STR Group

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# Modeling of III-Nitride MOVPE

May 2012

## Prehistory of STR:

1984: Start of the MOCVD modeling activities at Ioffe Institute, St. Petersburg, Russia

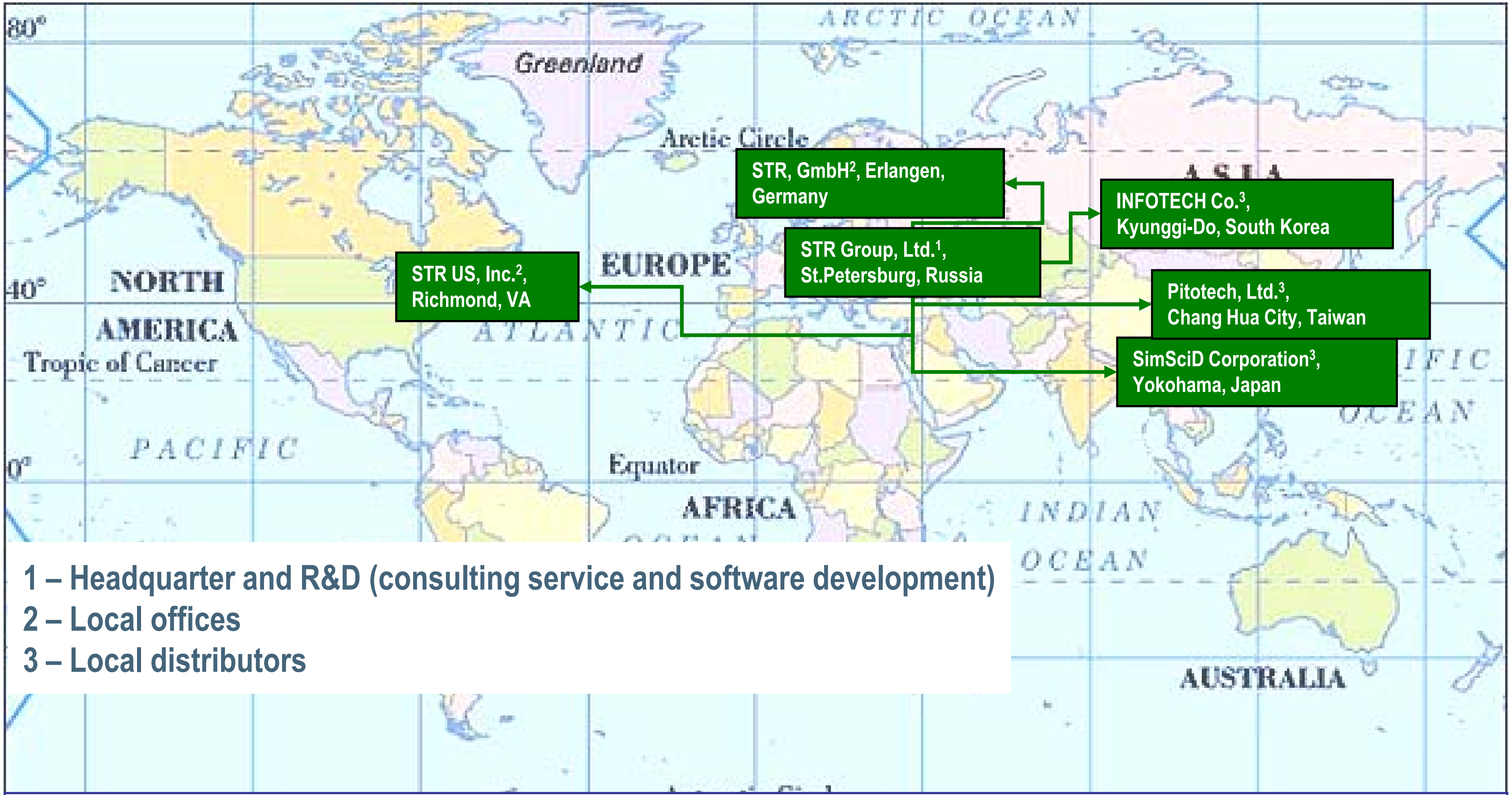
1993-1996: Group for modeling of crystal growth and epitaxy at University of Erlangen-Nuernberg, Germany

## History of software development

2000: Launch of development of the first specialized software
2003: First release of commercial software package
2004: First release of the software for device engineering

## STR Today:

More than 40 scientists and software engineers



STR, GmbH[2], Erlangen, Germany

STR Group, Ltd.[1], St.Petersburg, Russia

INFOTECH Co.[3], Kyunggi-Do, South Korea

STR US, Inc.[2], Richmond, VA

Pitotech, Ltd.[3], Chang Hua City, Taiwan

SimSciD Corporation[3], Yokohama, Japan

1 – Headquarter and R&D (consulting service and software development)
2 – Local offices
3 – Local distributors

Bulk crystal growth modeling (Si, Ge, SiGe, GaAs, InP, SiC, AlN, $Al_2O_3$, Optical Crystals)

Epitaxy and deposition modeling (Si, SiGe, SiC, AlGaAs, AlGaInP, AlGaInN, high-k oxides)

Modeling of device operation (LEDs, Laser Diodes, FETs/HEMTs Shottky diodes)

Software & consulting services :

- Modeling of crystal growth from the melts and solutions: CGSim
- Modeling of polysilicon deposition by Siemens process: PolySim
- Modeling of bulk crystal growth of SiC, AlN, GaN: ViR
- Modeling of epitaxy of compound semiconductors: CVDSim
- Modeling of optoelectronic and electronic devices: SimuLED

Customer base:

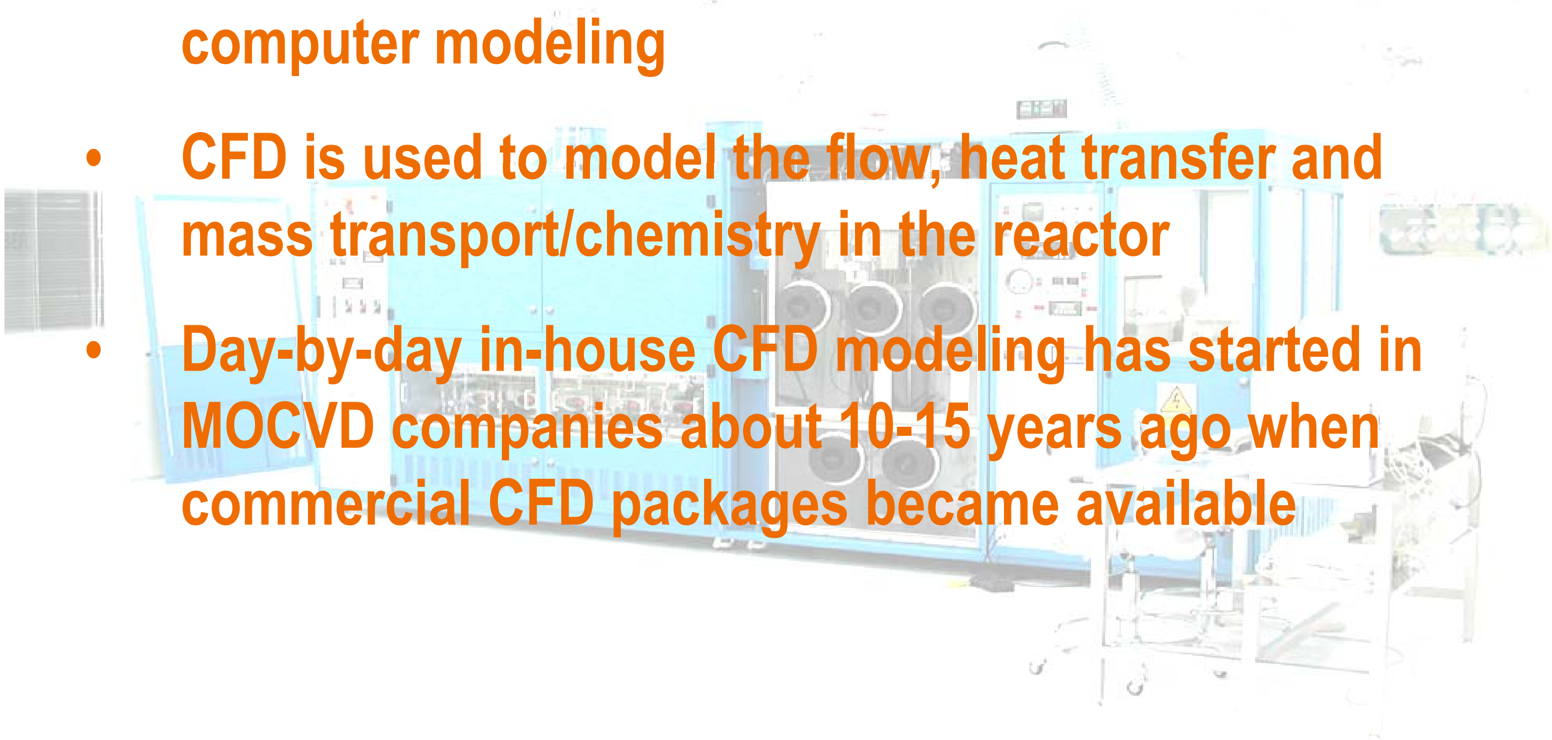
- More than 160 companies and universities worldwide
- Top LED, LD and solar cell manufacturers
- Top sapphire, GaAs, GaP, GaN, AlN and SiC wafer manufacturers
- Top MOCVD reactor manufacturers

# Outline

- Motivation for MOVPE modeling
- Specific features of nitride growth. CVDSim™ as the dedicated software for simulation of nitride growth by MOCVD
- Modeling of nitride growth in industrial reactors with focus on AlN/AlGaN growth in CCS reactor
- Unsteady effects in growth of GaN-based quantum-well heterostructures

# Basic overview of CFD modeling

- (C)omputation (F)luid (D)ynamics – approach to simulate a MOVPE reactor and process using computer modeling
- CFD is used to model the flow, heat transfer and mass transport/chemistry in the reactor
- Day-by-day in-house CFD modeling has started in MOCVD companies about 10-15 years ago when commercial CFD packages became available



# CFD modeling: what for?

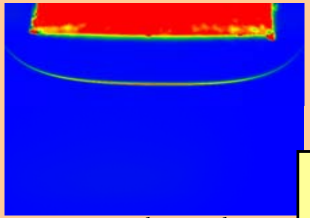
- Now CFD modeling is used by all the major MOCVD equipment manufacturers (Aixtron, Veeco, TNSC, Applied Materials…) to design the new reactors.
- CFD modeling is used also by MOCVD end-users as Hitachi Cable, Osram Opto, Philips Lumileds, Samsung LED and others.
- Modeling of flow and heat transfer is quite routine procedure now, <u>focus is shifted to the combination of CFD with advanced chemistry models…</u>

# Modeling of III-nitride MOVPE: main issues

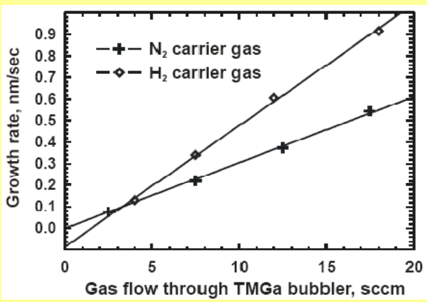
- Complicated gas-phase chemistry and gas-phase nucleation at high pressures
- Complicated surface chemistry – effect of temperature and carrier gas
- Parasitic deposition in wide range of temperature variation

Output from the modeling

- Optimization of the growth recipe
- Understanding of the underlying mechanisms
- Optimization of the reactor design
- Increase of the process yield



Creighton et al., (2004)



Zavarin et al., (2005)

Parikh et al., (2006)

