

Gas phase epitaxy

Example: AlGaInN growth by MOVPE

Michał Leszczyński

*Instytut Wysokich Ciśnień PAN
and TopGaN*

29 March 2022

Examples of questions

How does pressure in the reactor influence the growth rate of AlGaAs?

How does total flow influence the Mg incorporation into AlGaN?

How does temperature influence formation of vacancies in InGaN?

How do growth breaks between InGaAs and GaAs influence the homogeneity of the quantum wells?

Examples of questions

How does pressure in the reactor influence the growth rate of AlGaAs?

How does total flow influence the Mg incorporation into AlGaN?

How does temperature influence formation of vacancies in InGaN?

How do growth breaks between InGaAs and GaAs influence the homogeneity of the quantum wells?

How

- pressure
- temperature
- NH₃ flow
- TEGa flow
- TMIn flow
- H₂ flow
- N₂ flow
- Growth breaks
- etc

influence the InGa_N QW properties?

Properties: chemical composition, thickness, defect concentration, optical and electrical properties. etc

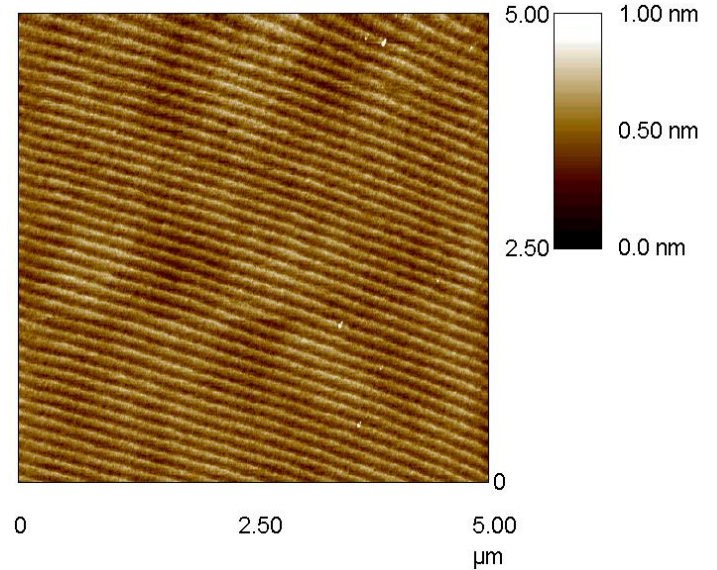
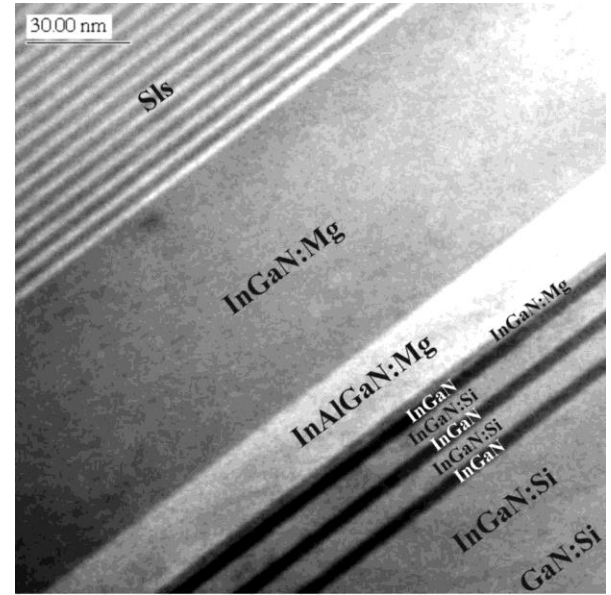
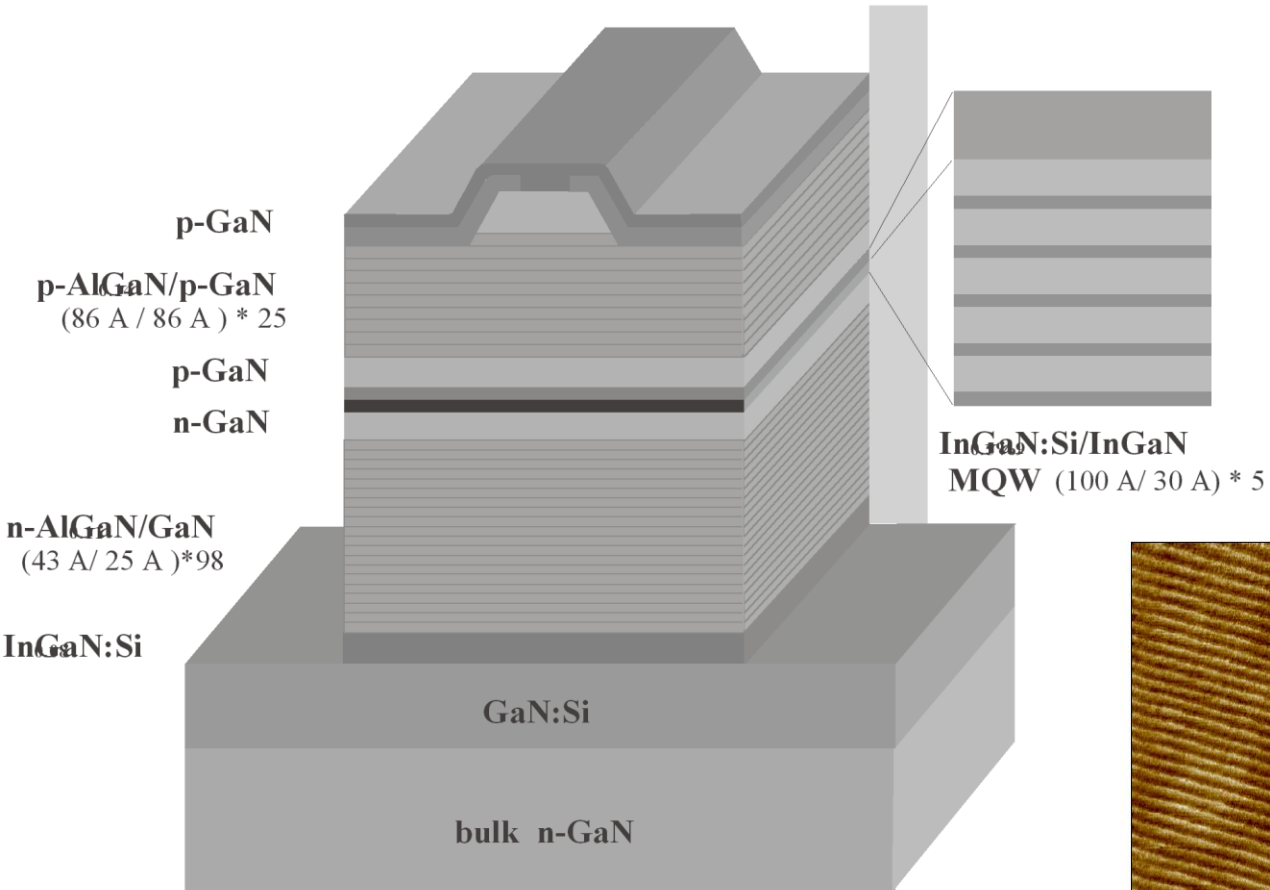
Growth parameters in MOVPE are not independent to each other.

If we wished to test all combinations for only 4 values, we would have to do 4^{10} experiments= 1 000 000

Outline

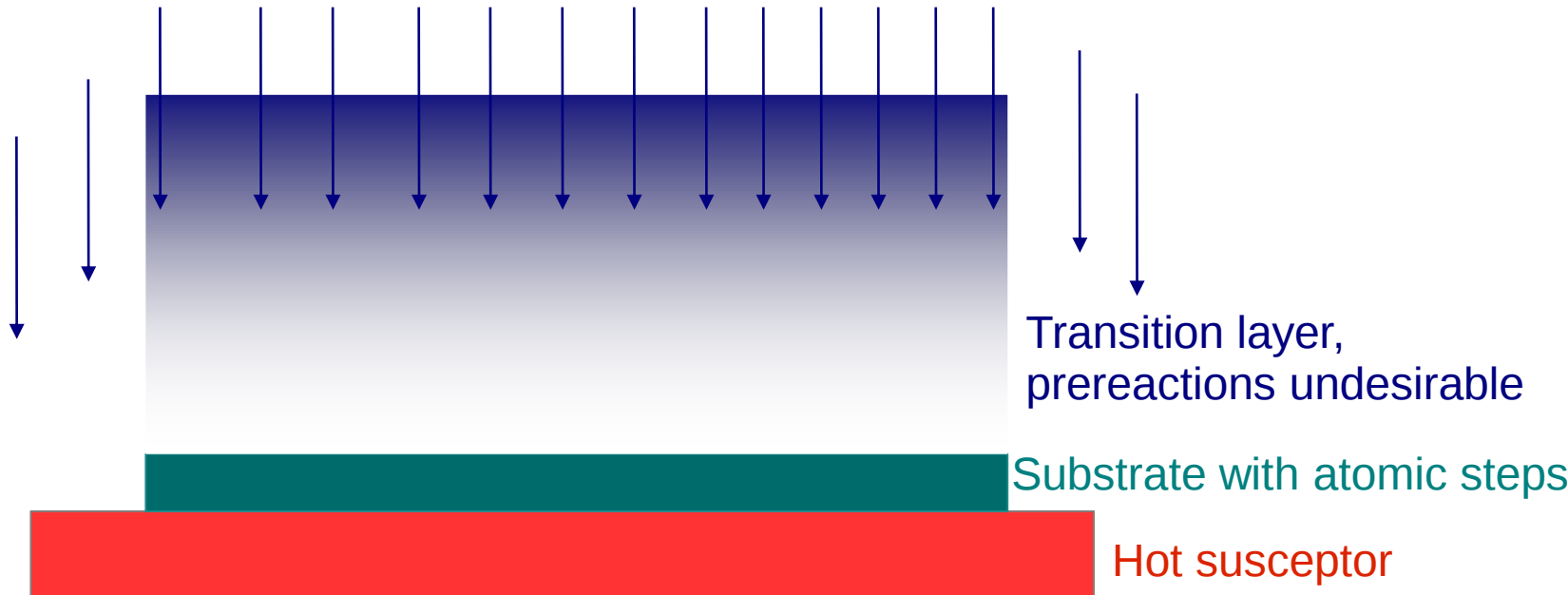
- 1. Effectiveness of atom incorporation into GaN, AlGaN, InGaN**
- 2. Example of influence of hydrogen on InGaN growth**
- 3. Examples of how properties of the epi layers can be modified by growth of other layers.**

What do we wish to grow? For example, laser diode epi structure.



MOVPE growth of nitride semiconductors

N_2 , H_2 , NH_3 , TEGa , TMGa , TMAI , TMIIn , SiH_4 , Cp_2Mg

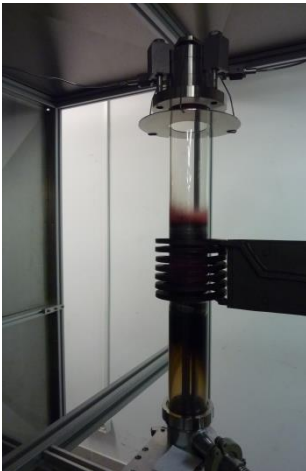


As a result, we have a layer which has certain:

- * chemical composition
- * thickness
- * morphology
- * uniformity

1. Effectiveness of atom incorporation into GaN, AlGaIn, InGaIn

MOVPE reactors used



Home made (HM)
2000 growth runs

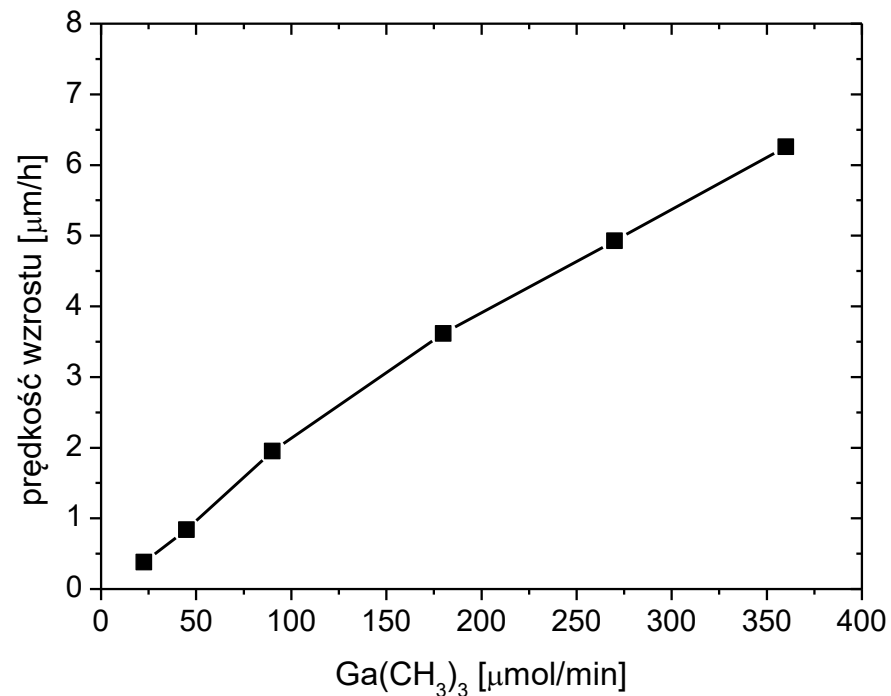
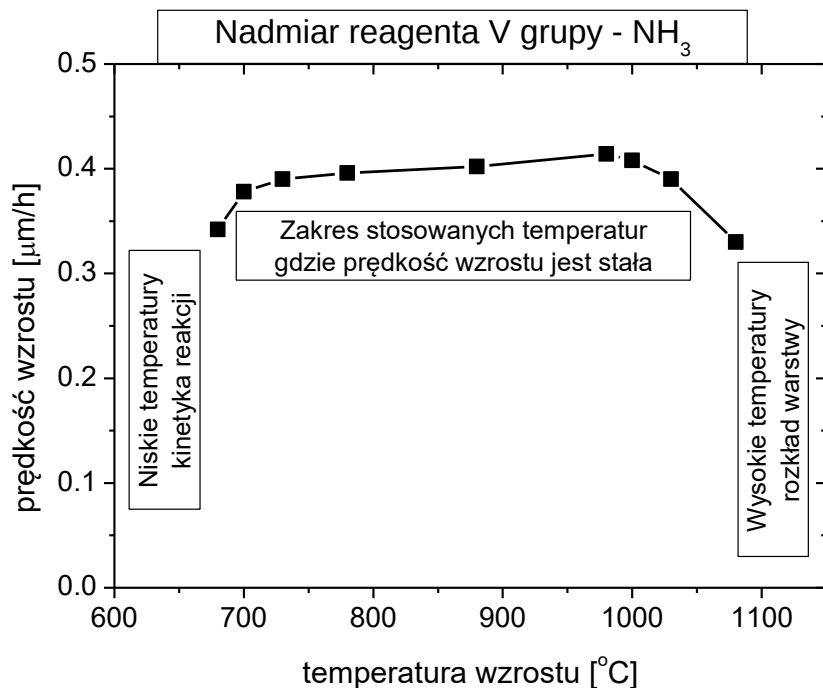


