

# Gas phase epitaxy

## Example: AlGaInN growth by MOVPE

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## **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?~~

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

How

- pressure
- temperature
- NH<sub>3</sub> flow
- TEGa flow
- TMIn flow
- H<sub>2</sub> flow
- N<sub>2</sub> flow
- Growth breaks
- What was grown before and after
- etc

influence the InGaN QW properties?

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

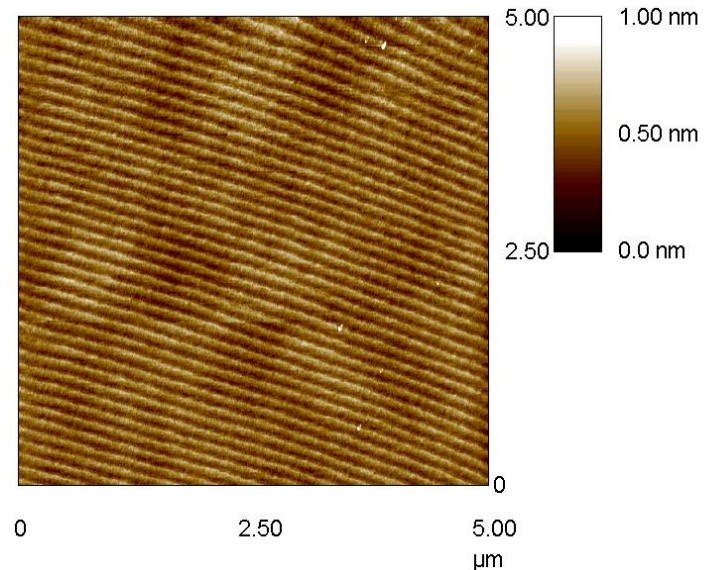
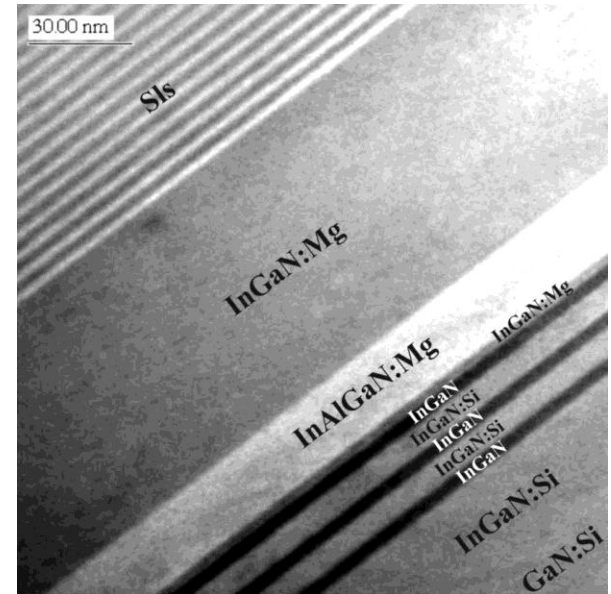
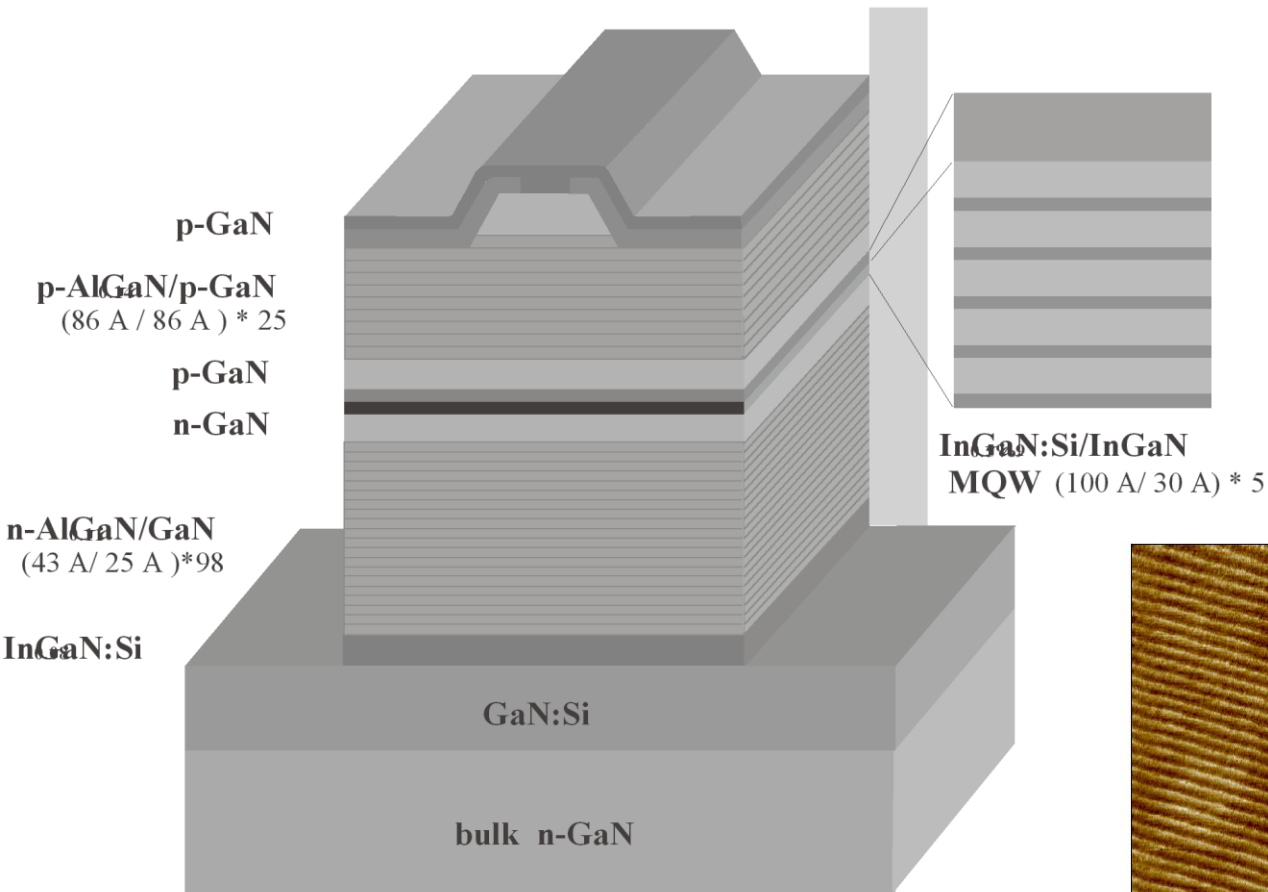
**Growth parameters in MOVPE are not independent to each other.**

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

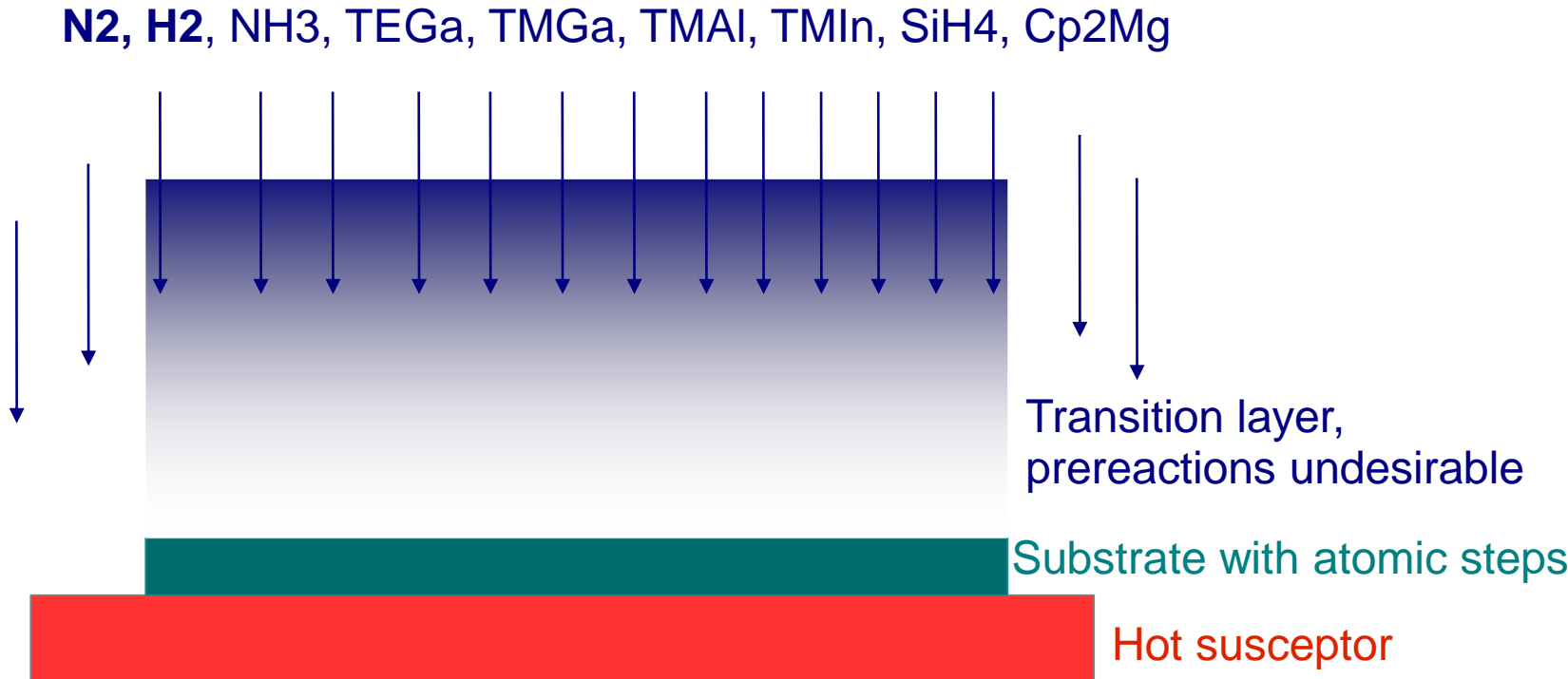
## **Outline**

- 1. Effectiveness of atom incorporation into GaN, AlGa<sub>N</sub>, InGa<sub>N</sub>**
- 2. Example of influence of hydrogen on InGa<sub>N</sub> growth**
- 3. Examples of how properties of the epi layers can be modified by growth of other layers.**
- 4. Diffusion of atoms during growth**

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



# MOVPE growth of nitride semiconductors

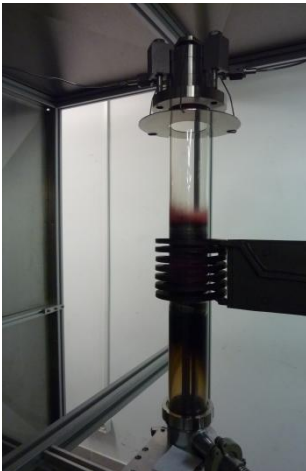


As a result, we have a layer which has certain:

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

# 1. Effectiveness of atom incorporation into GaN, AlGaN, InGaN

## MOVPE reactors used



Home made (HM)  
2000 growth runs



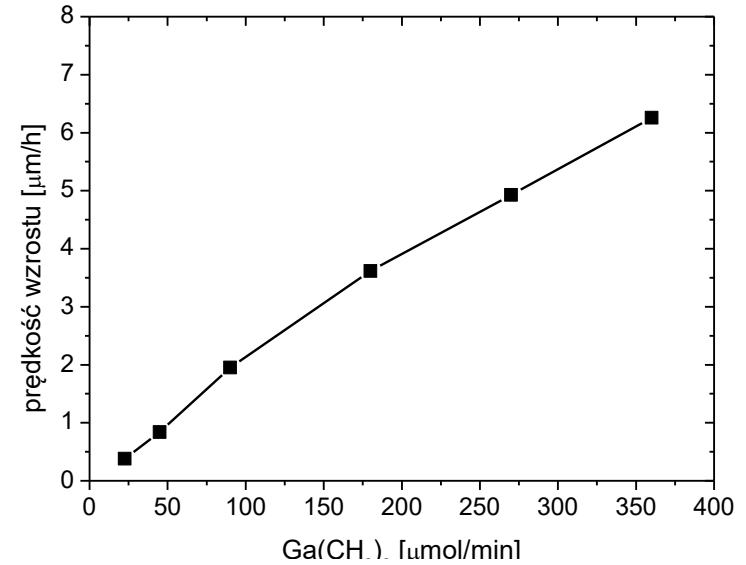
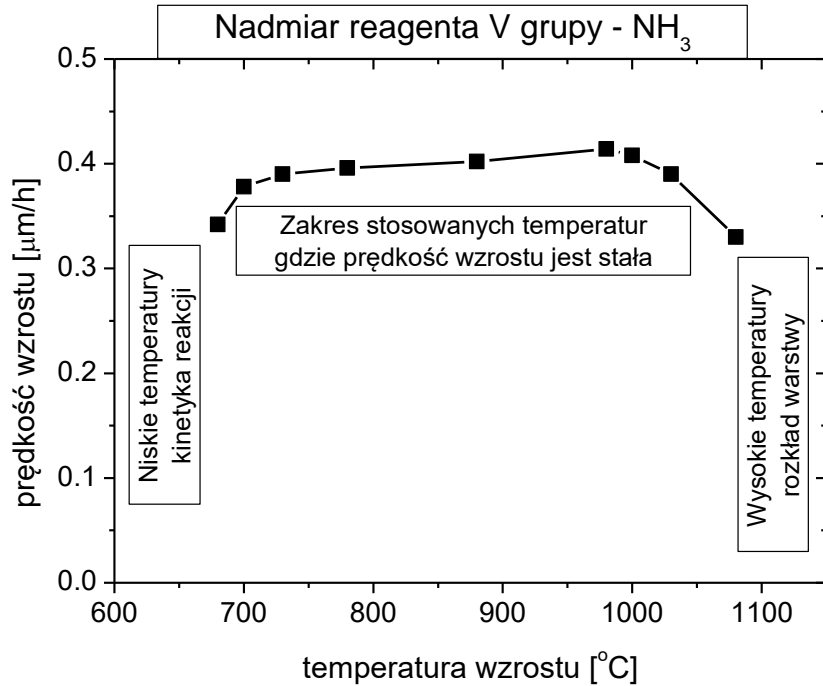
CCS Aixtron  
6000 growth runs



