Metalorganic Vapour Phase Epitaxy (MOVPE) of Nitrides and III-V Nano-heterostructures

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Outline

- Heterostructures
- MOVPE principle
- Reactor types
- In situ monitoring
- GaN epitaxy challenges
- Nanoheterostructure epitaxy (in FZU)

Compound semiconductors and heterostructures

Elements used in semiconductors

First, germanium and afterwards silicon were discovered to have semiconductor properties

	II.B	III.A	IV.A	V.A	VI.A
2		B	C	N	O
3		Al	**Si**	P	S
4	Zn	Ga	**Ge**	As	Se
5	Cd	In	Sn	Sb	Te
6	Hg	Tl	Pb	Bi	Po

Elements used in semiconductors

Later, in 60-ties and 70-ties also III-V semiconductors were prepared also in layered structures (so called heterostructures)

	II.B	III.A	IV.A	V.A	VI.A
2		B	C	N	O
3		**Al**	**Si**	**P**	S
4	Zn	**Ga**	**Ge**	**As**	Se
5	Cd	In	Sn	**Sb**	Te
6	Hg	Tl	Pb	Bi	Po

Elements used in semiconductors

II-VI semiconductors were discovered approx ten years later

	II.B	III.A	IV.A	V.A	VI.A
2		B	C	N	O
3		**Al**	**Si**	**P**	**S**
4	**Zn**	**Ga**	**Ge**	**As**	**Se**
5	**Cd**	In	Sn	**Sb**	**Te**
6	**Hg**	Tl	Pb	Bi	Po

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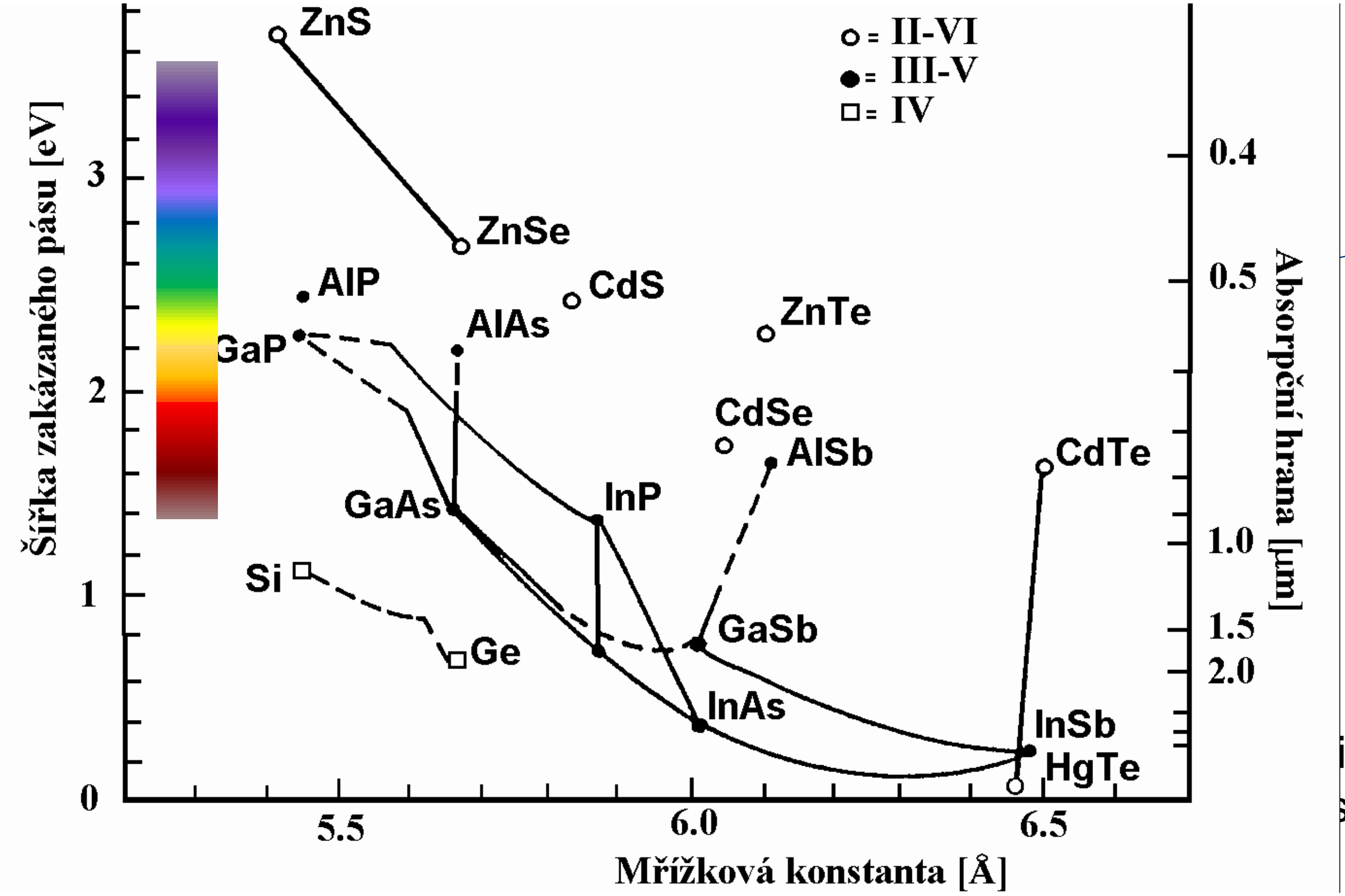
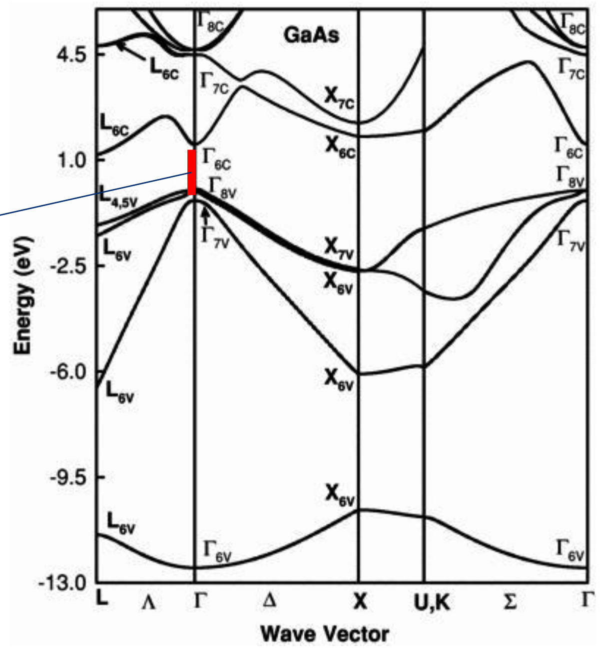
Elements used in semiconductors

Finally, nowadays semiconductors employ also the small atoms in the first raw with strong bounds and large band gaps

	II.B	III.A	IV.A	V.A	VI.A
2		B	C	N	O
3		Al	Si	P	S
4	Zn	Ga	Ge	As	Se
5	Cd	In	Sn	Sb	Te
6	Hg	Tl	Pb	Bi	Po

Older types of binary and ternary compound semiconductors





icond. alloys – dashed lines represents
s since only semiconductors with similar

Binary and ternary compound semiconductors

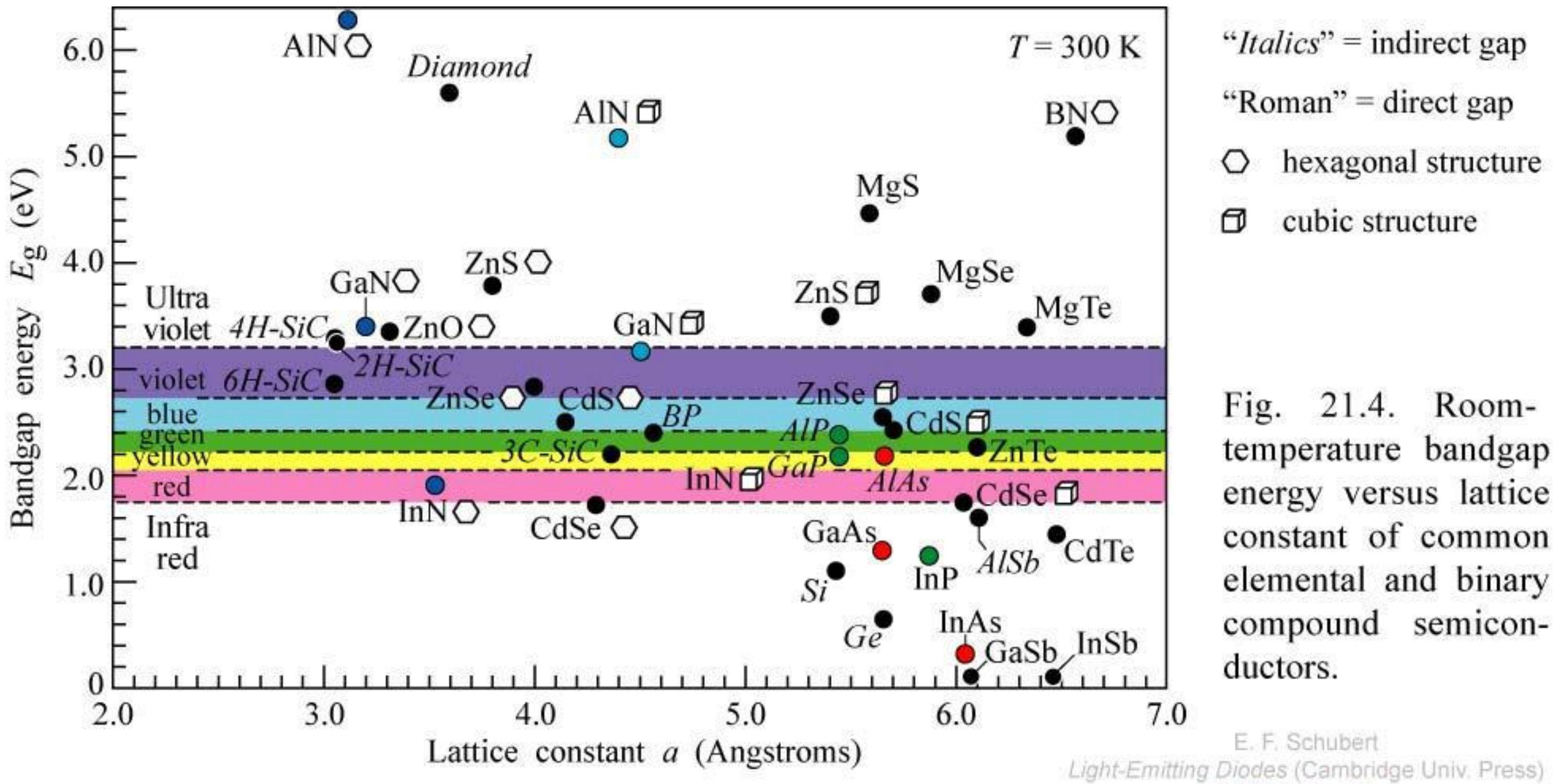


Fig. 21.4. Room-temperature bandgap energy versus lattice constant of common elemental and binary compound semiconductors.

E. F. Schubert
Light-Emitting Diodes (Cambridge Univ. Press)
www.LightEmittingDiodes.org

Many semiconductors are still missing in this graph .