CCS Aixtron
4000 growth runs



High Pressure (HP)
200 growth runs

Effectiveness of Ga incorporation into GaN vs temperature and TMGa flow in HM



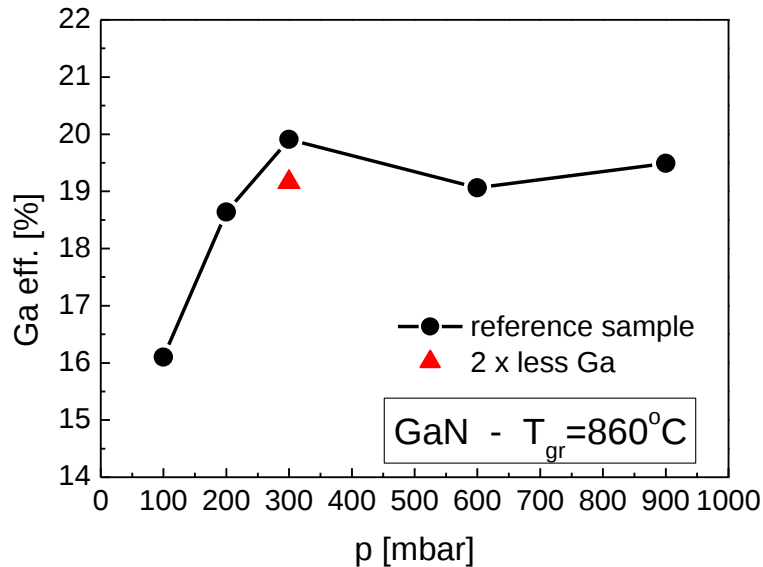
Growth rate proportional to TMGa or TEGa flow

Low temperature – low ammonia decomposition

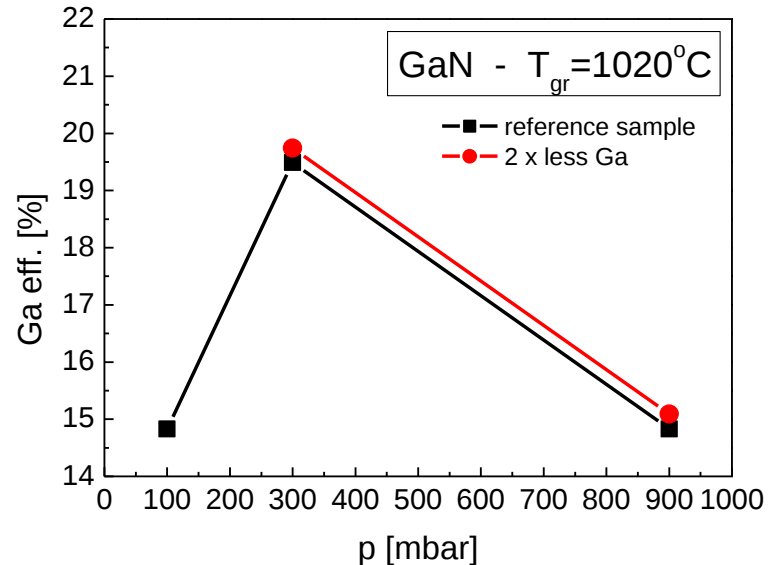
High temperature- decomposition

Effectiveness of Ga incorporation into GaN vs pressure

Efficiency= number of atoms incorporated into the epi layer/ number of atoms in gas phase



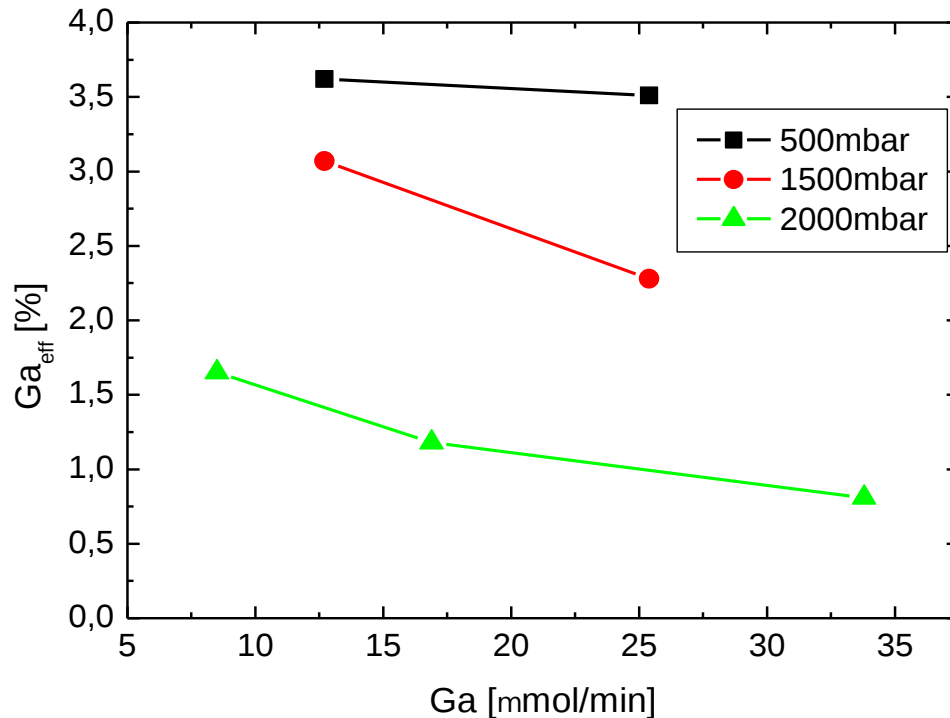
At low pressure, the Ga atoms are blown away from the surface.



At high pressure and temperature, the rate of prereactions increase which prevents Ga incorporation

Efficiency of Ga incorporation independent on amount of TEGa

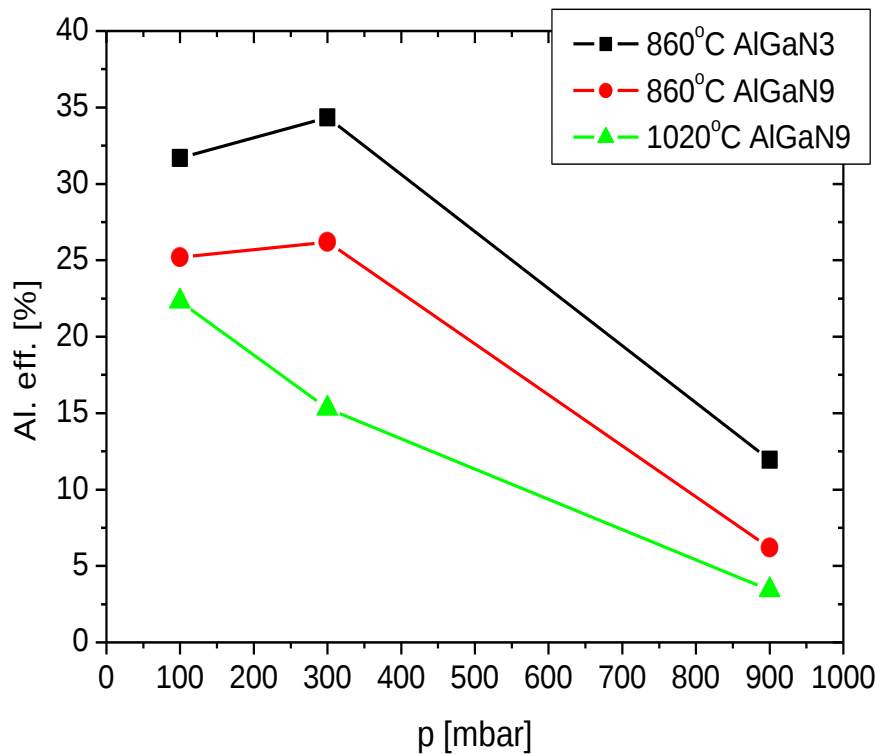
Efficiency of Ga incorporation into GaN in HP



Much lower efficiencies of Ga incorporation than in HM and CCS

At high pressure, prereactions lower the Ga-incorporation efficiency

Efficiency of Al incorporation into AlGa_N in HM



Efficiency of Al incorporation falls down with TMAI flow increase

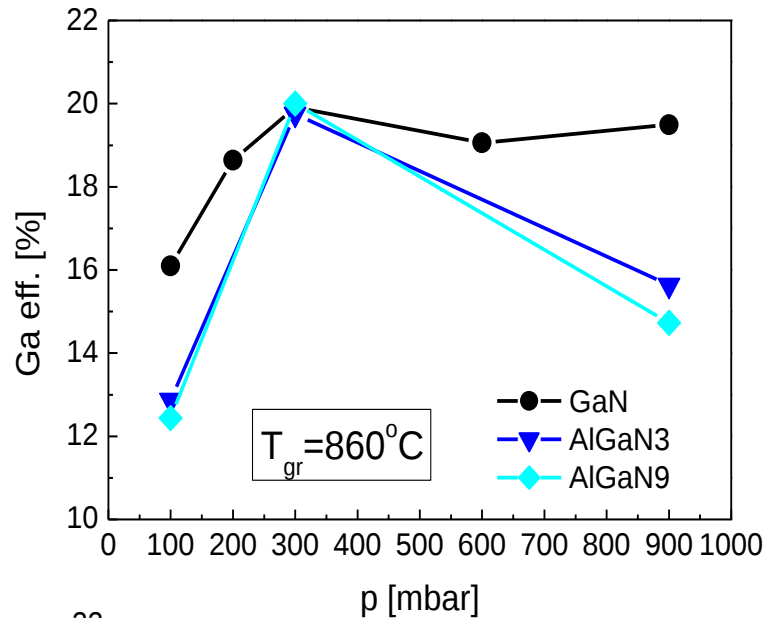
Prereactions rate higher than in the case of GaN

More prereactions at high temperature and pressure

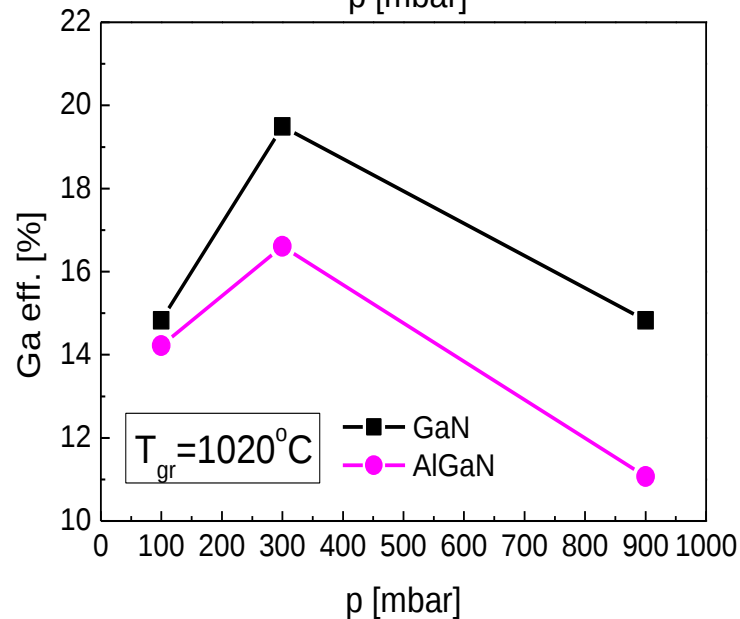
3 sccm of TMAI

9 sccm of TMAI

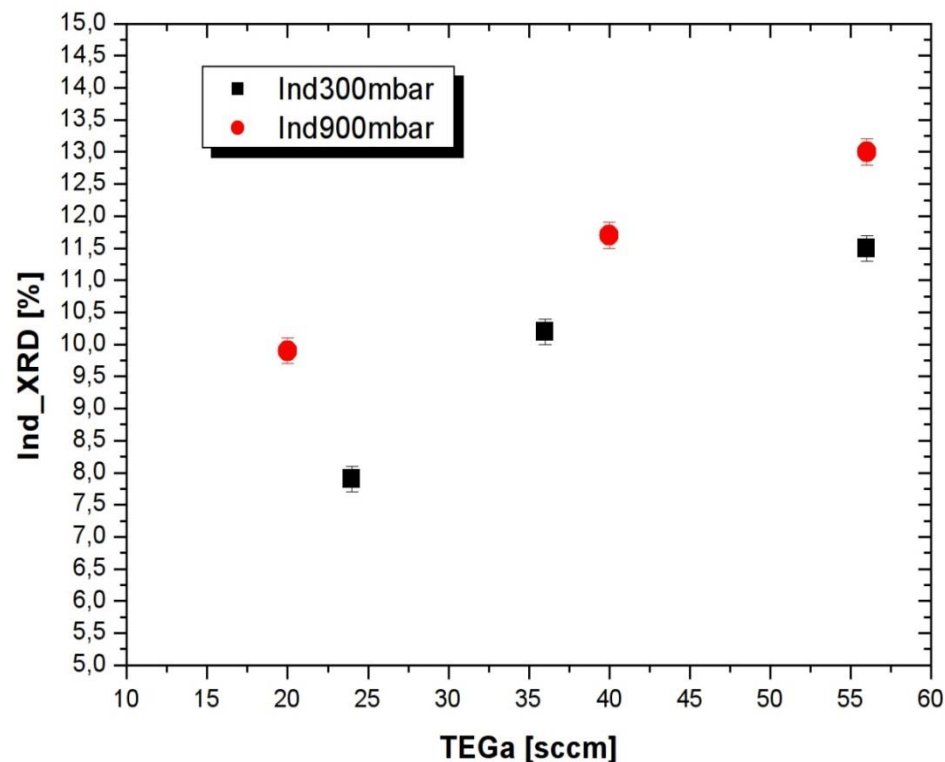
Efficiency of Ga incorporation into AlGaN in HM