High Pressure (HP)  
200 growth runs



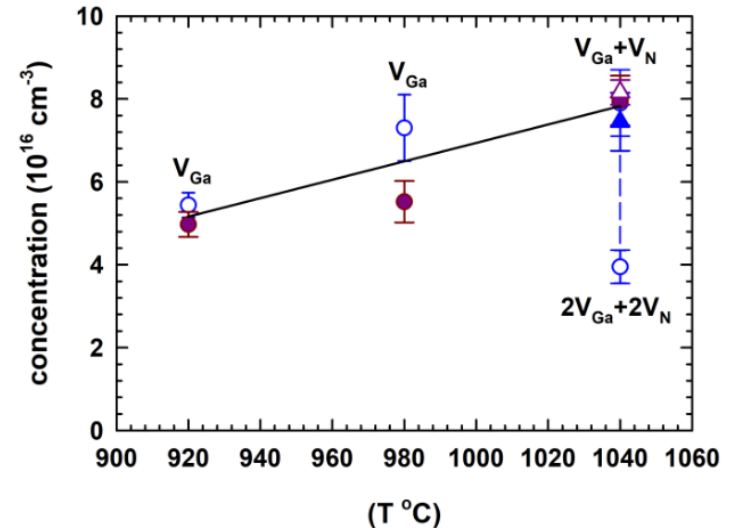
# Effectiveness of Ga incorporation into GaN vs temperature and TMGa flow in HM



Growth rate proportional to TMGa or TEGa flow

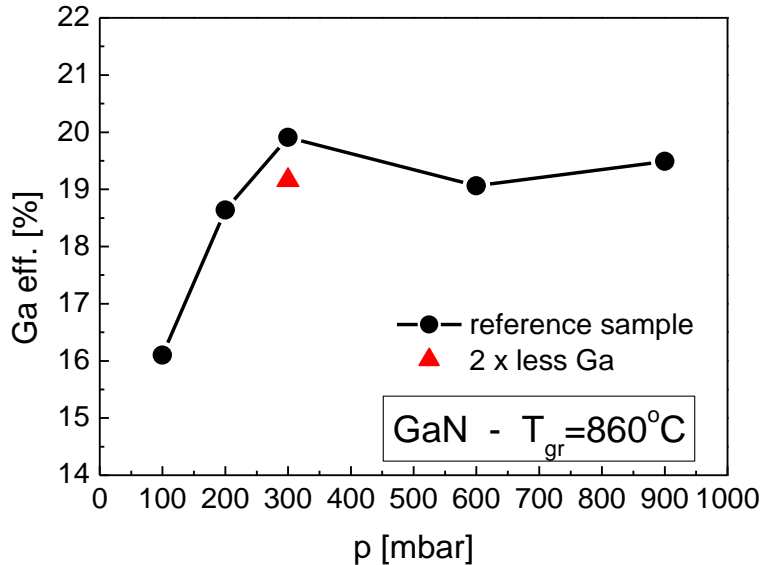
Low temperature – low ammonia decomposition

High temperature- decomposition

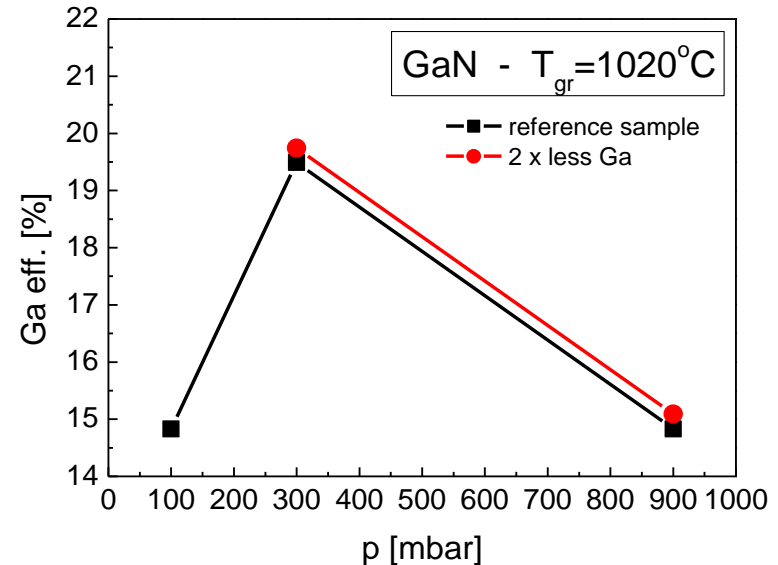


# Effectiveness of Ga incorporation into GaN vs pressure

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



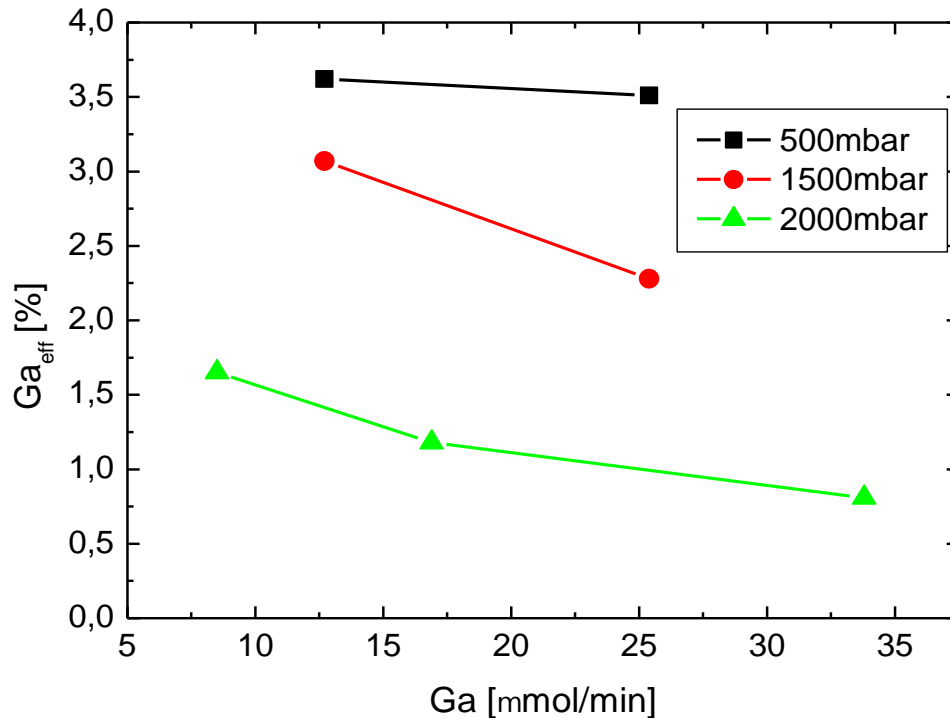
At low pressure, the Ga atoms are blown away from the surface.



At high pressure and temperature, the rate of pre-reactions increase which prevents Ga incorporation

**Efficiency of Ga incorporation independent on amount of TEGa**

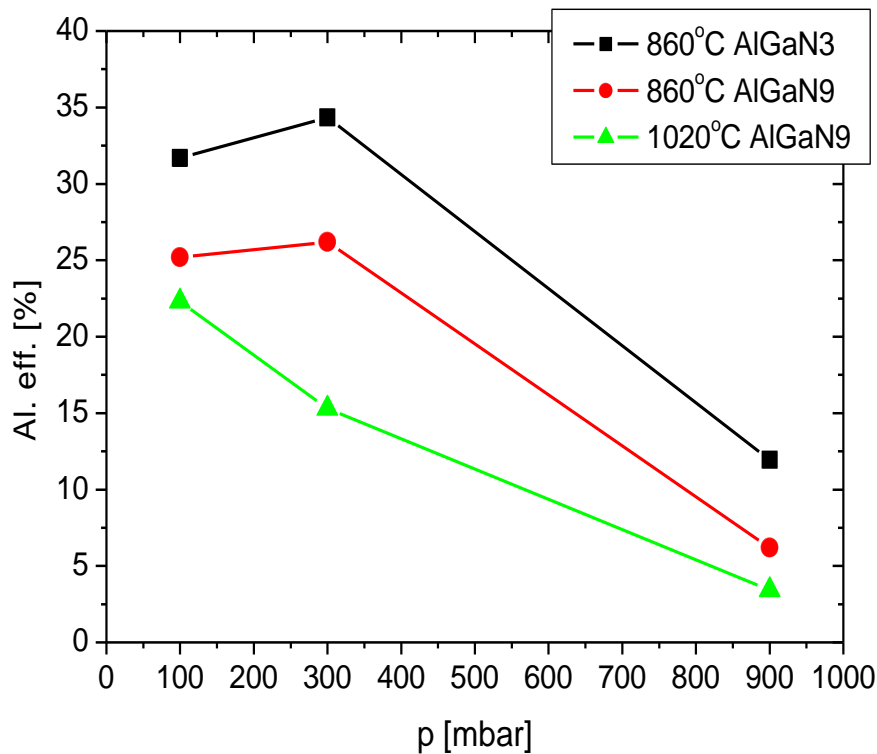
# Efficiency of Ga incorporation into GaN in HP



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 AlGaN in HM



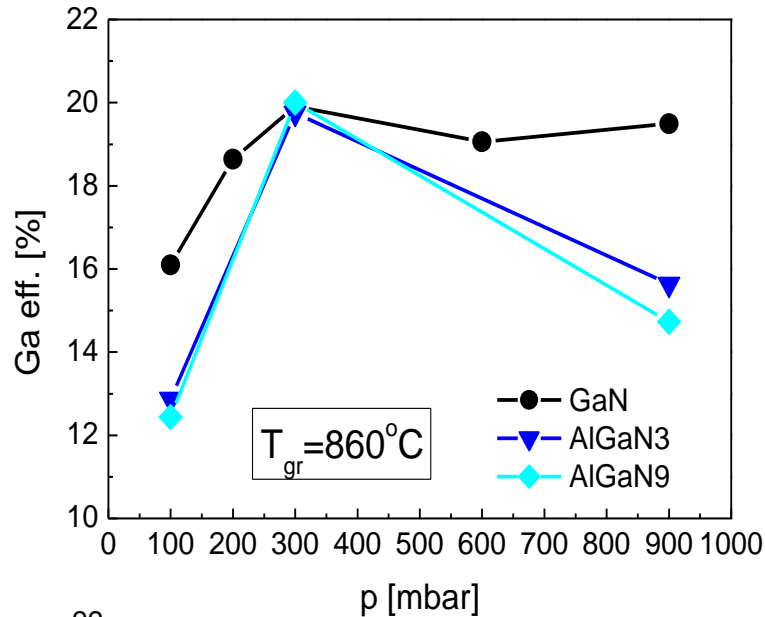
Efficiency of Al incorporation falls down with TMAI flow increase

Prereactions rate higher than in the case of GaN

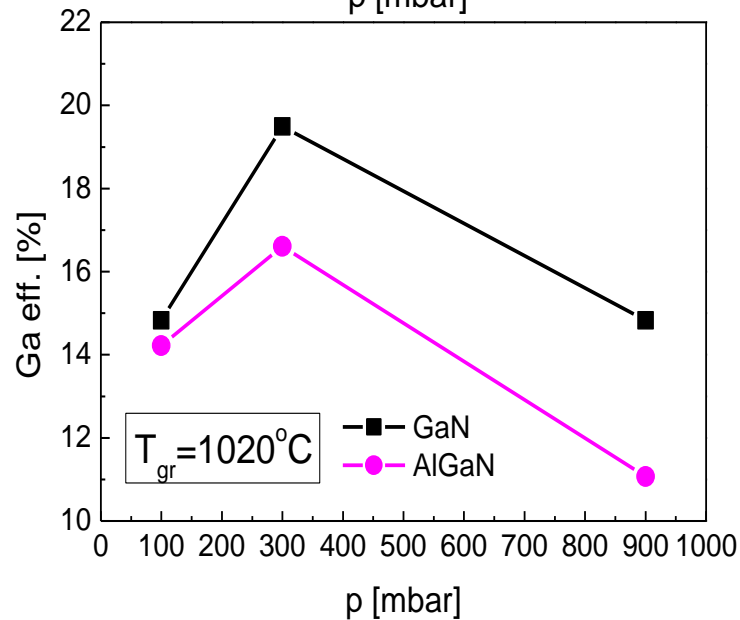
More prereactions at high temperature and pressure

3 sccm of TMAI  
9 sccm of TMAI

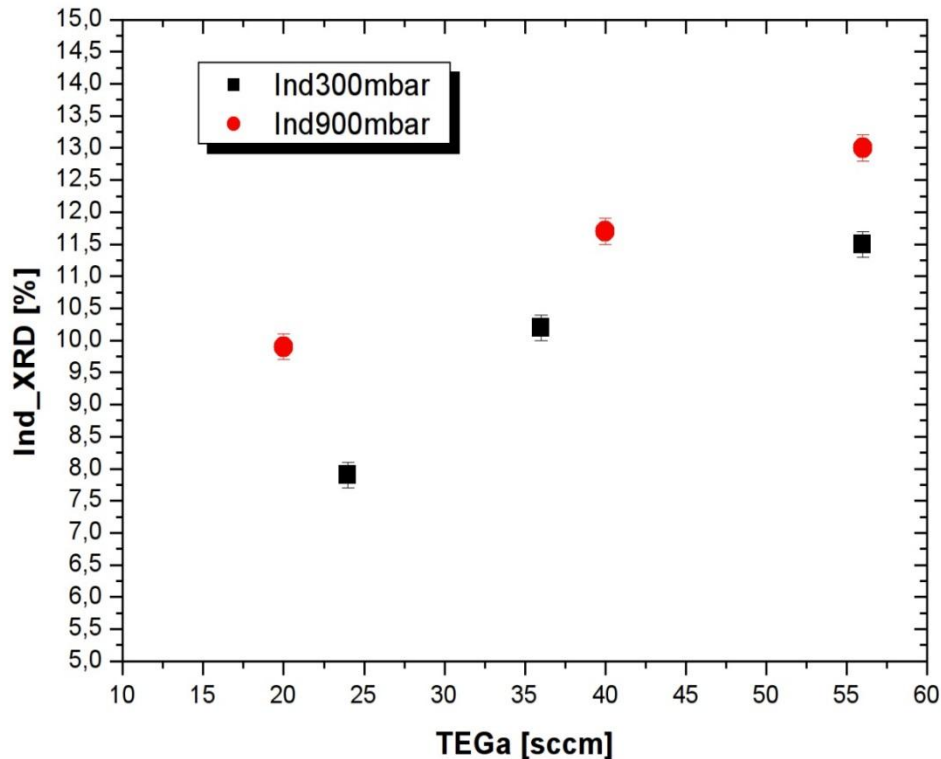
# Efficiency of Ga incorporation into AlGaN in HM



**Prereacted TMAI and NH3 molecules block Ga incorporation**



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

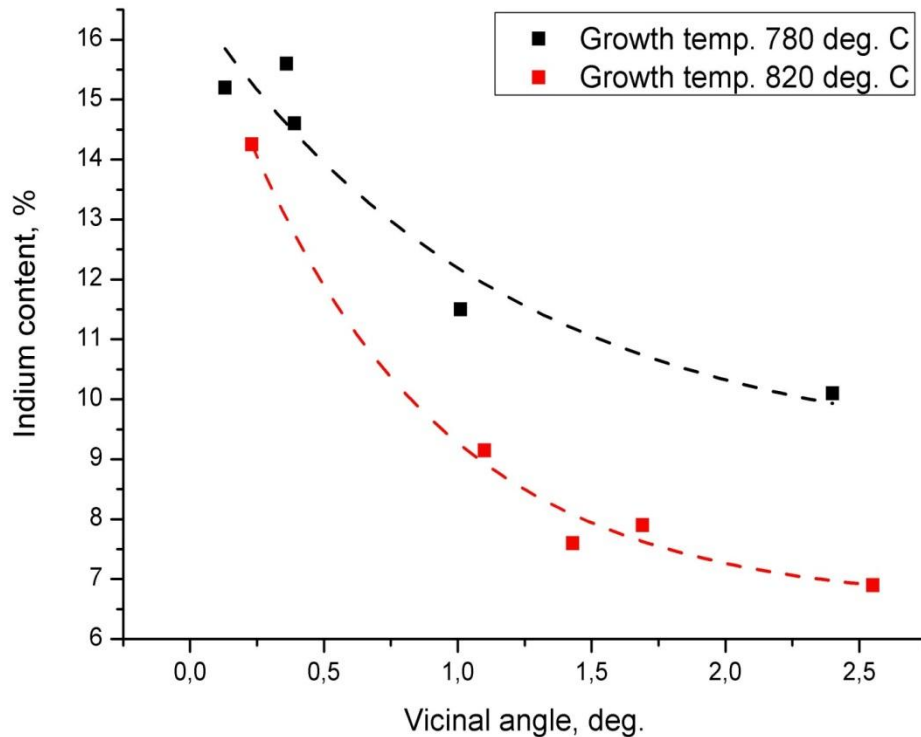


More Ga source in the gas phase,  
but more In in InGaN solid phase.