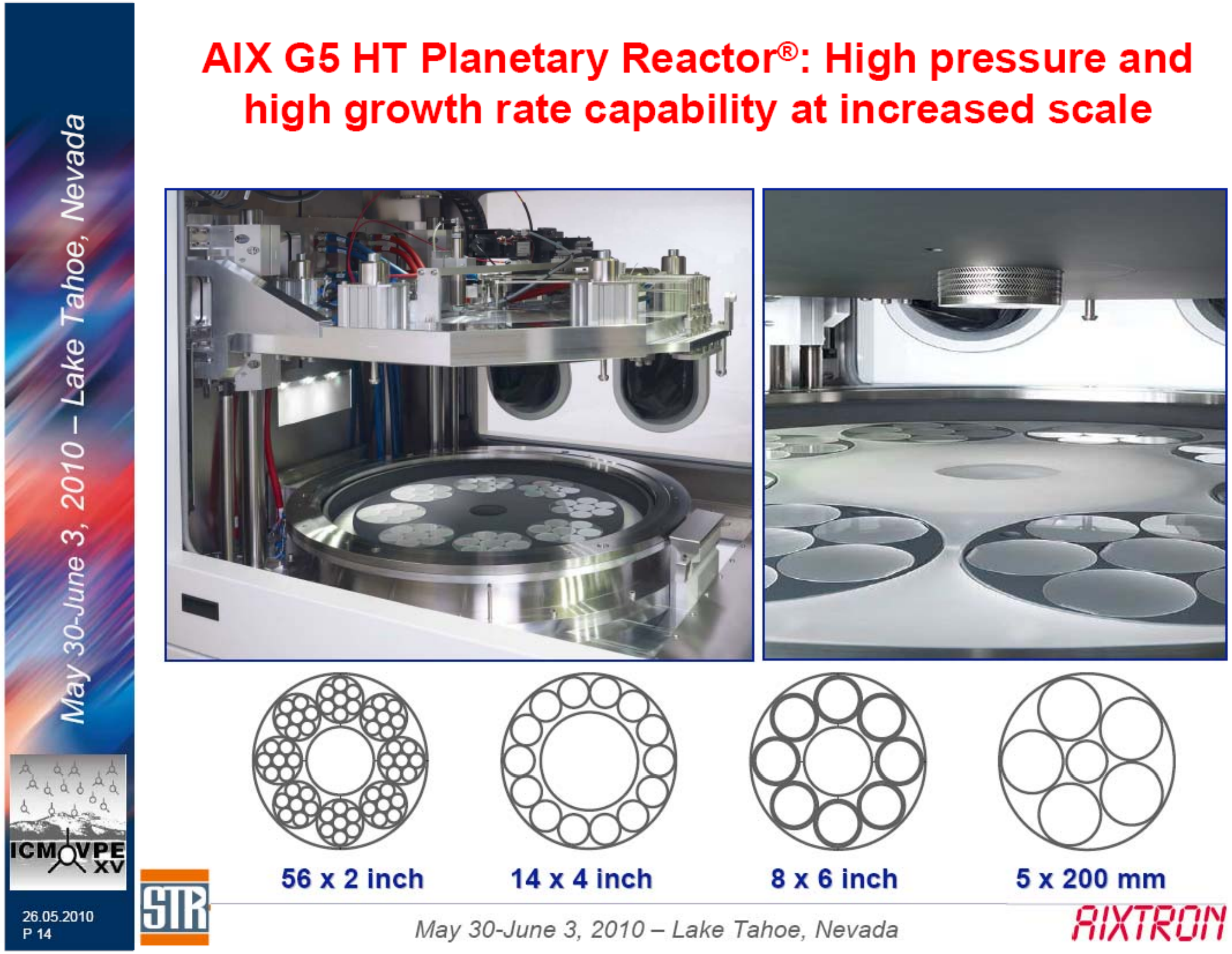
# CVDSim™

## Chemical Vapor Deposition Simulator

## Simulation Tool for Modeling of CVD Processes in Industrial Reactors

### CVDSim Nitride Edition:

- Prediction of the growth rate and composition
- Parasitic reactions and particle formation
- Parasitic deposition on injectors and walls (low temperature kinetics, condensation of the adducts and non-volatile products)
- Effect of the lattice mismatch on alloy composition



## AIX G5 HT Planetary Reactor®: High pressure and high growth rate capability at increased scale

56 x 2 inch

14 x 4 inch

8 x 6 inch

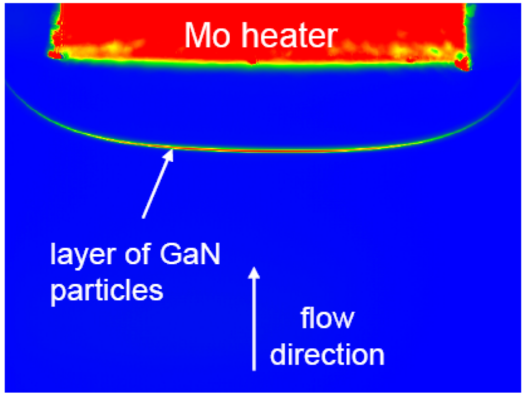
5 x 200 mm

May 30-June 3, 2010 – Lake Tahoe, Nevada

26.05.2010
P 14

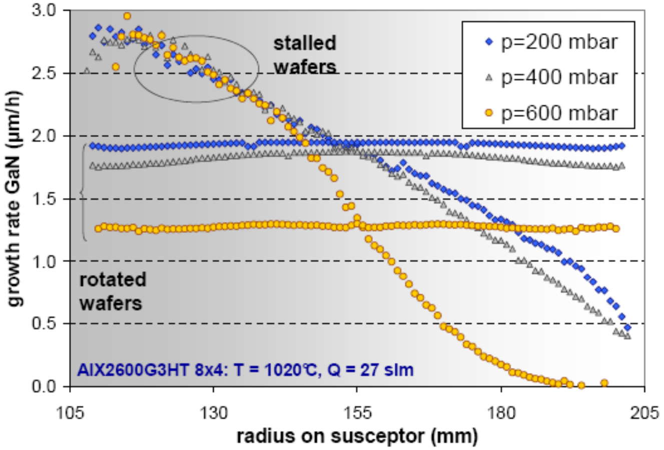
Joint Aixtron/STR presentation at ICMOVPE XV, 2010

# Evidence of gas phase nucleation in MOVPE of III-Nitrides



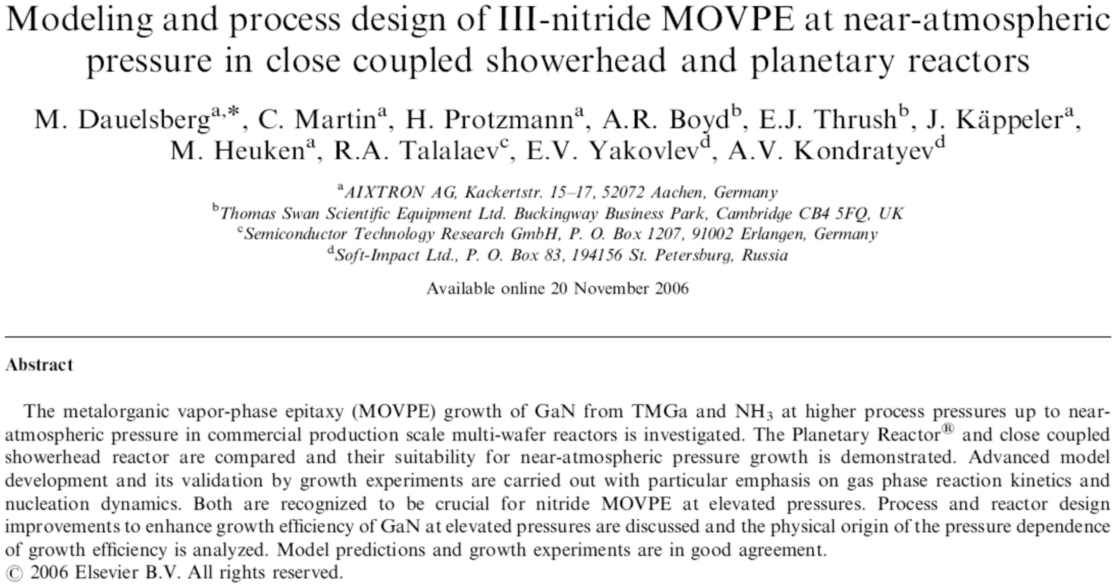
from: J. Randall Creighton et al. JCG 261 (2004) 204

- Laser scattering experiments at standard MOVPE conditions using conventional precursors
- Particle size and density identified
- Parametric dependencies and formation mechanism analysed



Production scale reactor
(e. g. Planetary Reactor® 8 x 4 inch)

- Indirect effect on growth efficiency and layer thickness profiles
- often abrupt, sudden depletion
- deviation from mass transport limited growth characteristic



# Modeling and process design of III-nitride MOVPE at near-atmospheric pressure in close coupled showerhead and planetary reactors

M. Dauelsberg[a,*], C. Martin[a], H. Protzmann[a], A.R. Boyd[b], E.J. Thrush[b], J. Käppeler[a], M. Heuken[a], R.A. Talalaev[c], E.V. Yakovlev[d], A.V. Kondratyev[d]

[a] *AIXTRON AG, Kackertstr. 15–17, 52072 Aachen, Germany*
[b] *Thomas Swan Scientific Equipment Ltd. Buckingway Business Park, Cambridge CB4 5FQ, UK*
[c] *Semiconductor Technology Research GmbH, P. O. Box 1207, 91002 Erlangen, Germany*
[d] *Soft-Impact Ltd., P. O. Box 83, 194156 St. Petersburg, Russia*

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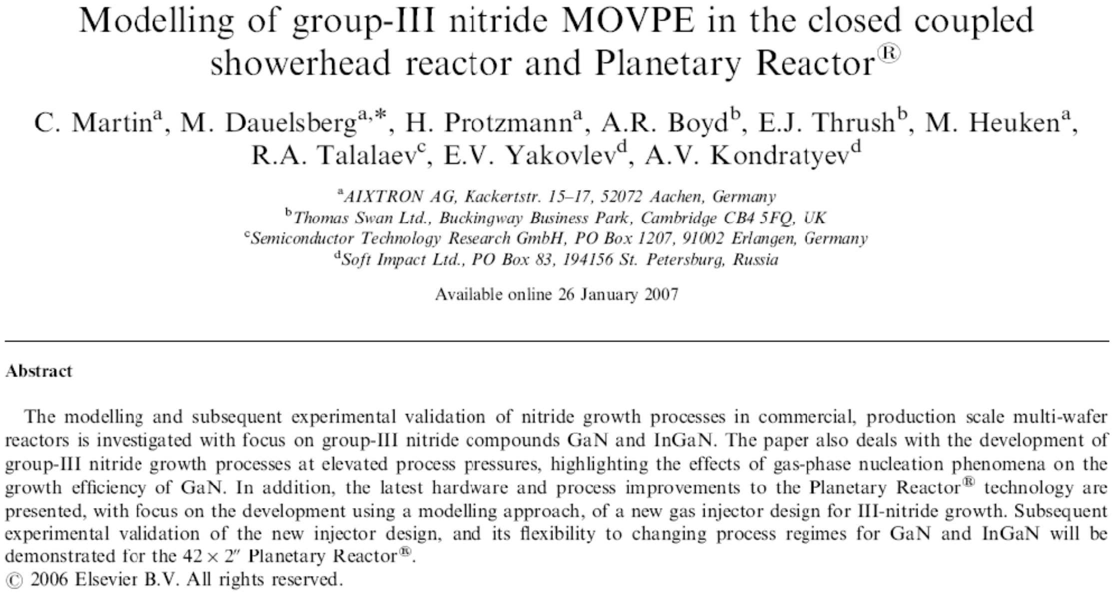
**Abstract**

The metalorganic vapor-phase epitaxy (MOVPE) growth of GaN from TMGa and $NH_3$ at higher process pressures up to near-atmospheric pressure in commercial production scale multi-wafer reactors is investigated. The Planetary Reactor® and close coupled showerhead reactor are compared and their suitability for near-atmospheric pressure growth is demonstrated. Advanced model development and its validation by growth experiments are carried out with particular emphasis on gas phase reaction kinetics and nucleation dynamics. Both are recognized to be crucial for nitride MOVPE at elevated pressures. Process and reactor design improvements to enhance growth efficiency of GaN at elevated pressures are discussed and the physical origin of the pressure dependence of growth efficiency is analyzed. Model predictions and growth experiments are in good agreement.



# Modelling of group-III nitride MOVPE in the closed coupled showerhead reactor and Planetary Reactor®

C. Martin[a], M. Dauelsberg[a,*], H. Protzmann[a], A.R. Boyd[b], E.J. Thrush[b], M. Heuken[a], R.A. Talalaev[c], E.V. Yakovlev[d], A.V. Kondratyev[d]