Prereacted TMAI and NH₃ molecules block Ga incorporation



Efficiency of In incorporation into InGaN versus TEGa (growth rate) flow in HM

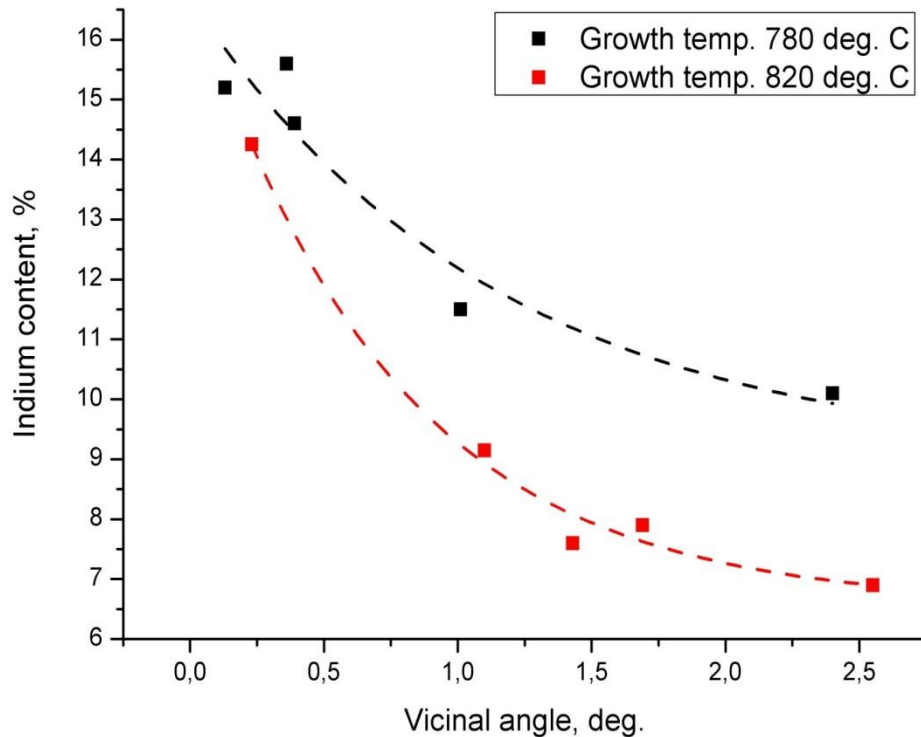


More Ga source in the gas phase,
but more In in InGaN solid phase.

More indium at elevated pressure.

In atoms to be incorporated must
be surrounded by Ga atoms

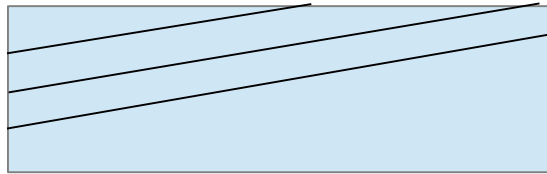
In incorporation into InGaN layers versus GaN substrate off-orientation



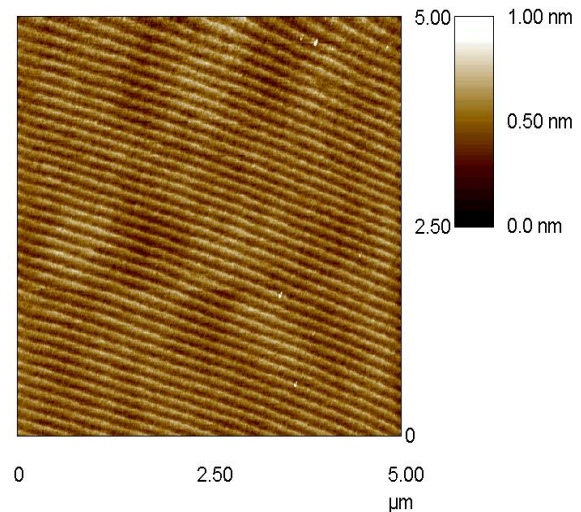
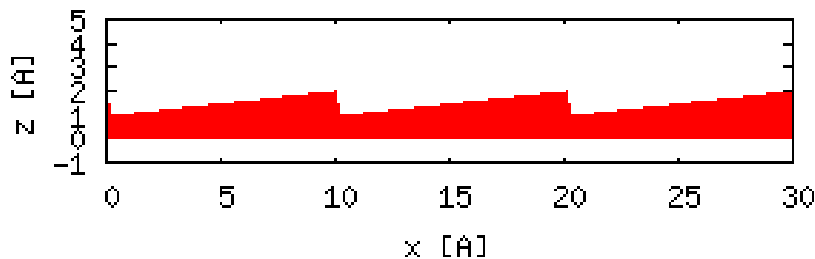
If we have bad morphology
(steps are not identical), we
deal with In inhomogeneous
incorporation

GaN substrate off-orientation

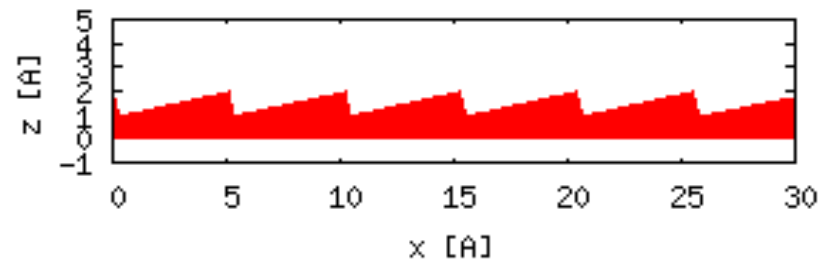
- The steps flow slower
- **Many AlGaN and InGaN parameters are strongly influenced**



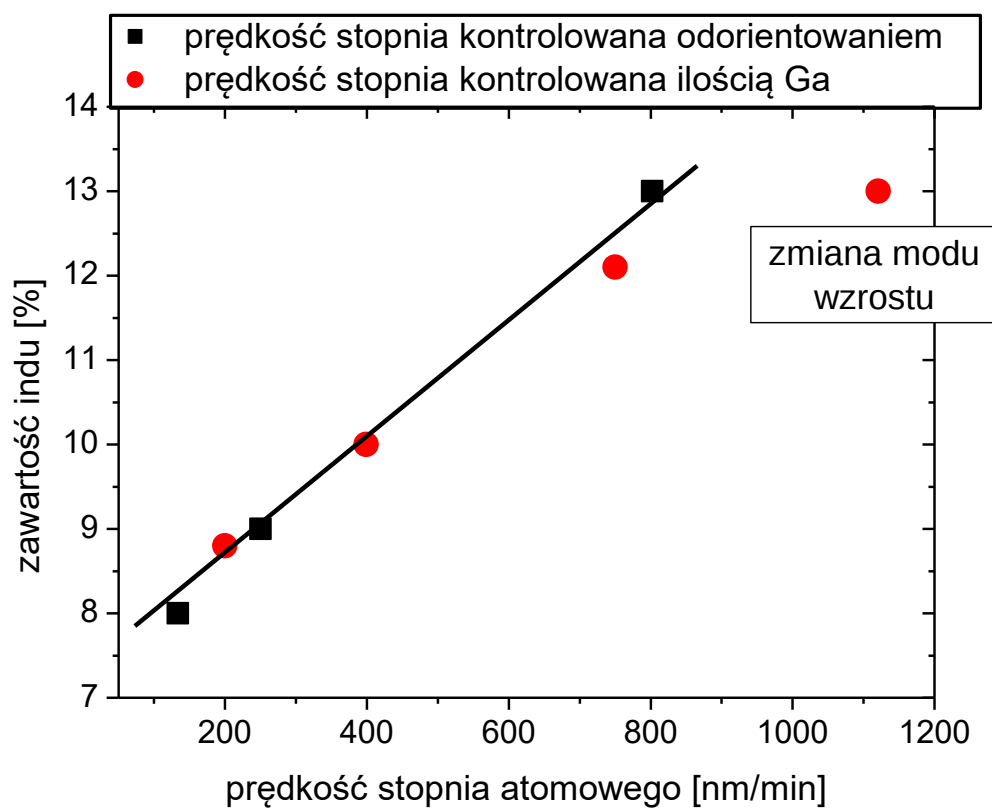
Low misorientation - fast atomic steps



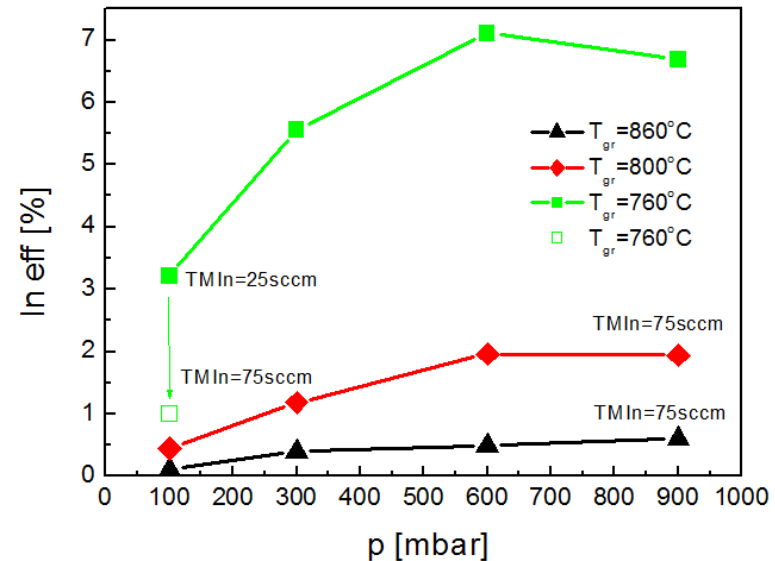
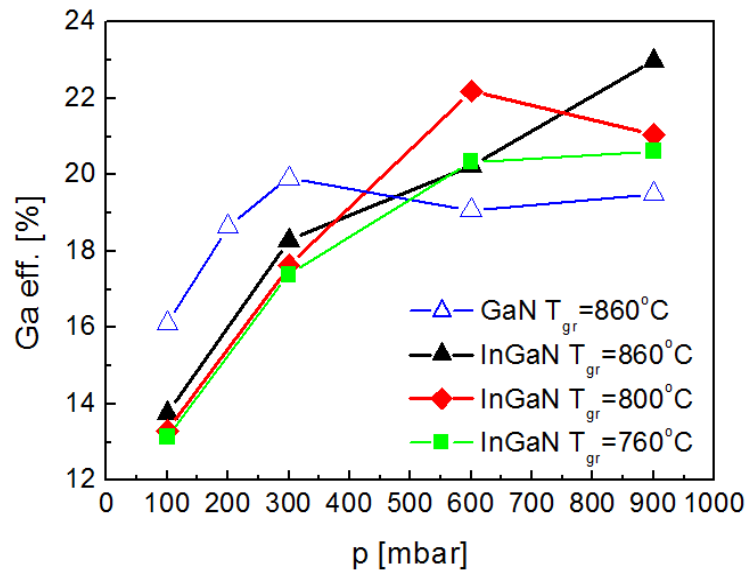
Higher misorientation - slower atomic steps



Incorporation into InGaN versus velocity of the steps in step-flow growth



Efficiency of Ga and In incorporation into InGaN in HM

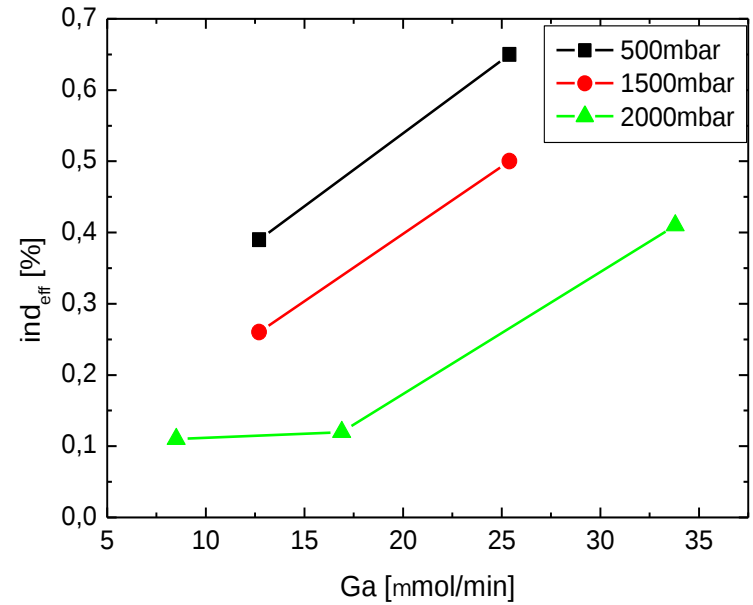
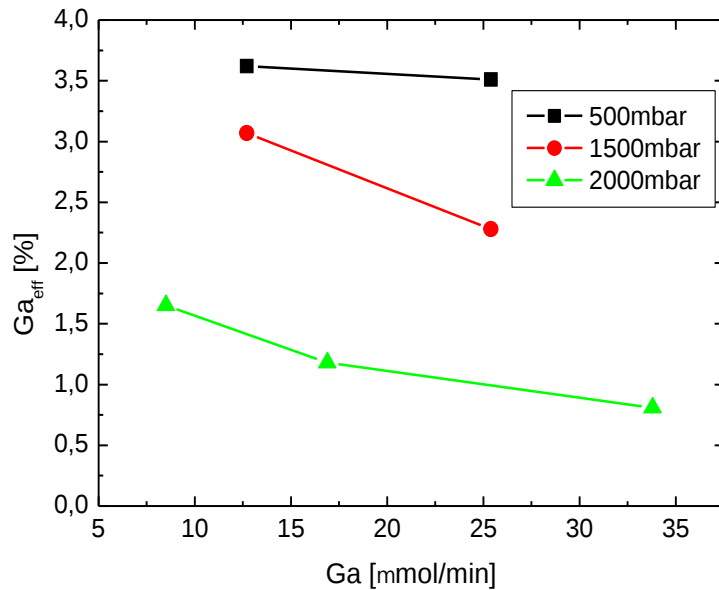


Indium increases Ga incorporation.