More indium at elevated pressure.

In atoms to be incorporated must  
be surrounded by Ga atoms

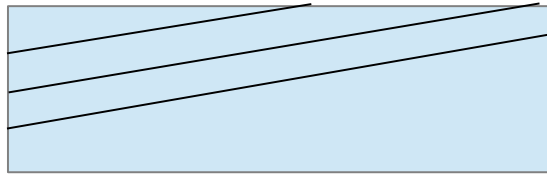
# In incorporation into InGaN layers versus GaN substrate off-orientation



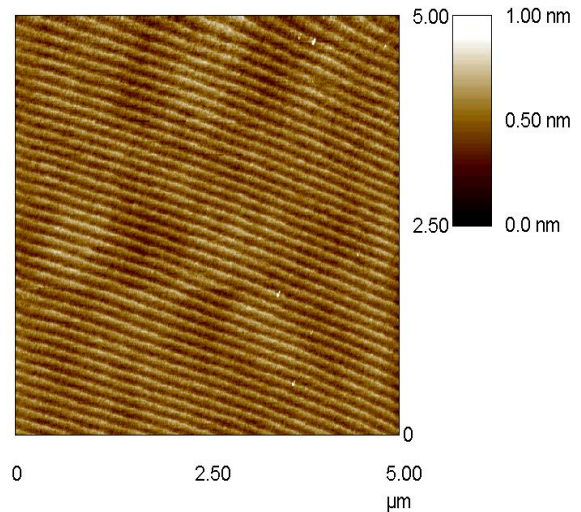
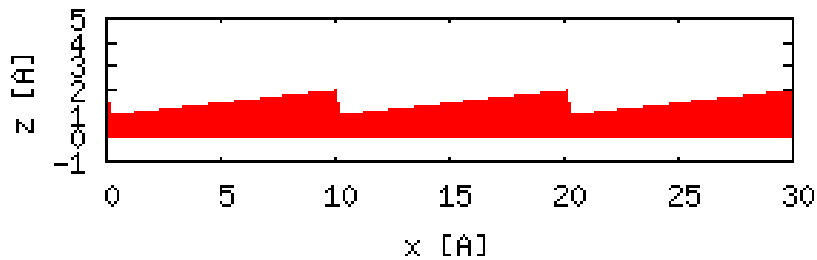
If we have bad morphology (steps are not identical), we deal with In inhomogeneous incorporation

# GaN substrate off-orientation

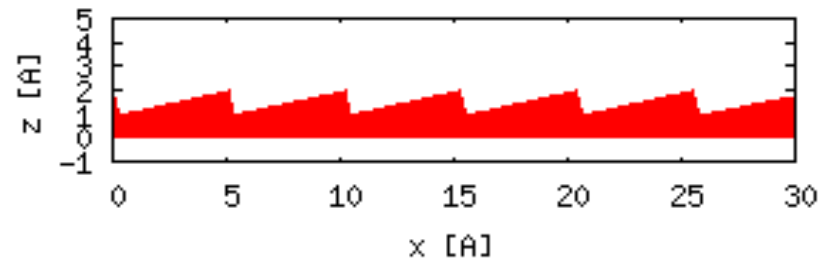
- The steps flow slower
- **Many AlGaN and InGaN parameters are strongly influenced**



Low misorientation - fast atomic steps

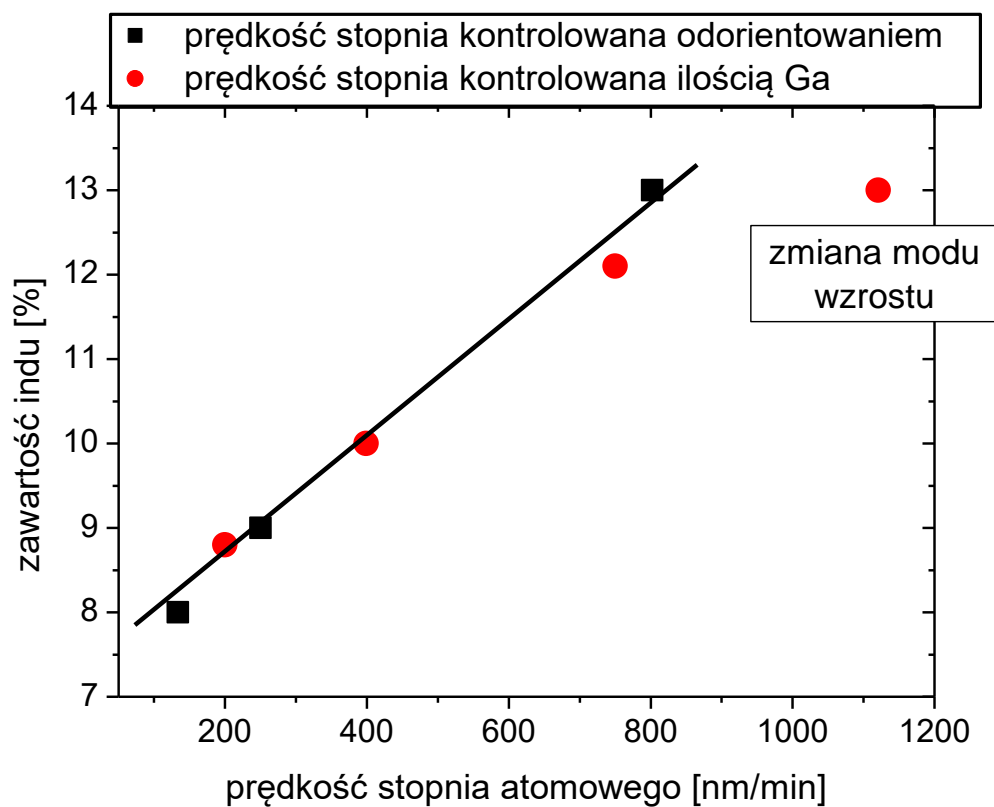


Higher misorientation - slower atomic steps

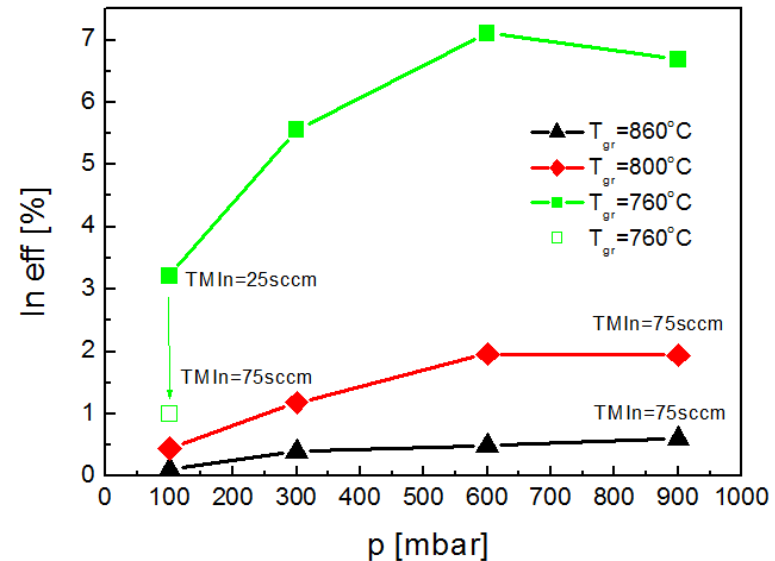
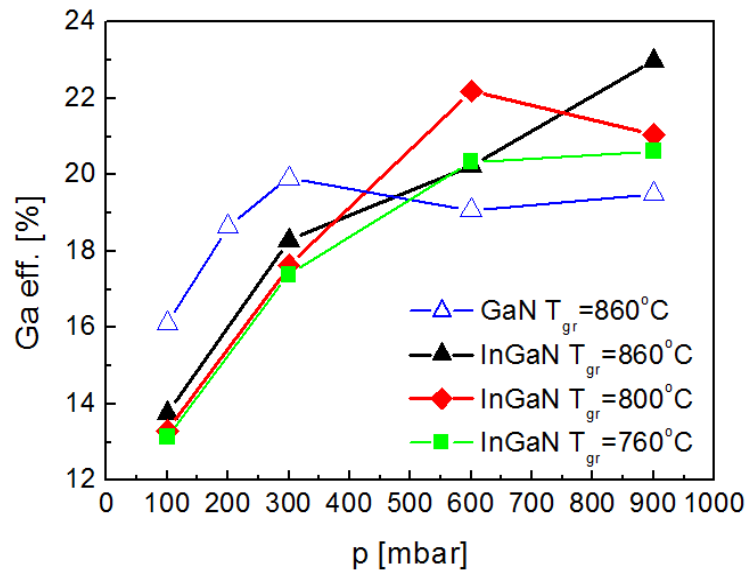




## Incorporation into InGaN versus velocity of the steps in step-flow growth



# Efficiency of Ga and In incorporation into InGaN in HM

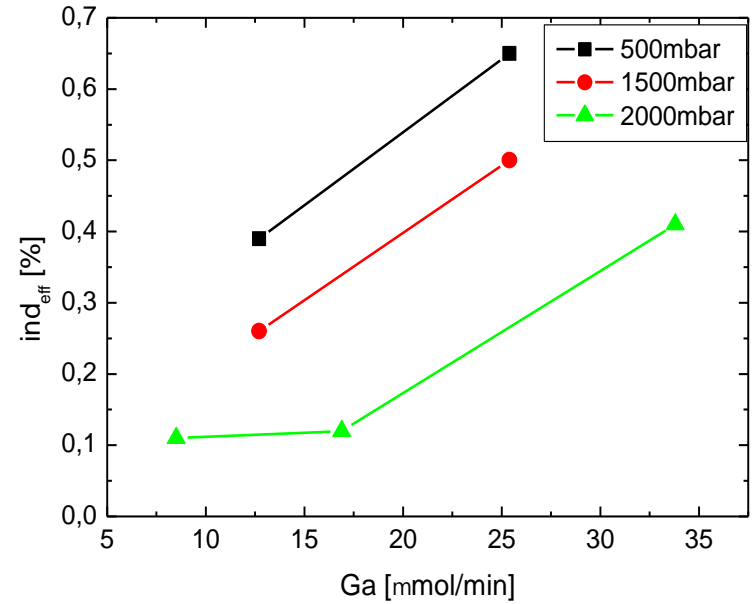
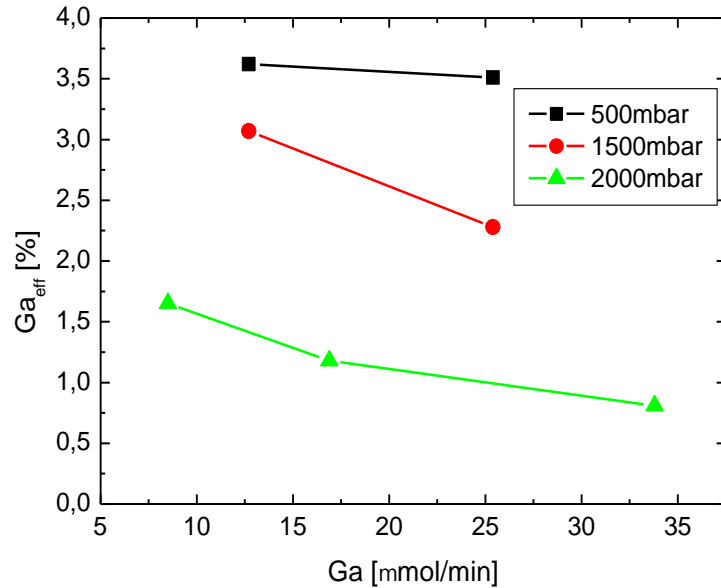


**Indium increases Ga incorporation.**

**In incorporation efficiency increases for:**

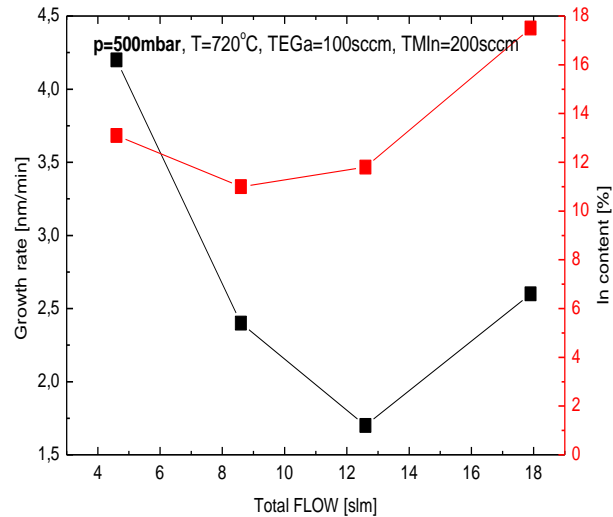
- \* **lower TMIn-flow**
- \* **lower temperature**
- \* **higher pressure (seems to be a maximum)**

