH radicals and the chemisorption process occur when the hydrogen is released.

## 3.-Proposal

Based on the previous discussed results we can identify two paths for the intermediate reactions for the growth of GaN on GaN(0001)B substrates. One of them is produced on the gallided surface; on this surface occurs the chemisorption of the radical NH. The second path occurs on the nitrided surface passivated with hydrogen, where the gallium reacts in one physisorbed with another chemisorbed state.

Only one path occurs on the GaN(0001)A gallided surface, on this face the ammonia gas is physisorbed on Ga [$NH_3$(ph. on Ga)], physisorbed Ga catalyzes the $NH_3$ cracking process producing solid GaN. The last process completes the cycle of gallided GaN(0001)A surface. The described process guarantees the gallided state of this face.

Therefore we have for both cases the next elements, resulting from the above discussion.

i).- There exist an adsorcion layer where the distinct chemical species interact with each other and with the GaN surface.

ii).- The GaN(0001) surfaces are clearly distinguished by their different chemical behavior in GaN(0001)A and GaN(0001)B.

iii).- The surface of GaN(0001)A always kept the gallided state, regardless of sample history.

iv).- The surface of GaN(0001)B show the gallided and nitrided states. The nitrided state disappear when the sample is heated in vacuum.

v).- On the gallided surface exist a physisorbed state of Ga on Ga, this physisorbed atoms behave almost like a liquid film on the surface.

vi).- The ammonia decomposition is a catalytic surface activated process. Two species can be distinguished $NH_3$(ph) and NH(ch)

vii).-The nitrided surface is hydrogen passivated with . The N-H bonds are in a chemisorbed state produced by the decomposition of the ammonia physisorbed on the gallided surface. When the sample is heated the radicals are desorbed and the surface will be in a gallided state again.

viii).- The physisorbed gallium atoms arriving to the nitrided surface are quickly desorbed or chemisorbed, in the last case release a hydrogen atom is observed.

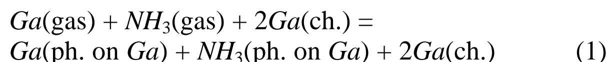
In our model the growth runs are considered as the stationary processes in which the gallided and nitrided surface sites become the same sites after the growth cycle. The reaction path in the LT-MOCVD growth process of *GaN* on the (0001) A plane can be written as having two stages by:

$$Ga(\text{gas}) + NH_3(\text{gas}) + 2Ga(\text{ch.}) = Ga(\text{ph. on } Ga) + NH_3(\text{ph. on } Ga) + 2Ga(\text{ch.}) \quad (1)$$

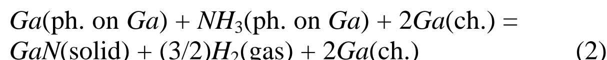
$$Ga(\text{ph. on } Ga) + NH_3(\text{ph. on } Ga) + 2Ga(\text{ch.}) = GaN(\text{solid}) + (3/2)H_2(\text{gas}) + 2Ga(\text{ch.}) \quad (2)$$

where *Ga* (gas), $NH_3$ (gas) and $H_2$ (gas) are the *Ga* atoms, $NH_3$ and $H_2$ molecules in the gaseous phase, respectively, *Ga* (ph. on *Ga*) and $NH_3$ (ph. on *Ga*) are the physisorbed *Ga* atoms and $NH_3$ molecules on the gallided surface sites, respectively, *GaN* (solid) is the molecule *GaN* in the solid phase. Thus, formation of *GaN* molecule is considered as the result of the reaction between the physisorbed *Ga* atom and $NH_3$ molecule.