In incorporation efficiency increases for:

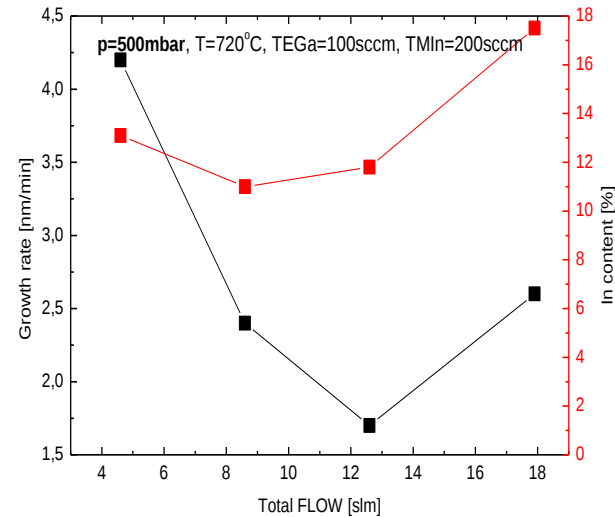
- * lower TMIn-flow
- * lower temperature
- * higher pressure (seems to be a maximum)

Efficiency of Ga and In incorporation into InGaN in HP

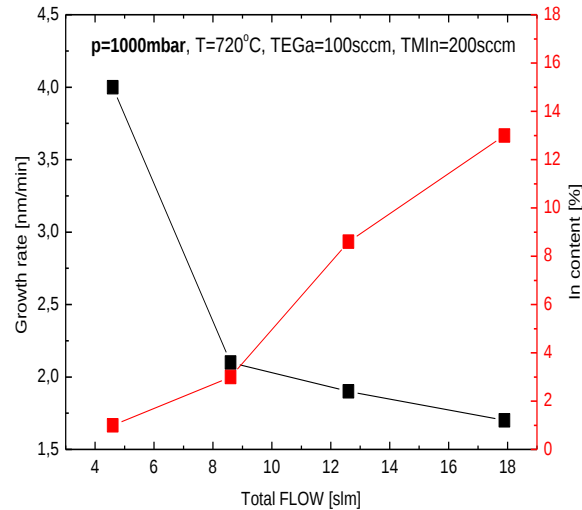


Prereactions in HP reactor- main source of troubles

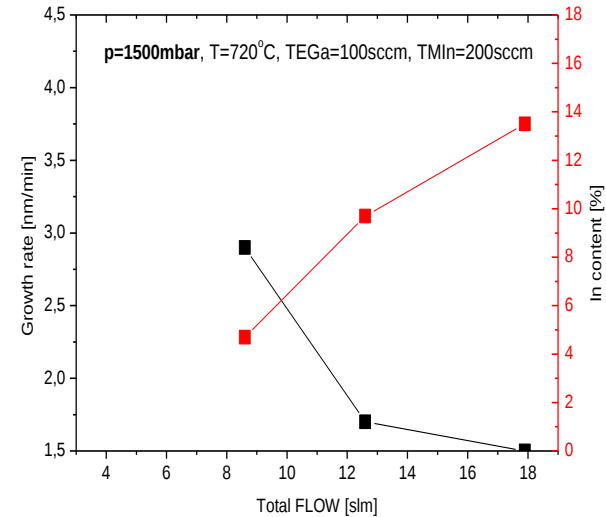
Influence of total flow on the InGaN growth rate and In incorporation in HP



500 mbar



1000 mbar

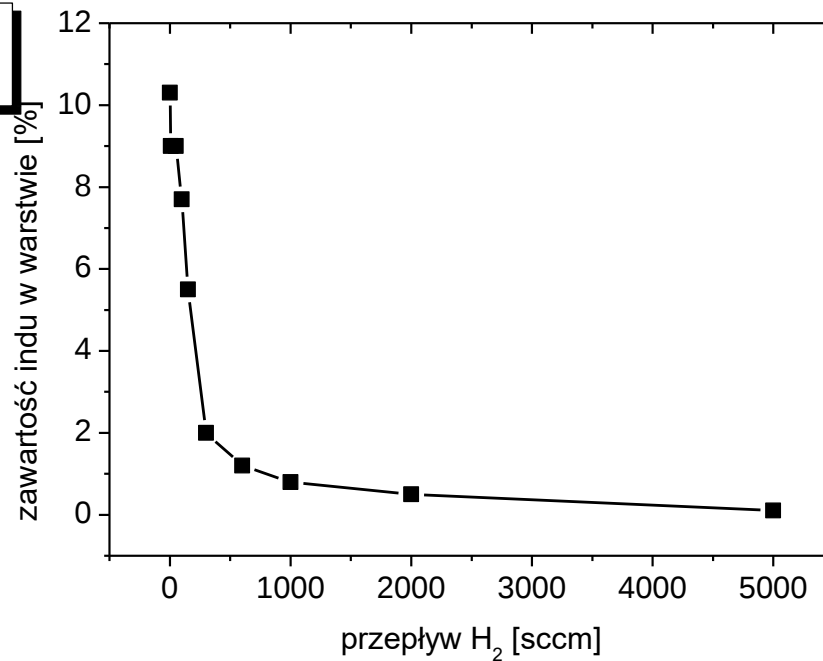
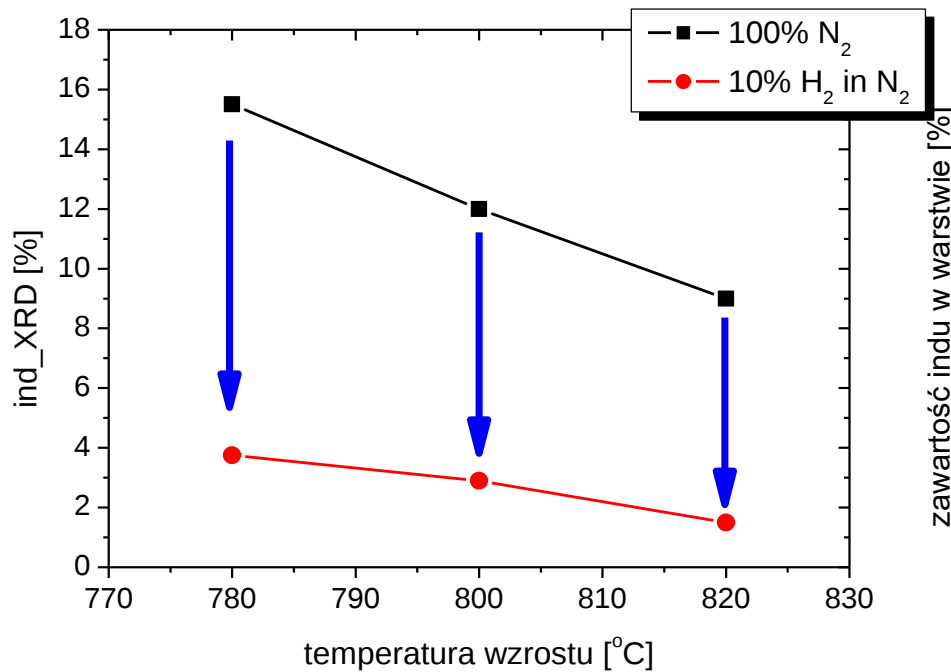


1500 mbar

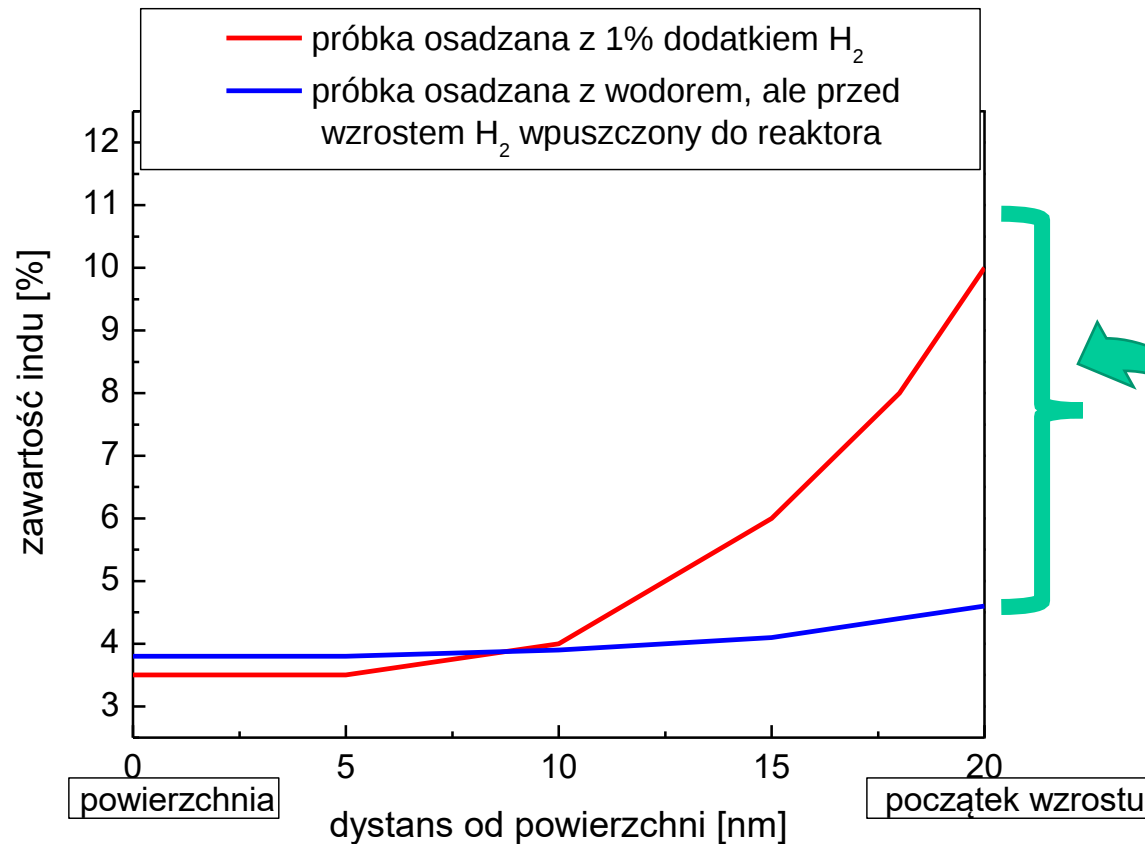
Growth rate decreases with total flow- TEGa and TMIn are blown away more efficiently

In content increases. Lower real temperature? Different NH₃/NH₂ on the surface? Lower prereaction rate?

Influence of hydrogen used in the carrier gas



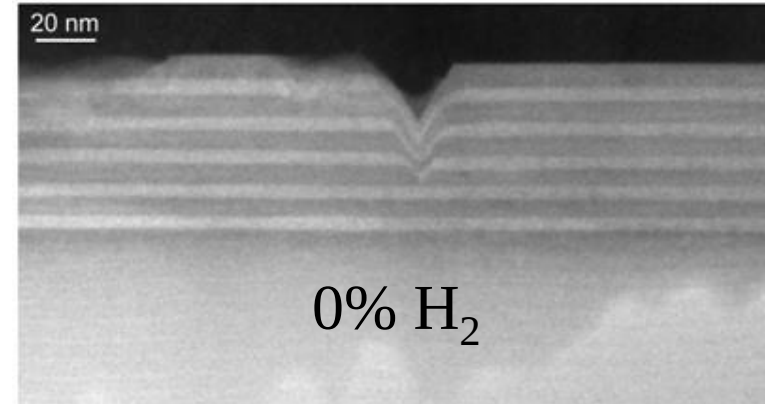
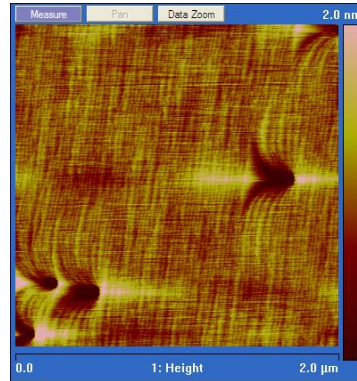
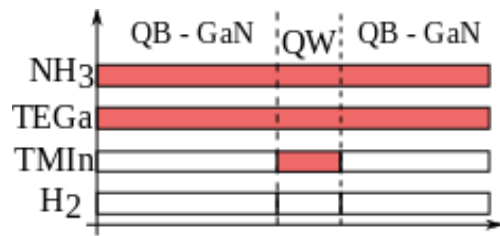
Gradient of In content in InGaN layers grown with H₂ in the carrier gas



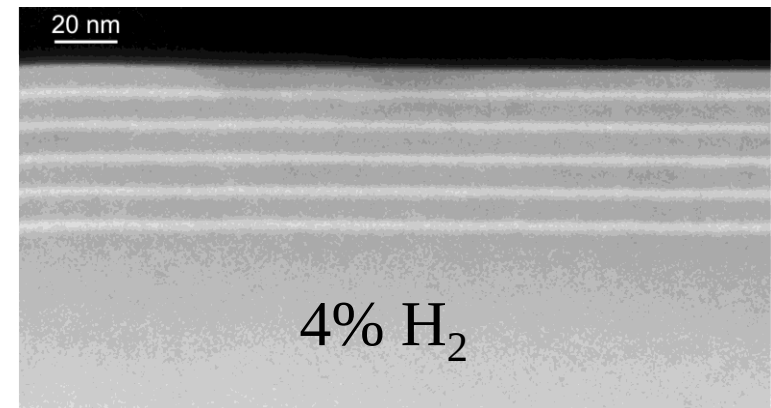
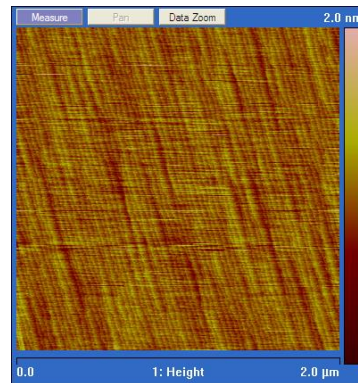
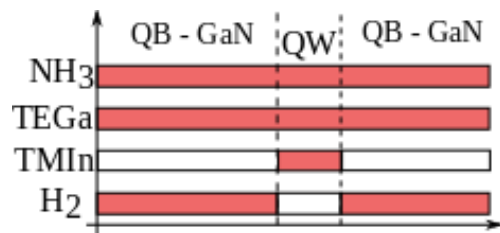
Hydrogen passivates the surface and In is not incorporated