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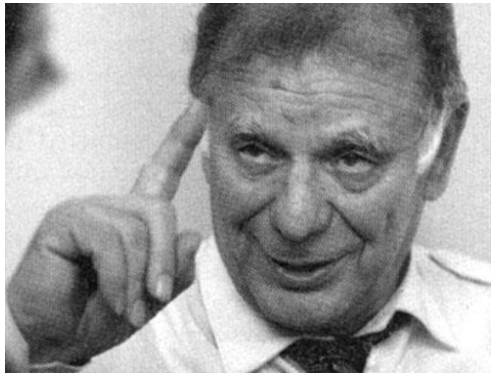
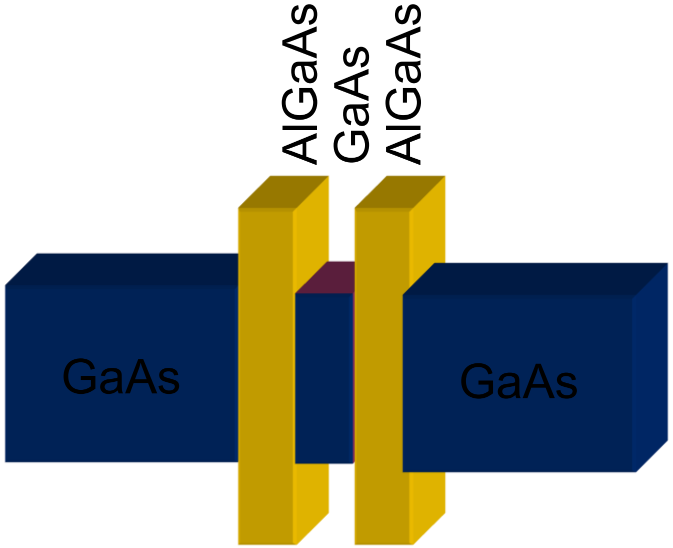
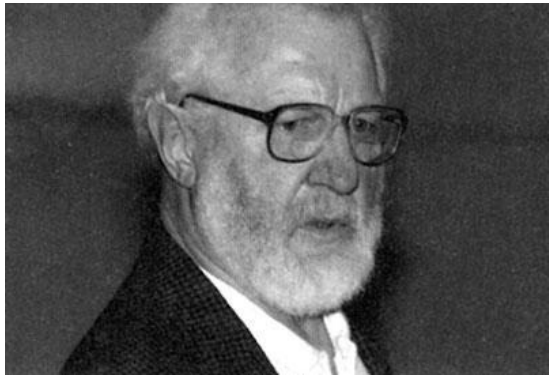
AlGaAs/GaAs double heterosructures



Žores Aljorov

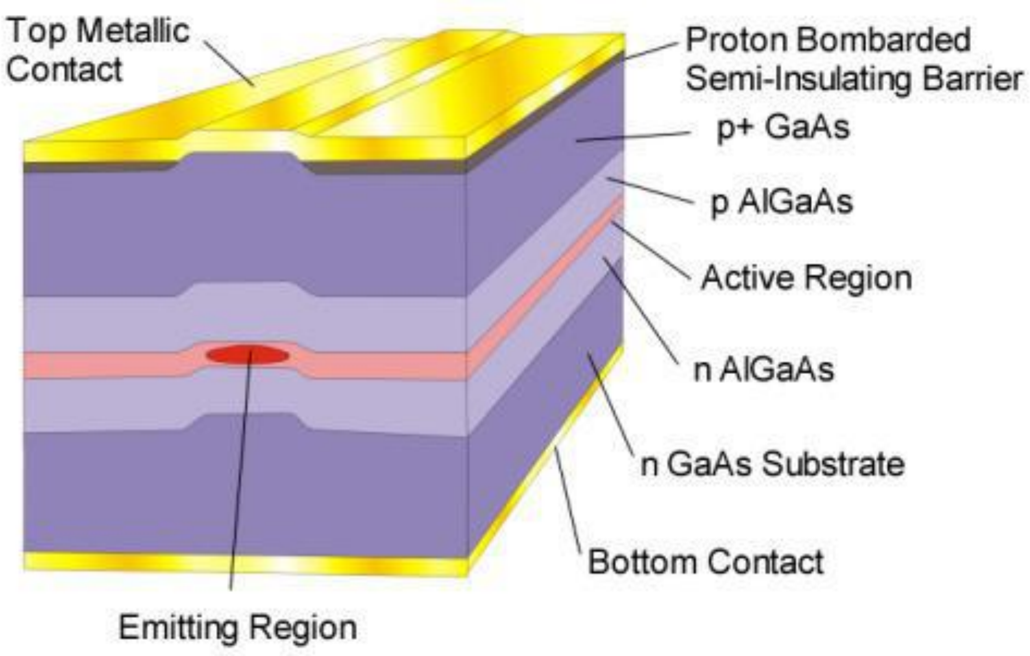




Herbert Kroemer

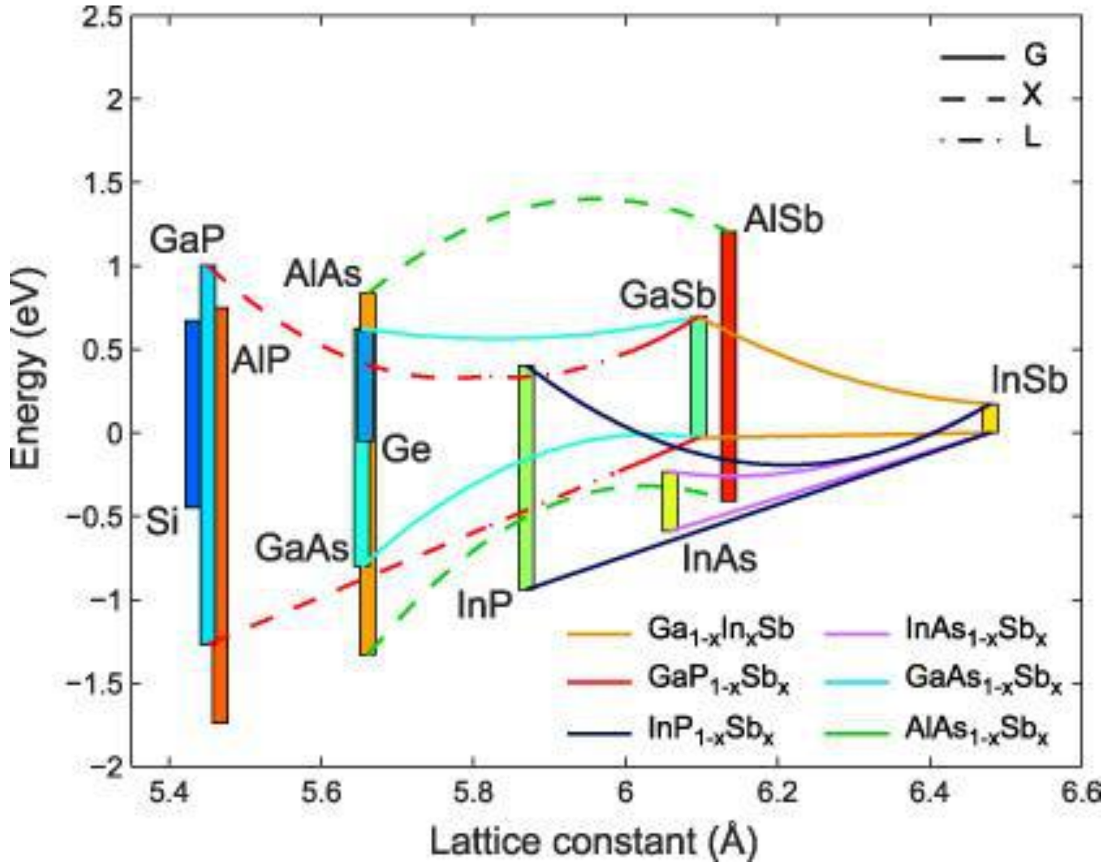
The first heterostructure was designed Ž. Alfjorov and H. Kroemer. They succeeded to substantially increased emission intensity and prepared first laser diodes. **Nobel Prize**

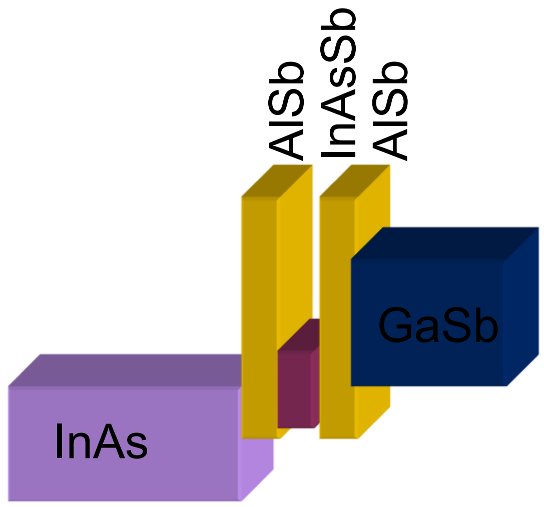
Separate confinment of electrons and photons



Separate confinment of electrons and photons
– another increase of emission intensity of laser diodes