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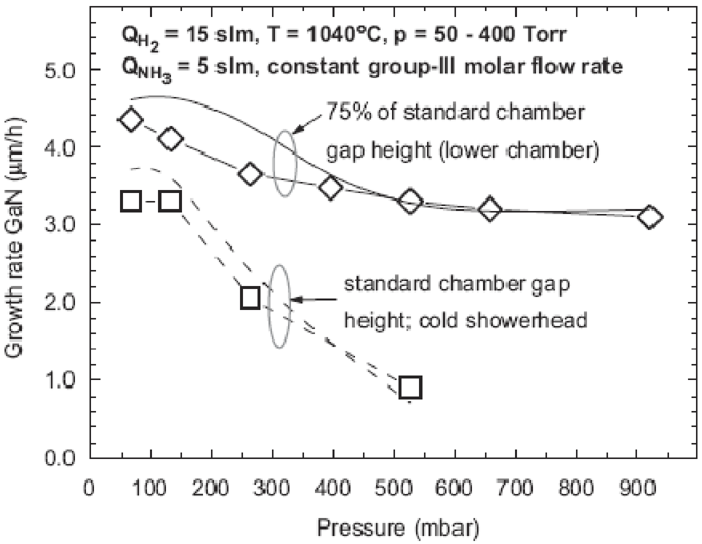
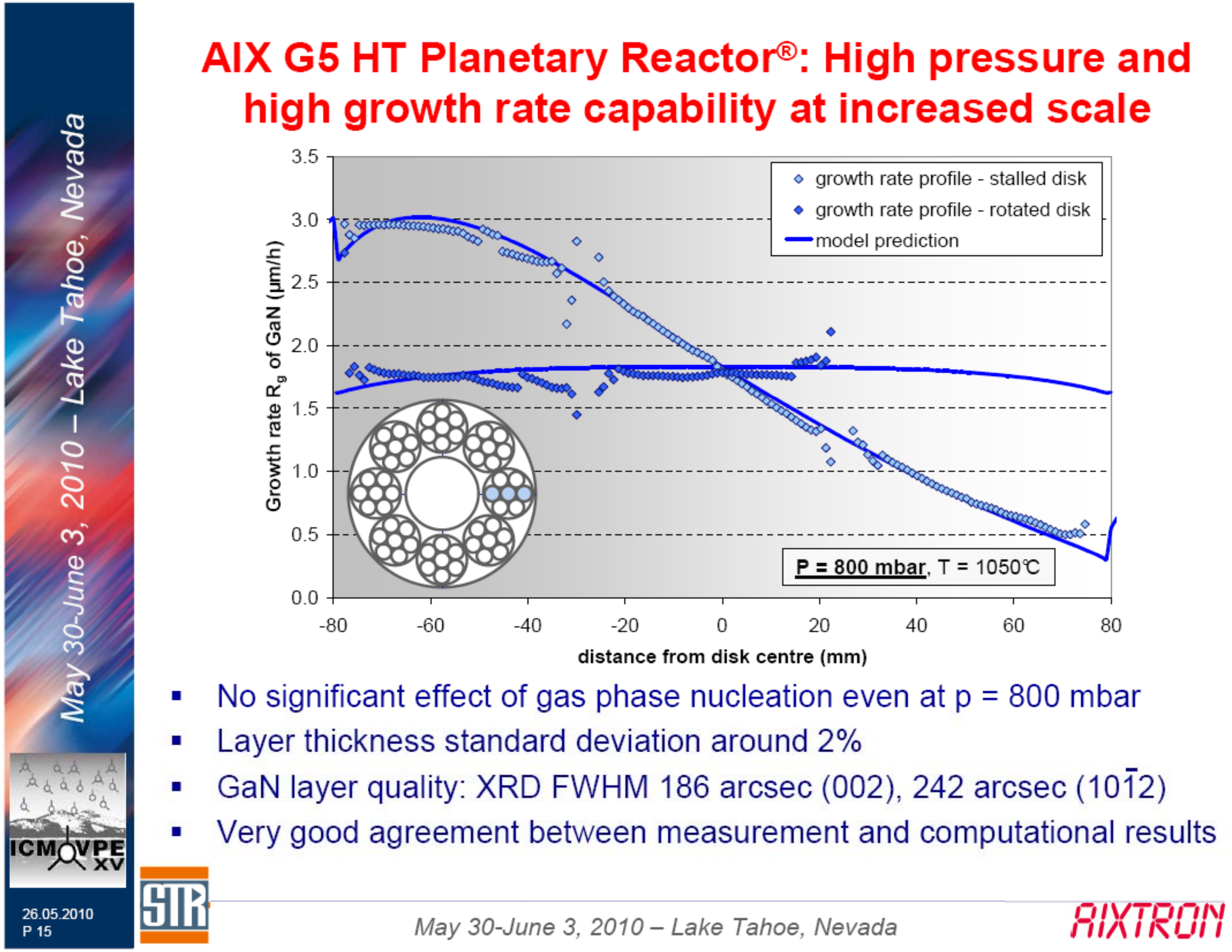
**Abstract**

The modelling and subsequent experimental validation of nitride growth processes in commercial, production scale multi-wafer reactors is investigated with focus on group-III nitride compounds GaN and InGaN. The paper also deals with the development of group-III nitride growth processes at elevated process pressures, highlighting the effects of gas-phase nucleation phenomena on the growth efficiency of GaN. In addition, the latest hardware and process improvements to the Planetary Reactor® technology are presented, with focus on the development using a modelling approach, of a new gas injector design for III-nitride growth. Subsequent experimental validation of the new injector design, and its flexibility to changing process regimes for GaN and InGaN will be demonstrated for the 42 × 2″ Planetary Reactor®.

## Modeling is actively used for the process optimization and design of commercial production-scale multi-wafer reactors

### GaN growth rate vs pressure in 6x2” CCS reactor





May 30-June 3, 2010 – Lake Tahoe, Nevada

ICMOVPE XV

26.05.2010
P 15

## AIX G5 HT Planetary Reactor®: High pressure and high growth rate capability at increased scale

- No significant effect of gas phase nucleation even at p = 800 mbar
- Layer thickness standard deviation around 2%
- GaN layer quality: XRD FWHM 186 arcsec (002), 242 arcsec $(10\bar{1}2)$
- Very good agreement between measurement and computational results

May 30-June 3, 2010 – Lake Tahoe, Nevada

AIXTRON

# Numerical and Experimental Study on Metal Organic Vapor-Phase Epitaxy of InGaN/GaN Multi-Quantum-Wells

**Changsung Sean Kim**
**Jongpa Hong**
**Jihye Shim**
**Bum Joon Kim**
**Hak-Hwan Kim**
**Sang Duk Yoo**
**Won Shin Lee**

Corporate R&D Institute CAE Group,
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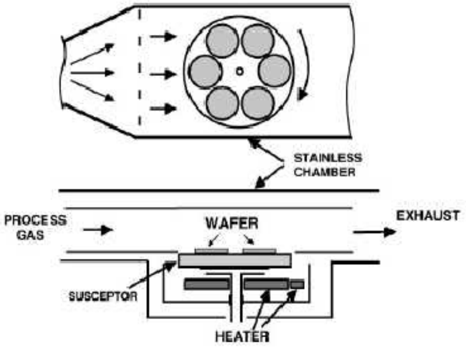
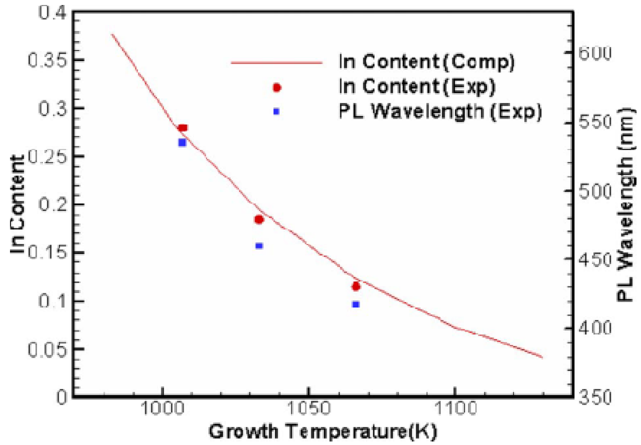
*A numerical and experimental study has been performed to characterize the metal organic vapor-phase epitaxy (MOVPE) growth of InGaN/GaN multi-quantum-wells. One of the major objectives of the present study is to predict the optimal operating conditions that would be suitable for the fabrication of GaN-based light-emitting diodes using three different reactors, vertical, horizontal, and planetary. Computational fluid dynamics (CFD) simulations considering gas-phase chemical reactions and surface chemistry were carried out and compared with experimental measurements. Through a lot of CFD simulations, the database for the multiparametric dependency of indium incorporation and growth rate in InGaN/GaN layers has been established in a wide range of growth conditions. Also, a heating system using radio frequency power was verified to obtain the uniform temperature distribution by simulating the electromagnetic field as well as gas flow fields. The present multidisciplinary approach has been applied to the development of a novel-concept MOVPE system as well as performance enhancement of existing commercial reactors.* [DOI: 10.1115/1.2956513]

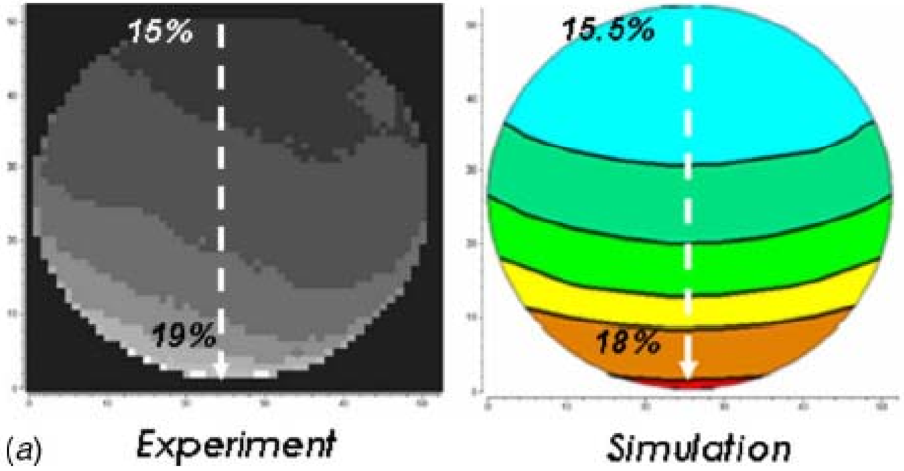
*Keywords: metal organic vapor-phase epitaxy, InGaN, multi-quantum-well, light-emitting diode, surface chemistry, radio frequency power, electromagnetic field*



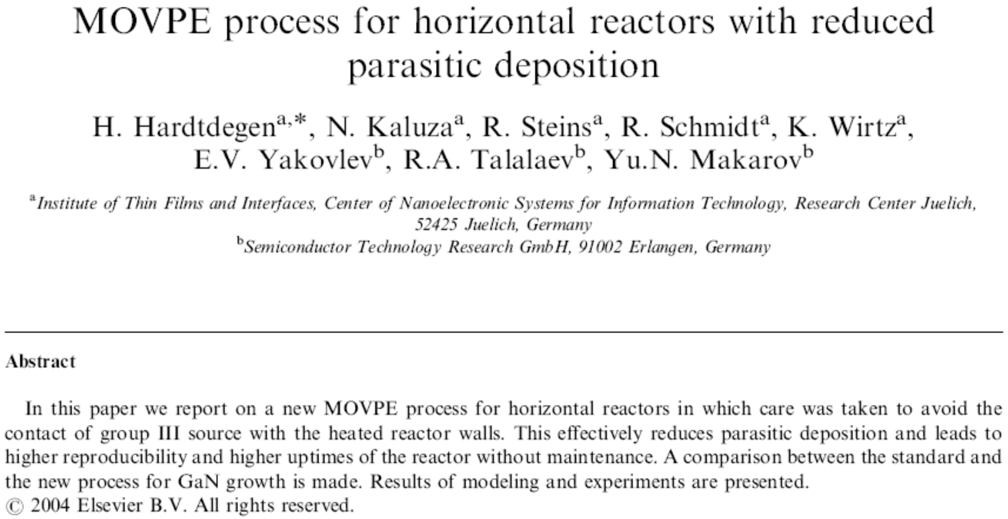
**Combination of simulation and experimental analysis has been applied to improve the performance of the existing reactors and to develop a novel reactor concept**



Contour lines of indium composition



(a) Experiment Simulation



# MOVPE process for horizontal reactors with reduced parasitic deposition

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E.V. Yakovlev[b], R.A. Talalaev[b], Yu.N. Makarov[b]

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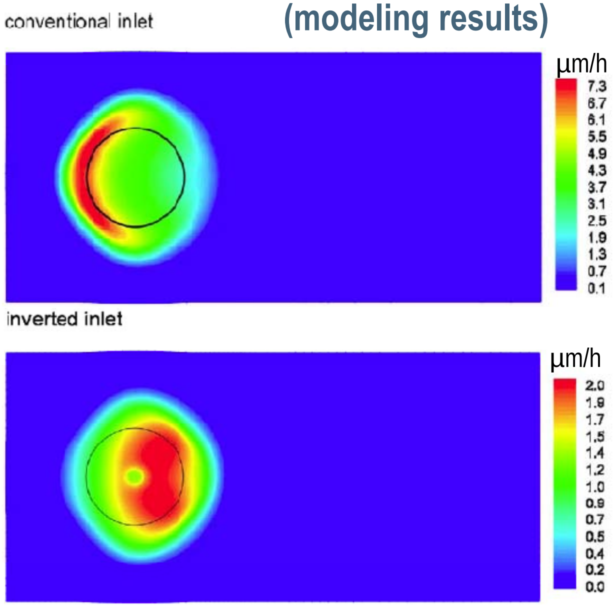
[b] *Semiconductor Technology Research GmbH, 91002 Erlangen, Germany*

**Abstract**

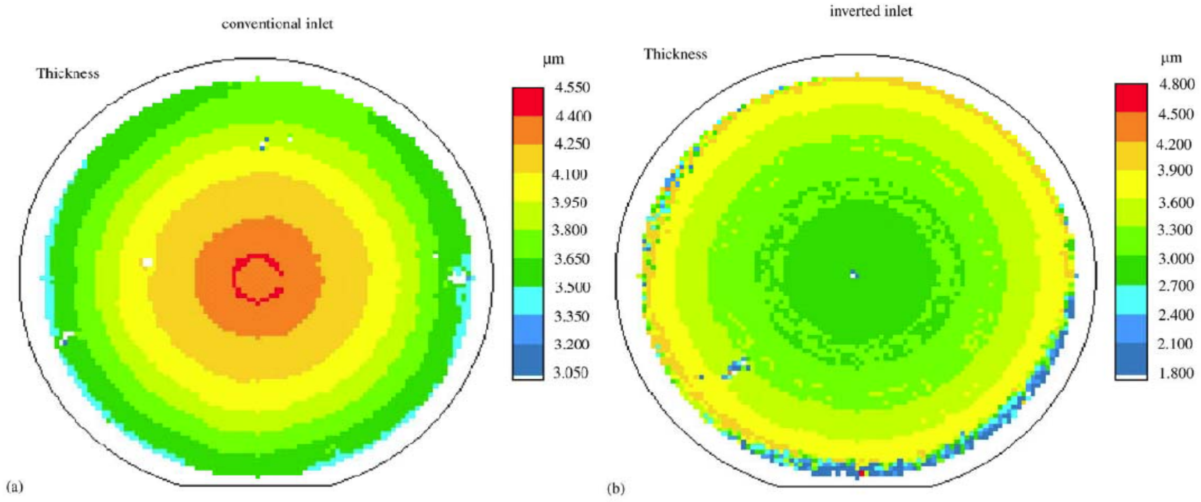
In this paper we report on a new MOVPE process for horizontal reactors in which care was taken to avoid the contact of group III source with the heated reactor walls. This effectively reduces parasitic deposition and leads to higher reproducibility and higher uptimes of the reactor without maintenance. A comparison between the standard and the new process for GaN growth is made. Results of modeling and experiments are presented.