The affinities of reactions (1) and (2) are written as:



$$A_{1.1} = \mu_{Ga}^{g} + \mu_{NH_3}^{g} - \mu_{Ga}^{ph} - \mu_{NH_3}^{ph} \quad (3)$$



$$A_{2.1} = \mu_{Ga}^{ph} + \mu_{NH_3}^{ph} - \mu_{GaN}^{s} - \frac{3}{2}\mu_{H_2}^{g} \quad (4)$$

In line with above mentioned, the physisorbed *Ga* atoms are considered as the liquid state atoms disposed on the uncharged part of the surface sites during the growth process. The chemical potentials of the ammonia molecules

in the gaseous and physisorbed states should be very close one another since the *V/III* ratio at LT-MOCVD of *GaN* is substantially larger than unity. Therefore, almost all physisorbed ammonia molecules should return in the gaseous phase. Thus, the affinity of reaction (1) in the developed model can be rewritten as:

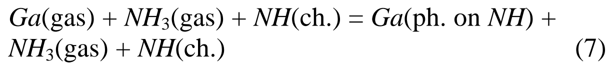
$$A_{1.1} = \mu_{Ga}^{g} - \mu_{Ga}^{ph}$$
$$= \mu_{Ga}^{0g} - \mu_{Ga}^{0l} - RT \ln\left(\frac{\Theta_{(0001)A}}{(1-\Theta_{(0001)A})\, p_{Ga}}\right) \qquad (5)$$

where $\mu_{Ga}^{0g}$ and $\mu_{Ga}^{0l}$ are the chemical potentials of the gaseous and liquid *Ga* in the standard state, $\Theta_{(0001)A}$ is the coverage of the physisorbed *Ga* atoms, $p_{Ga}$ is the pressure of the *Ga* atoms.

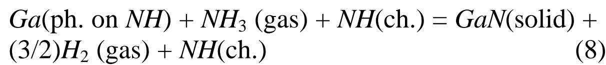
The affinity of reaction (2) is given as:

$$A_{2.1} = \mu_{Ga}^{0l} + \mu_{NH_3}^{0g} - \mu_{GaN}^{0s} - \frac{3}{2}\mu_{H_2}^{0g} + RT \ln\left(\frac{\Theta_{(0001)A}\, P_{NH_3}}{(1-\Theta_{(0001)A})\, P_{H_2}^{\frac{3}{2}}}\right) \qquad (6)$$

The reaction paths on the (0001) B plane are considered taking into account the nitrided and gallided surface sites. The reaction path on (0001) B nitrided surface is given in two stages as:

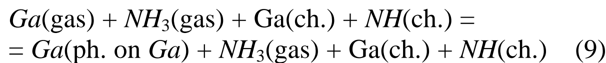


*Ga*(gas) + $NH_3$(gas) + *NH*(ch.) = *Ga*(ph. on *NH*) + $NH_3$(gas) + *NH*(ch.) (7)

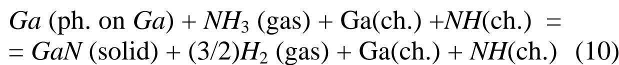


*Ga*(ph. on *NH*) + $NH_3$ (gas) + *NH*(ch.) = *GaN*(solid) + (3/2)$H_2$ (gas) + *NH*(ch.) (8)

The reaction path on (0001) B gallided surface is too given in two reactions:



*Ga*(gas) + $NH_3$(gas) + Ga(ch.) + *NH*(ch.) = = *Ga*(ph. on *Ga*) + $NH_3$(gas) + Ga(ch.) + *NH*(ch.) (9)



*Ga* (ph. on *Ga*) + $NH_3$ (gas) + Ga(ch.) +*NH*(ch.) = = *GaN* (solid) + (3/2)$H_2$ (gas) + Ga(ch.) + *NH*(ch.) (10)

where *Ga* (ph. on *NH*) is the physisorbed *Ga* atom on the nitrided surface site. If the growth process is considered as the stationary process then the physisorbed *Ga* coverages of gallided and nitrided surface sites should be conservated during the run. In such a case the chemical potentials of the *Ga* atoms on the gallided and nitrided surface sites are equal one another. Therefore, the affinity of reaction (7) should be equal the affinity of reaction (9). Accordingly, the affinities of reactions (8) and (10) are too equal one another. Moreover, the sum of the affinities of reactions (1) and (2) is equal the sums of the affinities of reactions (7) and (8) as well as reactions (9) and (10). Thus, it is necessary to estimate the affinity of one of reactions (7), (8), (9) or (10). Reaction (7) can be rewritten in the reduced form as:

*Ga*(gas) = *Ga* (ph. on *NH*) (11)

The affinity of reaction (7) is given as:

$$A_{1.2} = \mu_{Ga}^{g} - \mu_{Ga}^{ph.NH} = $$
$$= \mu_{Ga}^{0g} - \mu_{Ga}^{0l} + RT \ln \frac{p_{Ga}\,(1-\Theta_{(0001)B})}{\Theta_{(0001)B}} \qquad (12)$$

where $\Theta_{(0001)B}$ is the physisorbed *Ga* atoms coverage of the nitrided surface sites, respectively.