Binary and ternary compound semiconductors

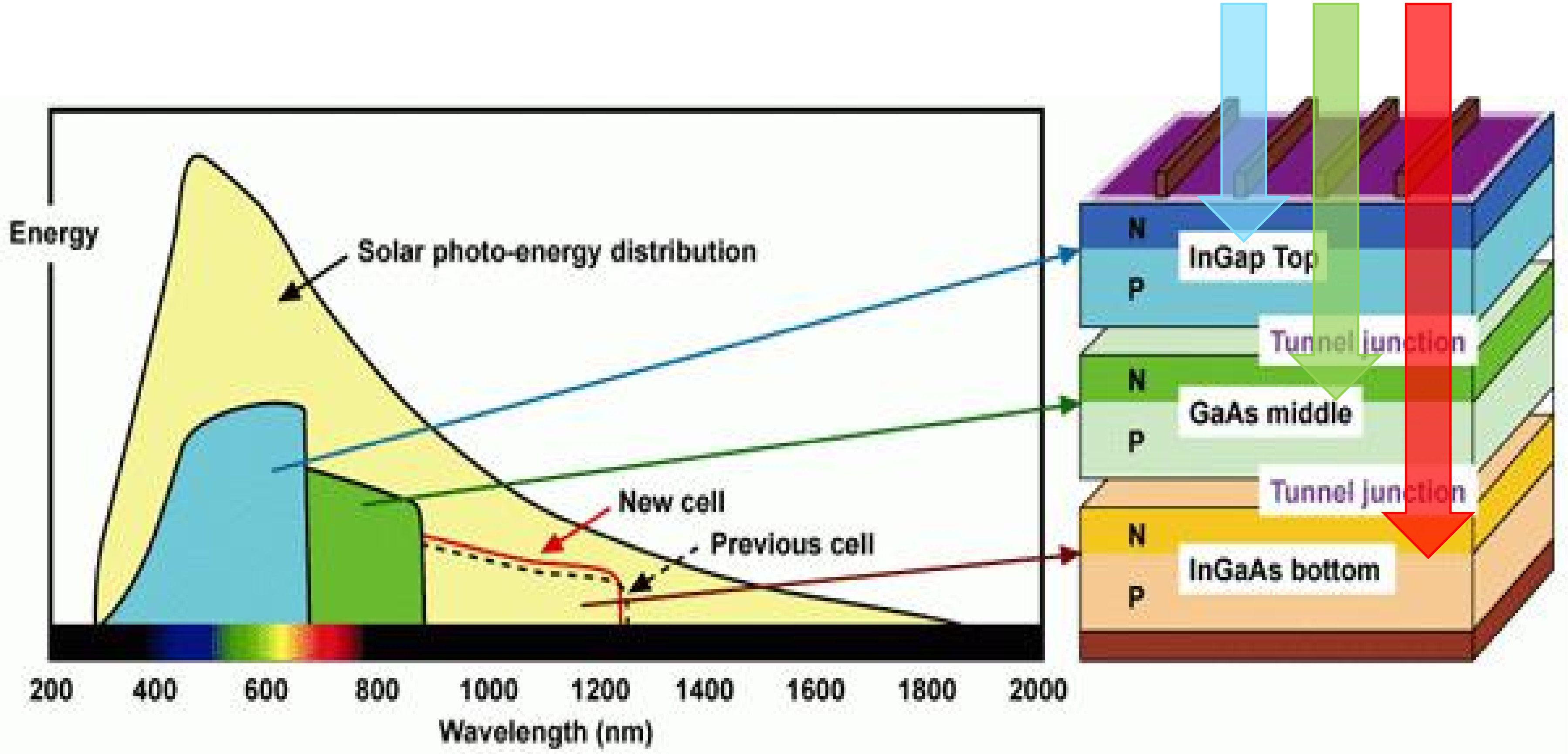




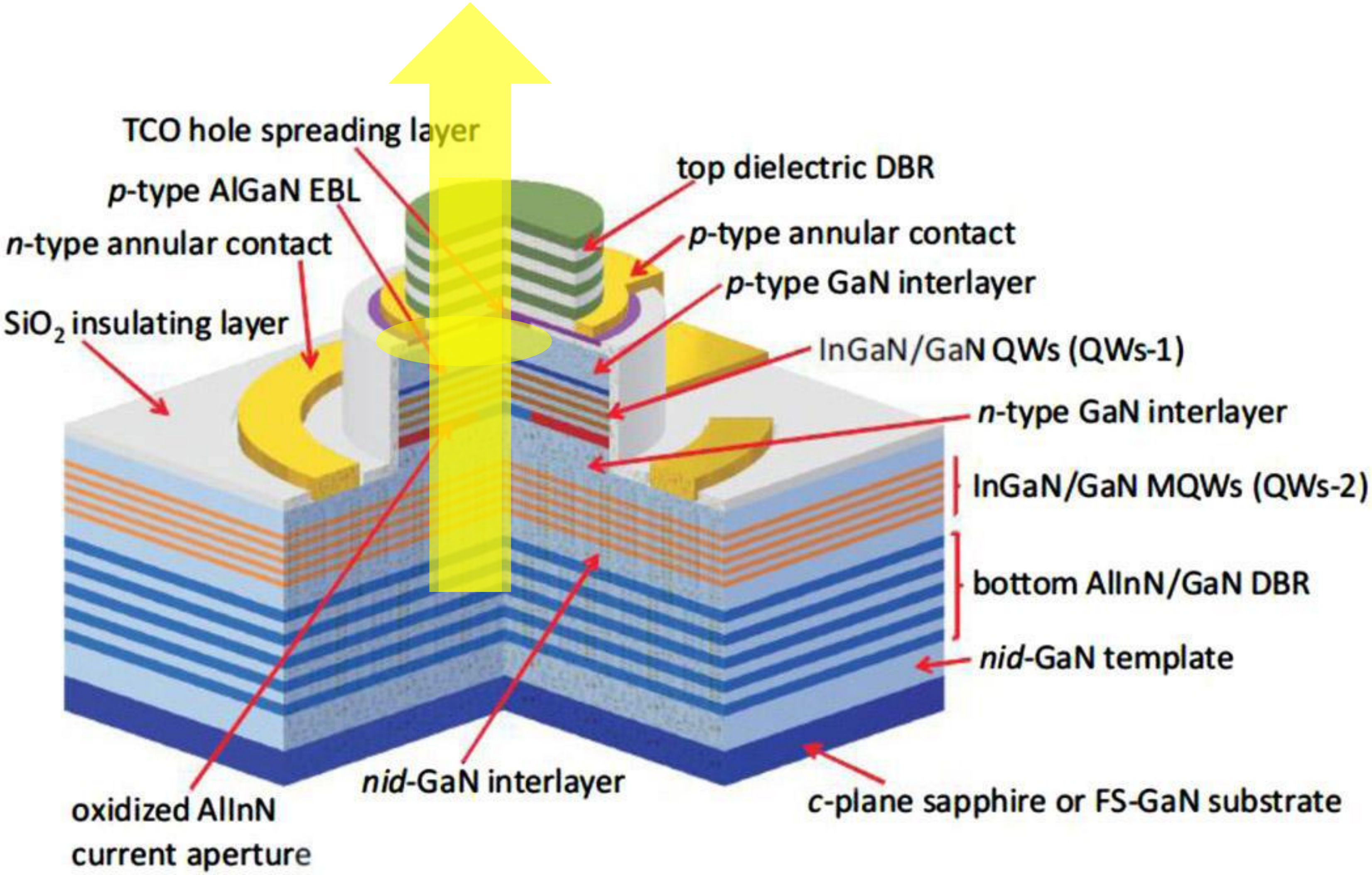
Semiconductors is a kind of toy for technologist: a set of brics from which you can bulit functional heterostructure

To design properly heterostructure with required properties you have to know the properties of bricks: position of conduction and valence band, lattice parameter, polarization, effective masses…

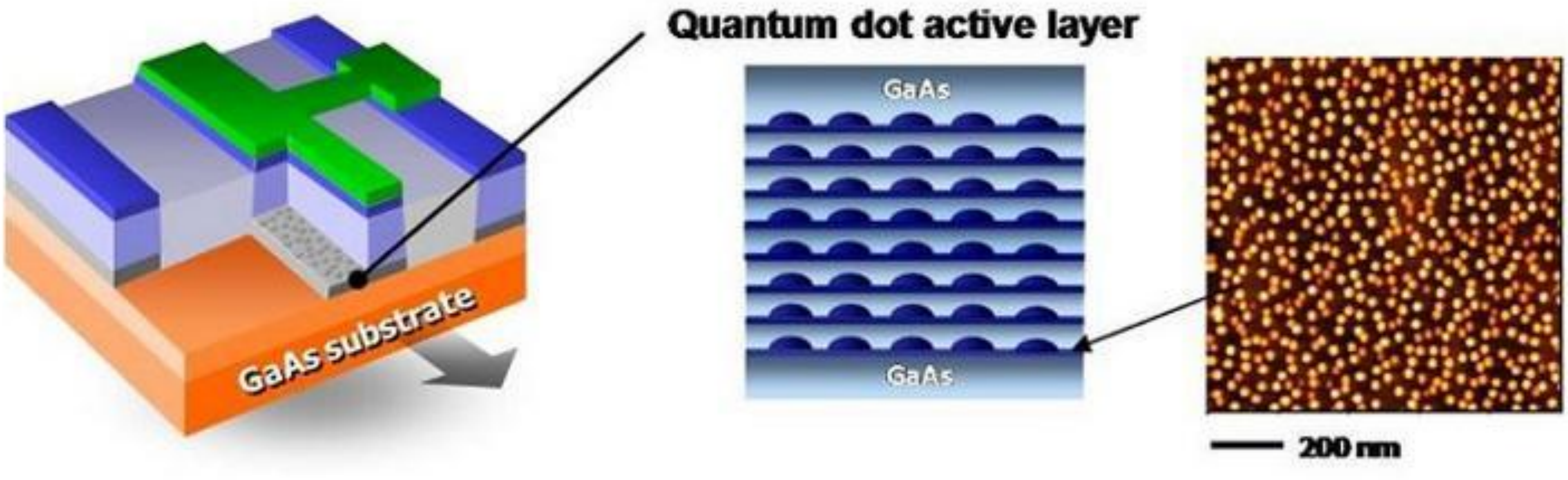
There are many other possibilities for heterostructure design and their applications such as: **Tandem solar cells**



Blue VCSEL structure



Structures with quantum dots



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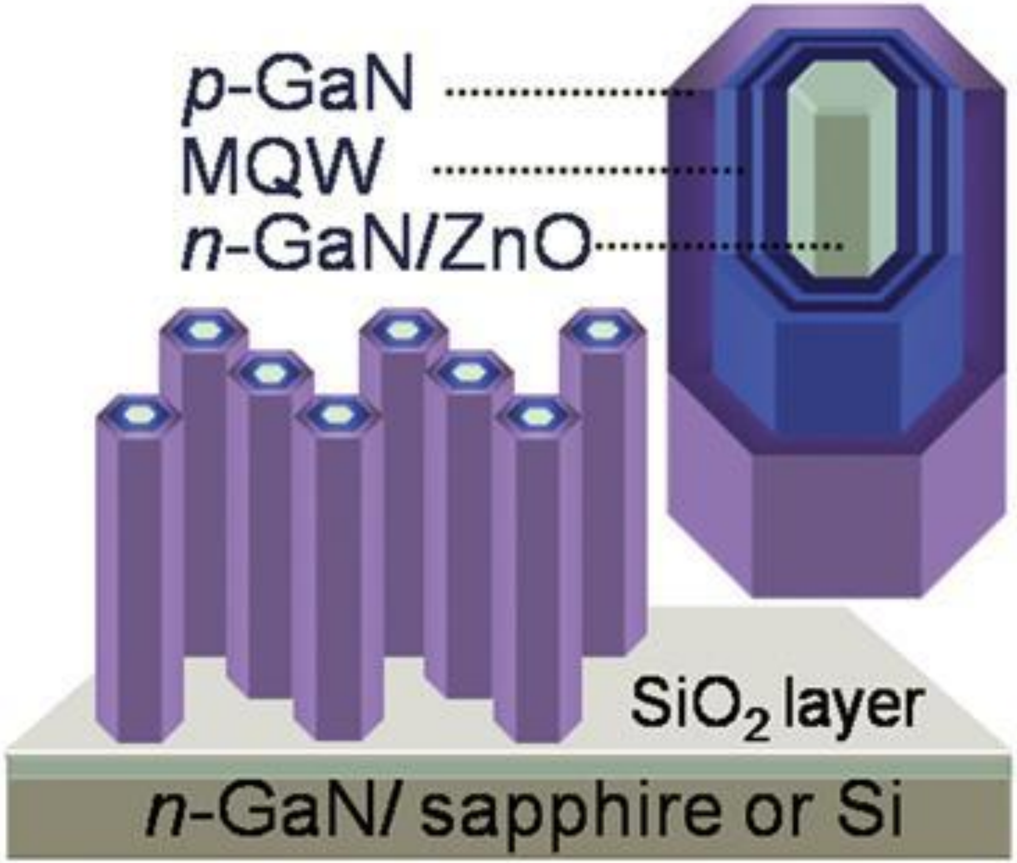
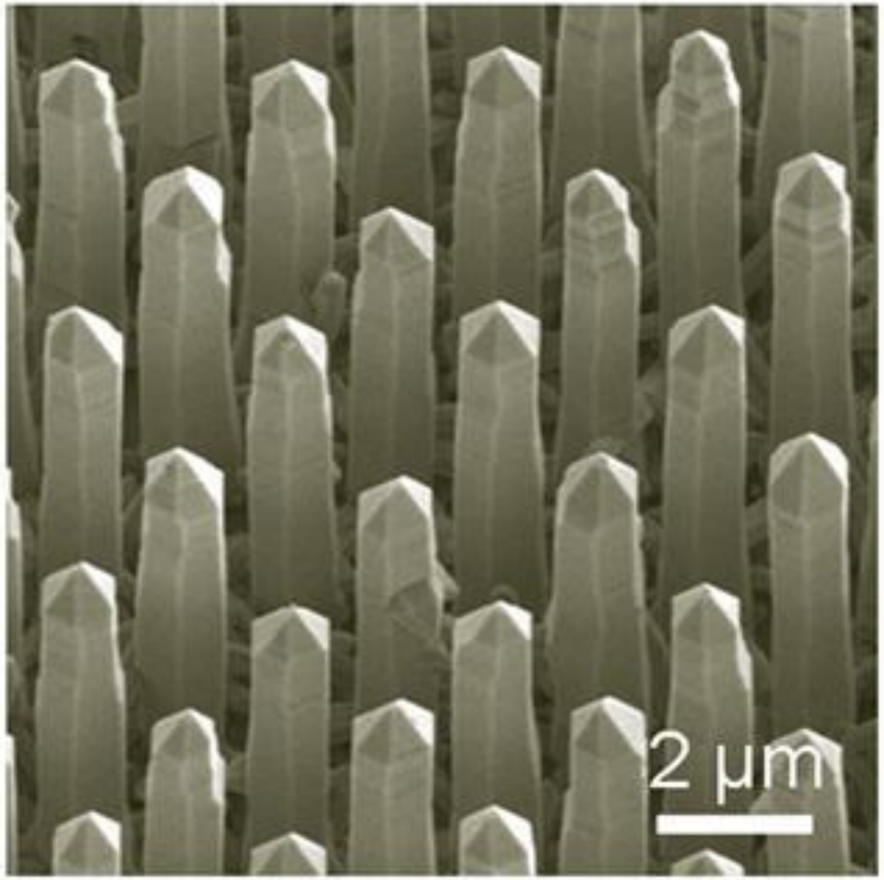
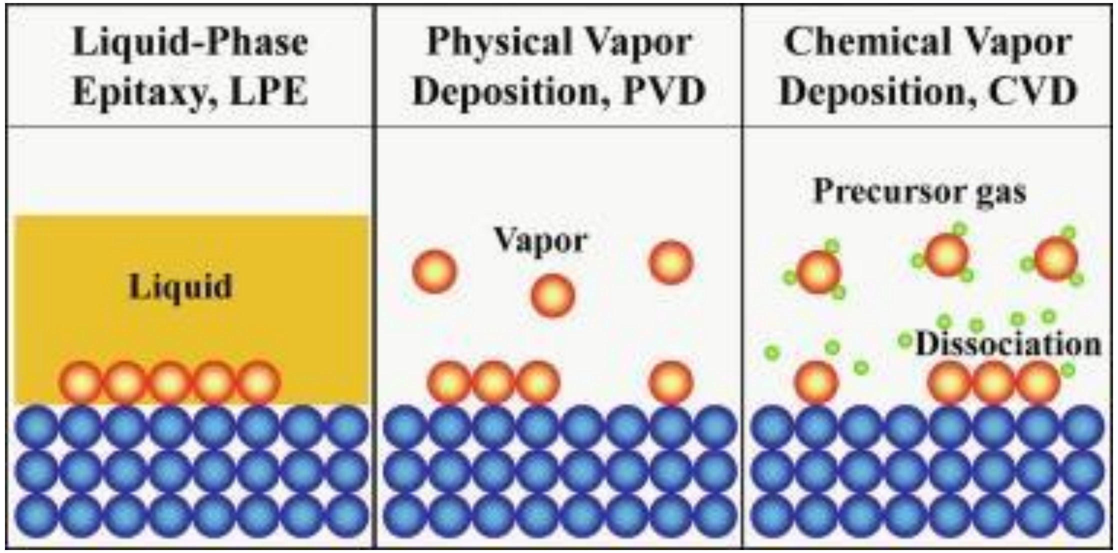
Sofisticated „core-shell“ structures