**The use of the inverted precursor supply allows 40 runs of 1.5 mm thick GaN without removing parasitic deposits instead of 10 growth runs for the conventional growth process**

## Deposition rate over the ceiling (modeling results)



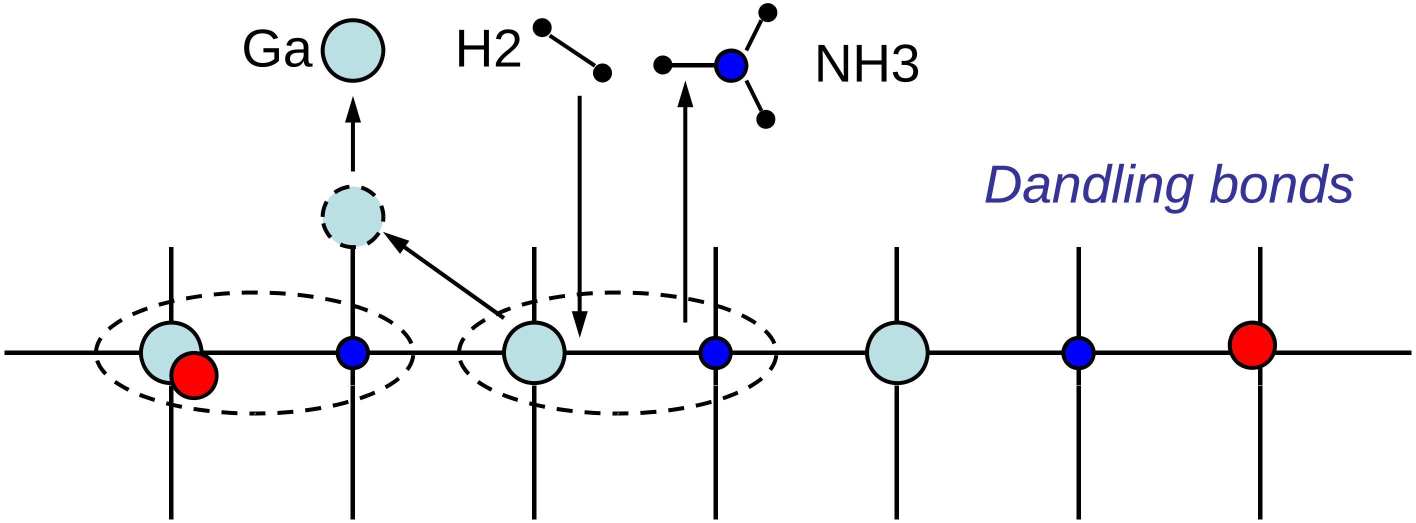
## Thickness mapping: from convex to concave profile



# AlN and AlGaN growth in Close Coupled Showerhead reactor

# Kinetic model for AlGaN deposition

- Adsorption and incorporation of all Ga- and some Al-containing species
- Etching of GaN part of AlGaN alloy, etching rate depends on composition of AlGaN



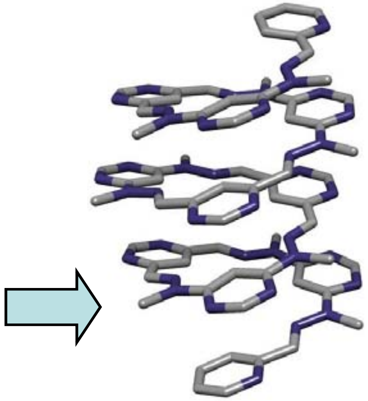
*Dandling bonds*

*Surface crystal lattice layer*

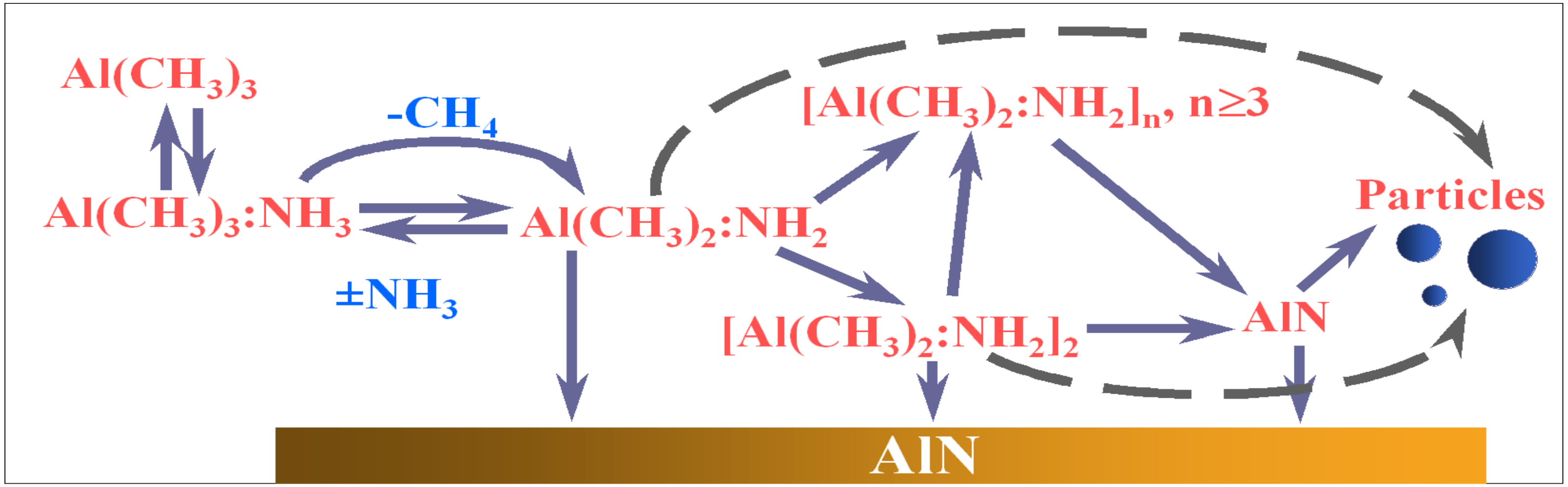
# Gas-phase reaction mechanism in AlN MOVPE

1. $TMAl + NH_3 \leftrightarrow TMAl{:}NH_3$
2. $TMAl{:}NH_3 \rightarrow DMAl{:}NH_2 + CH_4$
3. $TMAl{:}NH_3 + NH_3 \rightarrow DMAl{:}NH_2 + CH_4 + NH_3$
4. $2DMAl{:}NH_2 \rightarrow (DMAl{:}NH_2)_2$
5. $(DMAl{:}NH_2)_2 \rightarrow 2AlN + 4CH_4$

1. • **Adduct formation**
2. • **Elimination of methane**
3. • **Adduct reaction with ammonia**
4. • **Formation of oligomers**
5. • **AlN gaseous molecules formation from decomposition of dimers and trimers containing both Al and N**



# Gas-phase reaction and cluster nucleation mechanism in AlN MOVPE



Ways of aluminum losses:

formation of oligomers ($n\geq3$) and AlN particles

- Species initiating cluster nucleation: AlN vapor
- Nucleation and subsequent growth of clusters is due to reactions between AlN nuclei and Al-containing species such as AlN, $DMAl:NH_2$, $(DMAl:NH_2)_2$

# Gas phase nucleation and cluster growth/evaporation

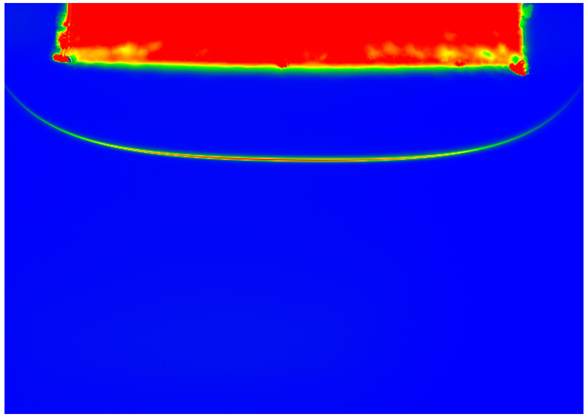
## Main assumptions used to simulate gas phase nucleation:

- Due to their small size, the clusters can be regarded as a pseudo gas of heavy molecules
- Transport of the clusters and their growth/evaporation are treated using the first three moments of the size distribution function
- Particle growth due to interactions with other group-III species

# Effect of the thermophoretic force

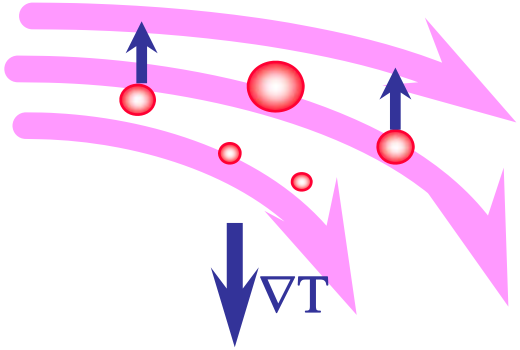
Thermophoretic force prevents particles from reaching the substrate, moving them in direction opposite to the temperature gradient

surface at ~1000°C

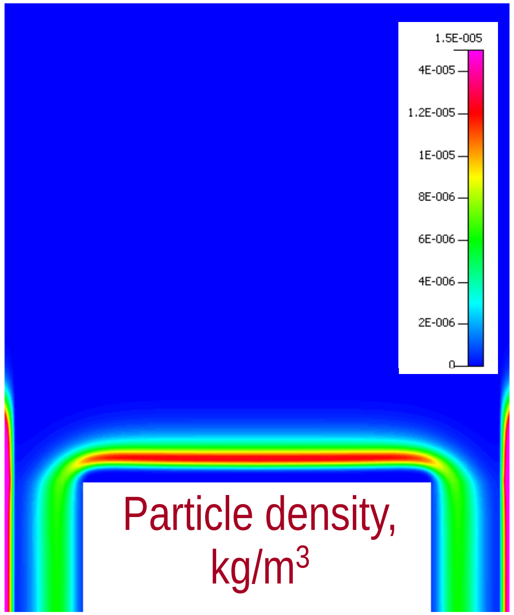


Laser scattering experiments, standard MOVPE conditions, conventional precursors (TMGa, TMAl, TMIn, ammonia); carrier gas - hydrogen/nitrogen

**J.R. Creighton et al, (2004)**



GaN particle size ranges from 10÷100 nm, density from 1÷6·$10^8$ $cm^{-3}$

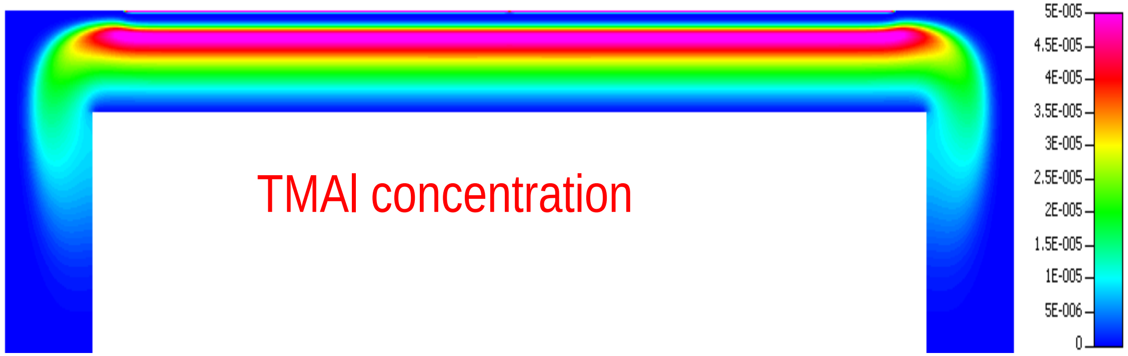


Particle density, $kg/m^3$

The AlN and AlGaN MOVPE models were previously successfully verified by the data obtained in the vertical rotating disk and planetary reactors