# Efficiency of Ga and In incorporation into InGaN in HP

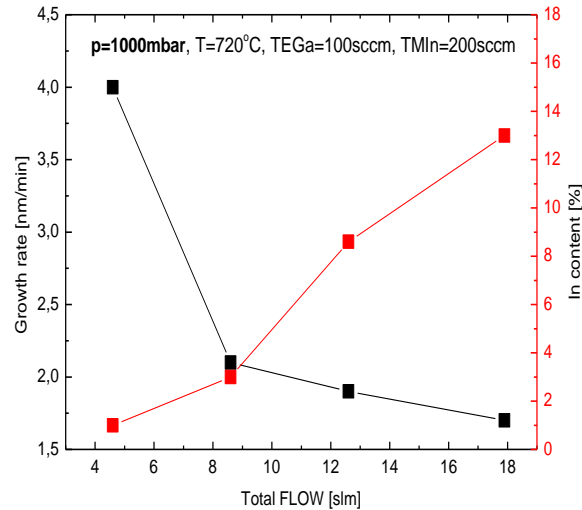


Prereactions in HP reactor- main source of troubles

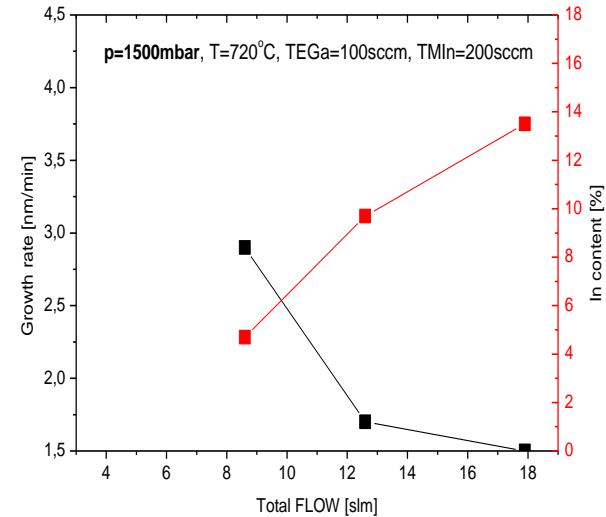
# Influence of total flow on the InGaN growth rate and In incorporation in HP



500 mbar



1000 mbar

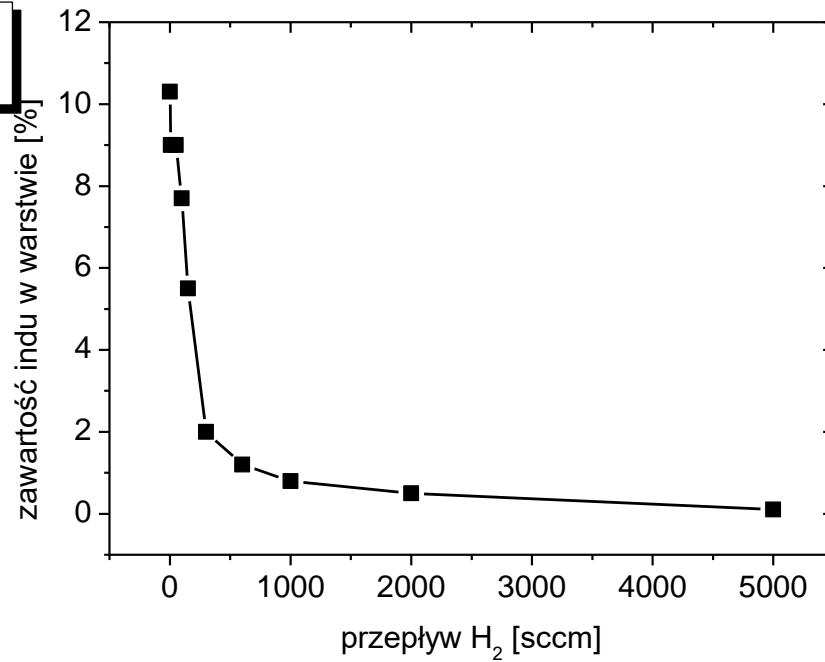
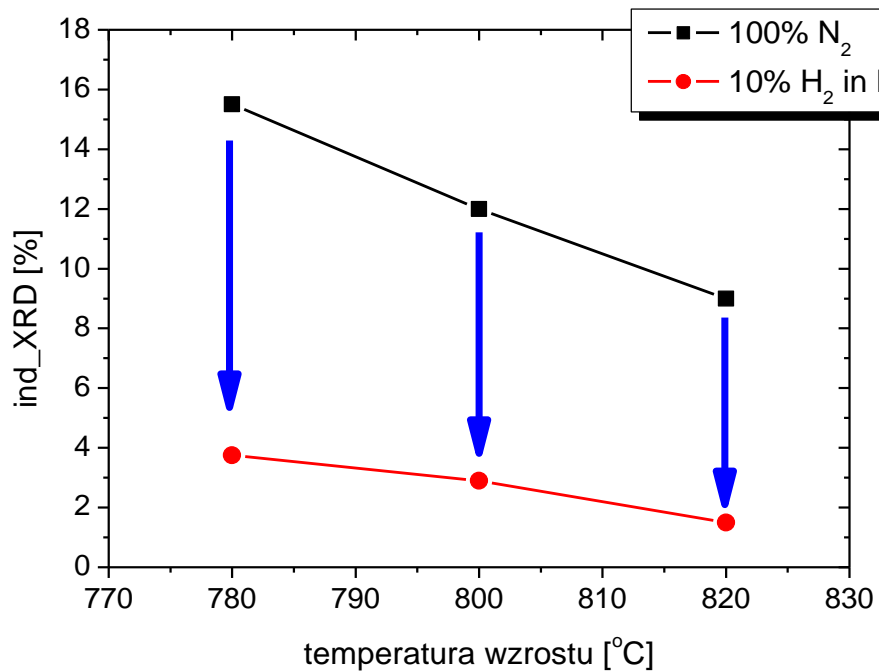


1500 mbar

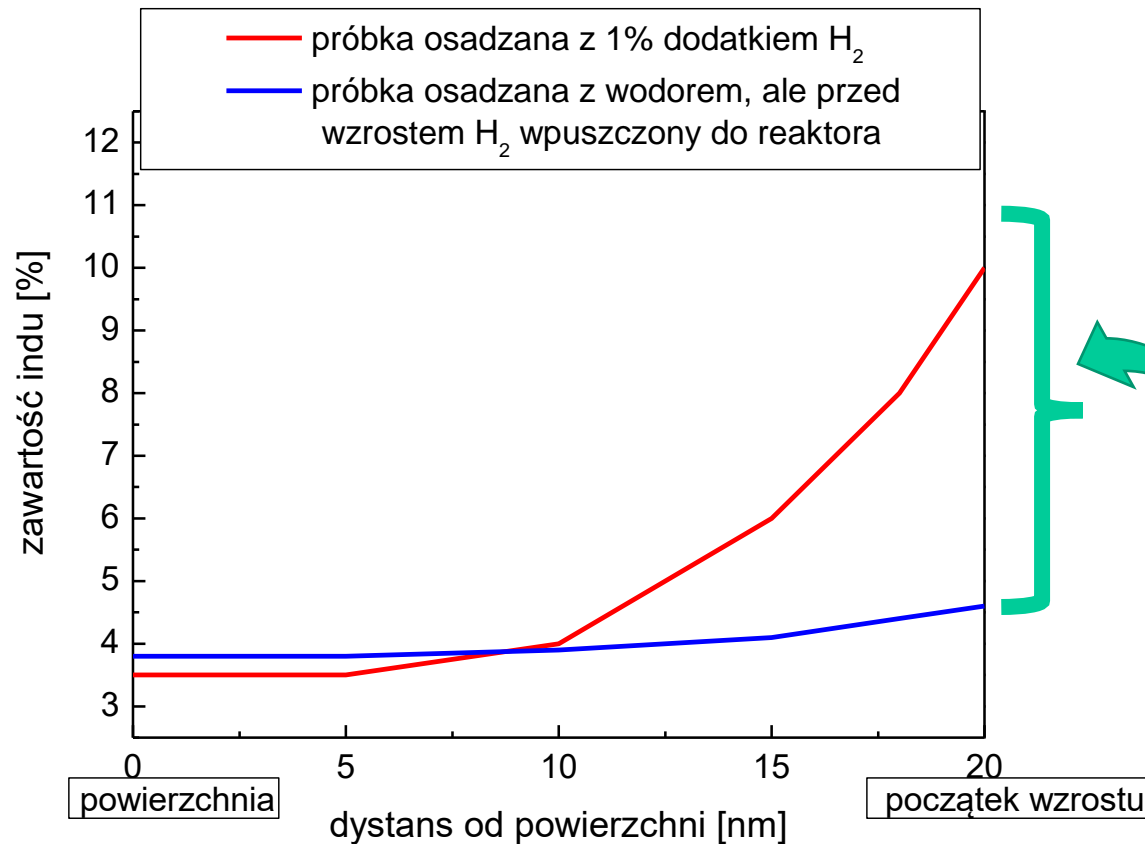
Growth rate decreases with total flow- TEGa and TMIn are blown away more efficiently

In content increases. Lower real temperature? Different NH<sub>3</sub>/NH<sub>2</sub> on the surface? Lower prereaction rate?

# Influence of hydrogen used in the carrier gas

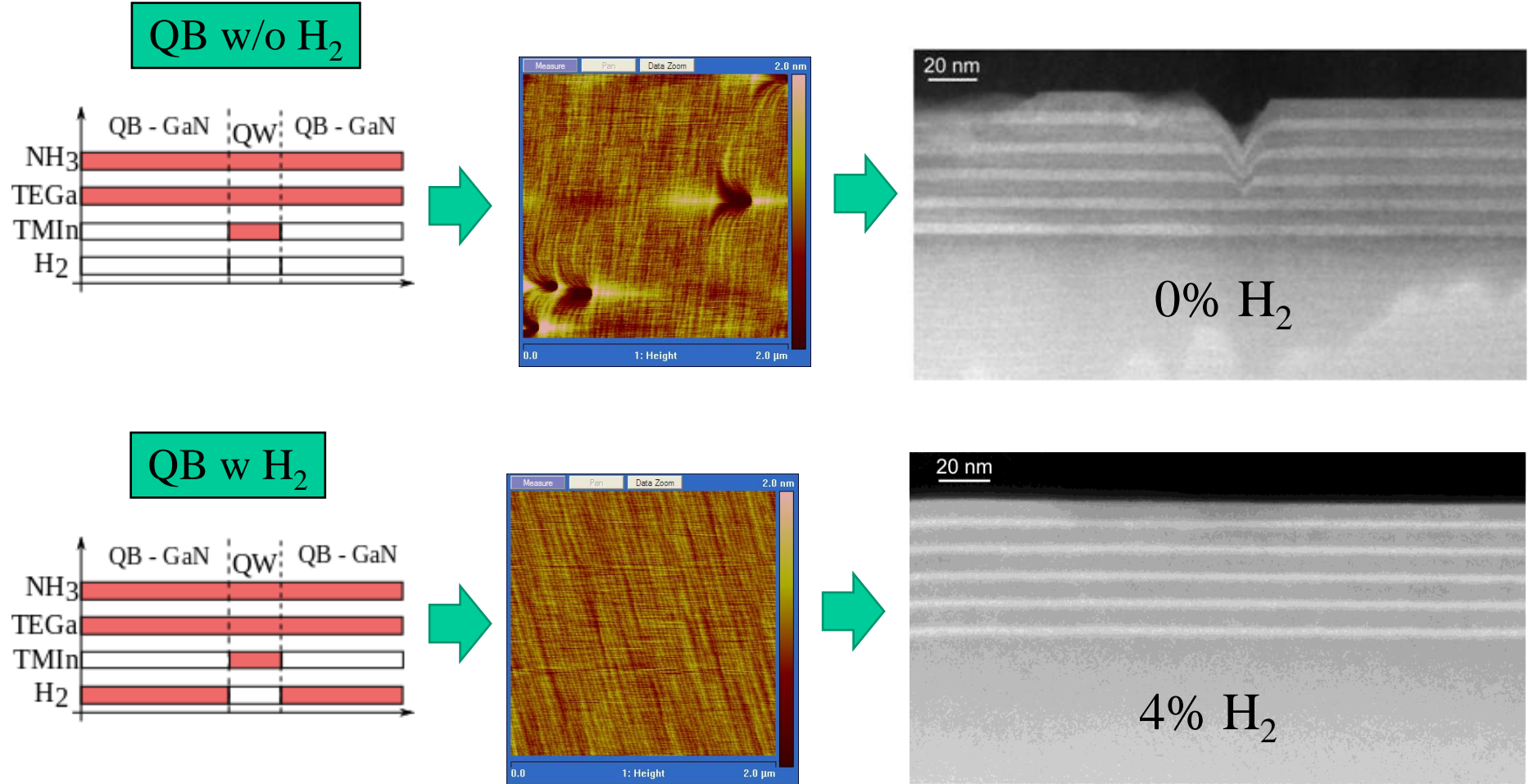


# Gradient of In content in InGaN layers grown with H<sub>2</sub> in the carrier gas



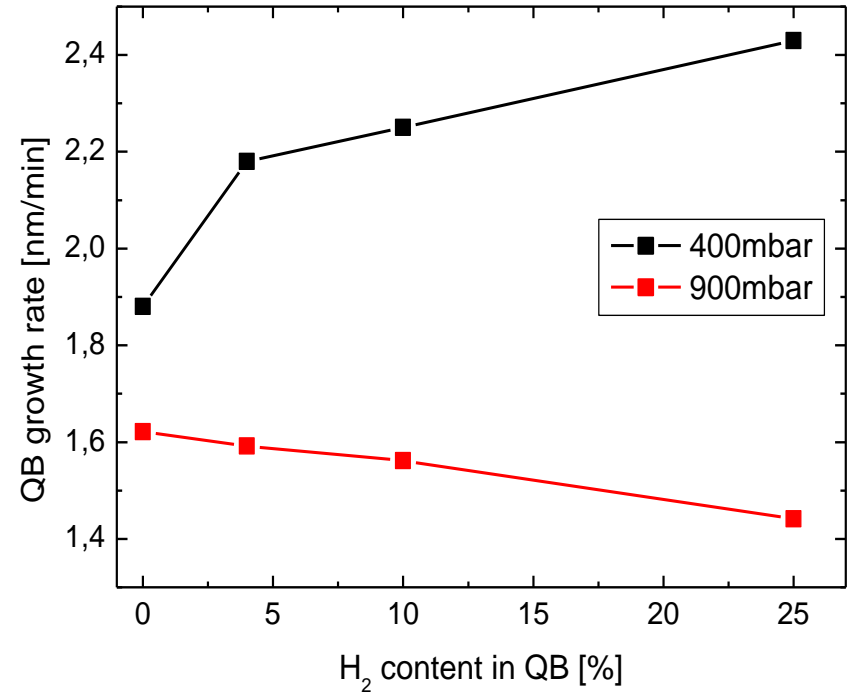
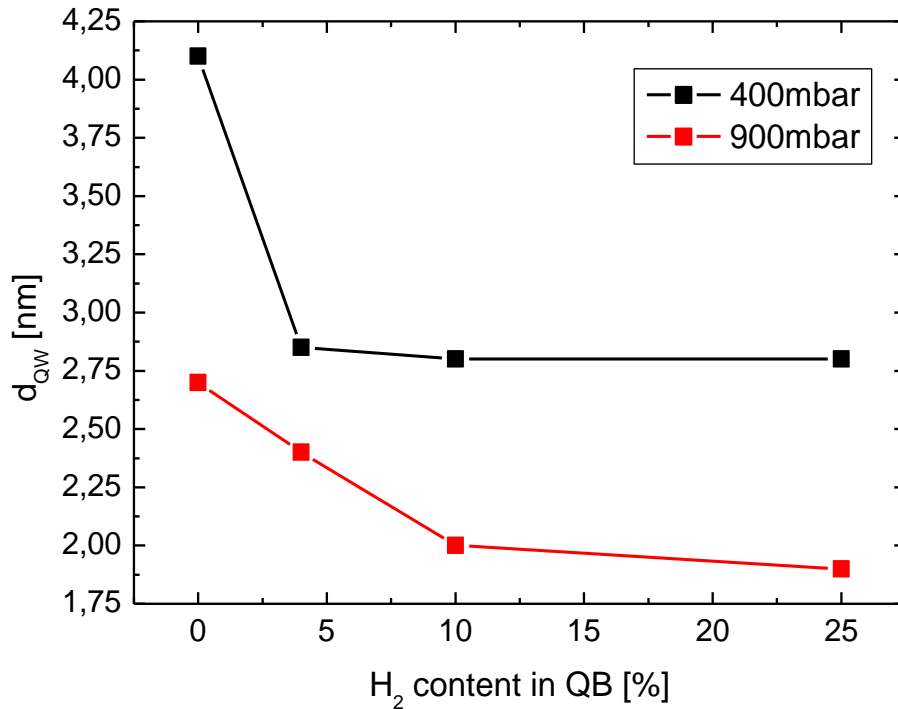
**Hydrogen passivates the surface and In is not incorporated**