The developed model was used for the quantitative estimations of the affinities of LT-MOCVD conditions of *GaN* described in [13]. The TMG and ammonia fluxes were kept constant, with flow rates of 3 *μmole/min* and 3 *slm*, respectively. The fluence of hydrogen was also kept constant with the flux rate of 2 slm. LT-MOCVD *GaN* was deposited at the temperature of 550 $^{o}$C, while the pressure was kept 76 *Torr,* and the average growth rate was measured to be 0.29 *μm/h*. Pressure of the *Ga* atoms in the gaseous phase can be estimated from the growth rate of *GaN* since the sticking coefficient of *Ga* at LT-MOCVD tends to unity. The interpolations for the chemical potentials of *Ga* in the gaseous and liquid states, *GaN* in the solid state as well as ammonia and hydrogen were taken from a database for thermodynamic properties of *GaN* and relevant species involved into the LT-MOCVD process [11]. The residence time of the physisorbed *Ga* atoms estimated from the results in [10,14] is substantially larger than the growth time of one monolayer. Therefore, the coverage of the physisorbed *Ga* atoms should be significant. In this study, the coverage of the physisorbed *Ga* atoms is considered in the wide region from 0.05 to 0.95. The dependencies of the ratios between the affinities of reactions (1), (2) as well as their sum and the temperature in the energy units on the *Ga* coverage are shown in Fig. 4.

As will be seen from Fig. 4, the considered reactions are far from thermodynamic equilibrium since the ratios between the affinities and temperature in the energy units substantially larger than unity. The large values of the affinities of reactions (2), (8) and (10) explain the formation of the thermodynamically metastable cubic modification of *GaN* in the LT-MOCVD runs. Accordingly to the theoretical estimations, the difference between the internal energy of the metastable cubic and stable hexagonal modifications of *GaN* may range from 207 to 454 *cal/mole* [15-17]. Thus, the difference between the internal energies is substantially smaller than the affinities of reactions (2), (8) and (10). Therefore, reason of crystallization of the metastable cubic *GaN* in LT-MOCVD runs is understandable

Ratio between the partial right and back reaction rates can be expressed by the affinity of the reaction and temperature in the energy units as [18]

$$\frac{w_r}{w_b} = \exp\left\{\frac{A}{RT}\right\}$$

In fact, the partial back reactions at the considered LT-MOCVD conditions are neglibibly small with comparison to the partial right reactions. By this is meant that the crystallized *GaN* cannot be described by the minimum condition of the free energy and much less by the condition of the heterogeneous equilibrium.

## 4. Conclusions

Low temperature metalorganic chemical vapor deposition of GaN with trimethylgallium and ammonia as the precursors is considered as the two stage nonequilibrium process. The description of the process is based on the analysis of the reaction affinities for a complete set of chemical reactions including the physisorbed and chemisorbed species.

The deviation from thermodynamic equilibrium is described by the affinities of the heterogeneous reactions. The values of the ratios between the thermodynamic affinities and temperature in the energy units estimated from the experimental data in the developed model are substantially larger than unity. Therefore the partial right reaction rates are significantly larger than the partial back reaction rates. Thus, each stage of the growth processes is far from thermodynamic equilibrium.

The peculiarities of the faces (0001)A and (0001)B of GaN are included in the model through the distinction between the physisorbed and chemisorbed states. The influence of the adsorption states on those surfaces is through the residence time an coverage factor.

The presented analysis can be used to explain the formation of the metaestable cubic modification of GaN at the discussed growth conditions.

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