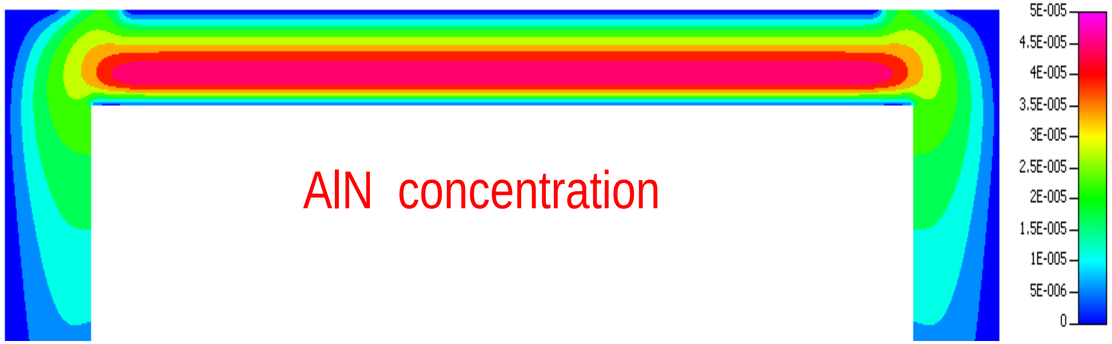
# AlN model verification: CCS 3x2" reactor

## Reaction pathways at different V/III ratios



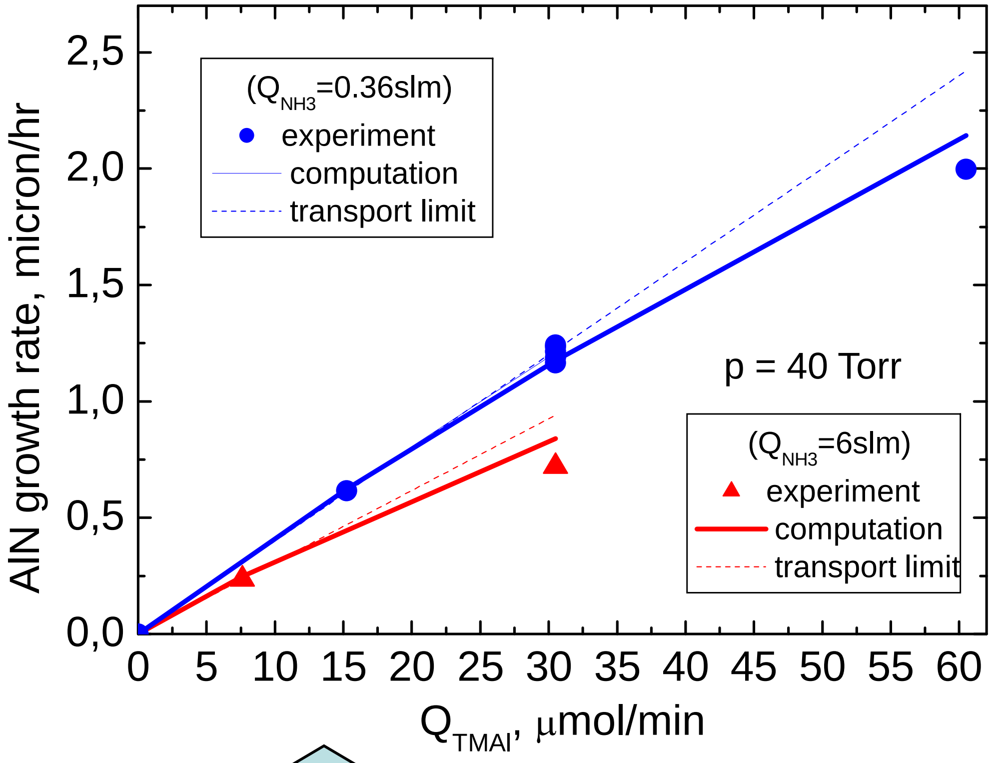
**Low $NH_3$ flow (0.36 slm):** TMAl - $TMAlNH_3$ equilibrium shifts back toward TMAl; growth efficiency is high

**High $NH_3$ flow (6 slm):** formation of heavy-molar-mass / low-diffusivity species (i.e. $[DMAlNH_2]_2$) followed by production of AlN vapor and AlN particles



# AlN model verification: CCS 3x2" reactor

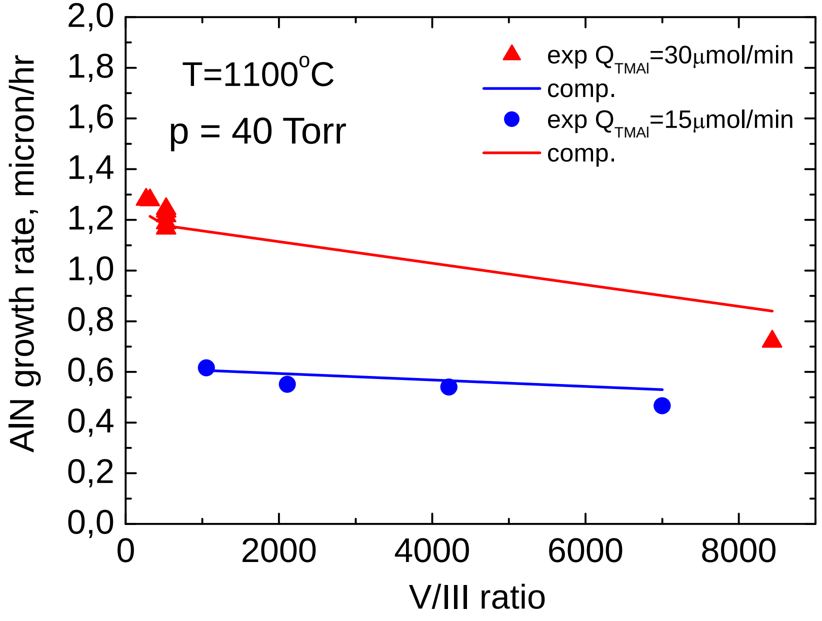
## Effect of the TMAl flow rate



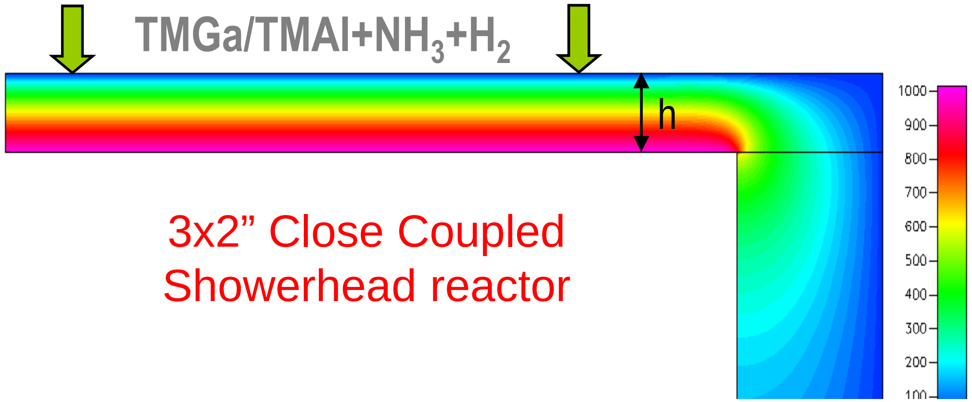
AlN Growth rate depends on ammonia flow rate

Increase of V/III ration results in increase of material loss and growth rate reduction

## Effect of the V/III ratio



# High growth rates of AlGaN in CCS 3x2" reactor (cooperation with TU Berlin)



3x2” Close Coupled Showerhead reactor

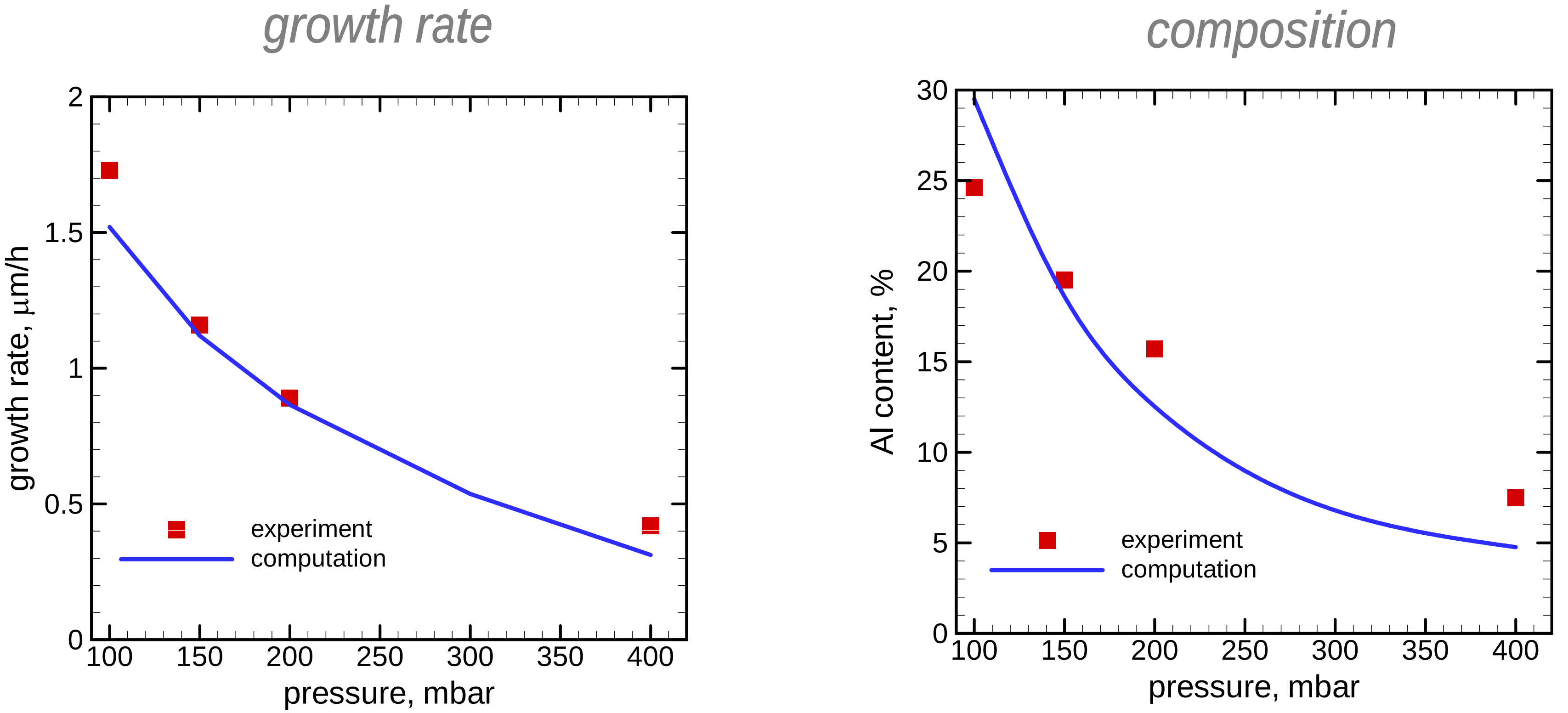
Additional losses of gallium: interaction of Ga-containing species with AlN particles (proceeds in kinetically-limited conditions)

**Measurements:**
*in-situ:* **EpiR-TT-DA-UV** system
*ex-situ:* **XRD**

**Process parameters:**
*Reactor height (h): 6-21 mm*
Total flow: 8 slm
Ammonia flow: 1.5 slm
Pressure: 50-500 mbar
Temperature: 1017 °C - 1052 °C
Templates GaN/$Al_2O_3$
Layer thickness: 100-700 nm

Target: growth of AlGaN layers with high aluminum content and growth rate

# Effect of the pressure on the AlGaN growth rate and composition (h=const)

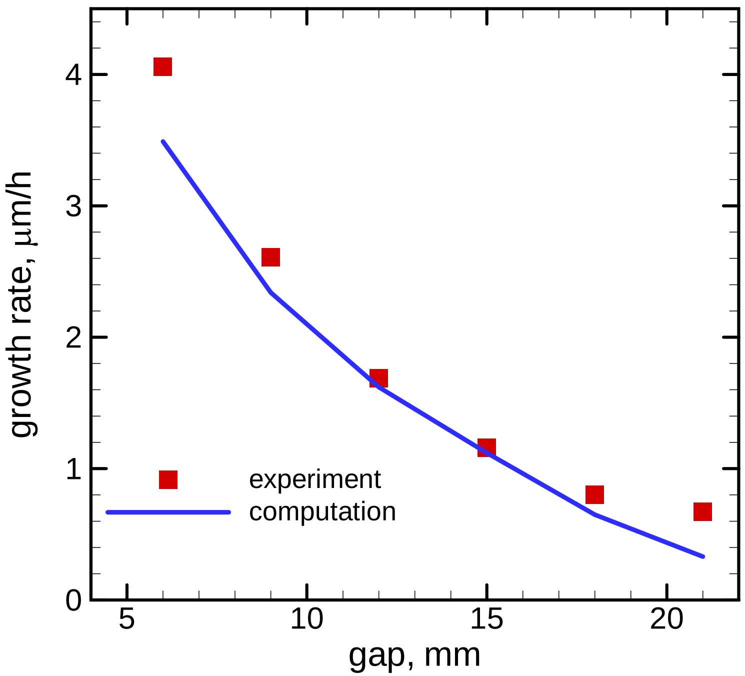


**Both growth rate and composition decrease with pressure due to enhanced intensity of particle generation in the gas phase**