# Growth of InGaN QWs with QBs grown with hydrogen



Hydrogen eliminates defects but influences also the QWs

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

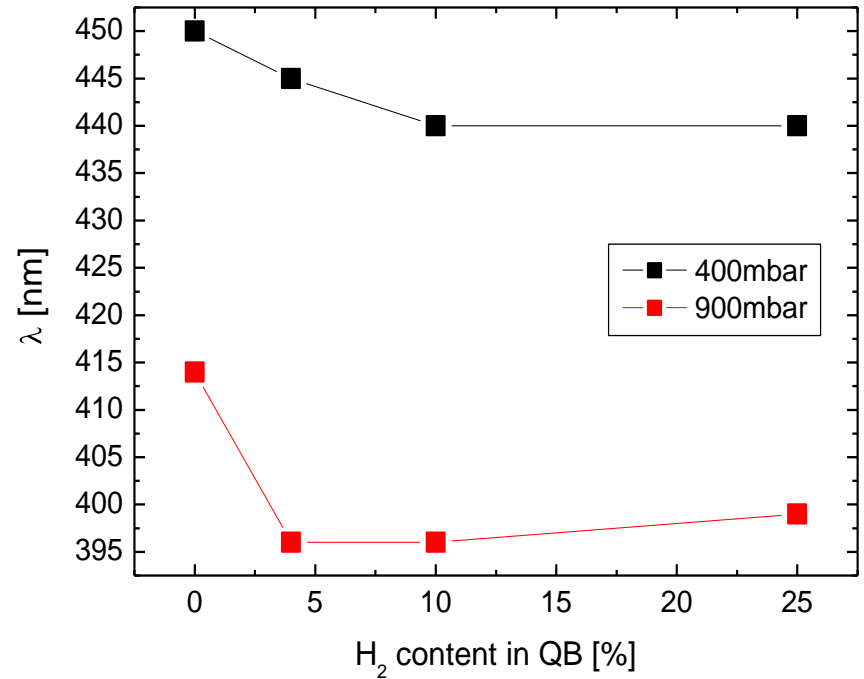
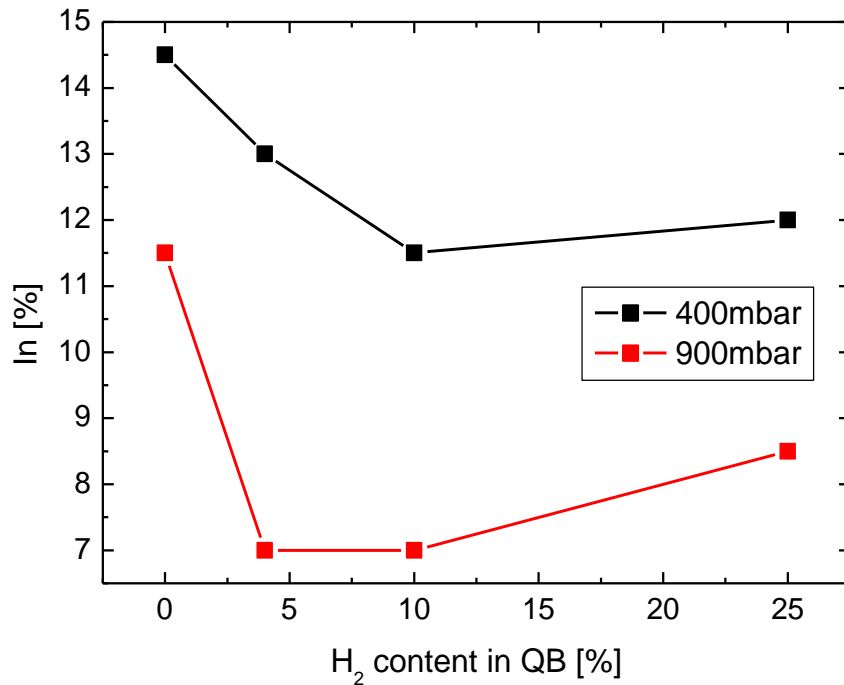


Hydrogen used in QB growth etches off InGaN QW more efficiently at high pressure

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

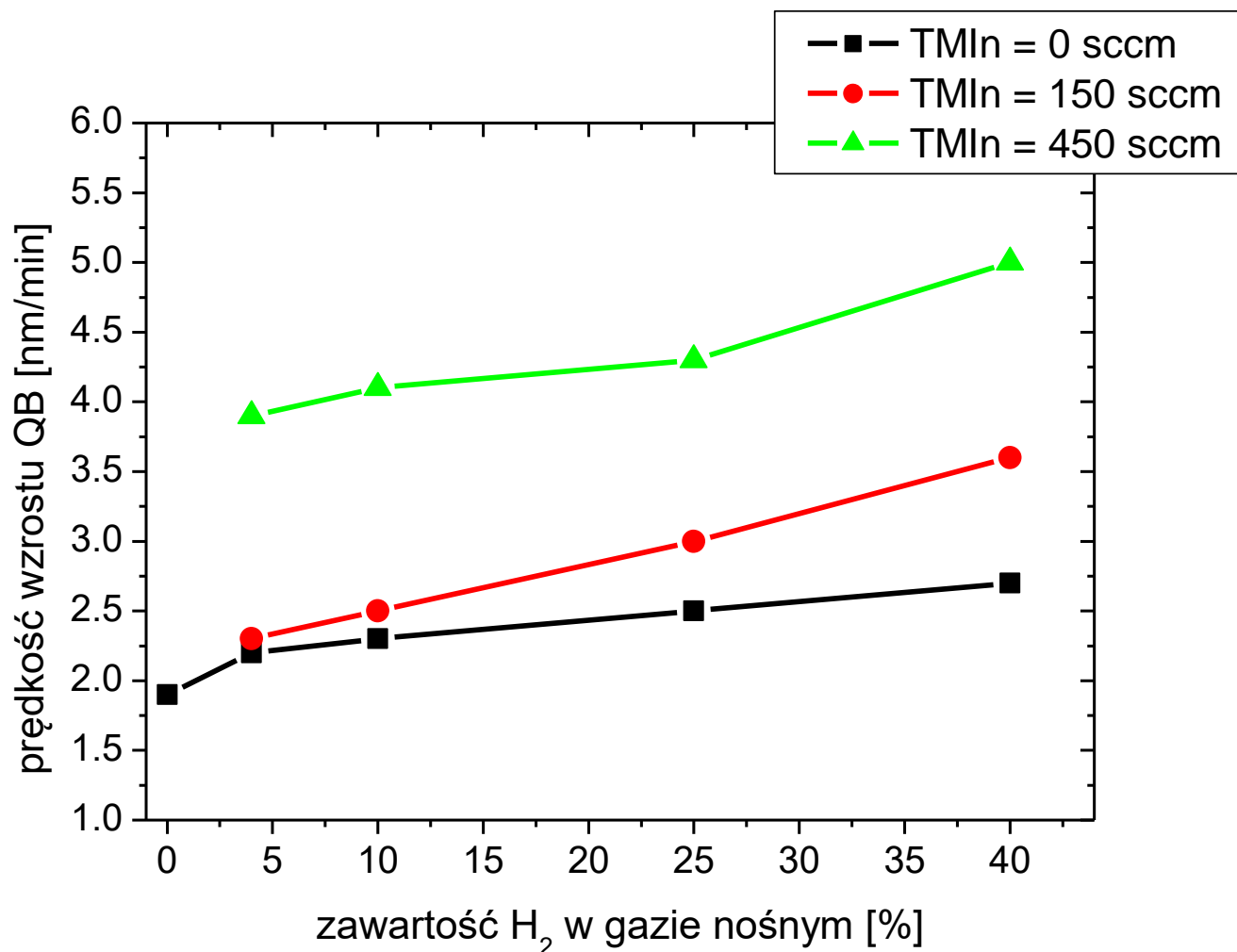


# Influence of hydrogen used in the carrier gas during GaN barrier growth in CCS



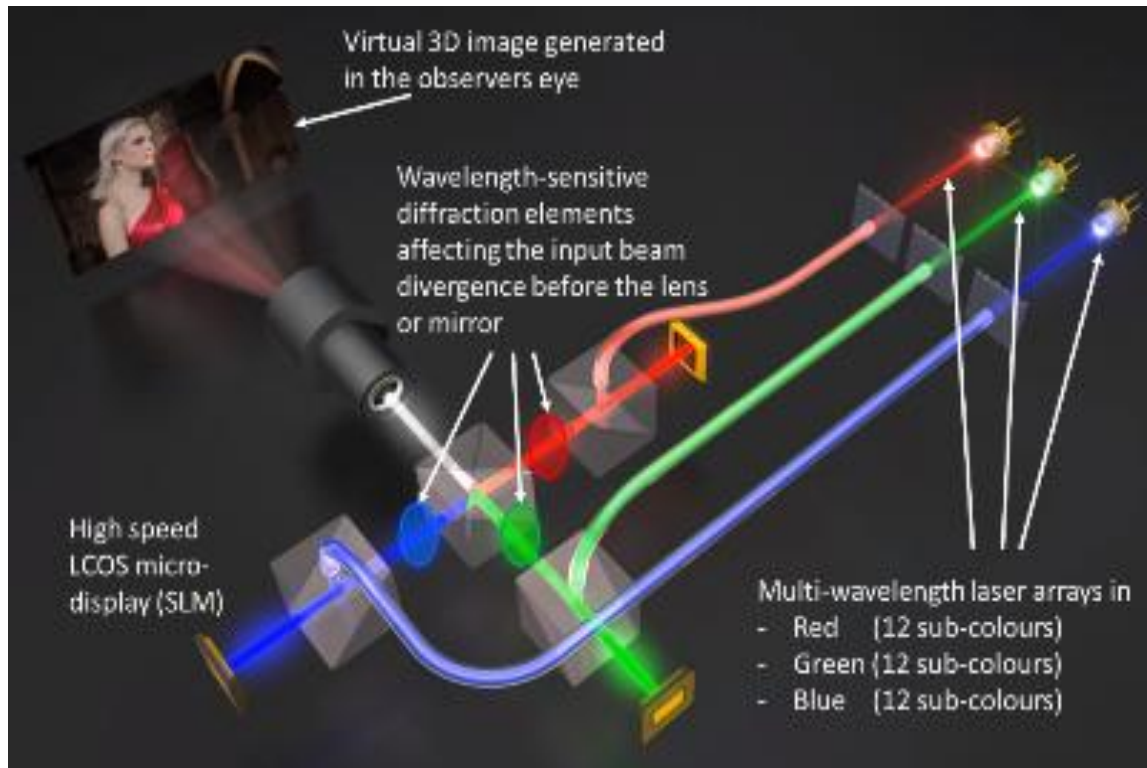
Hydrogen used in QB growth etches In off InGaN QW more efficiently at high pressure

# Influence of hydrogen and H2 on Ga incorporation



Effectiveness of Ga incorporation in CCS

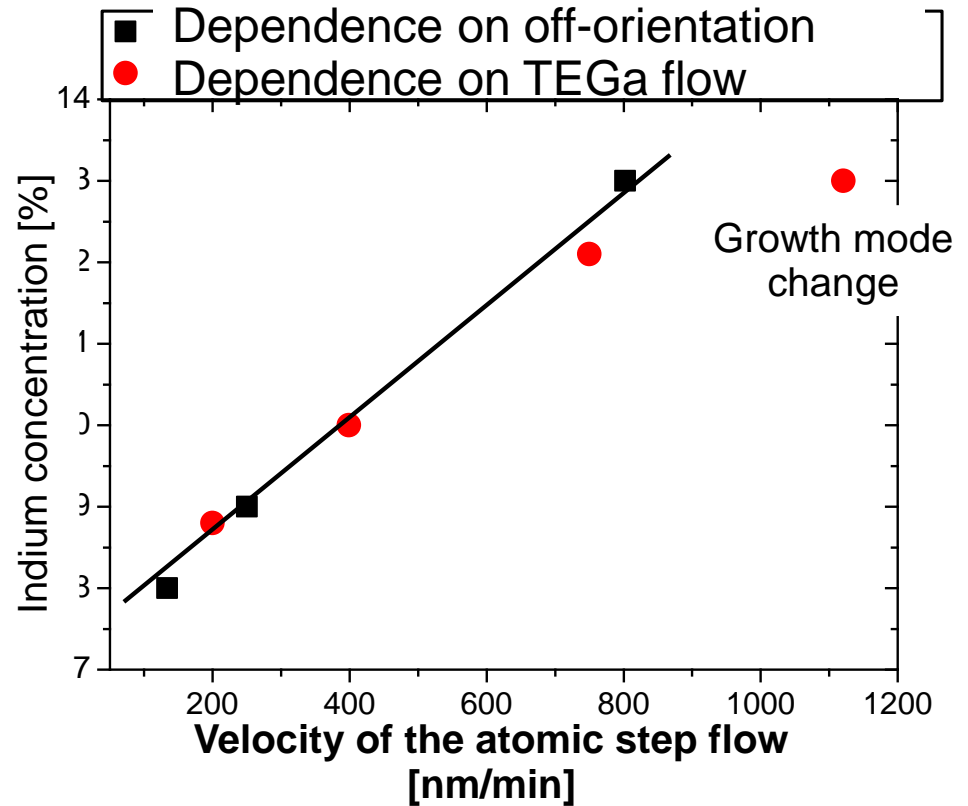
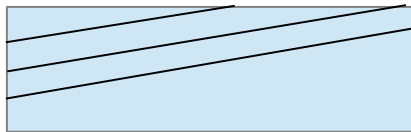
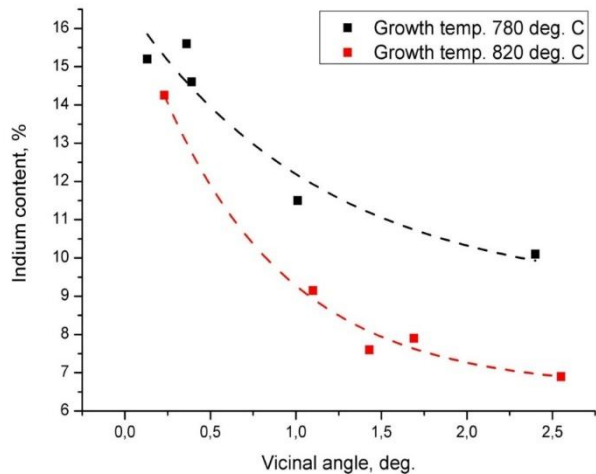
## 3-D Projectors without goggles- Holy Grail of optoelectronics