A growth of heterostructures is enabled by epitaxy

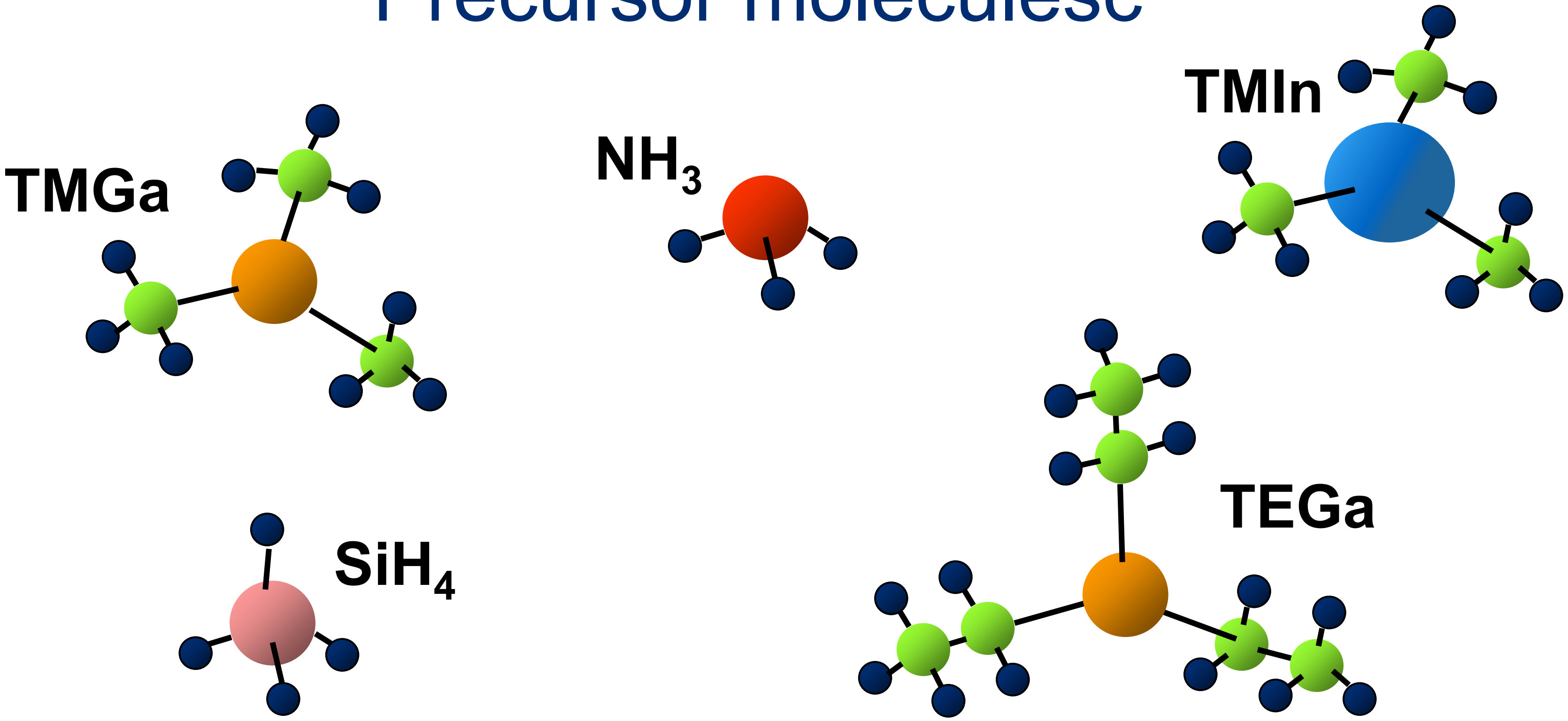


Many epitaxial techniques:

- Liquid phase epitaxy (LPE)
- Vapour phase epitaxy (HVPE, PVD, MBE, PAMBE, ALE, PECVD, **MOVPE (MOCVD)**)