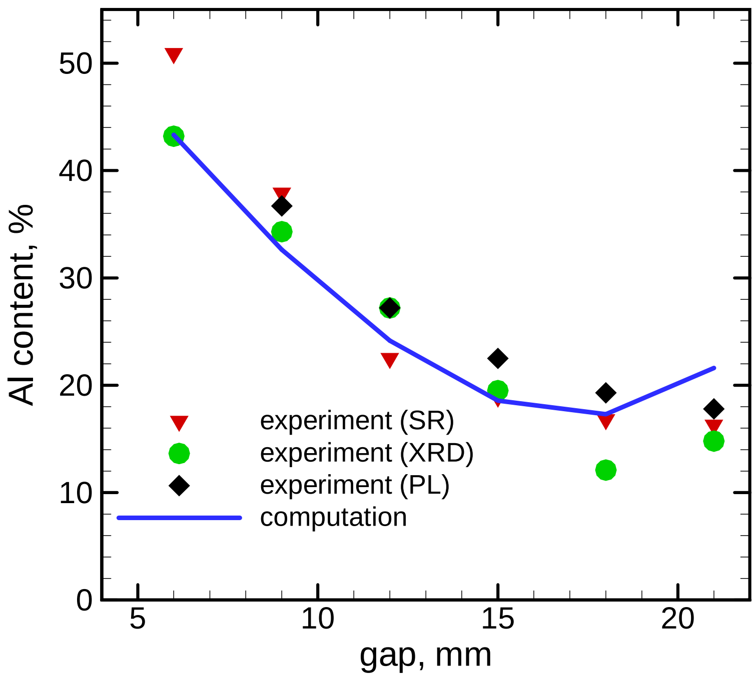
Data: J. Stellmach et al., Journal of Crystal Growth 315 (2011) 229
J. Stellmach et al., presented at ICMOVPE XV, 2010

# Effect of the gap height on the AlGaN growth rate and composition (p=const)

*growth rate*



*composition*

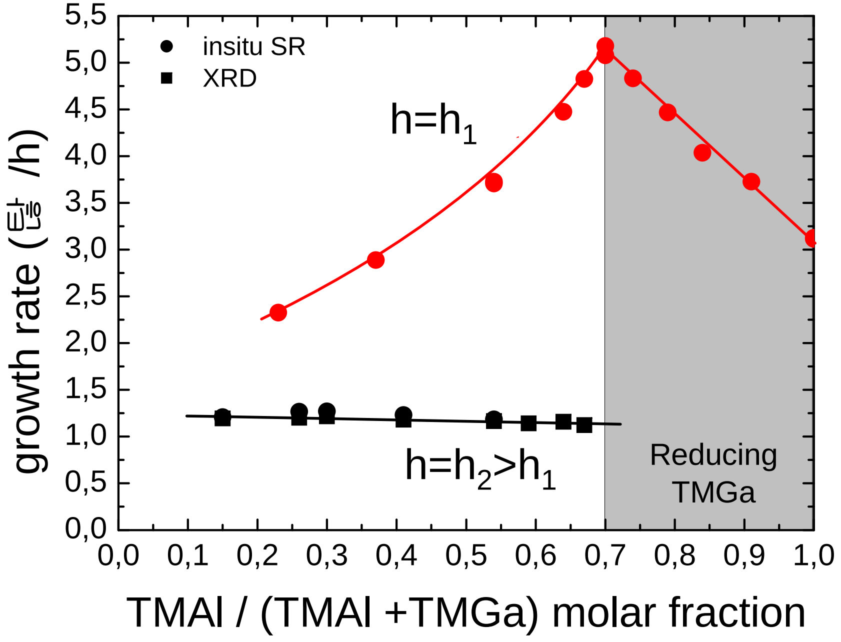


**Increase of the reactor height results in lowering the growth rate due to particle formation effects, however, the influence on the AlGaN composition is not so straightforward**

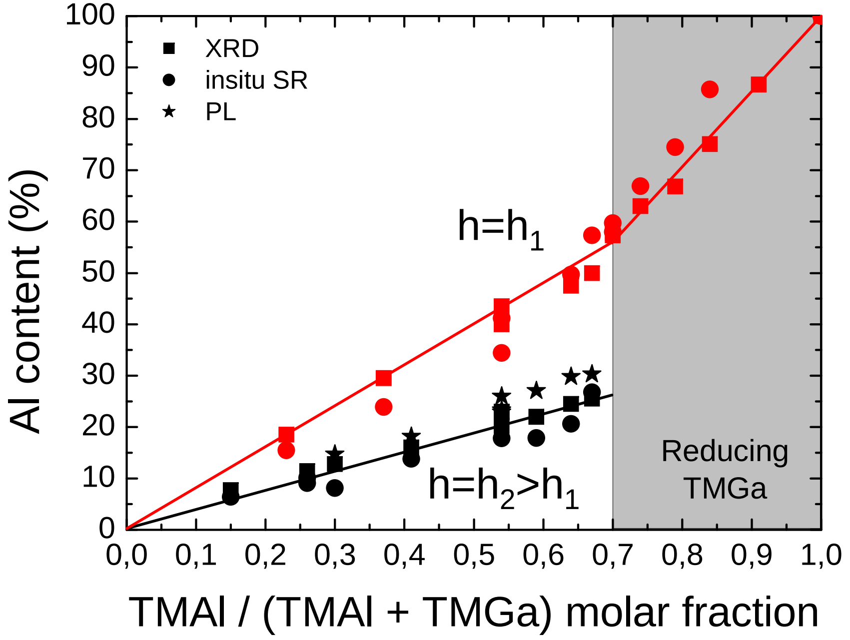
Data: J. Stellmach et al., Journal of Crystal Growth 315 (2011) 229
J. Stellmach et al., presented at ICMOVPE XV, 2010

# Further adjustment of the growth conditions

*growth rate*



*composition*

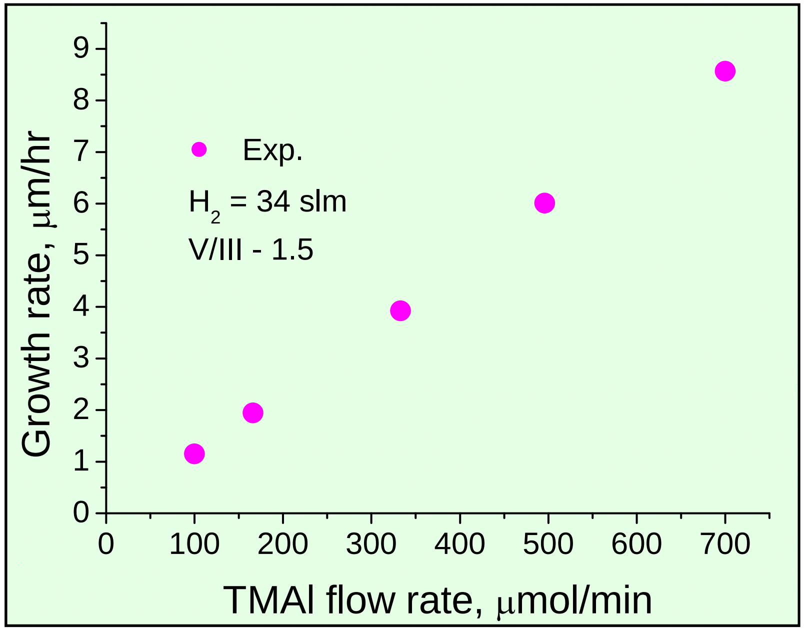


**Reproducible growth of AlGaN in the entire compositional range has been achieved with the growth rate above 3 µm/h**

Data: J. Stellmach et al., Journal of Crystal Growth 315 (2011) 229
J. Stellmach et al., presented at ICMOVPE XV, 2010

# High growth rates of AlN in planetary 6x2" reactor

Growth rate with TMAl flow

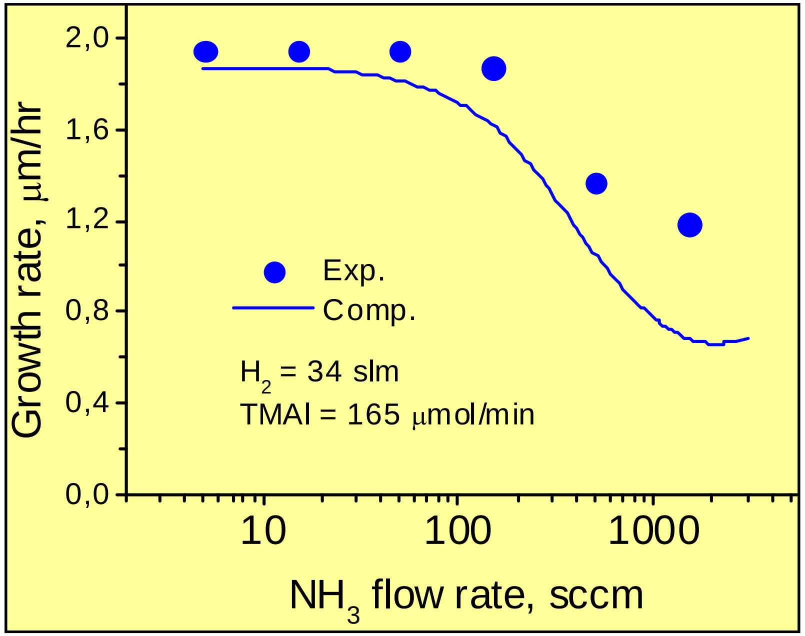


Prediction and explanation of the onset of parasitic chemistry for various V/III ratios, involving quite low V/III=1.5

**The conditions allowing AlN epitaxy with the growth rates exceeding 8μm/h have been found**

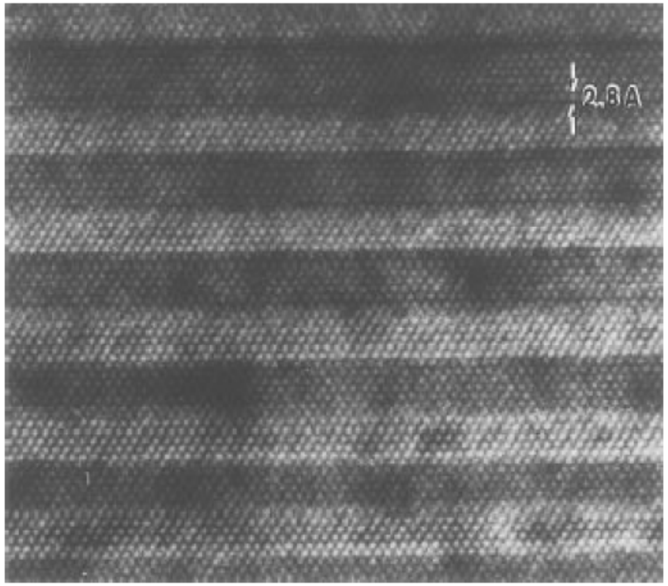
*P=100mbar, T=1045-1070°C*

Growth rate variation with ammonia



Data: Lundin et al., ACCGE 15, 2011, to be published in Journal of Crystal Growth

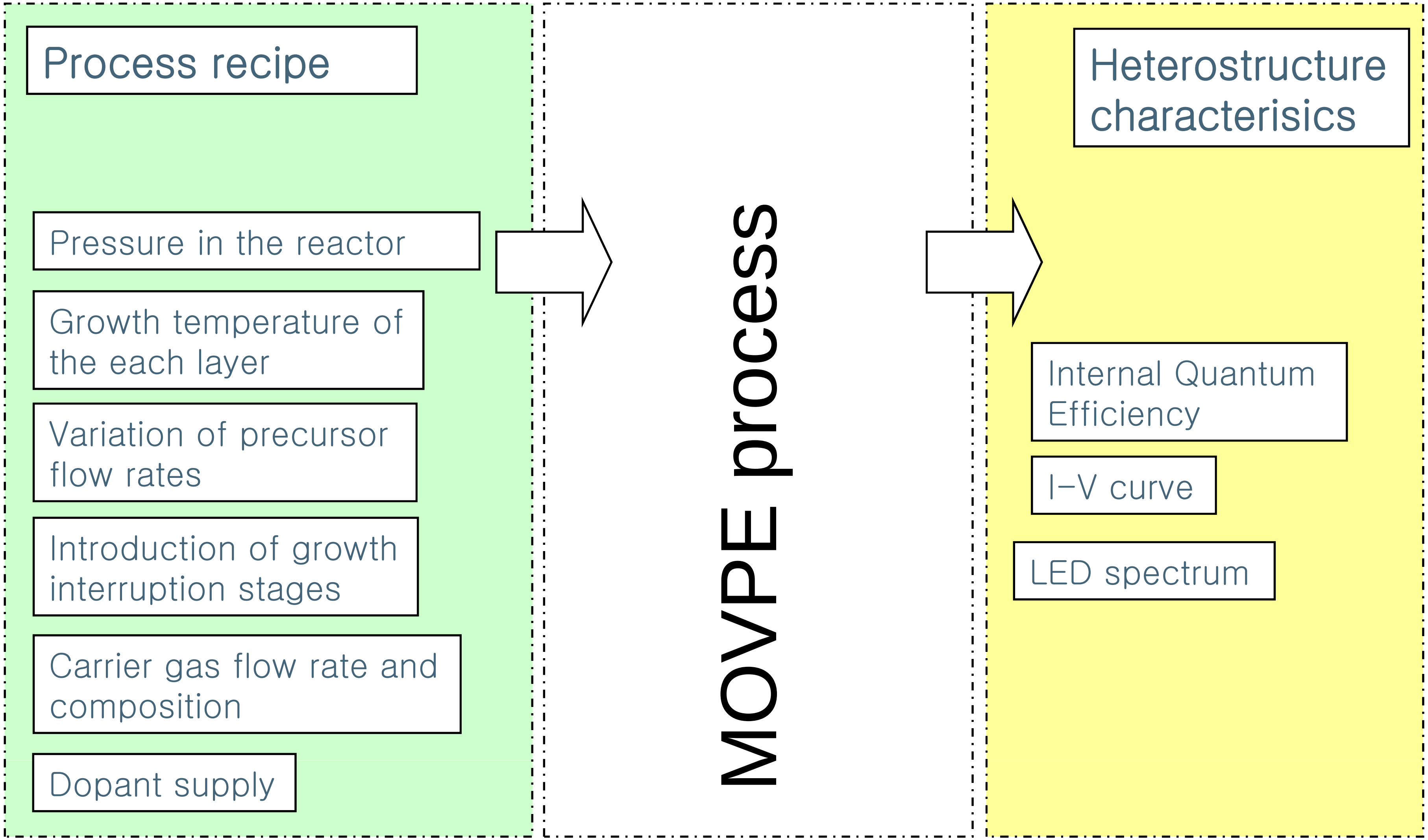
# Effect of growth conditions on characteristics of GaN-based quantum-well heterostructures



2012

STR-Group, Ltd.