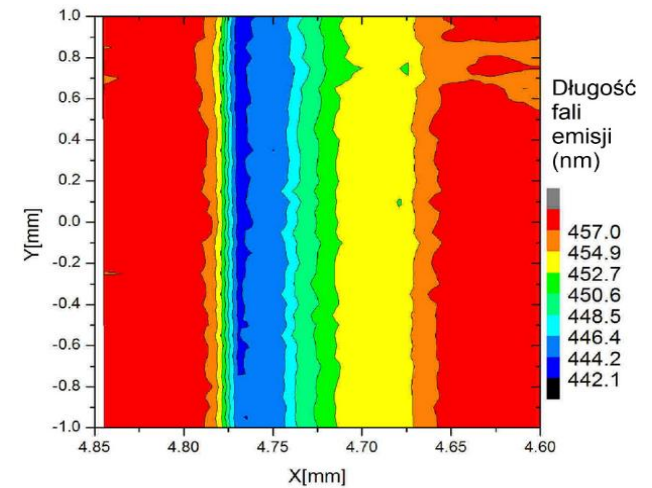
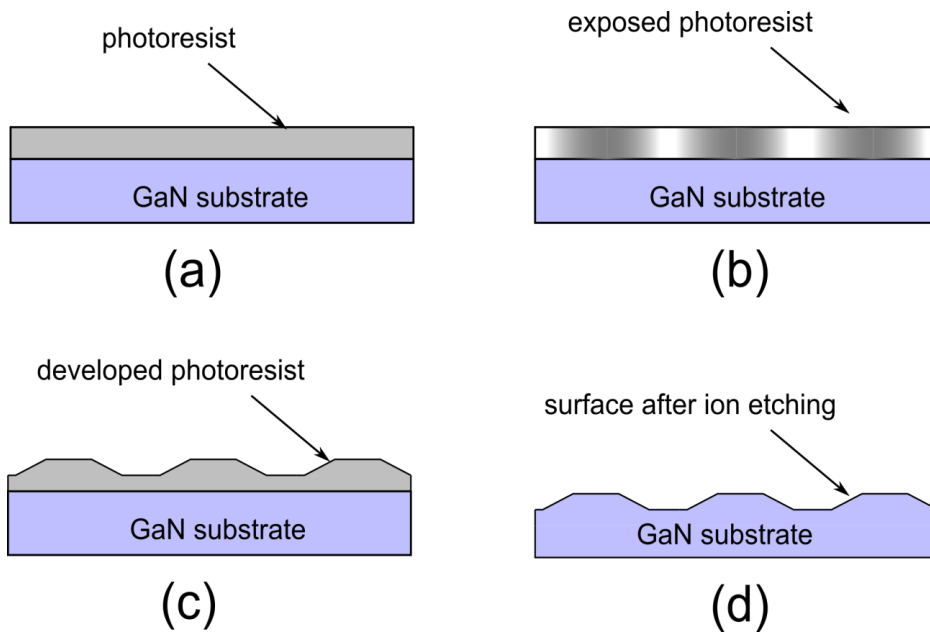
Nitrides:  
Blue 450-460 nm,  
step 1 nm  
Green 520-530 nm,  
step 1 nm

Arsenides/phosphides  
Red 630-640 nm,  
step 1 nm

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

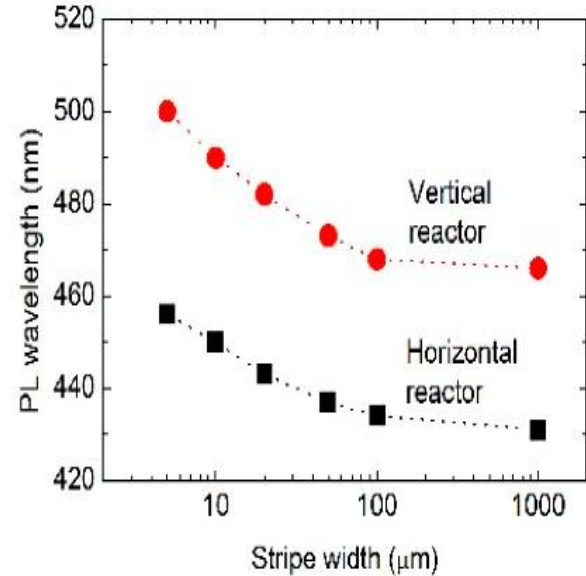
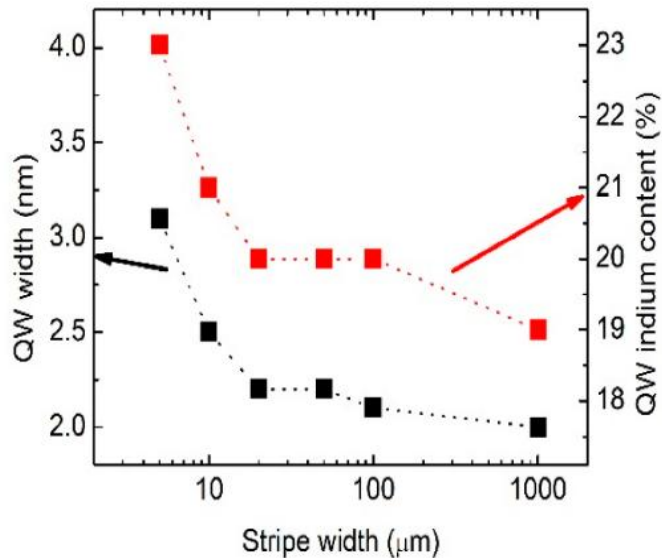
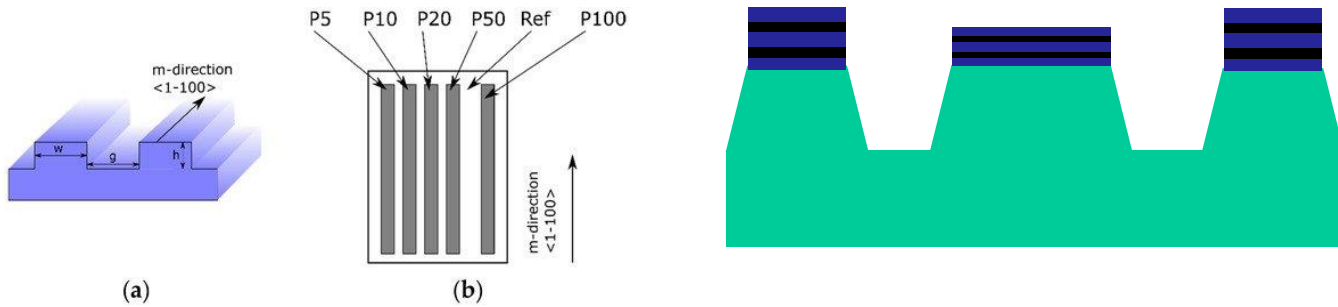


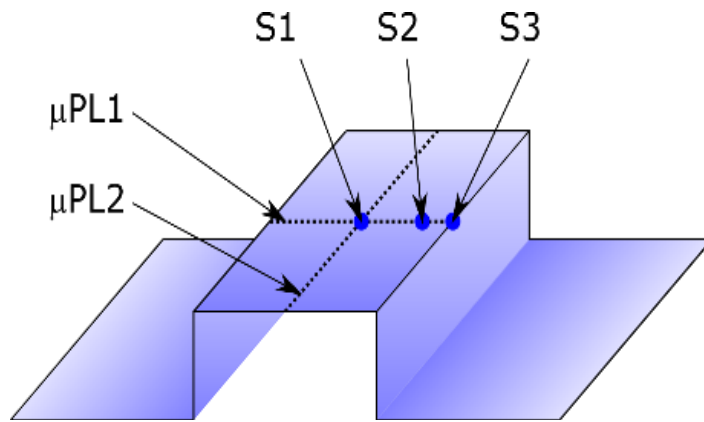
# Technology 1: Lateral patterning



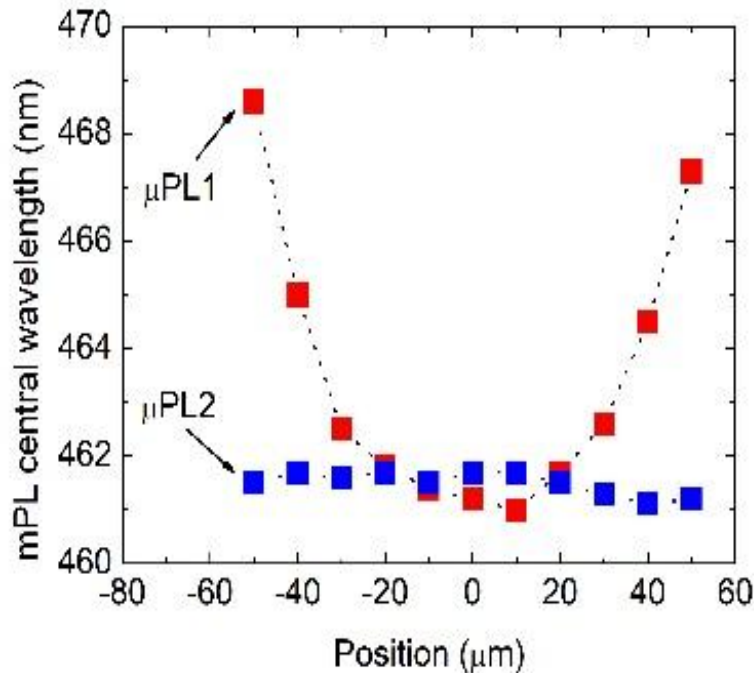
**M. Sarzynski idea**  
**Patented by TopGaN/Unipress**

# Technology 2. Growth of InGaN QWs on narrow stripes.





**Faster growth at the edges, more indium incorporated**



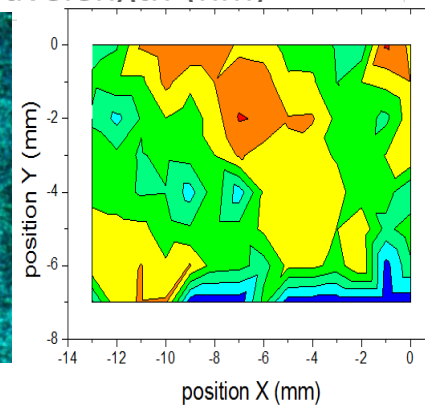
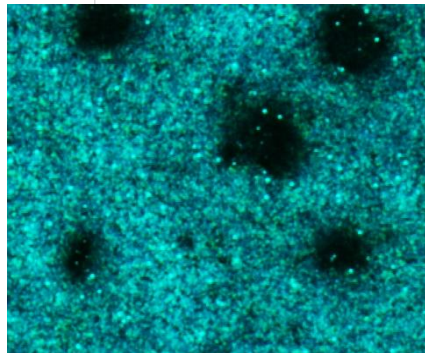
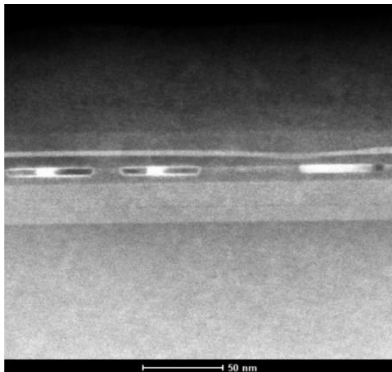
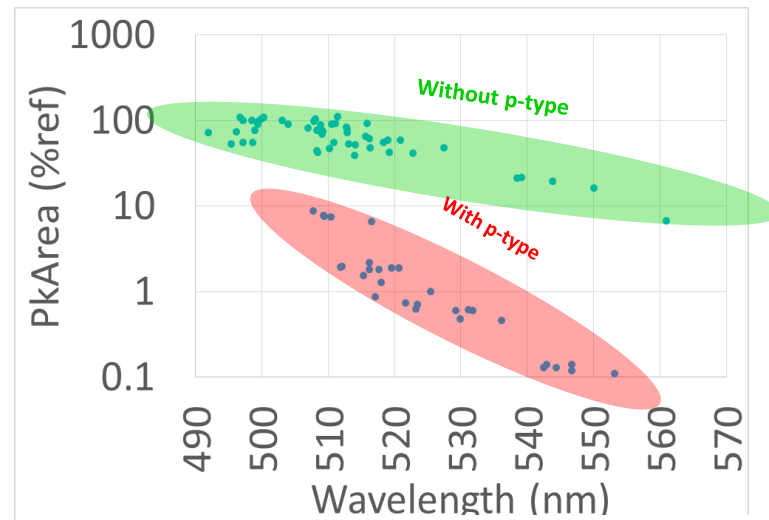
**Both technology 1 and 2 of blue multicolour arrays attract a big interest as they may lead to 3D projectors.**