Growth of InGaN QWs with QBs grown with hydrogen

QB w/o H_2

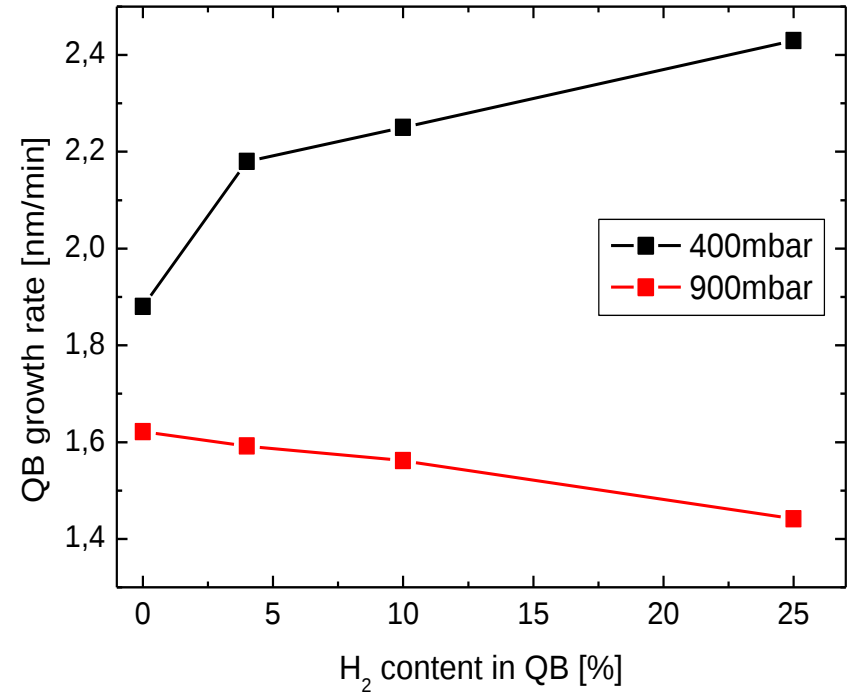
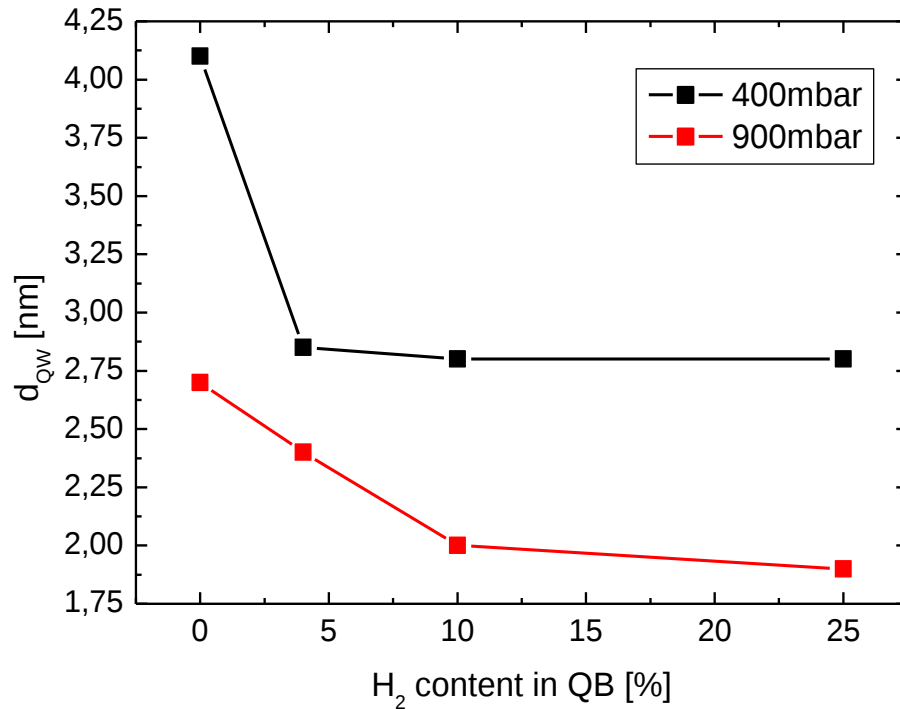


QB w H_2



Hydrogen eliminates defects but influences also the QWs

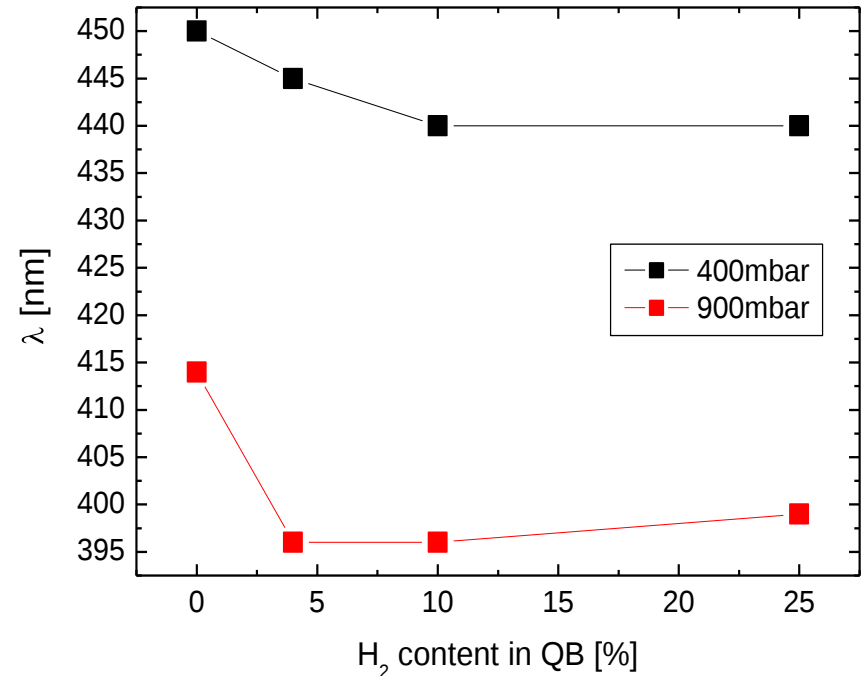
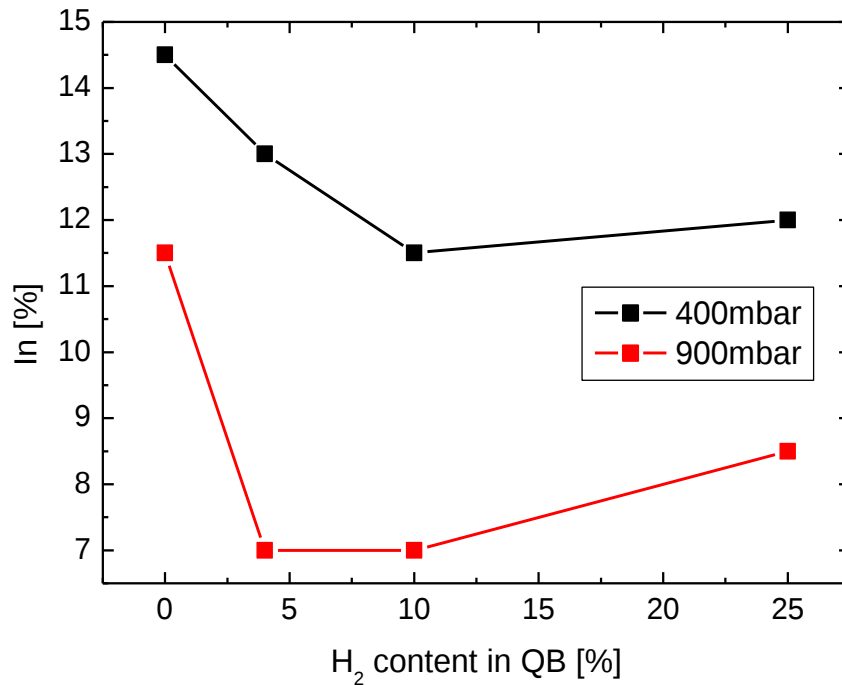
Influence of hydrogen used in the carrier gas during GaN barrier growth in CCS



Hydrogen used in QB growth etches off InGaN QW more efficiently at high pressure

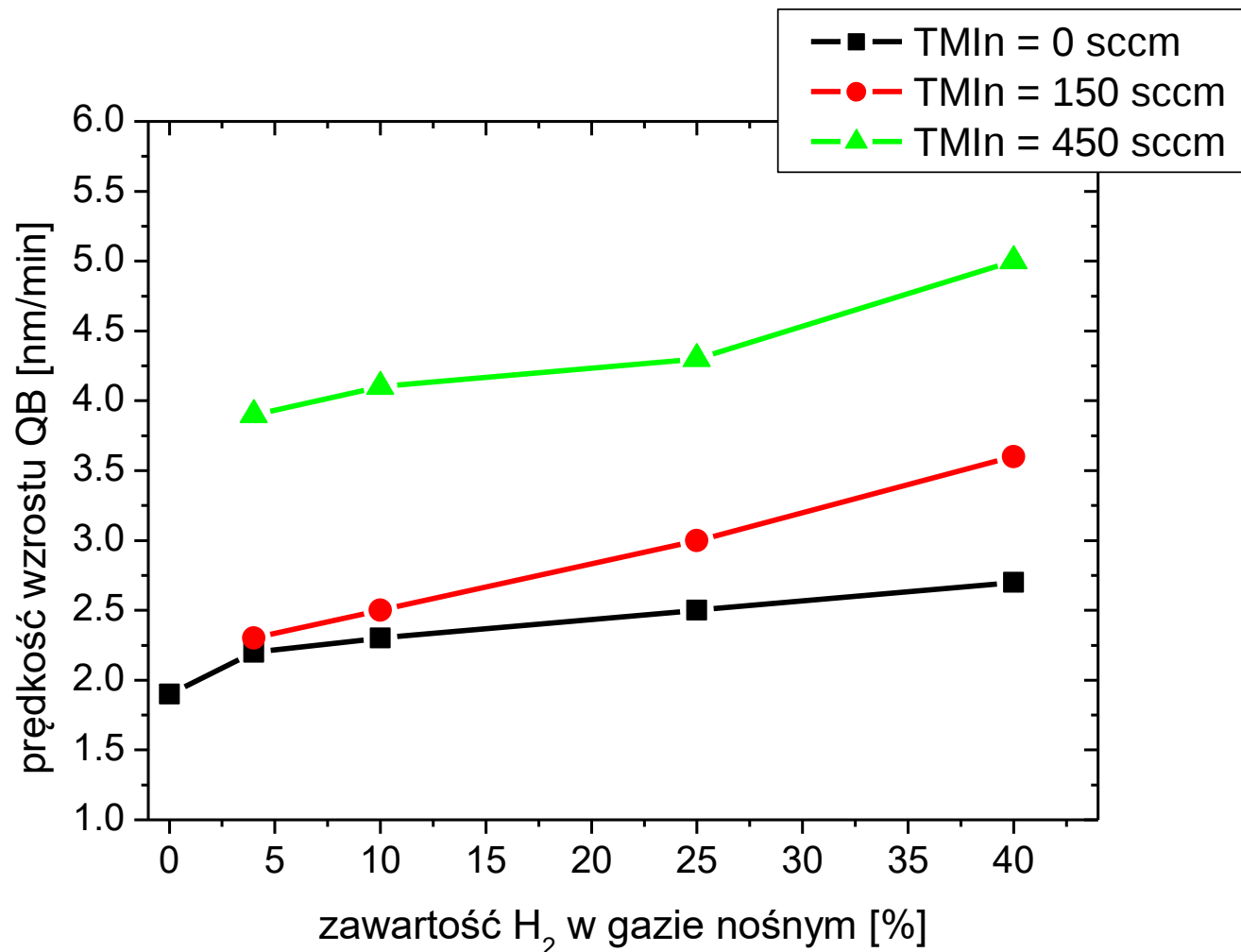
Hydrogen increases the growth rate of GaN (QB) at low pressure (???), decreases at higher pressure.

Influence of hydrogen used in the carrier gas during GaN barrier growth in CCS



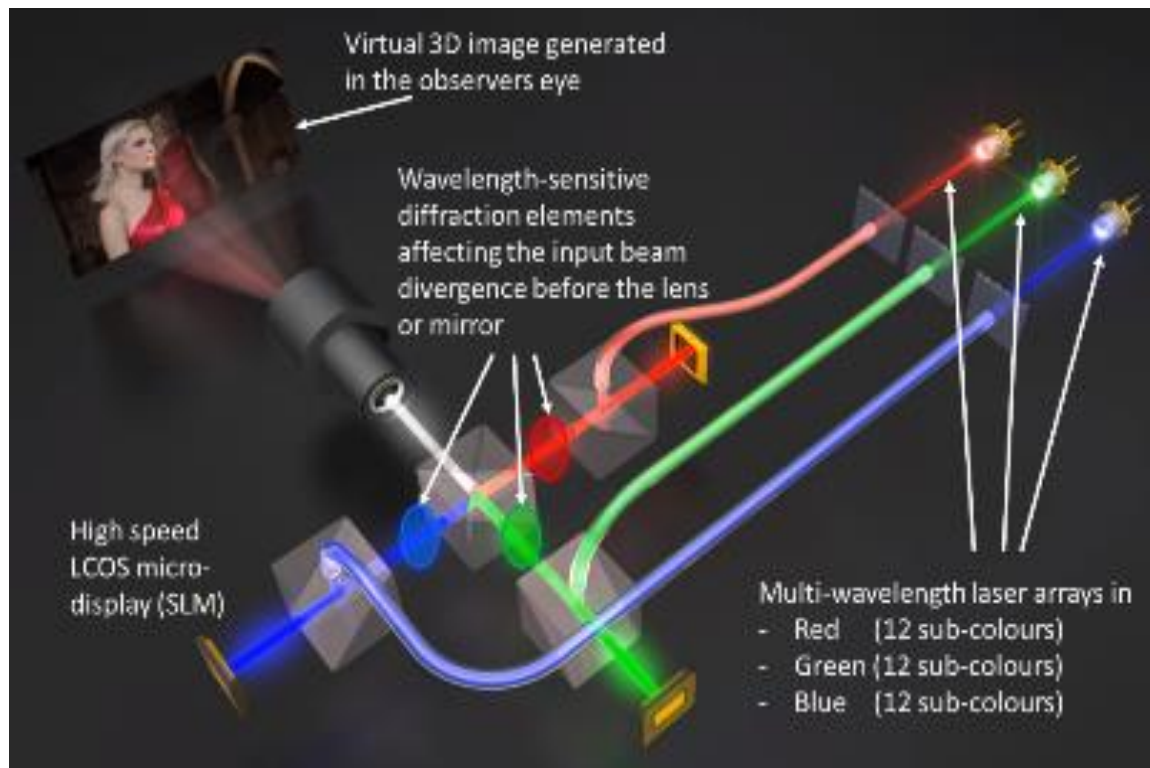
Hydrogen used in QB growth etches In off InGaN QW more efficiently at high pressure