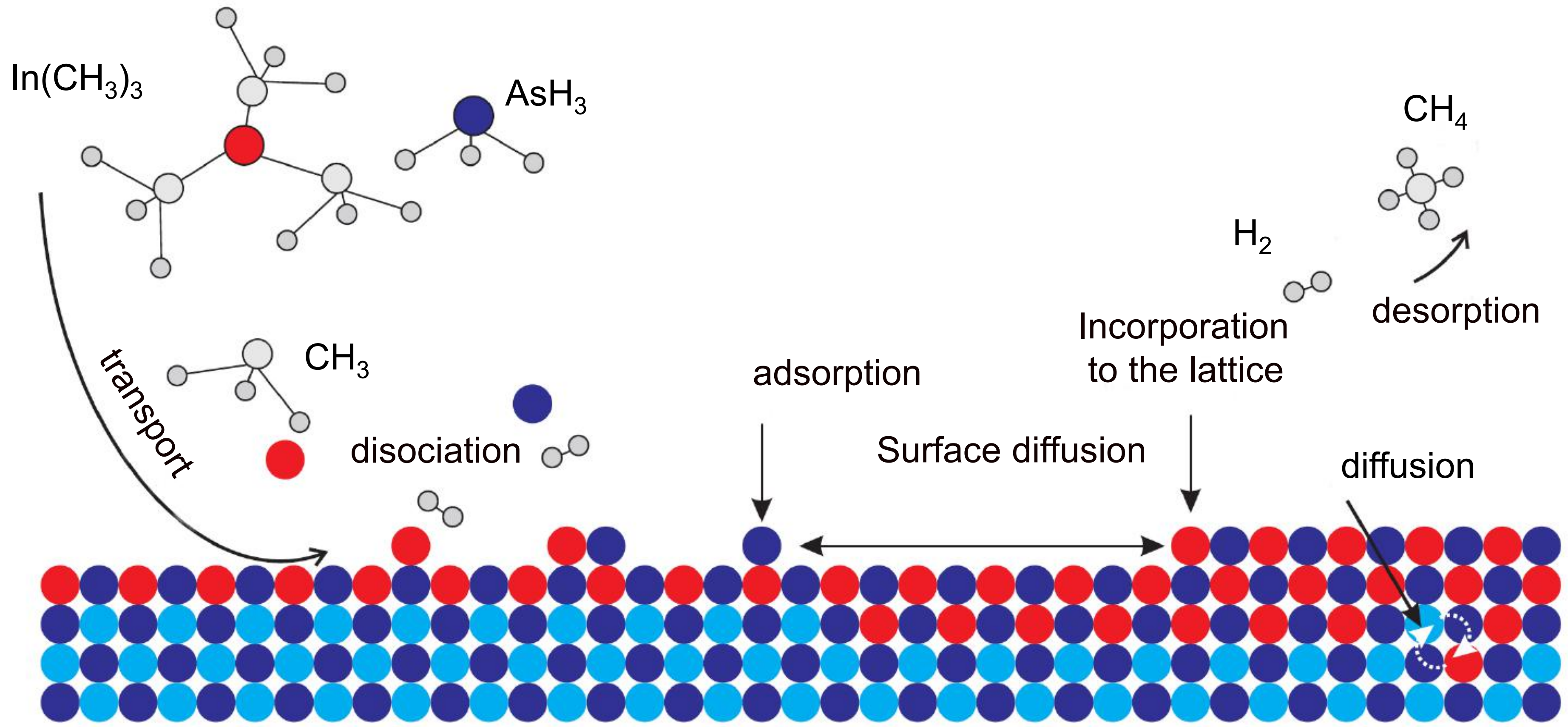
MOVPE - principle

MOVPE
Precursor moleculesc



$$\text{TMGa} + NH_3 \rightarrow \text{GaN} + 3\,CH_4$$

MOVPE
Physical and chemical processes



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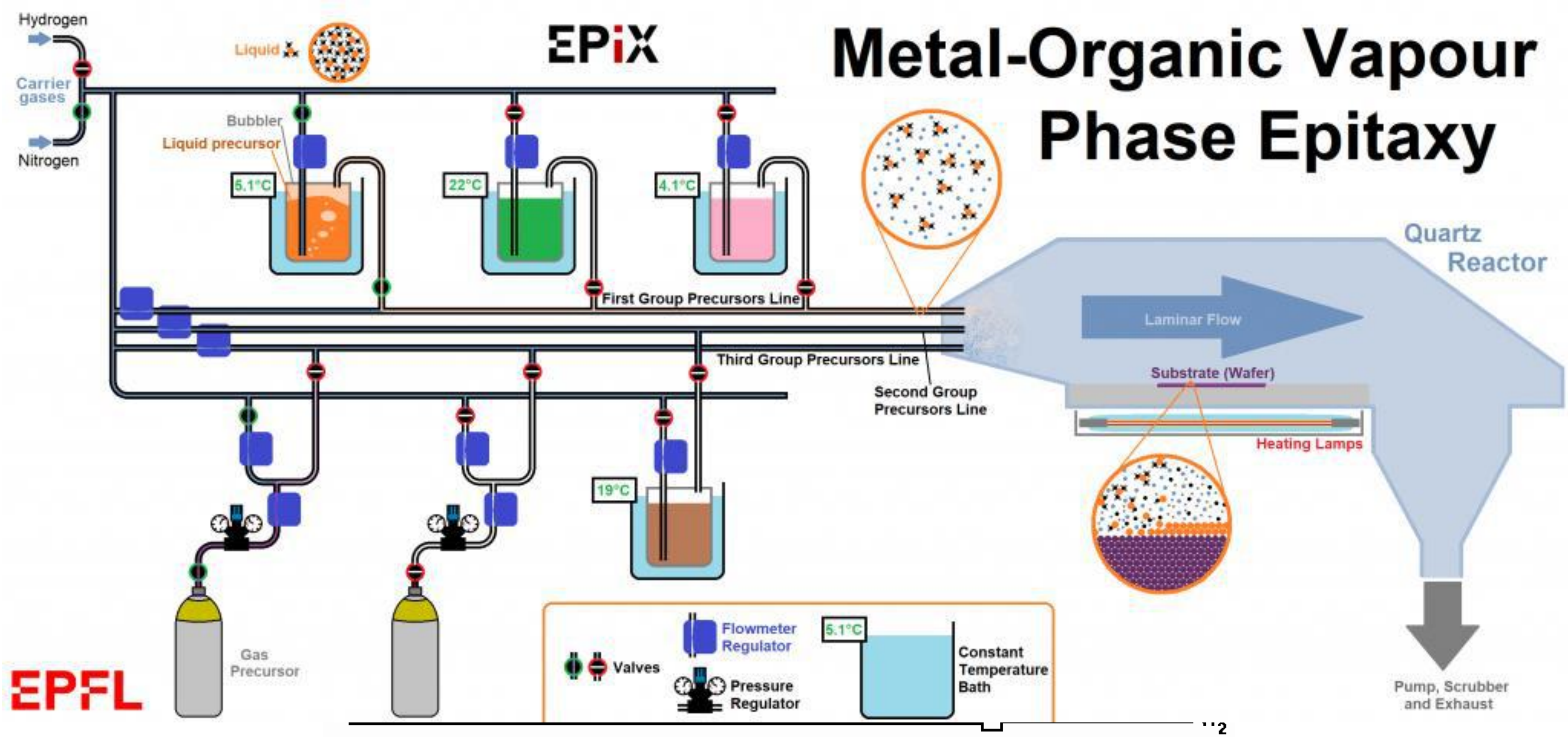
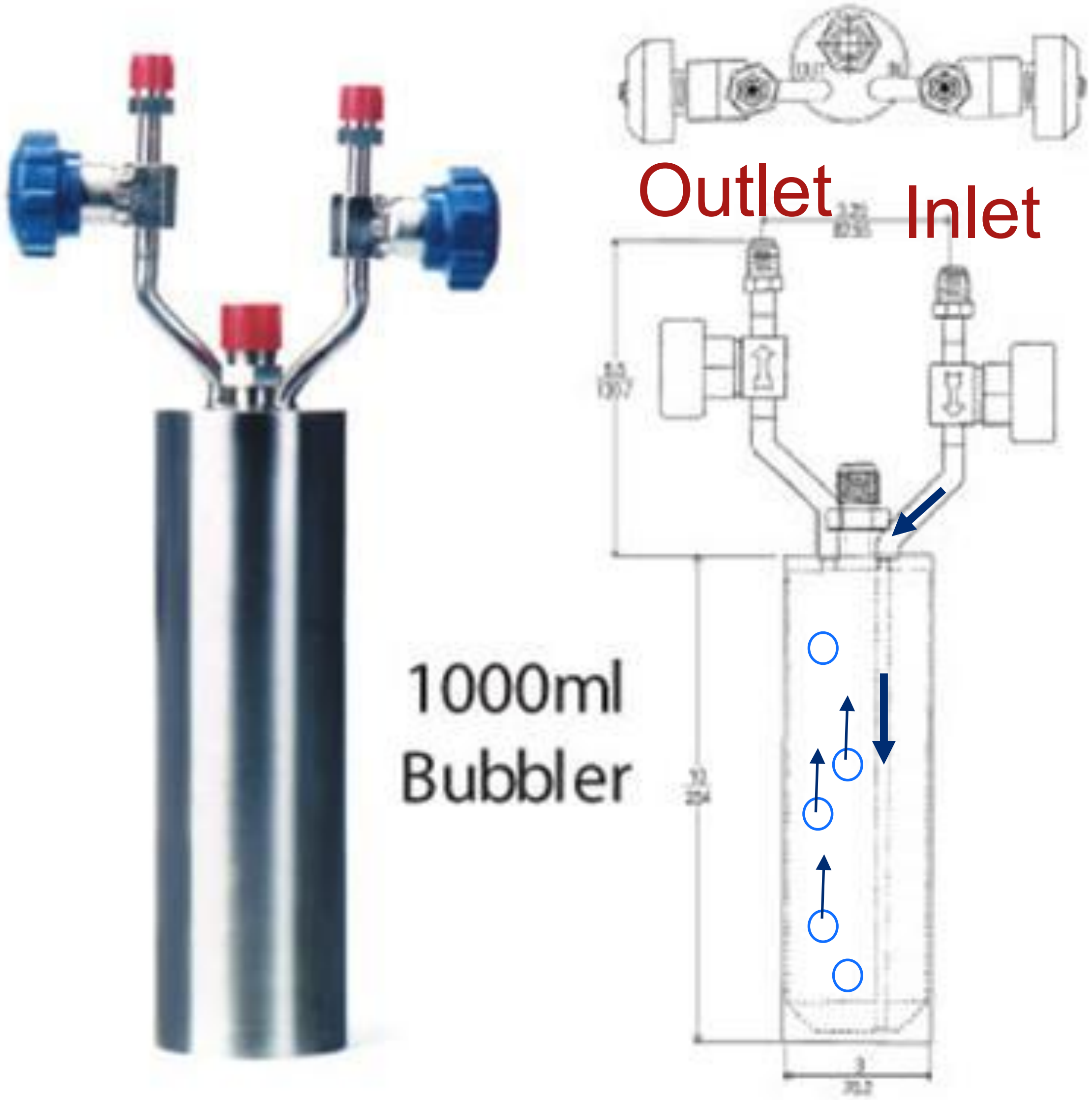
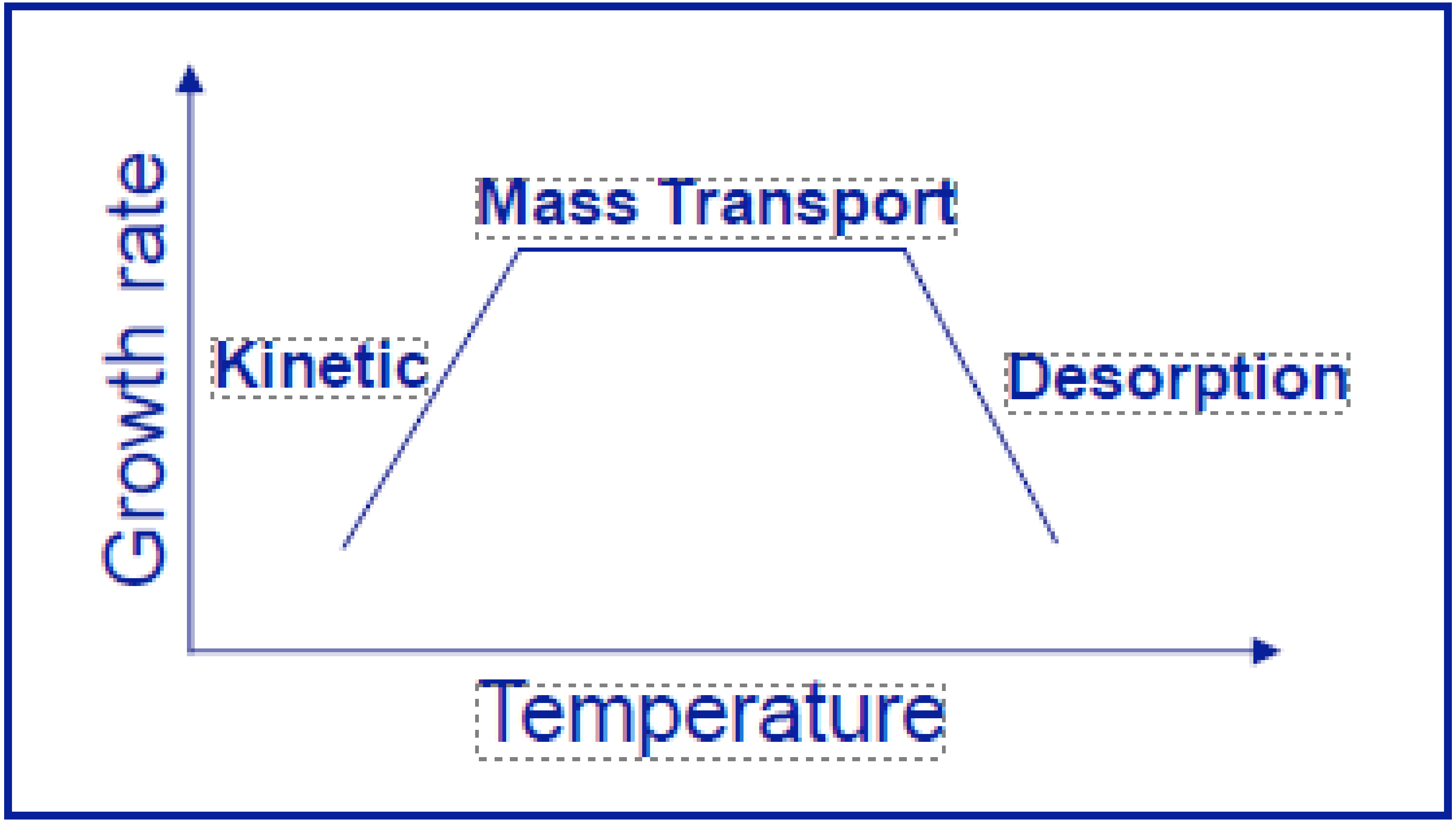
Principial scheme of



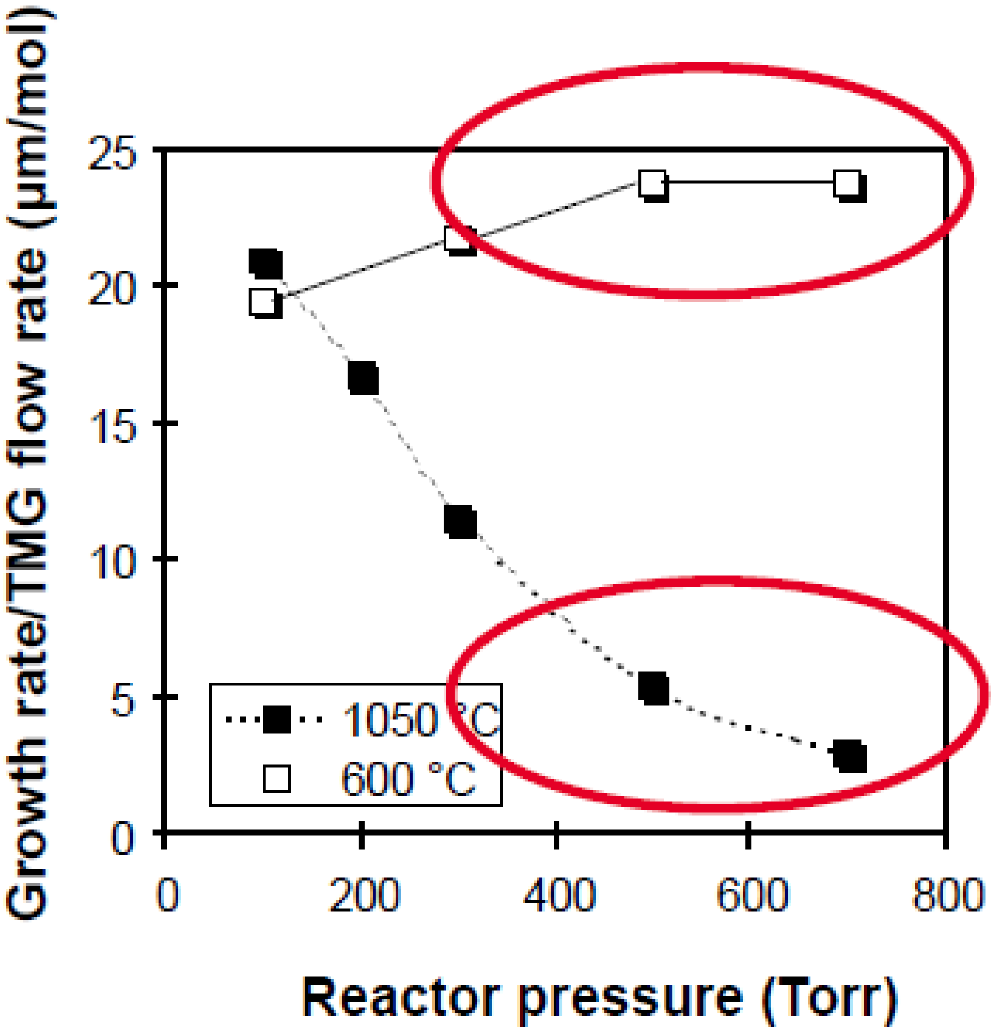
Bubblers – containers for metalorganics



Growth temperature



Growth temperature vs. pressure



Improved efficiency of precursor decomposition

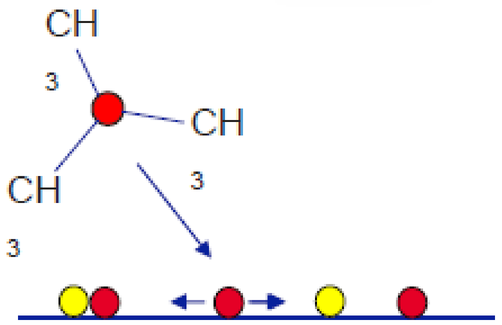
Parasitic reaction in gas phase

Substrate orientation

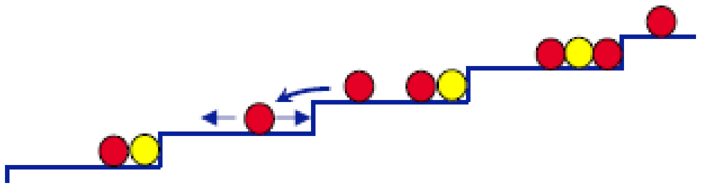
- Incorporation of atoms at step edges
  - Higher growth rates
  - Higher quality films