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

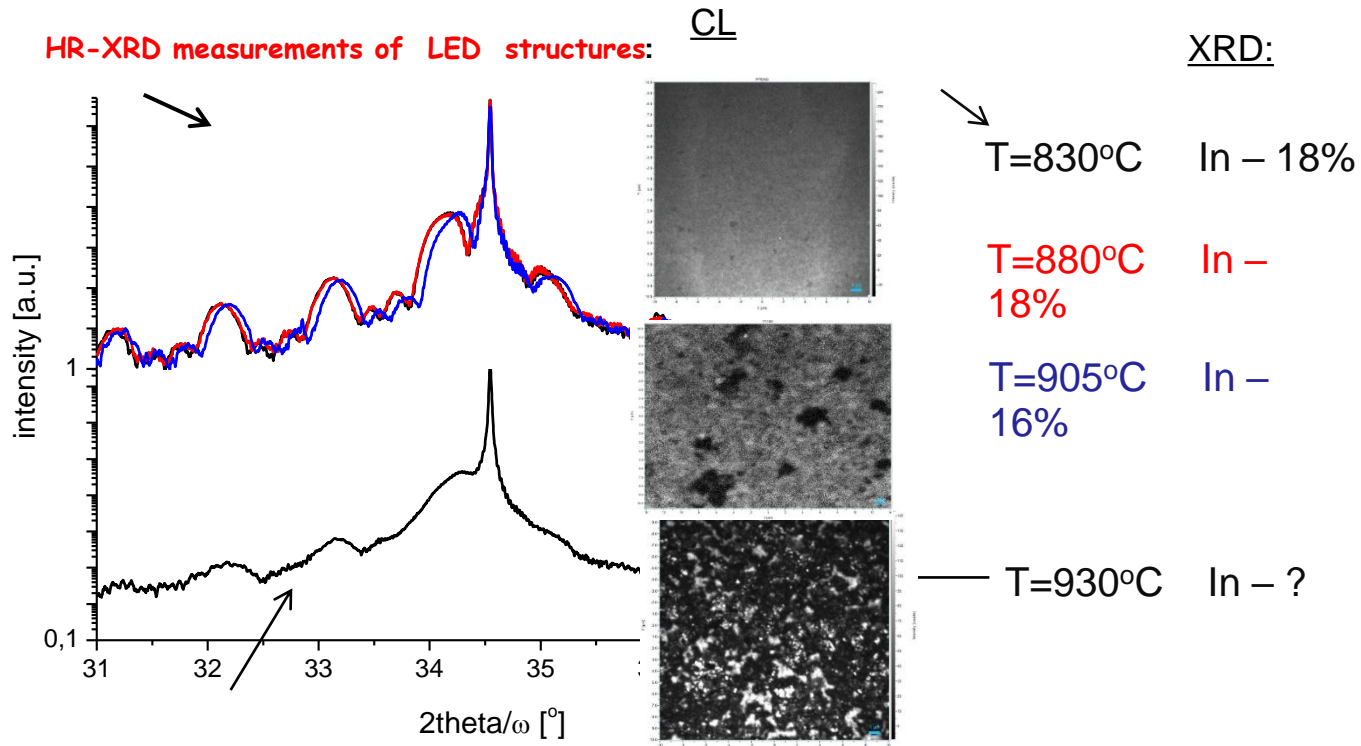


# InGaN MQW decomposition

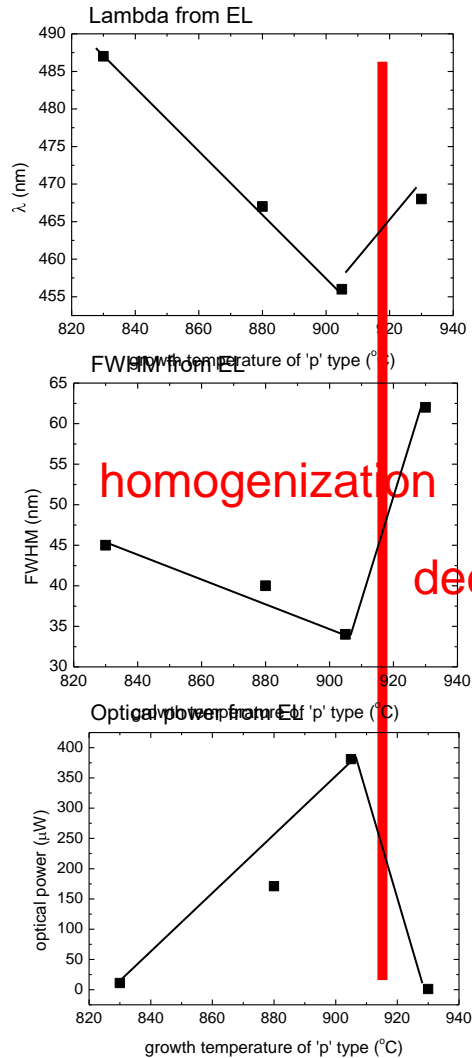


TEM: nanometer scale, Fluorescent microscopy: micrometers, MicroPL: m

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



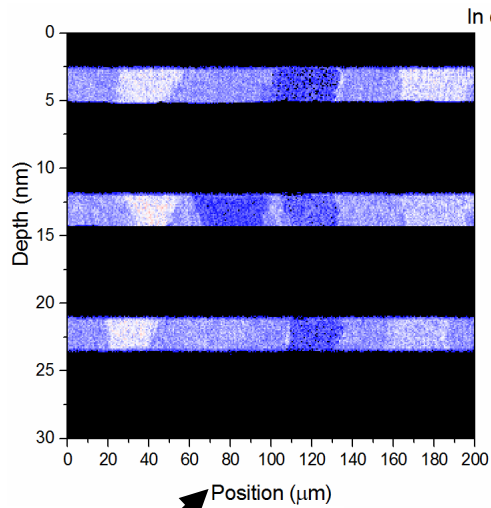
At high temperature satellite peaks becomes much more broader and disappear : QWs degradation occurs



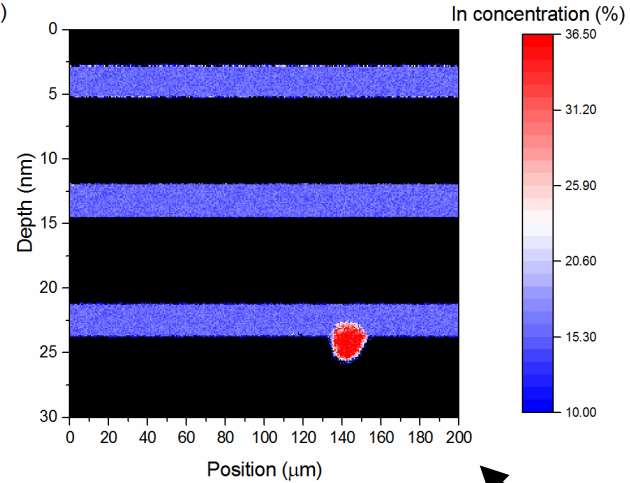
**For samples on sapphire (high dislocation density) we are able to homogenize InGaN QWs by growing p-type at high temperature.**

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

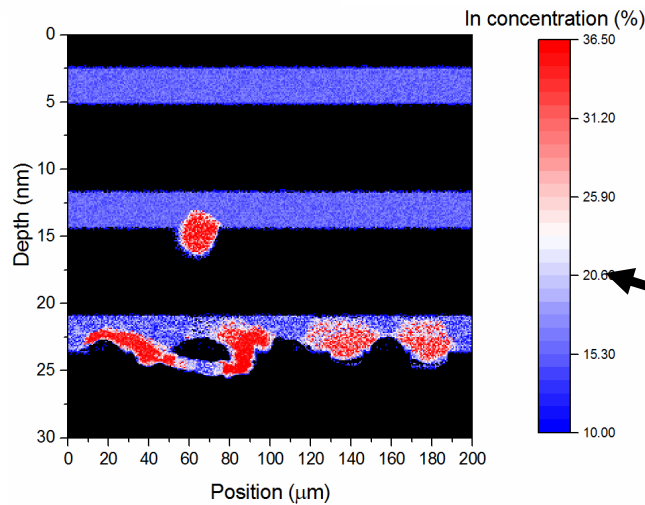
# SIMS data of In-content



as grown

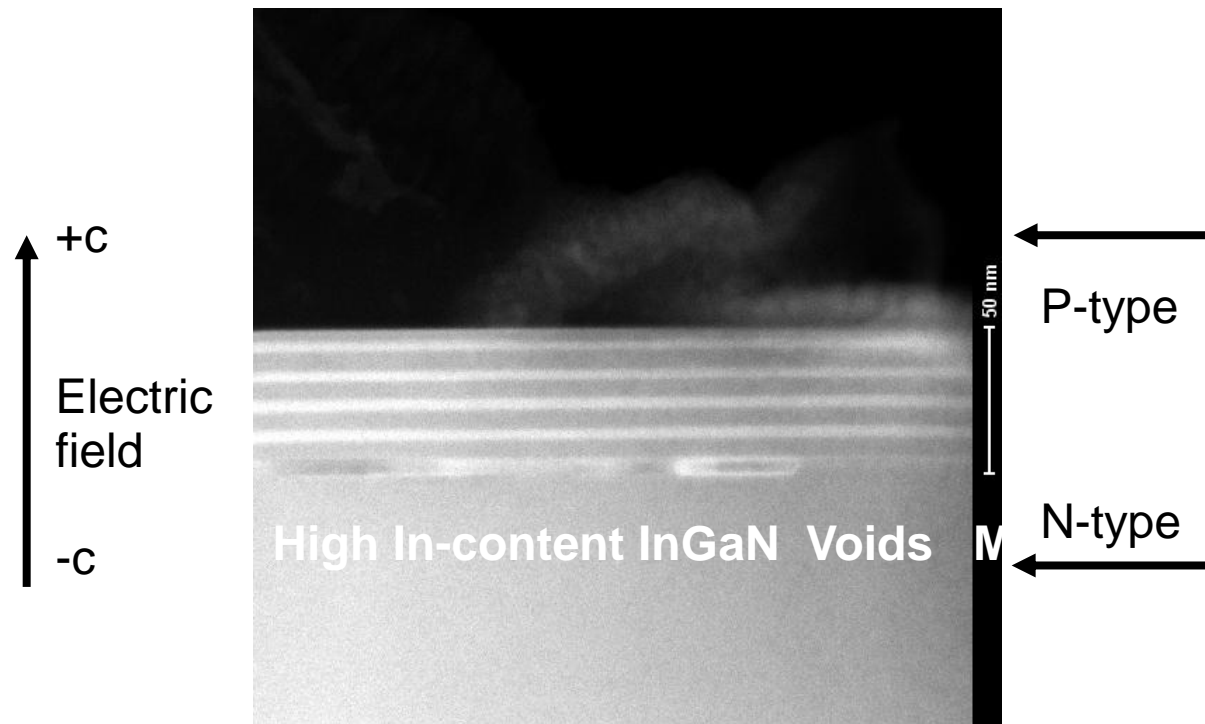


Homogenized  
905°C



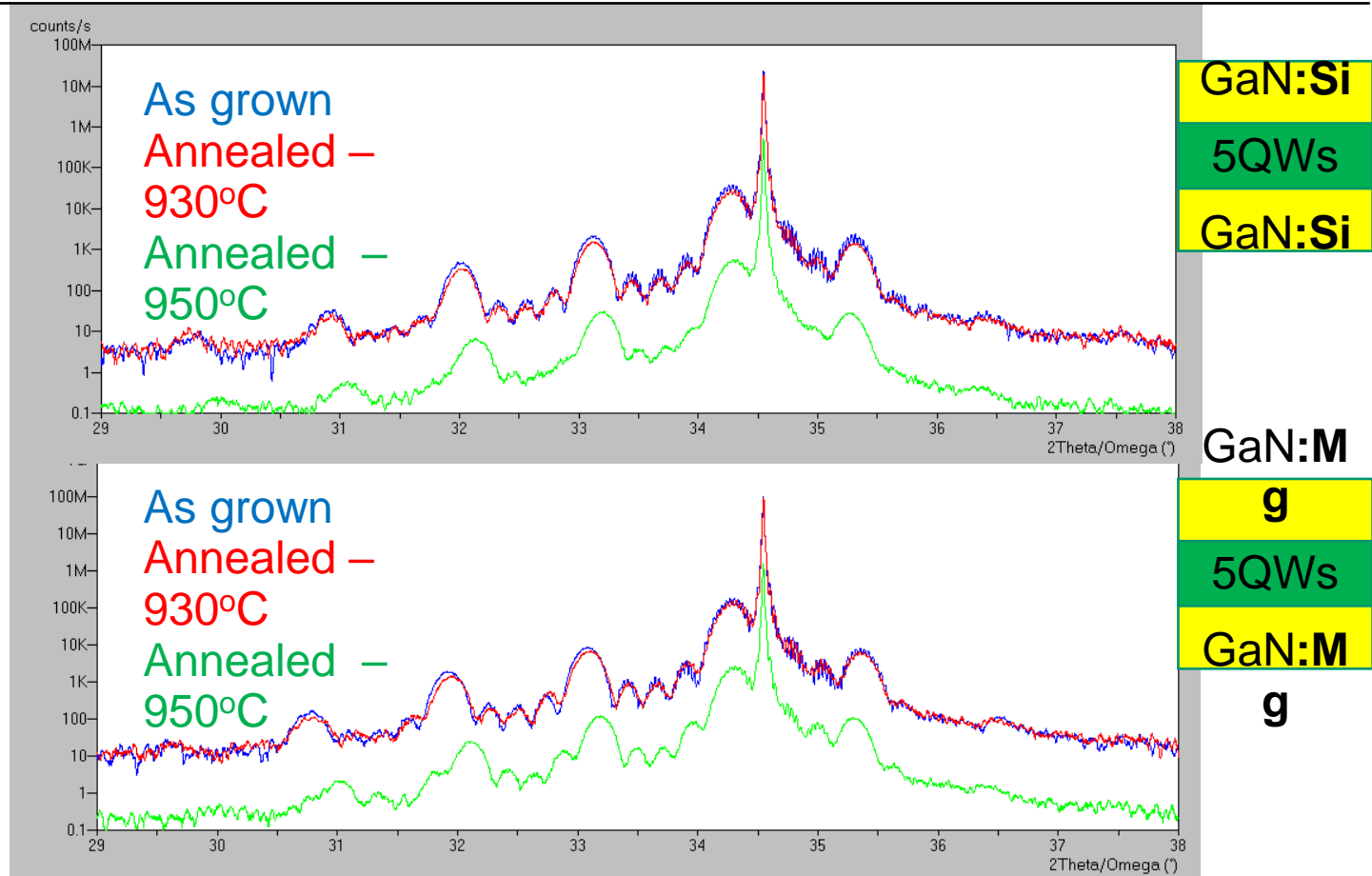
Decomposed  
930°C

Why does the decomposition start from the first QW?