Influence of hydrogen and H₂ on Ga incorporation



Effectivness of Ga incorporation in CCS

3-D Projectors without goggles- Holy Grail of optoelectronics



Nitrides:

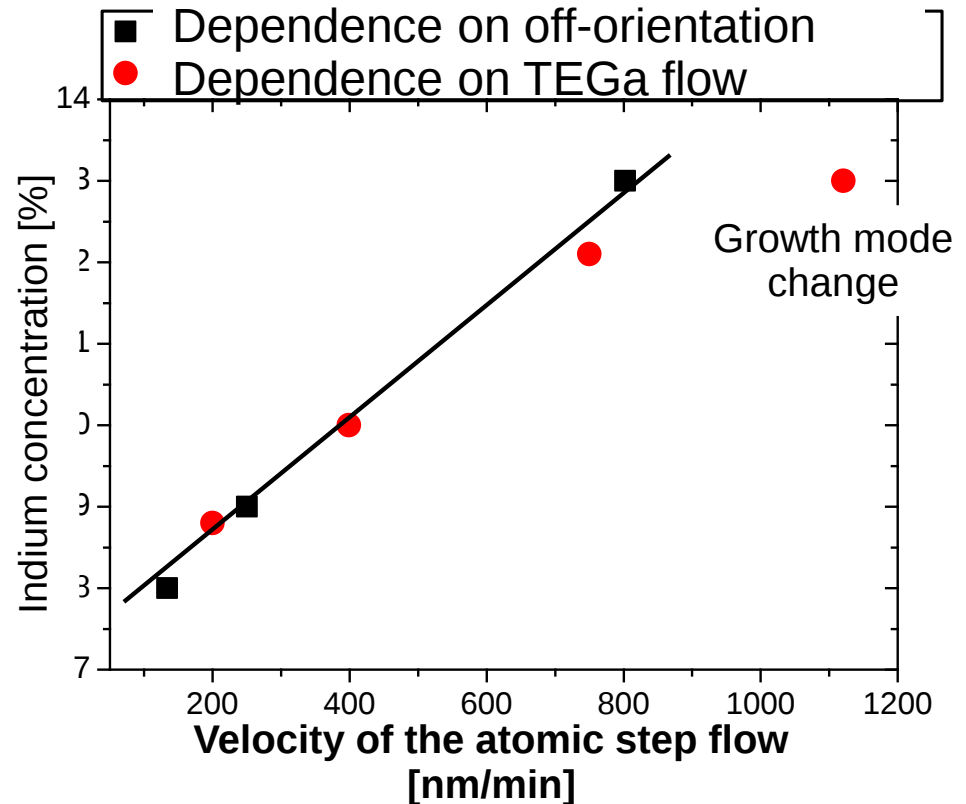
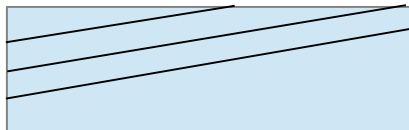
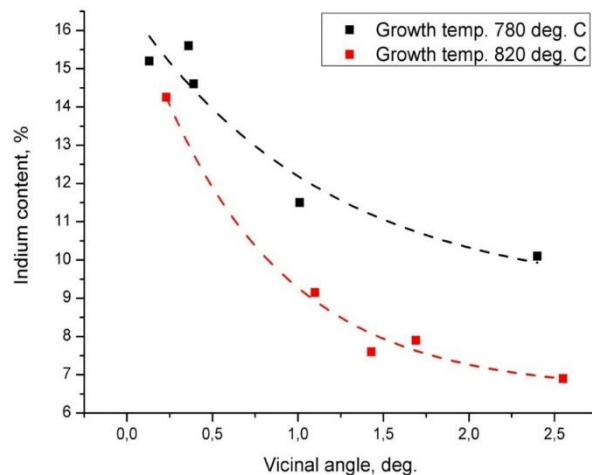
Blue 450-460 nm,
step 1 nm

Green 520-530 nm,
step 1 nm

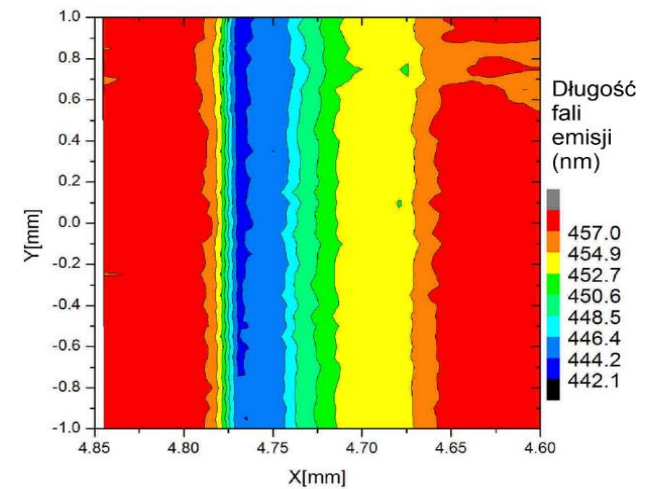
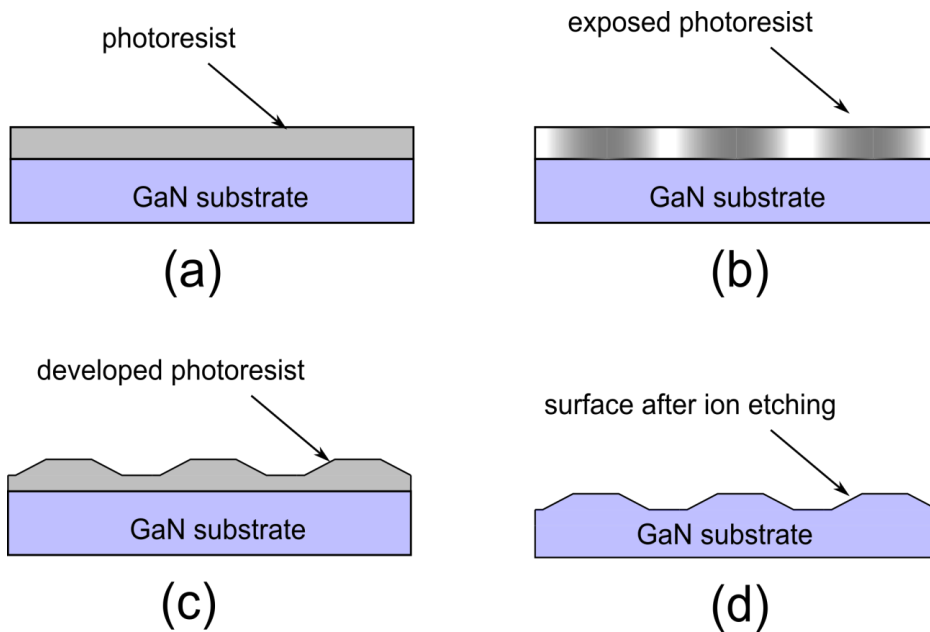
Arsenides/phosphides

Red 630-640 nm,
step 1 nm

In incorporation into InGaN layers versus GaN substrate off-orientation or growth rate

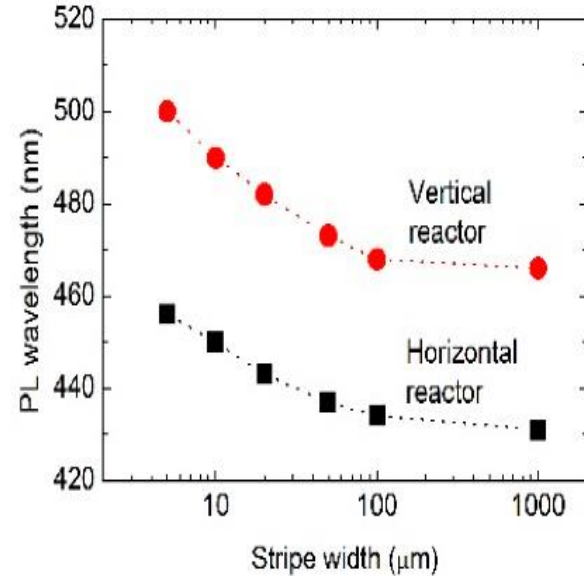
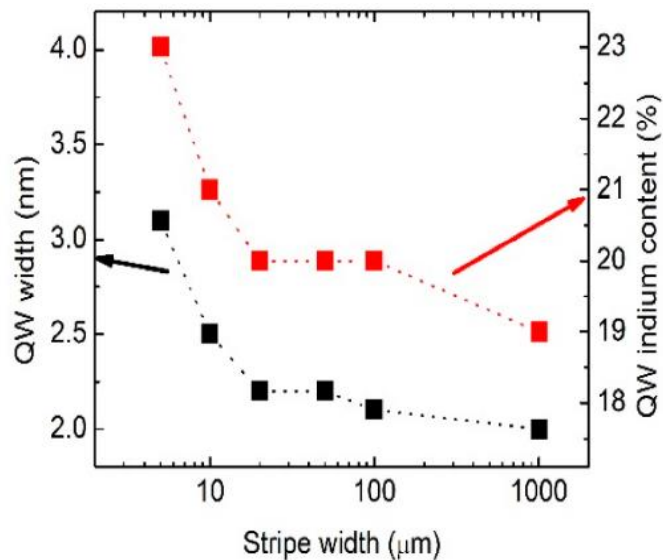
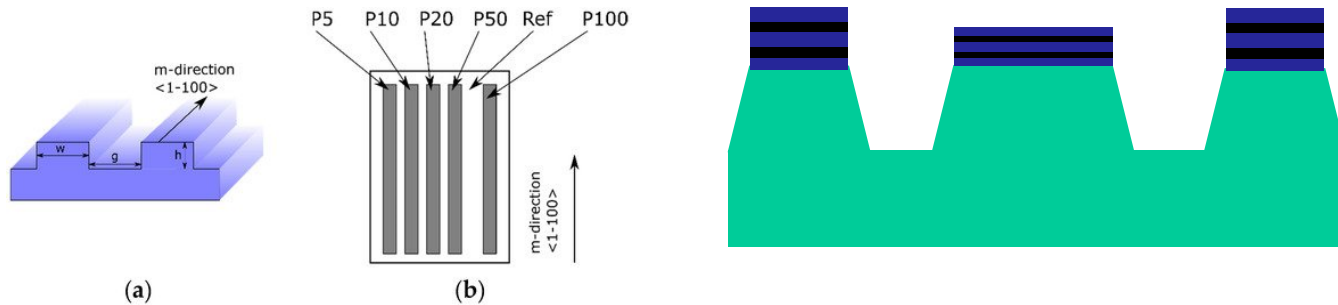


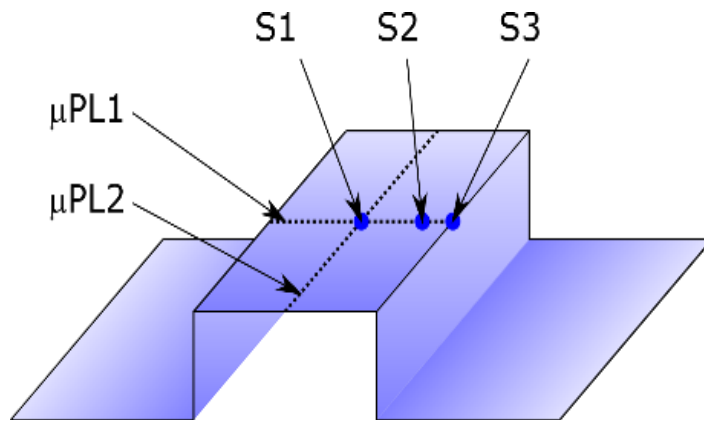
Technology 1: Lateral patterning



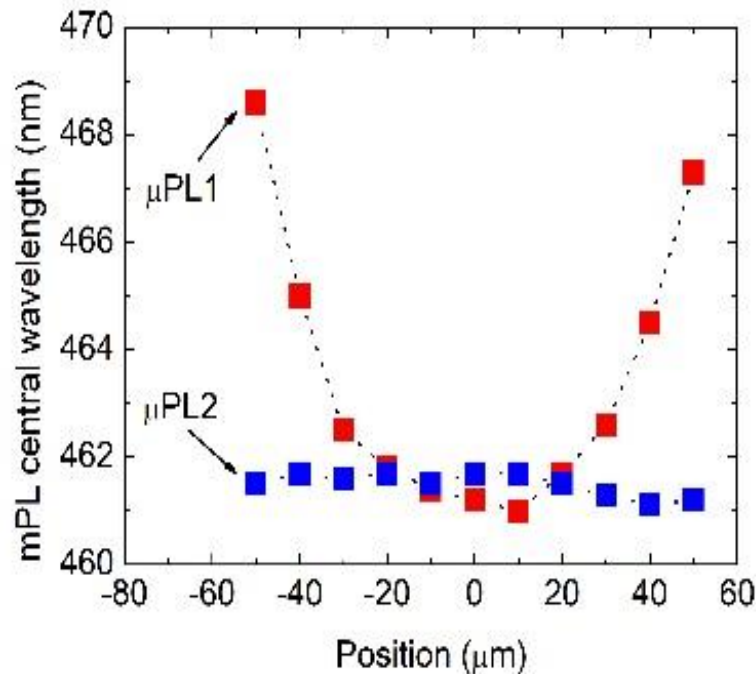
M. Sarzynski idea
Patented by TopGaN/Unipress

Technology 2. Growth of InGaN QWs on narrow stripes.