[bez názvu]

● Gallium
● Nitrogen



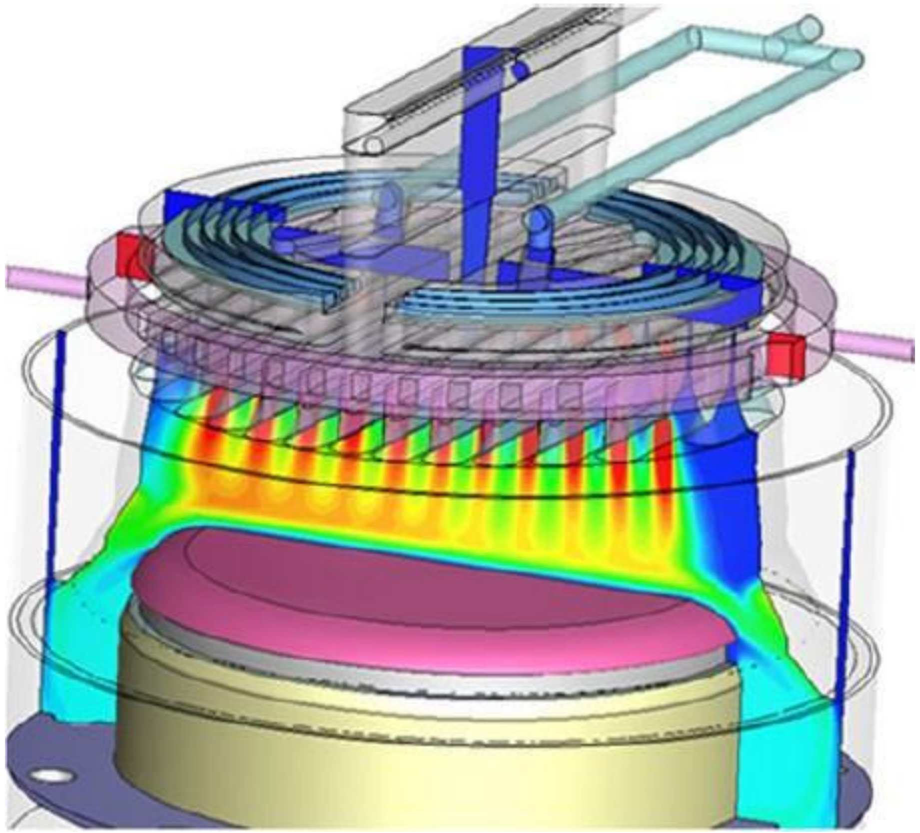
On-axis substrate



Misoriented (off-cut substrate)
Net surface diffusion of atoms
from high to low steps

MOCVD of compound semiconductors is usually performed on substrates misoriented by 0.1 to 3 towards a certain crystallographic direction

CCS 3x2 FlipTop reactor



Substrates are placed on the heated susceptor with pockets. The precursors are decomposed above heated substrates and the atoms are deposited on the surface.

MOVPE is dominant technology for nitride semiconductors

MOVPE aparature Aixtron CCS 3x2

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MOVPE reactor types

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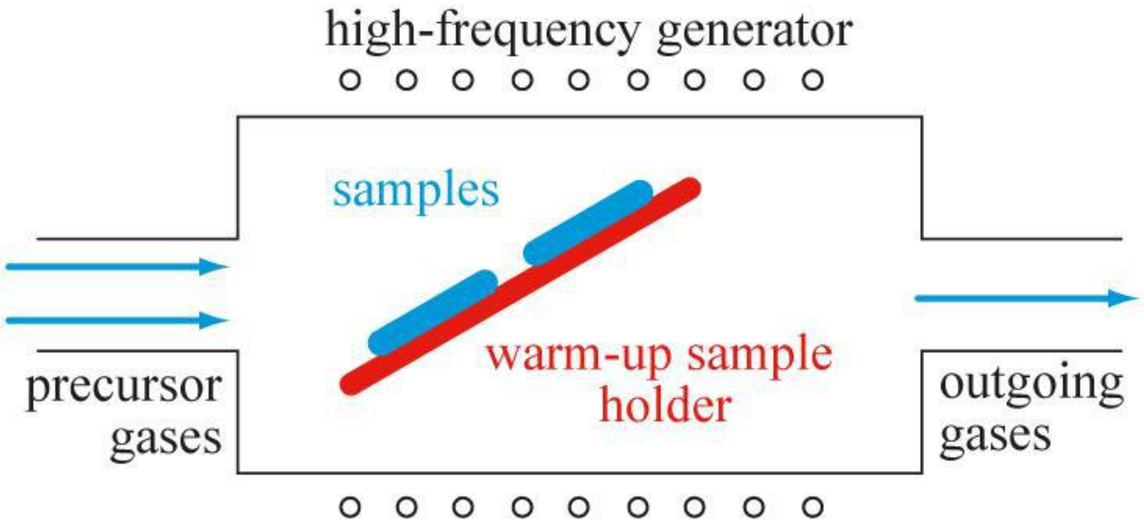
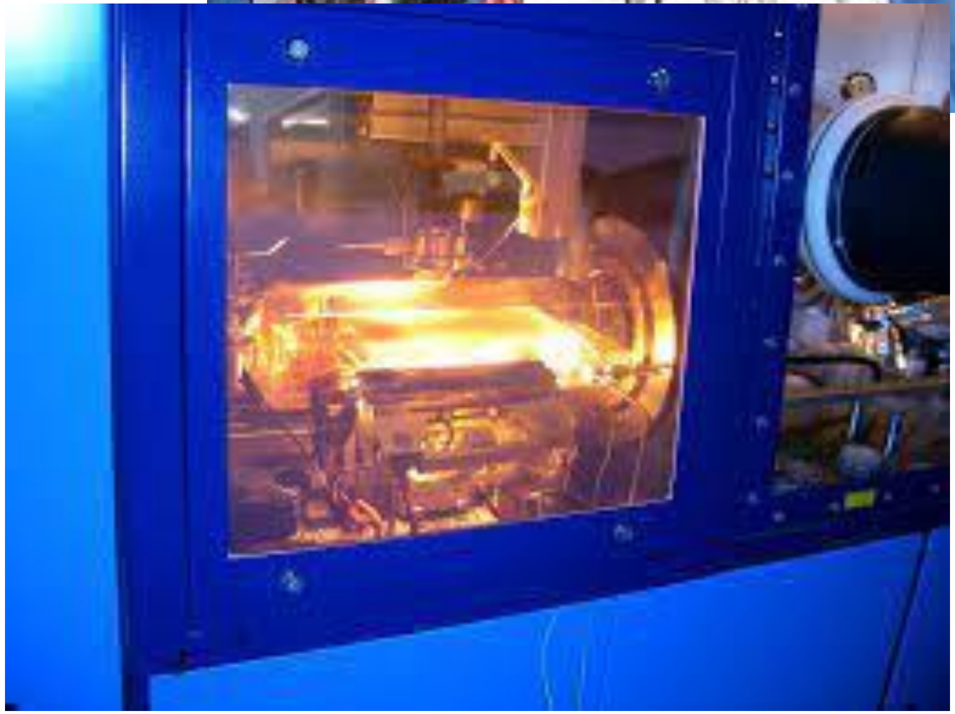
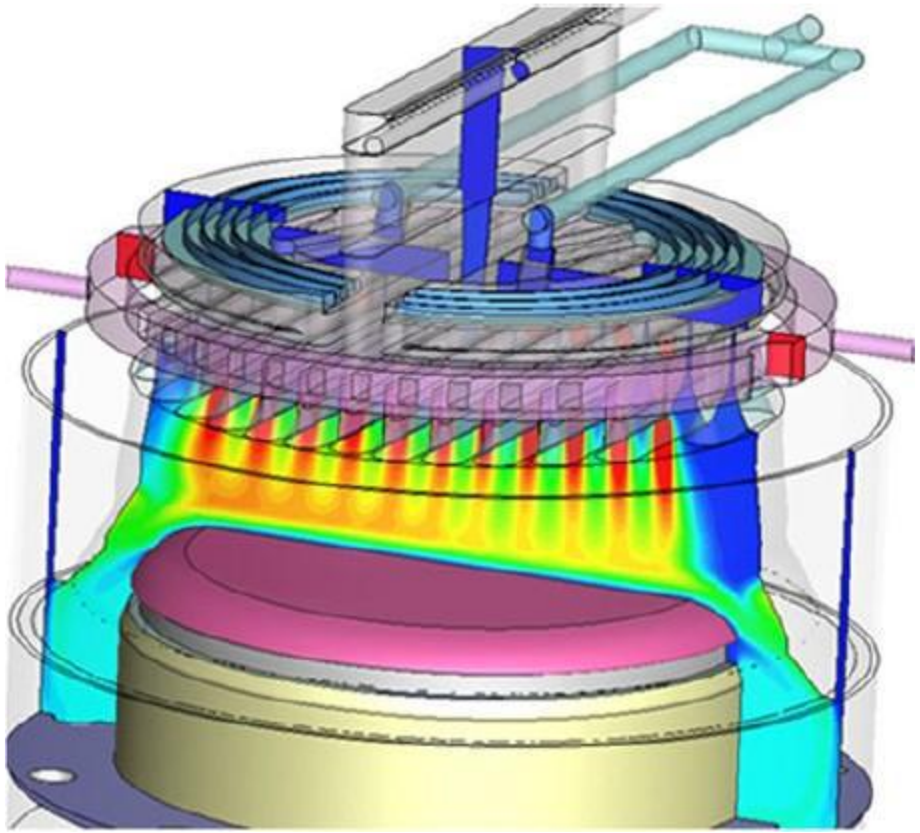
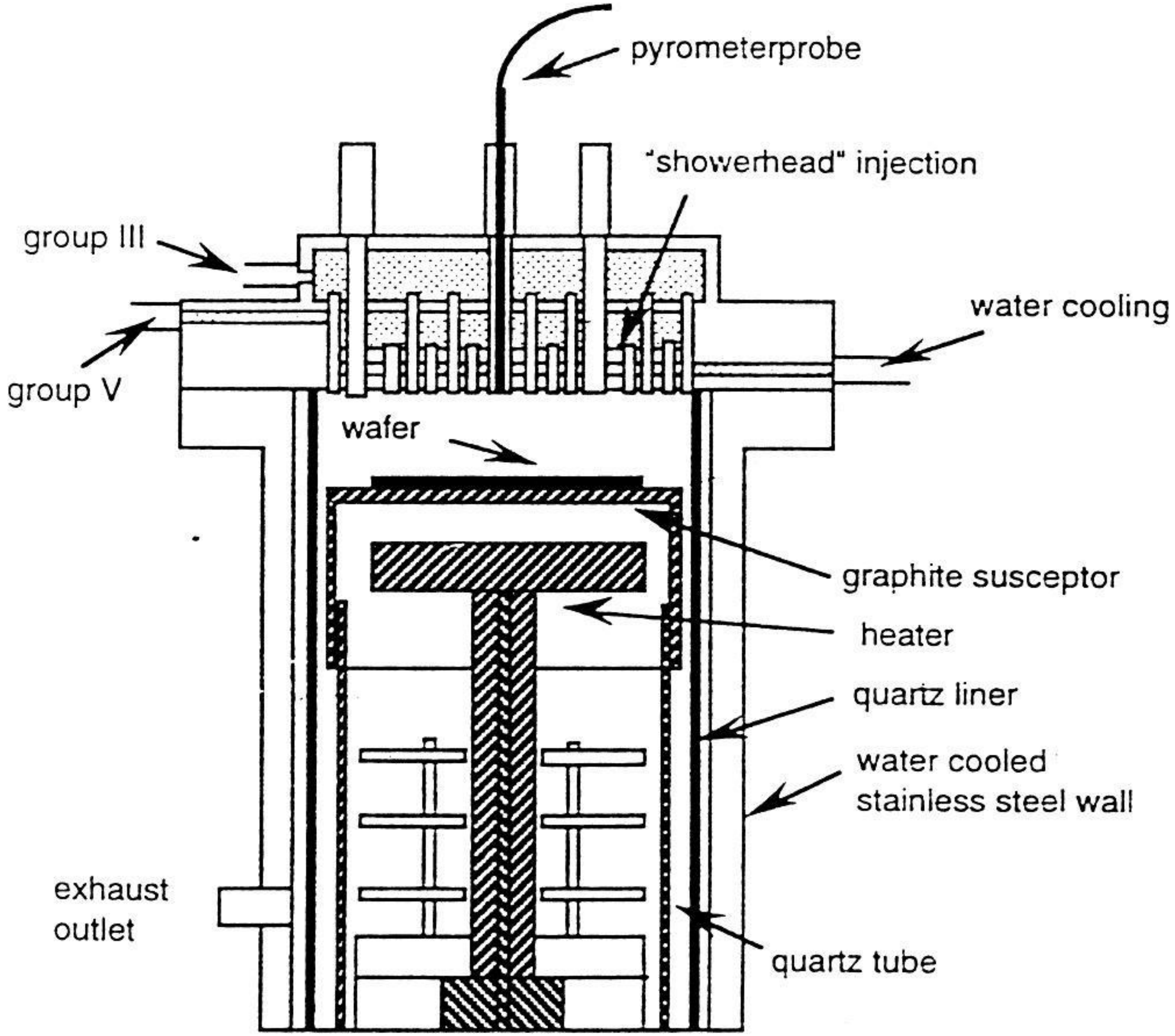
Horizontal reactors