# Diiferent doping below and above the InGaN/GaN MQWs

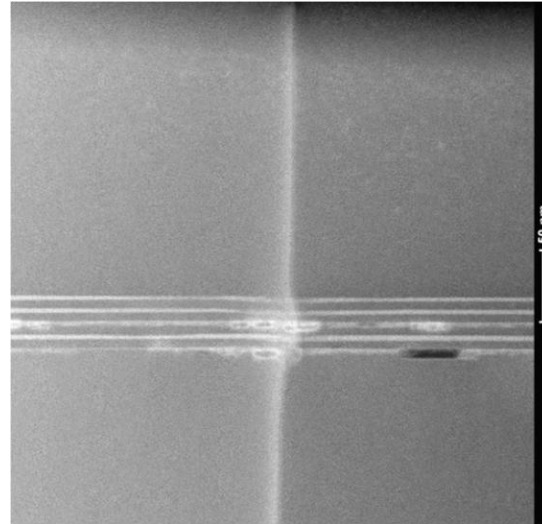
5QWs - (460 nm) - 17%In



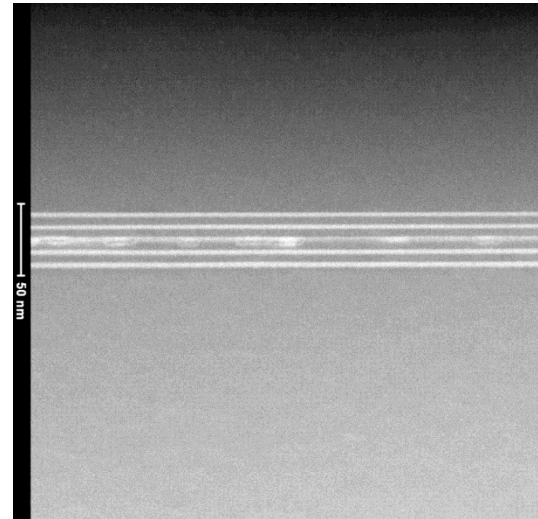
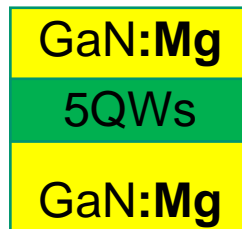
## After annealing at 950°C

No decomposition from the top

Electric field  
driven diffusion?  
Yes!



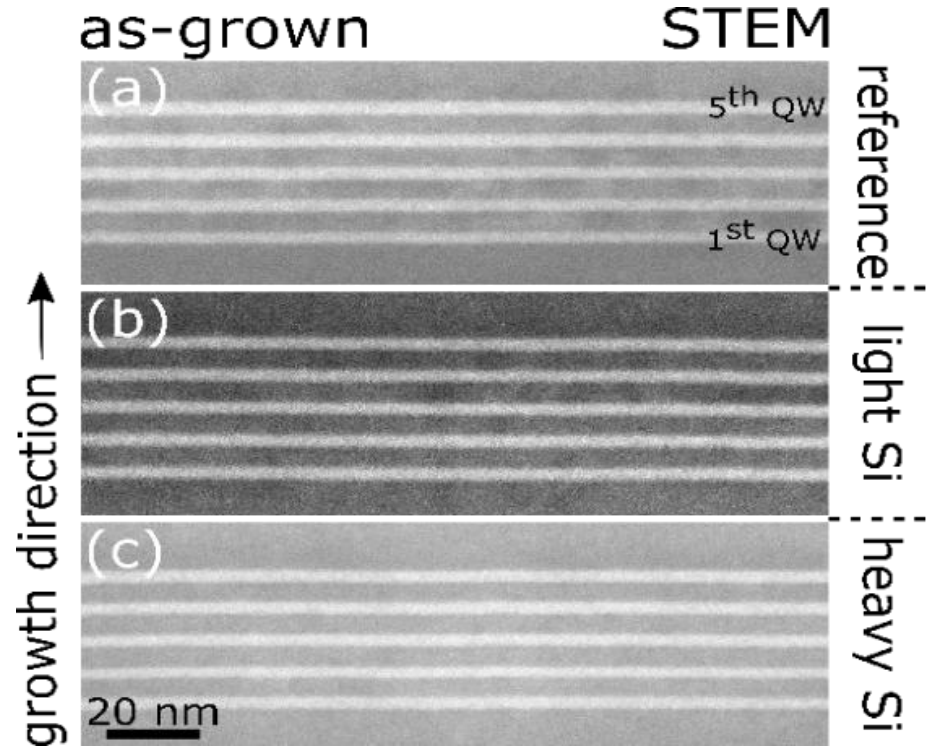
No decomposition  
above and below  
GaN:Mg



Ga-vacancies?  
Yes!

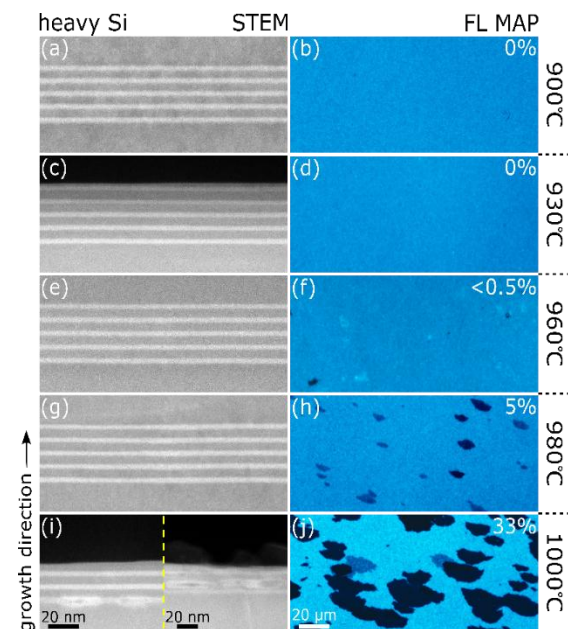
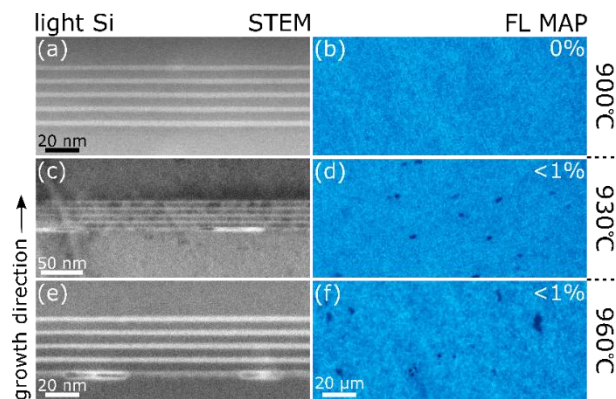
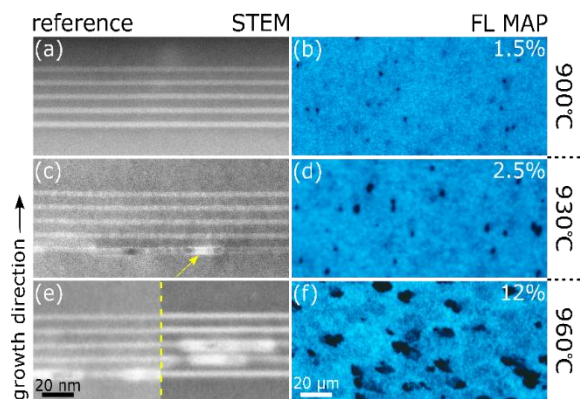
# Influence of Si-doping on InGaN QW decomposition

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

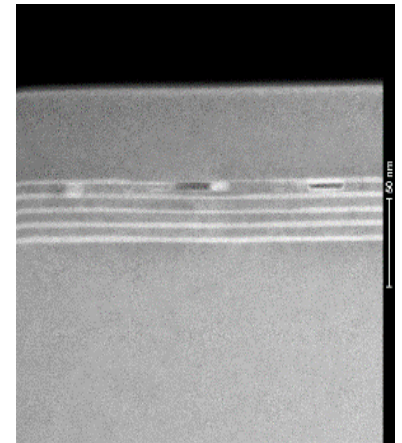
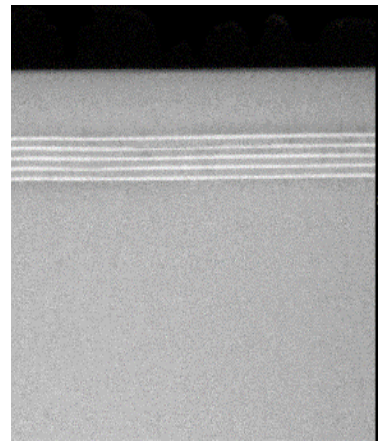
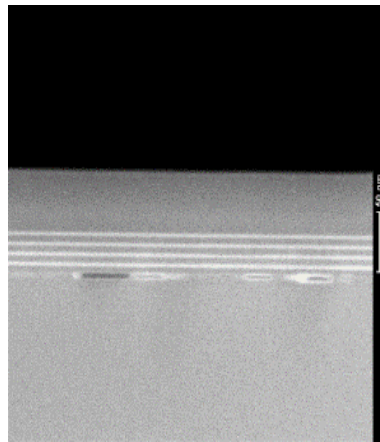
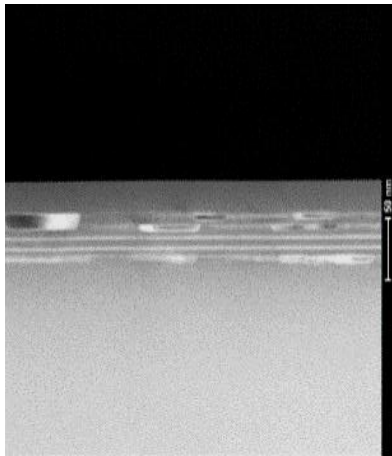




# High Si doping: decrease of V(Ga) mobility



## Influence of annealing atmosphere



A

B

C

D

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

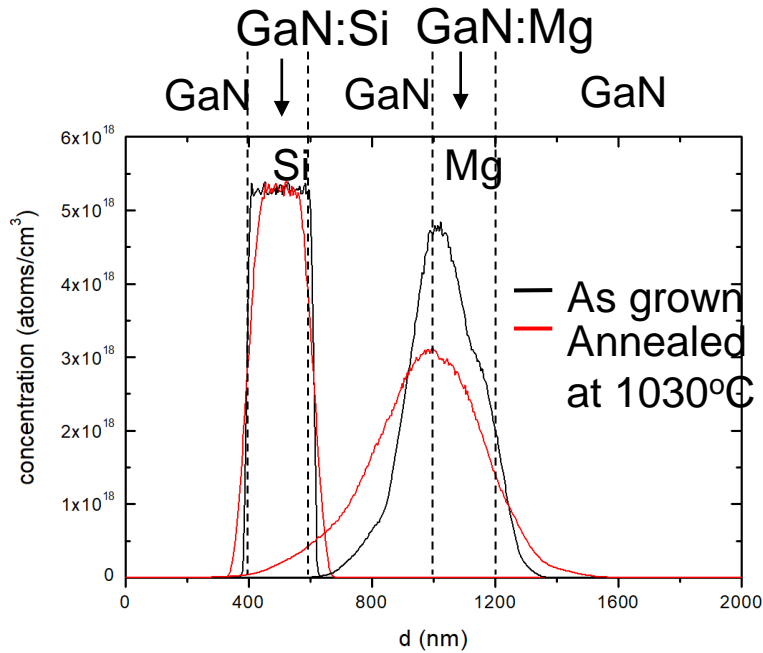
***A: in NH<sub>3</sub>+H<sub>2</sub> atmosphere,***

***B: in TEGa+NH<sub>3</sub>+H<sub>2</sub>,***

***C: in TEGa+NH<sub>3</sub>+H<sub>2</sub>, the barrier before the first QW doped with Si,***

***D: in NH<sub>3</sub>+H<sub>2</sub>, the barrier before the first QW doped with Si.***

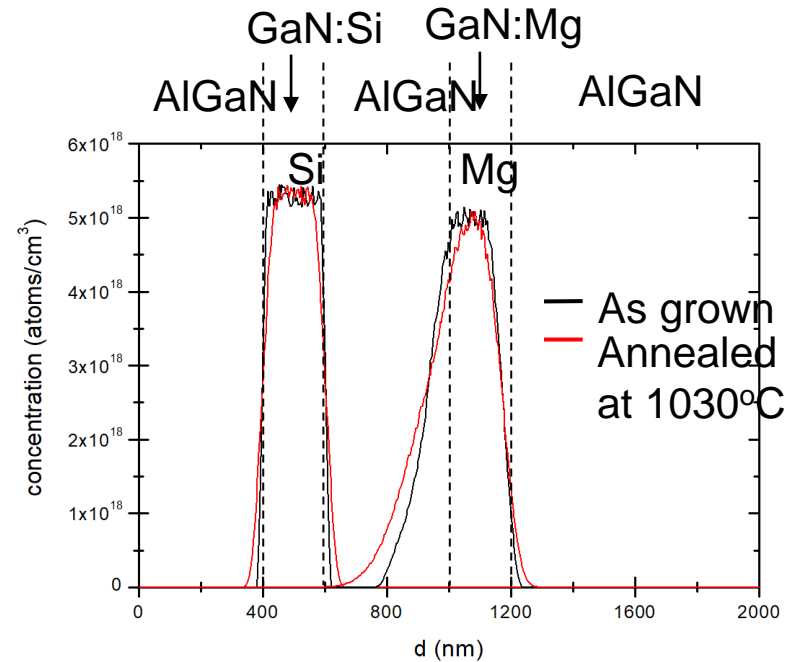
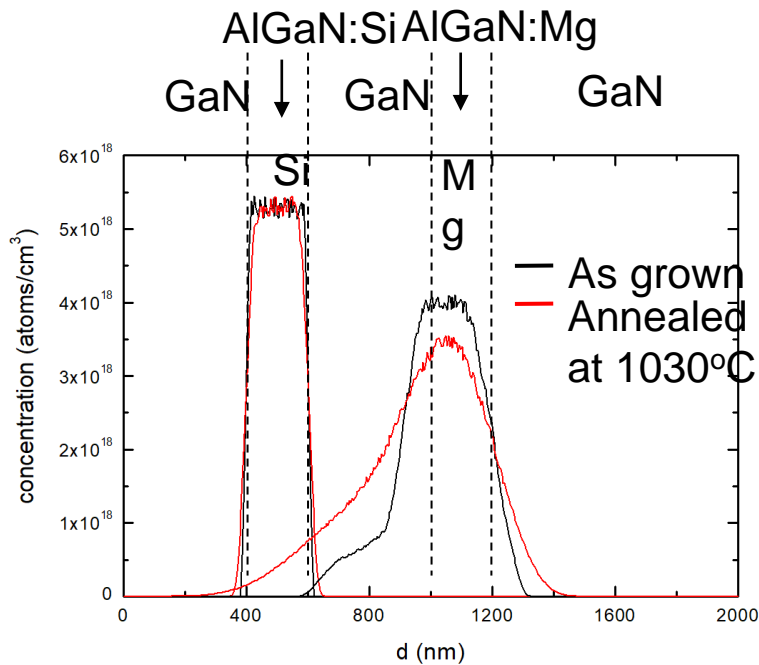
# Atoms diffuse during growth!



Why Mg diffuses easier than Si?  
Interaction of Mg, H, V?

Reactor memory. Why Mg is better remembered than Si?

# Mg diffuses easier in GaN than in AlGaN?



## 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.