Faster growth at the edges, more indium incorporated

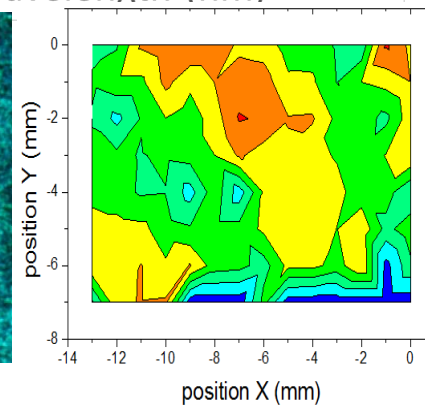
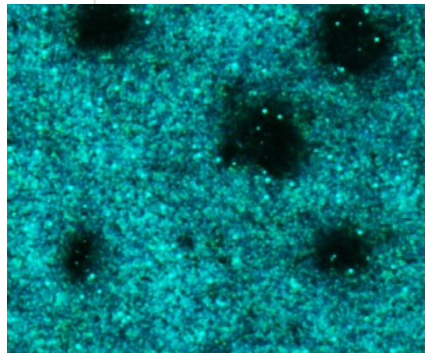
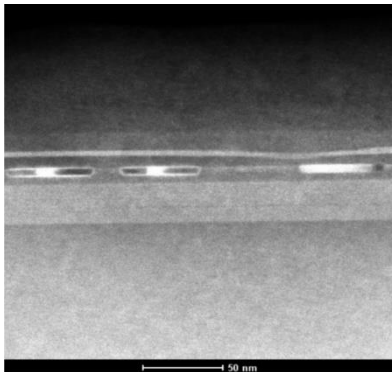
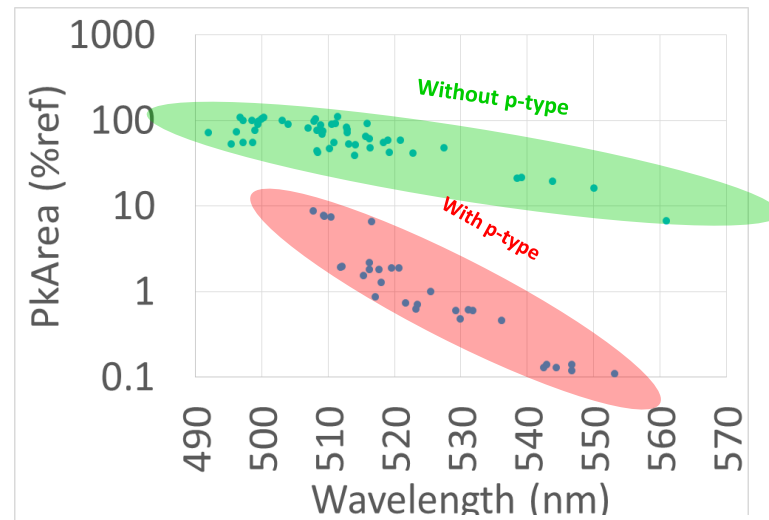


Both technology 1 and 2 of blue multicolour arrays attract a big interest as they may lead to 3D projectors.

Decomposition and homogenization of InGaN QWs at high temperature

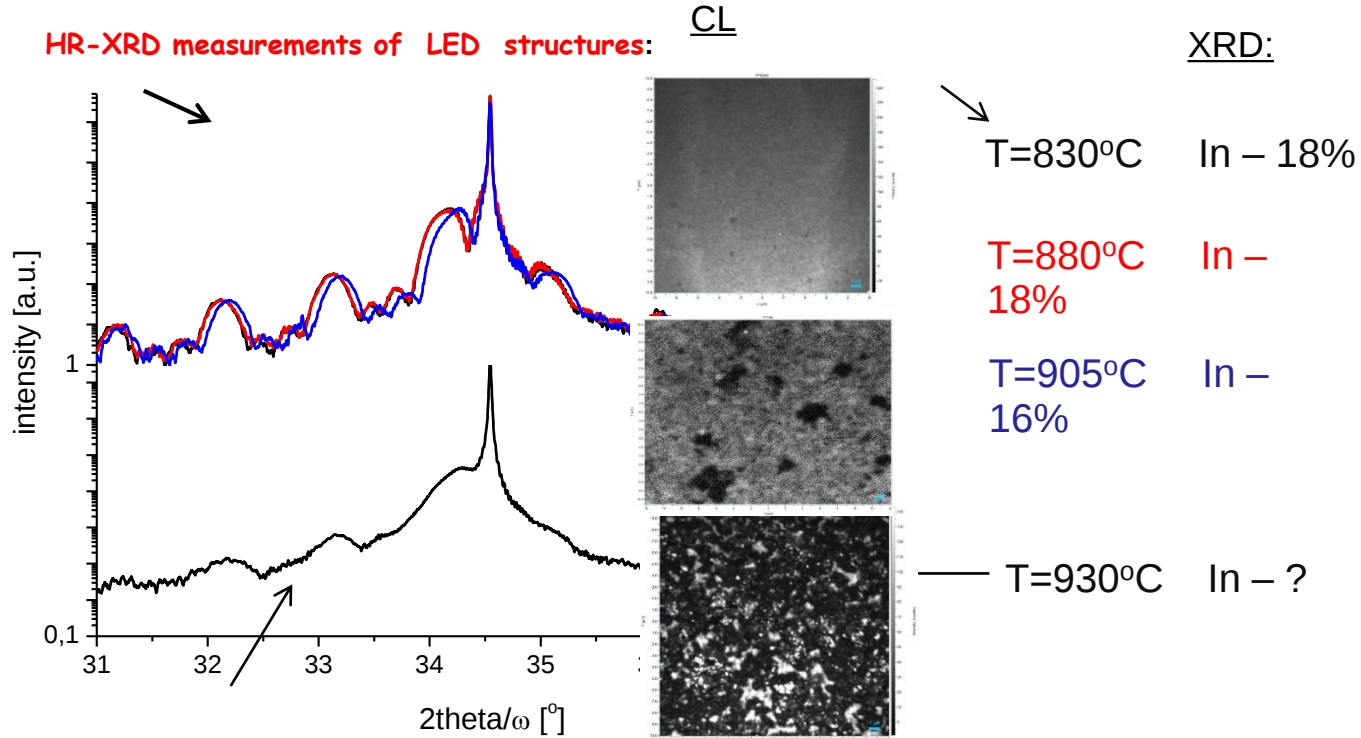
GaN:Mg	$T_{Gr} = XXXX^{\circ}C$
AlGaN:Mg	
GaN:Mg	
EBL - AlGaN:Mg	
Cap – GaN	
Cap – GaN	$T_{Gr} \text{ QW} < 740^{\circ}C$ $T_{Gr} \text{ QB} > 740^{\circ}C$ For In content > 15%
QW - InGaN	
QB – GaN	
InGaN	
GaN	$T_{Gr} = 1000^{\circ}C$
AlGaN:Si	
GaN:Si	
Substrate	

InGaN MQW decomposition

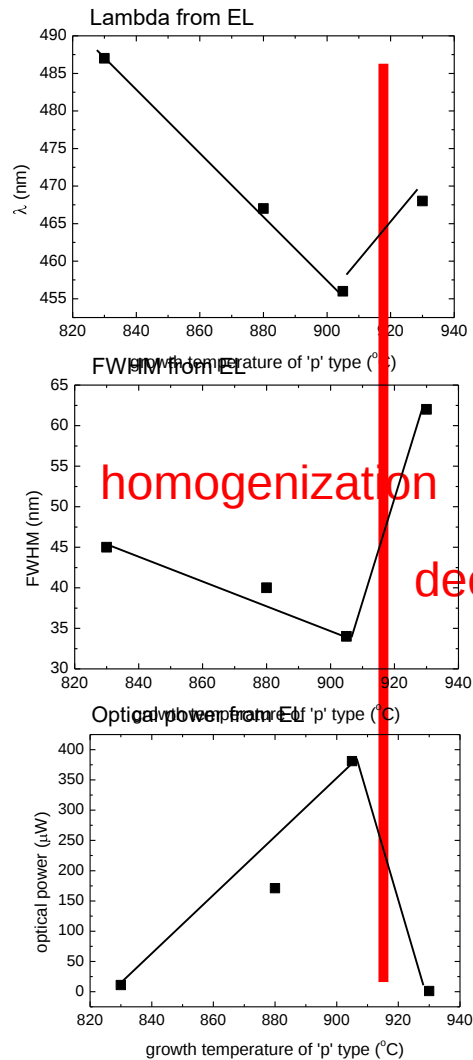


TEM: nanometer scale, Fluorescent microscopy: micrometers, MicroPL: m

Changes of the MQWs during p-type growth at high temperature: samples on sapphire



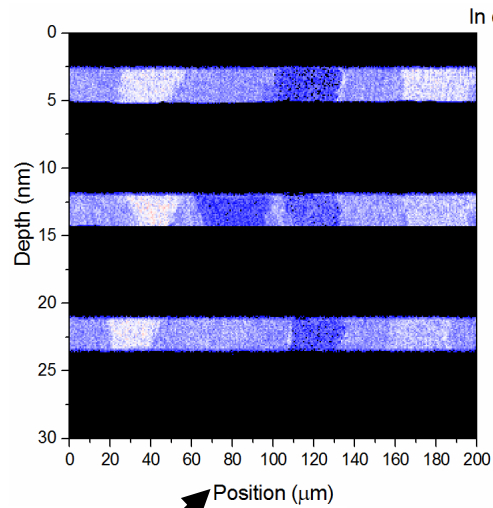
At high temperature satellite peaks becomes much more broader and disappear : QWs degradation occurs



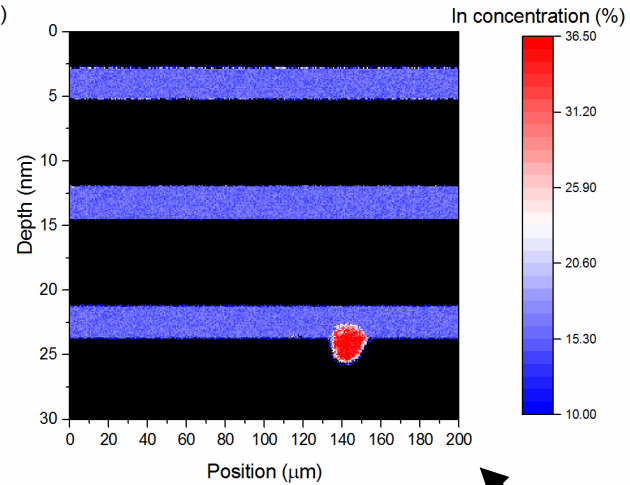
For samples on sapphire (high dislocation density) we are able to homogenize InGaN QWs by growing p-type at high temperature.