# Epitaxy-to-Device Engineering Modeling



Process recipe

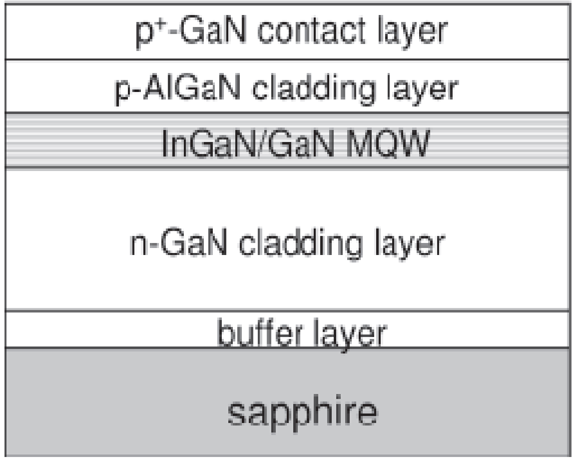
- Pressure in the reactor
- Growth temperature of the each layer
- Variation of precursor flow rates
- Introduction of growth interruption stages
- Carrier gas flow rate and composition
- Dopant supply

MOVPE process

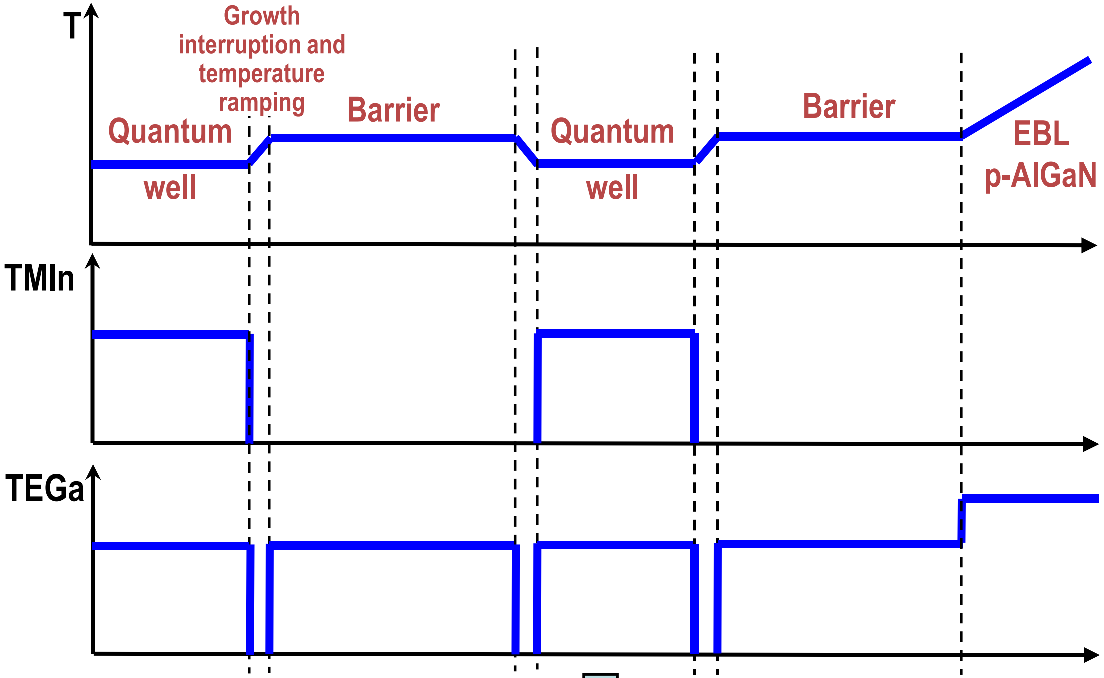
Heterostructure characterisics

- Internal Quantum Efficiency
- I–V curve
- LED spectrum

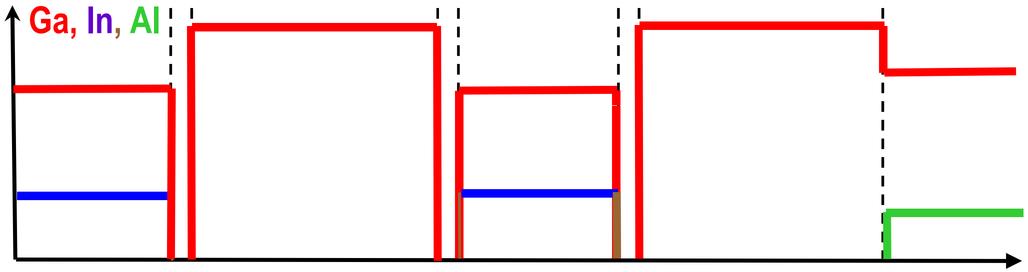
## Variation of the growth temperature and precursor supply specified by epi-engineer for growth of LED heterostructure



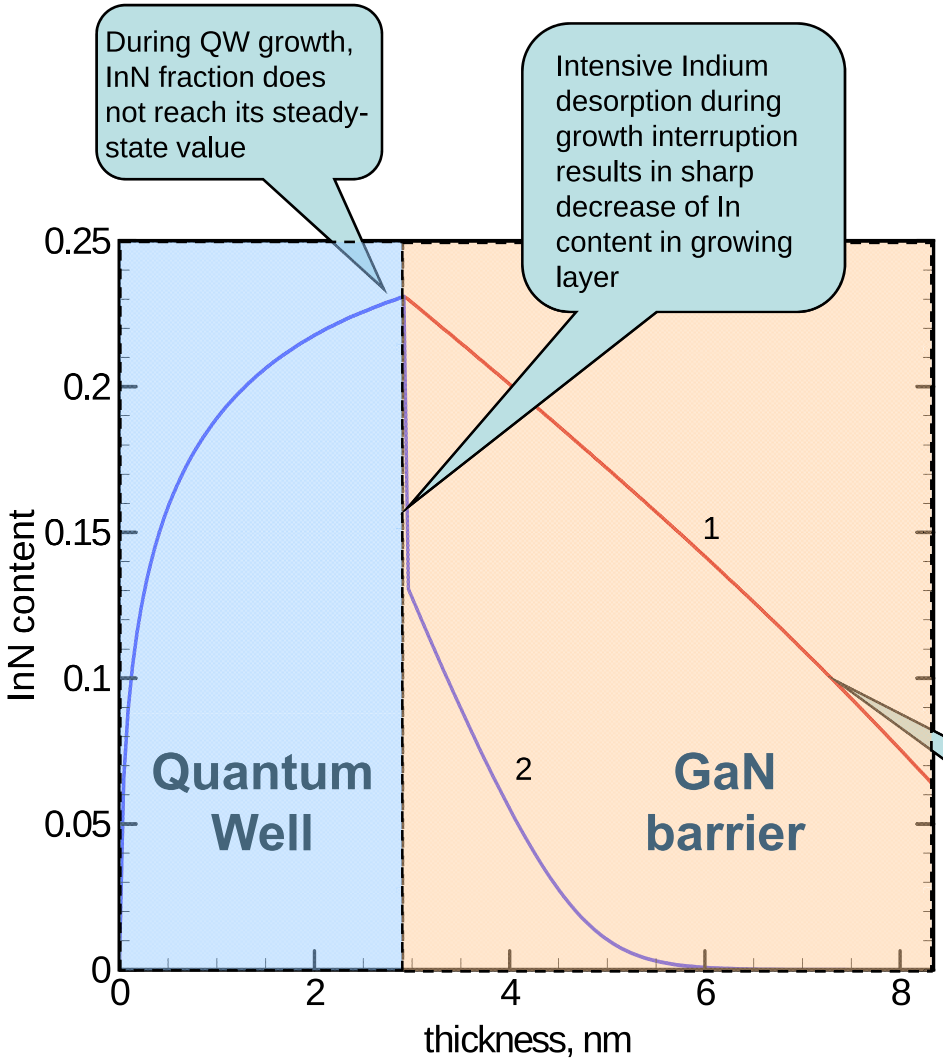
**Typical layer structures of state-of-the-art InGaN-based visible LEDs**



**Nominal structure, which can be projected from the steady-state calibration of the precursor flow rates**



# Composition profiles in QW, barrier, and EBL in blue SQW heterostructure grown under various conditions



During QW growth, InN fraction does not reach its steady-state value

Intensive Indium desorption during growth interruption results in sharp decrease of In content in growing layer

In fraction exhibits the presence of indium (In "tail") in the barrier

**Recipes simulated in growth of Single Quantum Well structure**

**1 - QW and barrier are grown at constant temperature, T=750°C: QW(750)/GaN(750)**

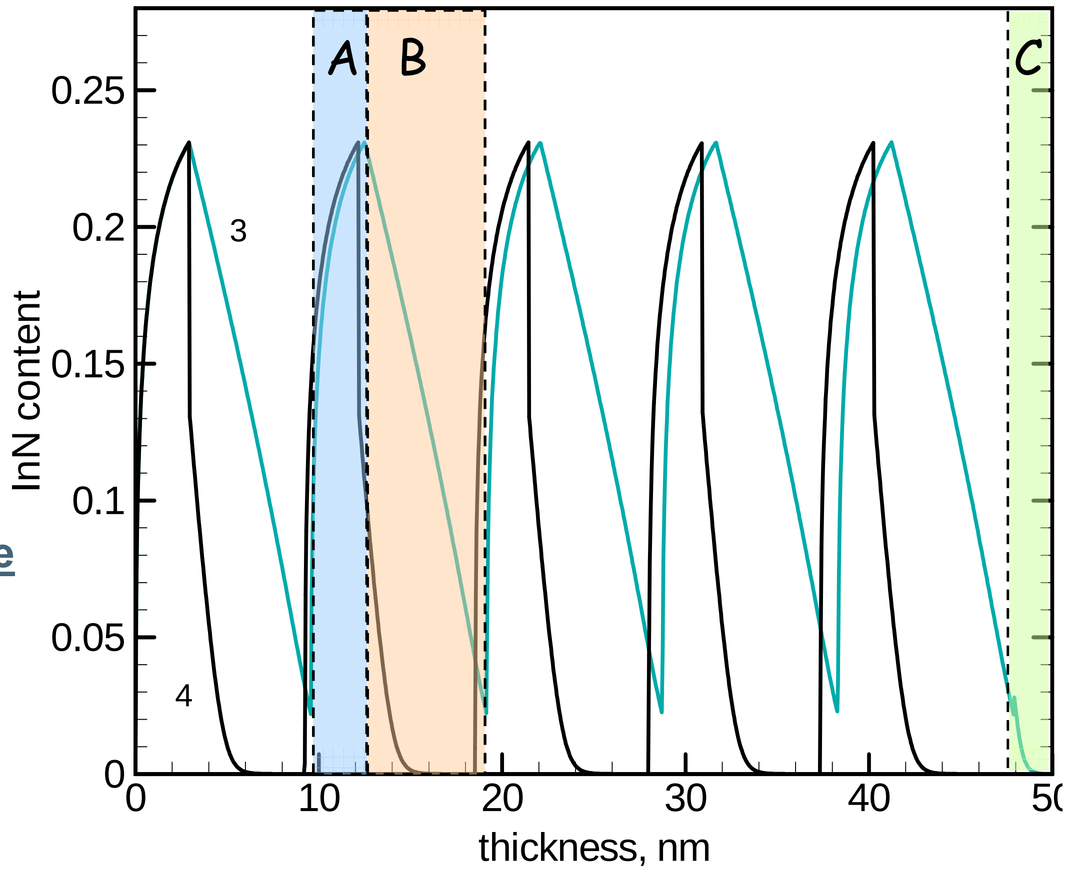
**2 - QW growth followed by interruption (GI) and next by barrier growth. QW is grown at 750°C. Temperature was ramped from 750°C up to 800°C during 30s. Barrier was grown at 800°C: QW(750)/GI/GaN(800)**