Vertical reactor





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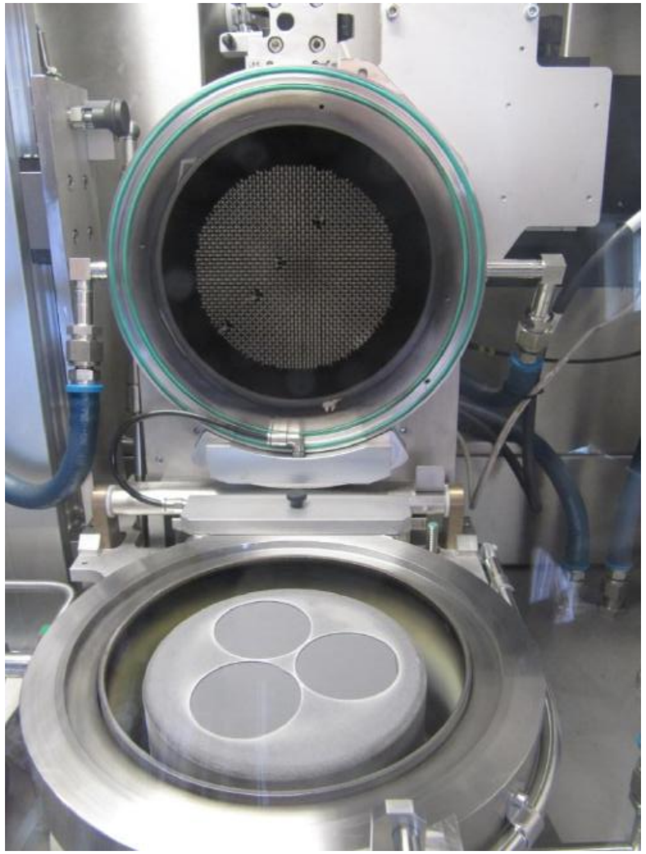
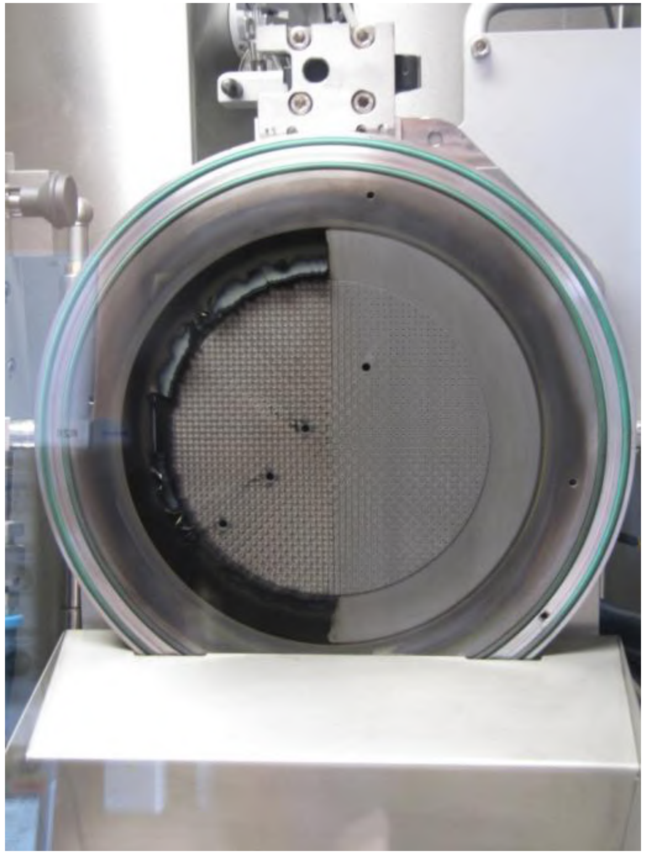
Growth chambre after epitaxy





Has to be cleaned after each run

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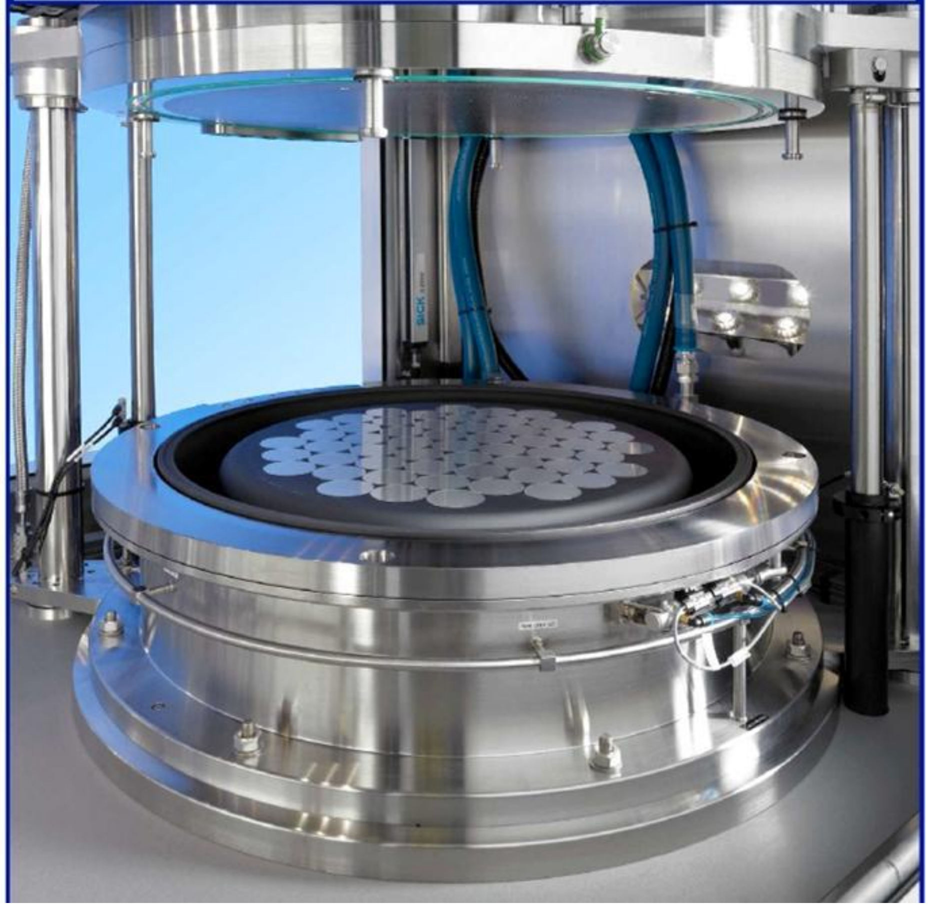
Industrial reactors

Integrated Concept System IC 2

Close Coupled Showerhead® 55x2”



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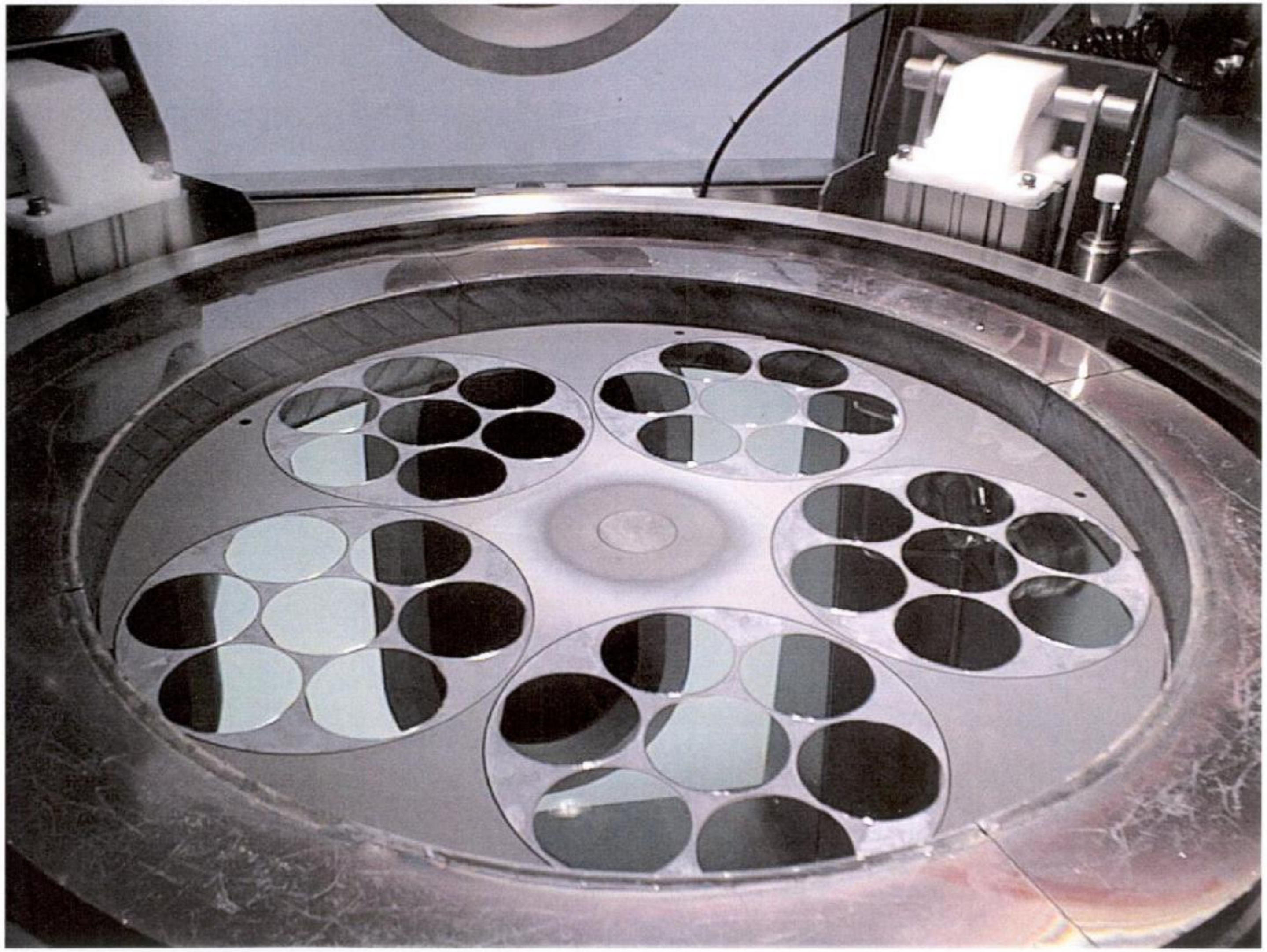
Cost of industial reactors cca 3 mil. EUR