If this temperature is too high, we deal with a catastrophic damage

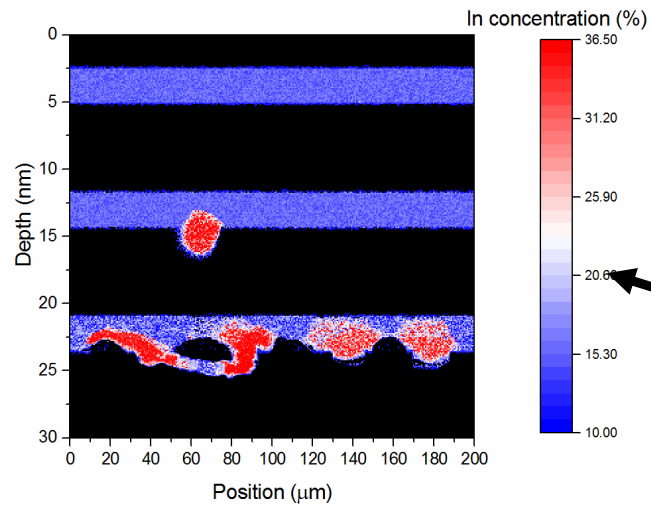
SIMS data of In-content



as grown

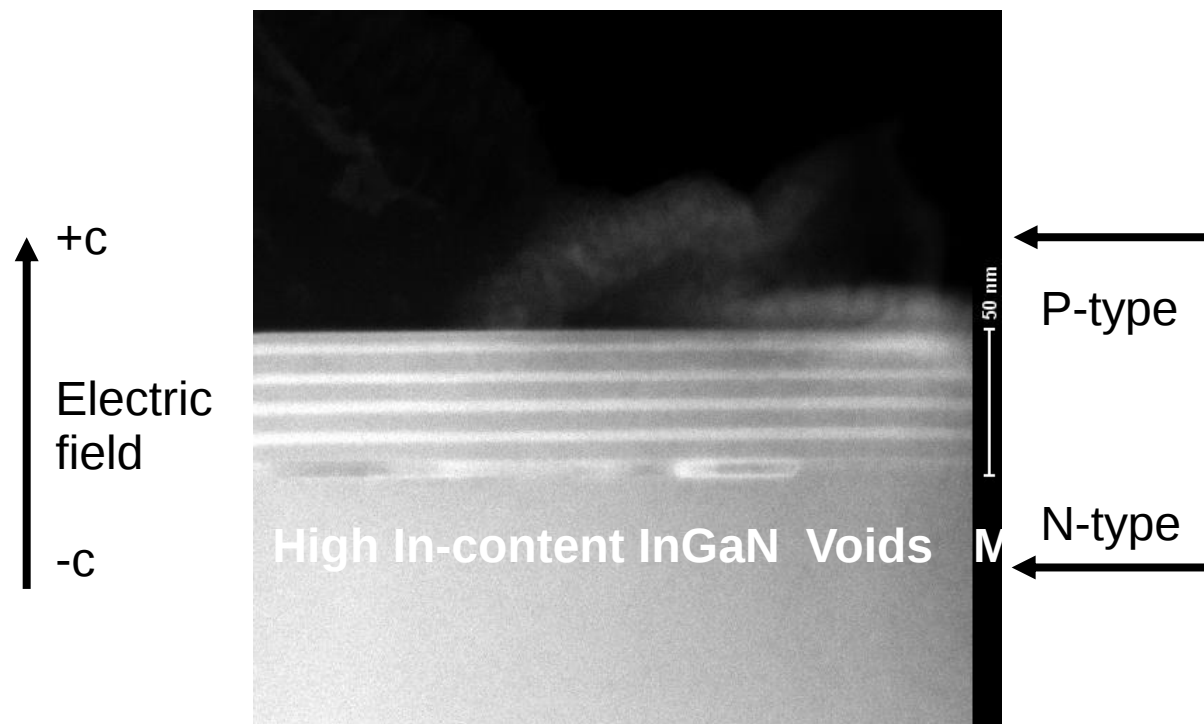


Homogenized
905°C



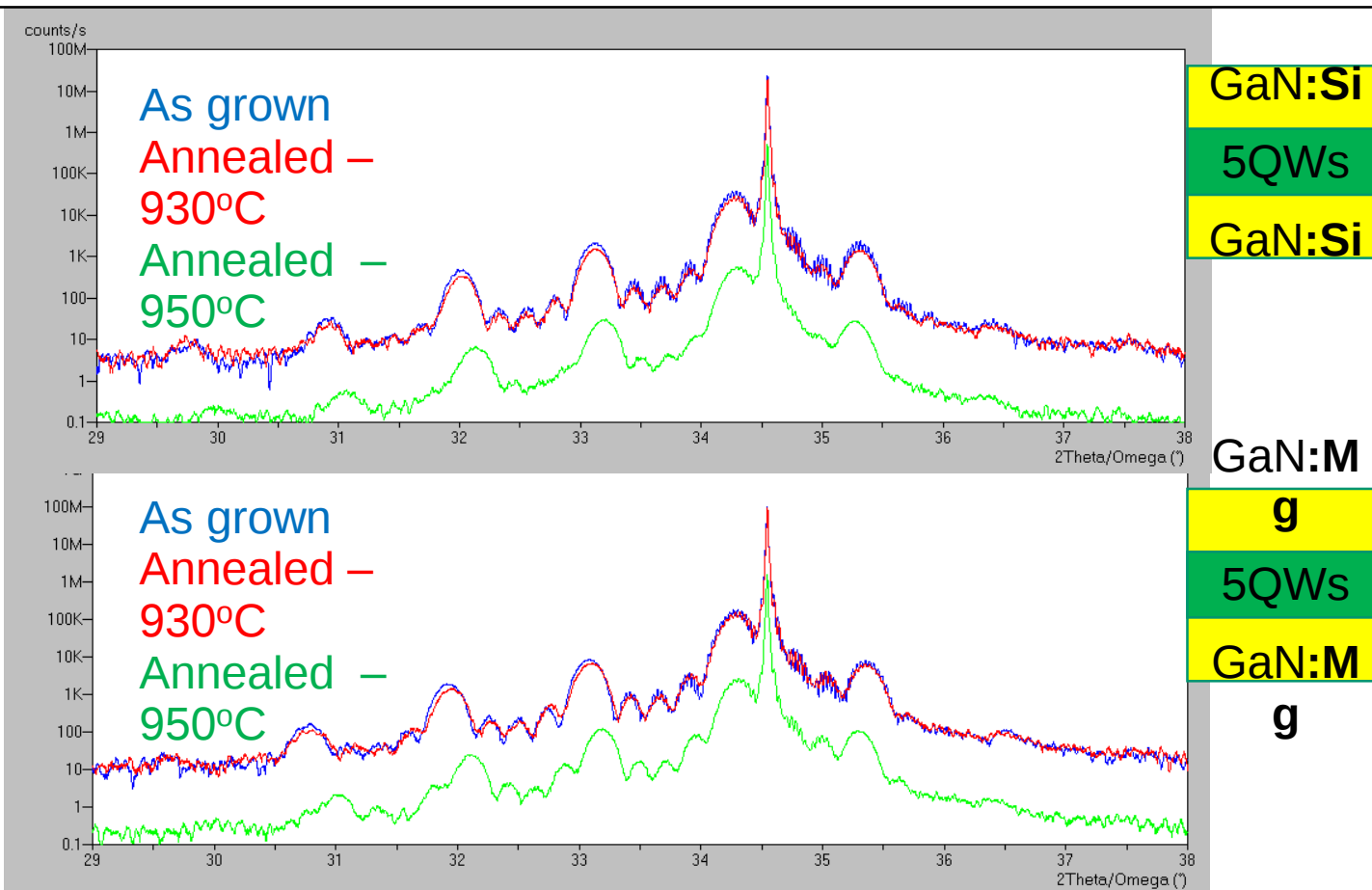
Decomposed
930°C

Why does the decomposition start from the first QW?



Diiferent doping below and above the InGaN/GaN MQWs

5QWs - (460 nm) - 17%In

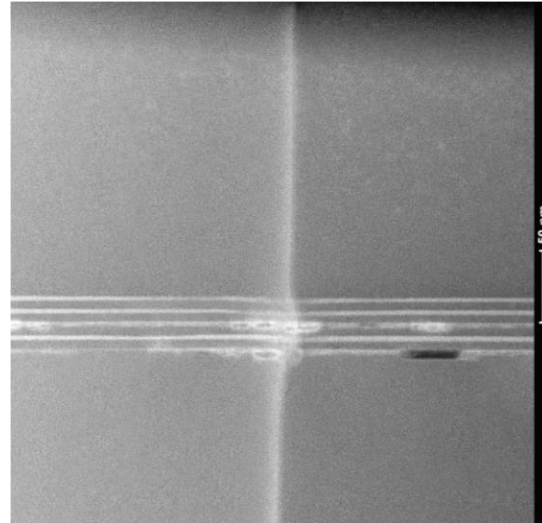


After annealing at 950°C

No decomposition from the top

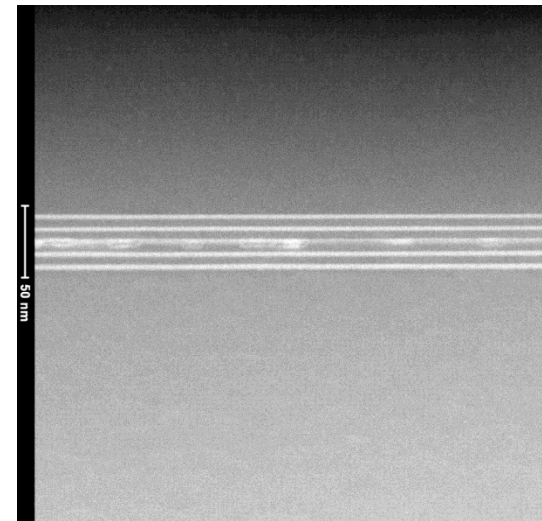
Electric field
driven diffusion?
Yes!

GaN:Si
5QWs
GaN:Si



No decomposition
above and below
GaN:Mg

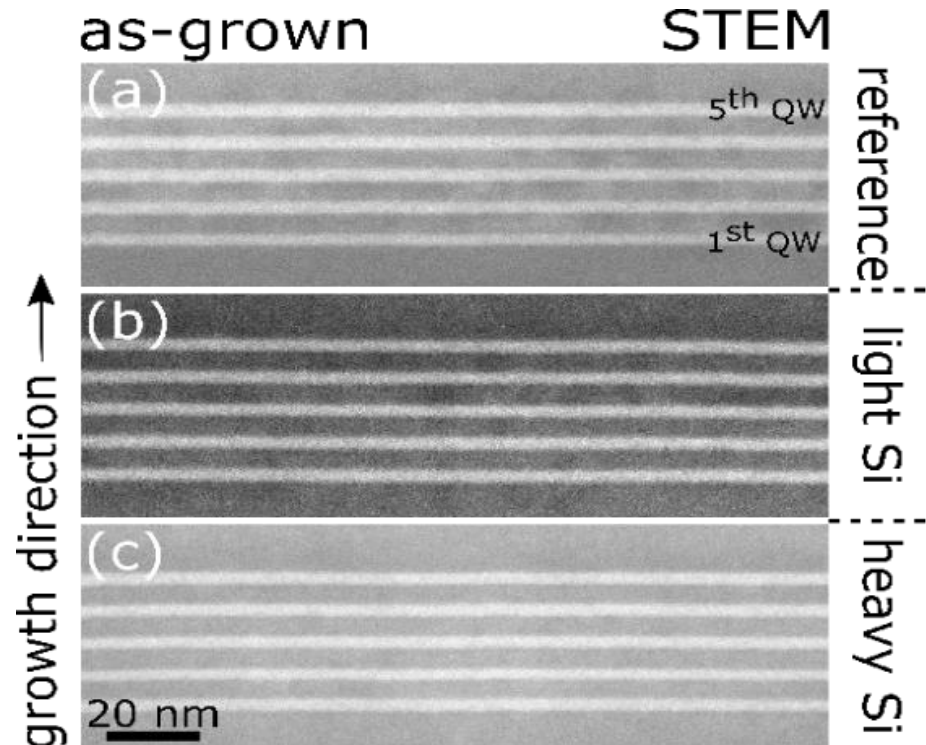
GaN:Mg
5QWs
GaN:Mg



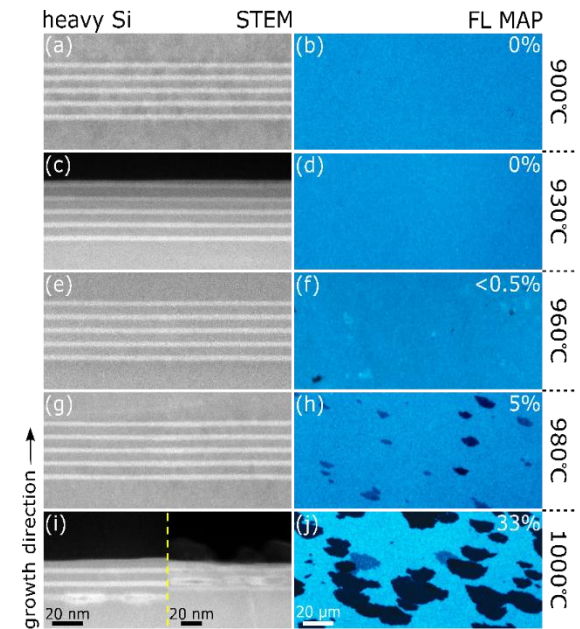
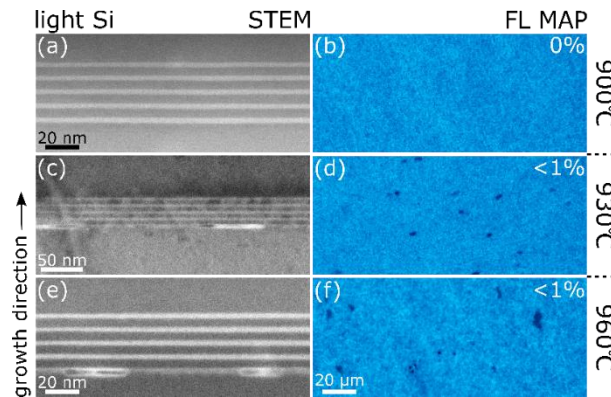
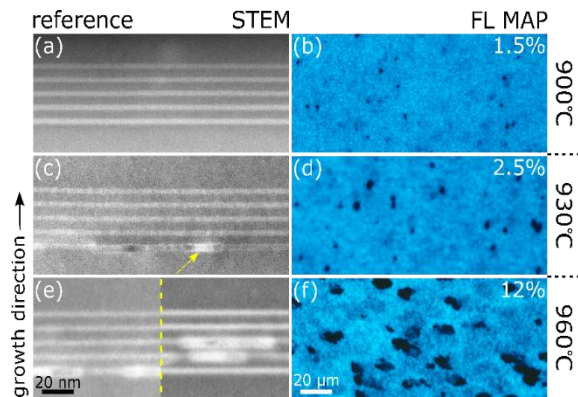
Ga-vacancies?
Yes!

Influence of Si-doping on InGaN QW decomposition

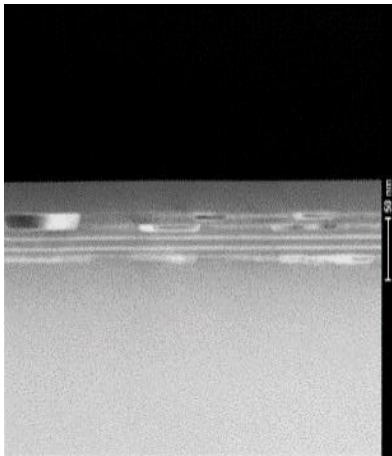
x5	cap	80nm GaN	850°C
	BL	4.5nm GaN: X	810°C
	QW	2.5nm In _{0.16} GaN	730°C
	BL	4.5nm GaN: X	810°C
	n-type	500nm GaN:Si	980°C
	buffer	1.5µm GaN	1050°C
	nucleation layer 100nm GaN (0001) sapphire		
structure		X doping in BLs	
reference		unintentional	
light Si		Si 10 ¹⁸ cm ⁻³	
heavy Si		Si 10 ¹⁹ cm ⁻³	



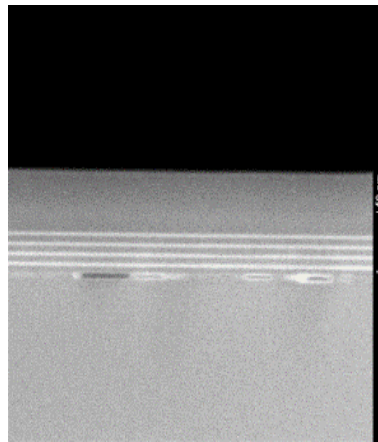
High Si doping: decrease of V(Ga) mobility



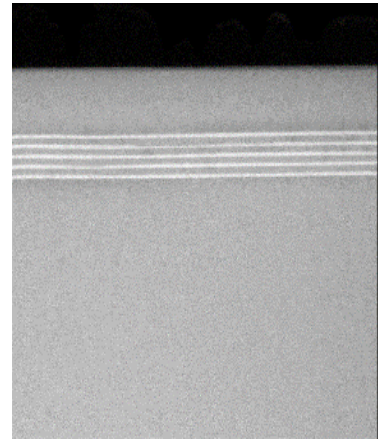
Influence of annealing atmosphere



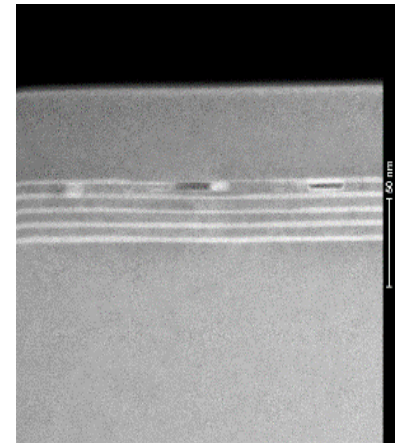
A



B



C



D

TEM topographs of InGaN/GaN QWs after annealing for 30 min. at 940°C and

A: in NH_3+H_2 atmosphere,

B: in $\text{TEGa}+\text{NH}_3+\text{H}_2$,

C: in $\text{TEGa}+\text{NH}_3+\text{H}_2$, the barrier before the first QW doped with Si,

D: in NH_3+H_2 , the barrier before the first QW doped with Si.

Closing remarks

1. The growth parameters in MOVPE are not independent to each other.
2. Growth is different in different reactors.
3. Incorporation of atoms is still not well understood.
4. The properties of the layers depend what has been grown below them and above them.