## Blue SQW LED

# Composition profiles in QW, barrier, and EBL in blue MQW heterostructures grown under various conditions

## Blue MQW LED

A- Quantum Well, B – GaN Barrier, C – AlGaN EBL

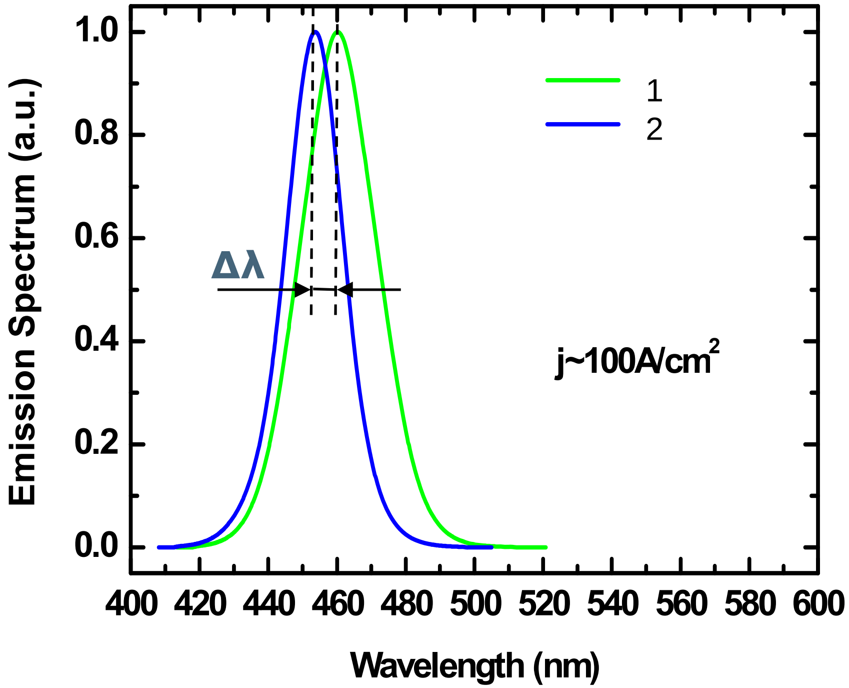


**Recipes simulated in growth of Single Quantum Well structure**

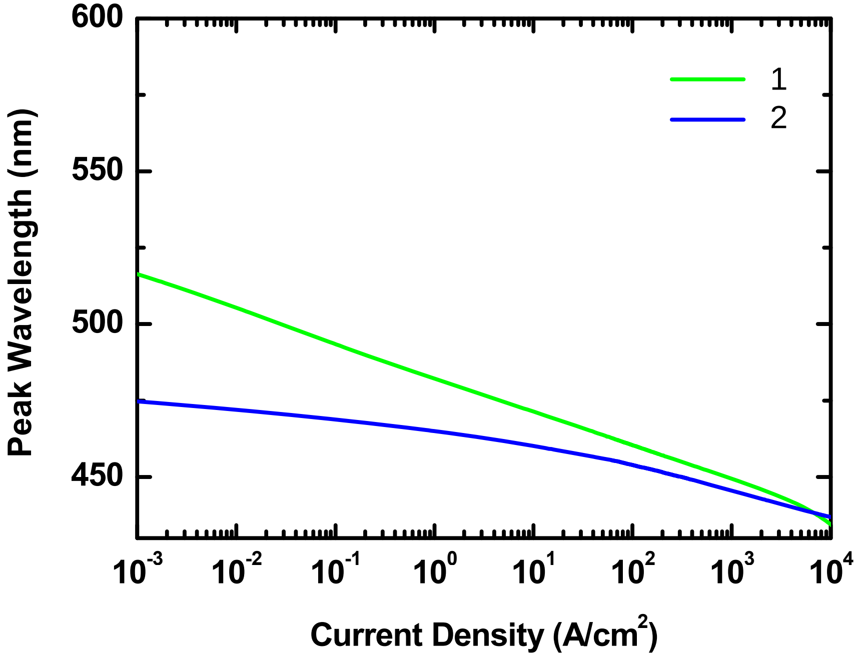
**3 – [QW(750)/GaN(750)]x5/AlGaN**

**4 – [QW(750)/GI/GaN]x5/AlGaN**

# Emission spectra and peak wavelength of SQW heterostructures grown under various conditions



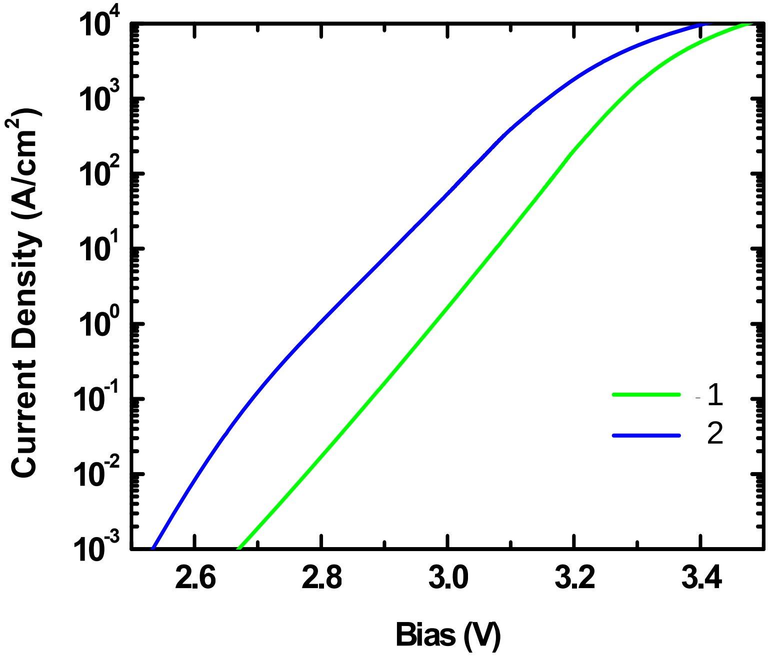
## Blue SQW LED

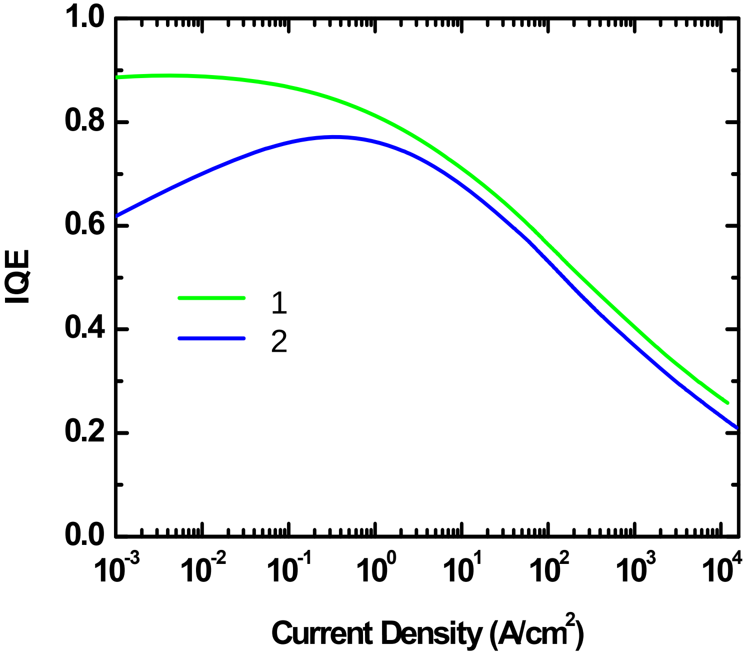


In comparison with isothermal growth of QW and barrier (1), the recipe with growth interruption followed by high-temperature barrier growth (2) results in some depletion of GaN barrier by Indium and as a result in a shift Δλ of dominant wavelength. Blue shift with current is suppressed

# I-V curve and Internal Quantum Efficiency of SQW heterostructures grown under various conditions

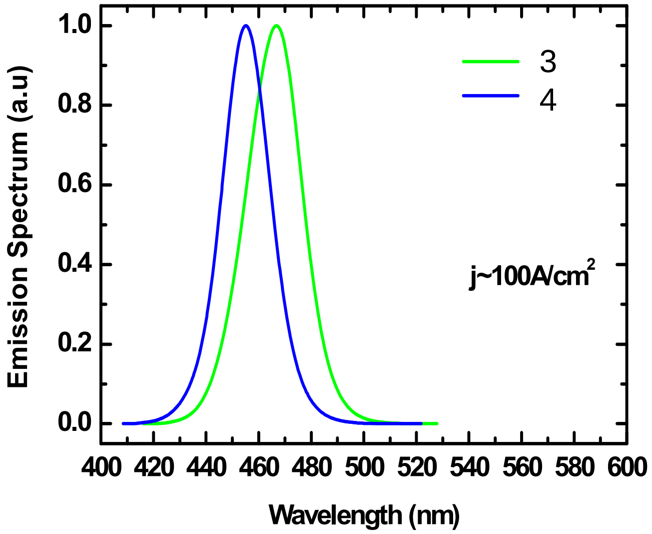
## Blue SQW LED

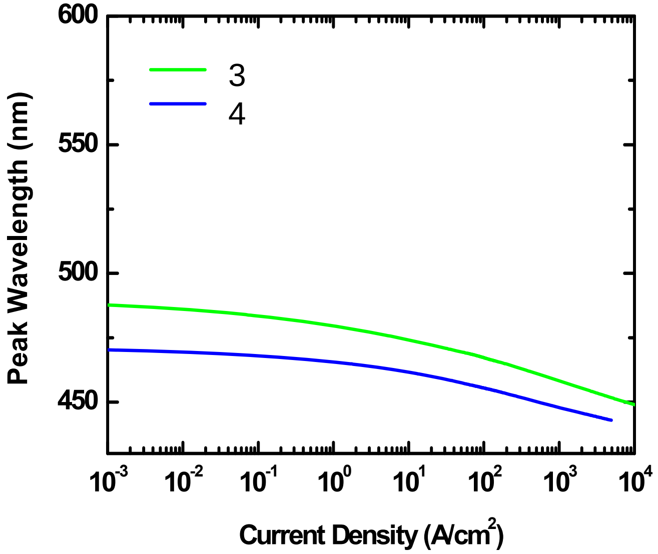




In comparison with isothermal growth of QW and barrier (1), the recipe with growth interruption followed by high-temperature barrier growth (2) results in some depletion of GaN barrier by Indium and decrease of forward voltage

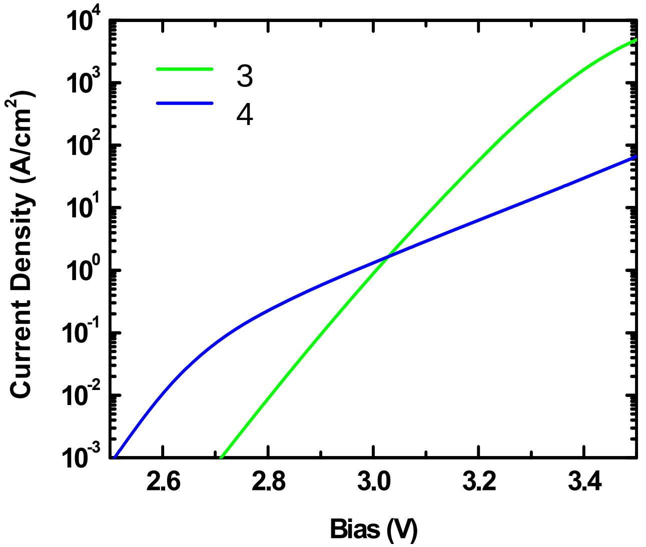
# Electrical-Optical characteristics of MQW heterostructures grown under various conditions

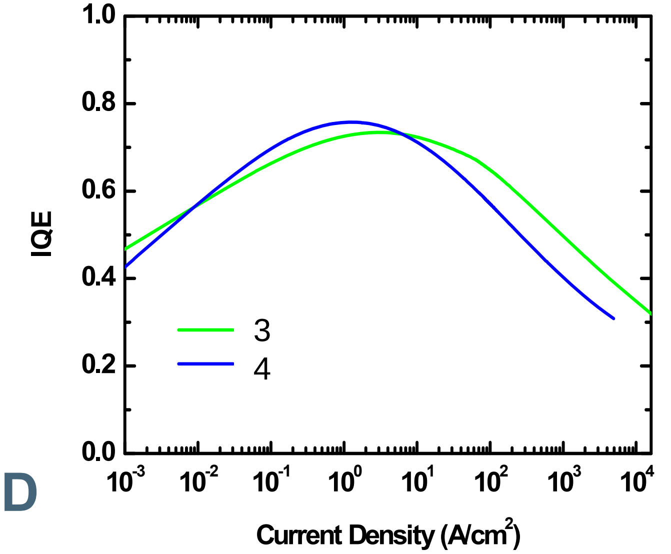




Along with position of dominant wavelength and blue shift of the emission spectrum with current, the recipe specified for growth of MQW LED has an effect on LED nonideality factor

## Blue MQW LED





**Electrical-Optical characteristics of heterostructures with the same nominal design depend on the recipe specified in MOCVD growth. In particular, Indium segregation results in:**

- **Shift of the emission spectra to longer wavelength**
- **Increased blue shift of the dominant wavelength with current**

**Simulations performed demonstrate that the detailed modeling of device structure growth, accounting for**

- **unsteady effects like surface segregation,**

**coupled with the**

- **computations of carrier transport, and**
- **light emission spectra**

**is a powerful tool for deliberate control of growth conditions and optimization of LED characteristics**

# Thank you for kind attention!