AIX 2600G3 Planetary Reactor® (35x2")



Industrial reactors – vertical Turbodisc reactor

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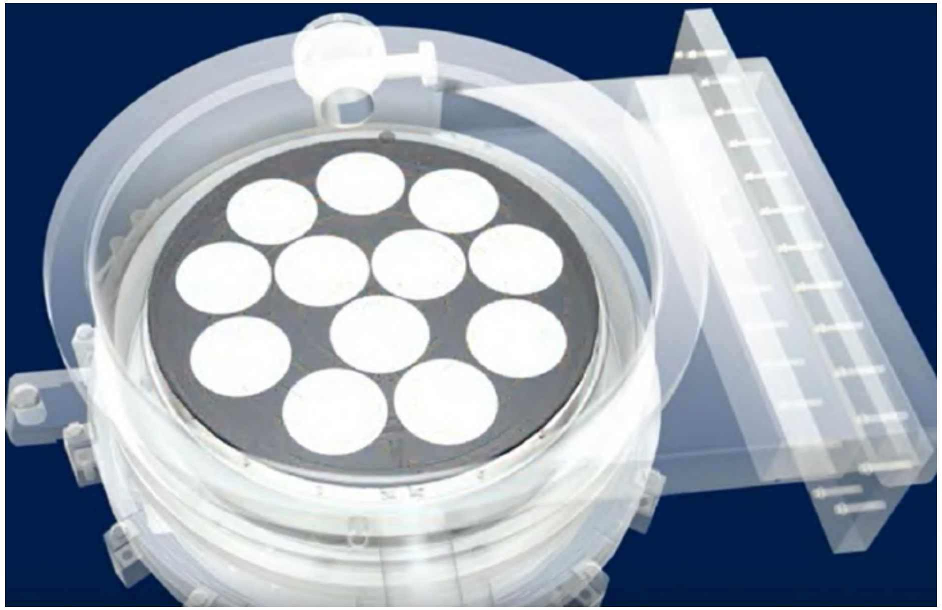
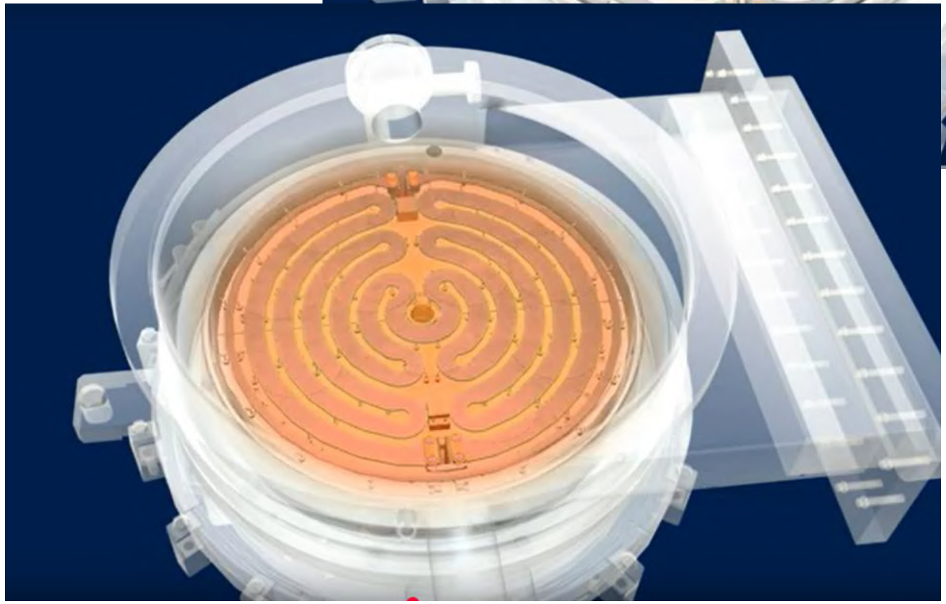


turbodisc



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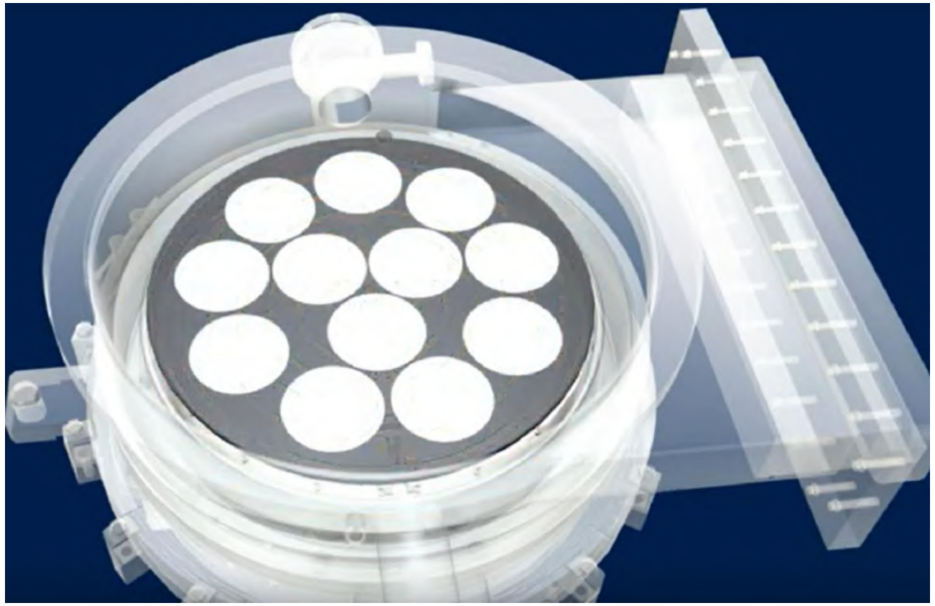
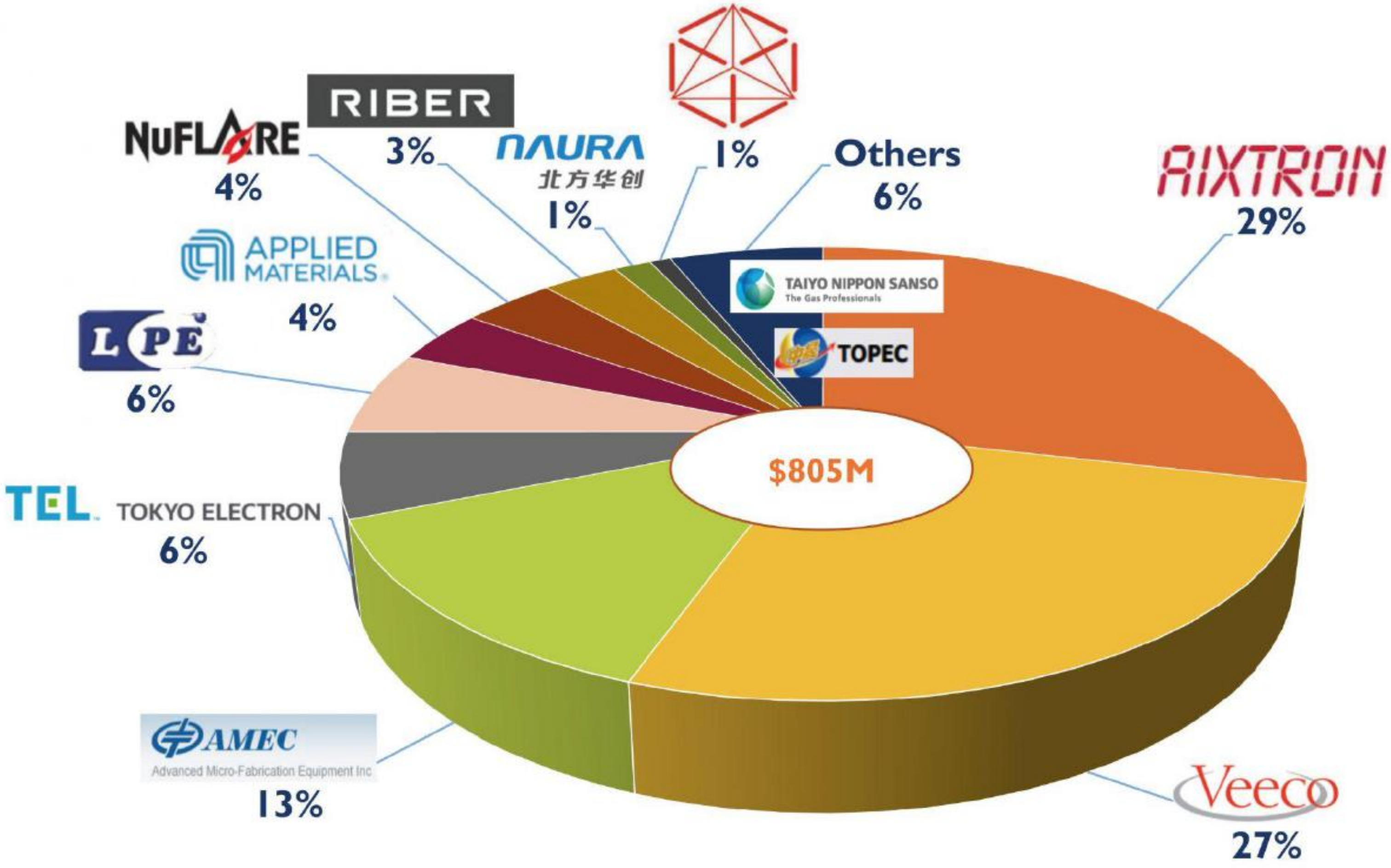
Industrial reactors – vertical Turbodisc reactor



2018 global epitaxy growth equipment market share

(Source: Epitaxy Growth Equipment for More Than Moore Devices Technology and Market Trends 2020 report, Yole Développement, 2020)



In situ monitoring

Reflectance

Curvature

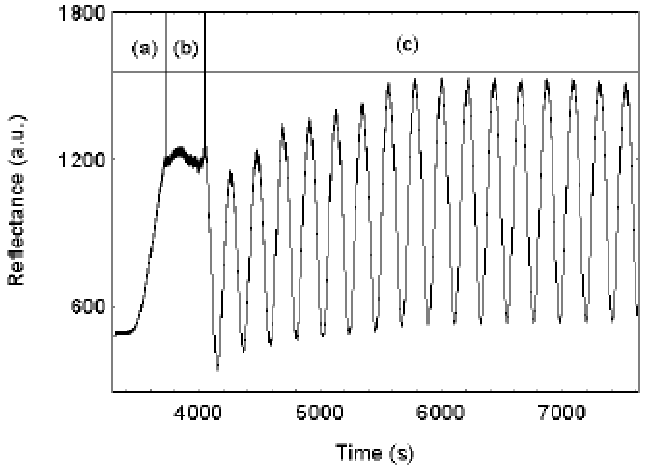
True temperature

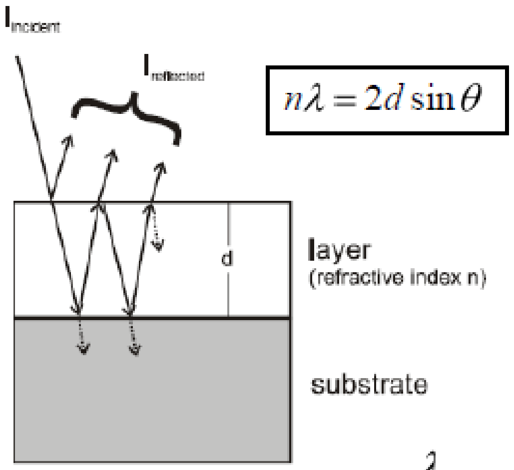
RAS – Reflectance anisotropy spectroscopy

Reflectivity

Growth Monitoring

- Reflectance interferometry
  - Phase difference of light
  - Constructive/destructive interference
  - Fabry-Perot oscillations
  - Measurable growth rate (periodicity)



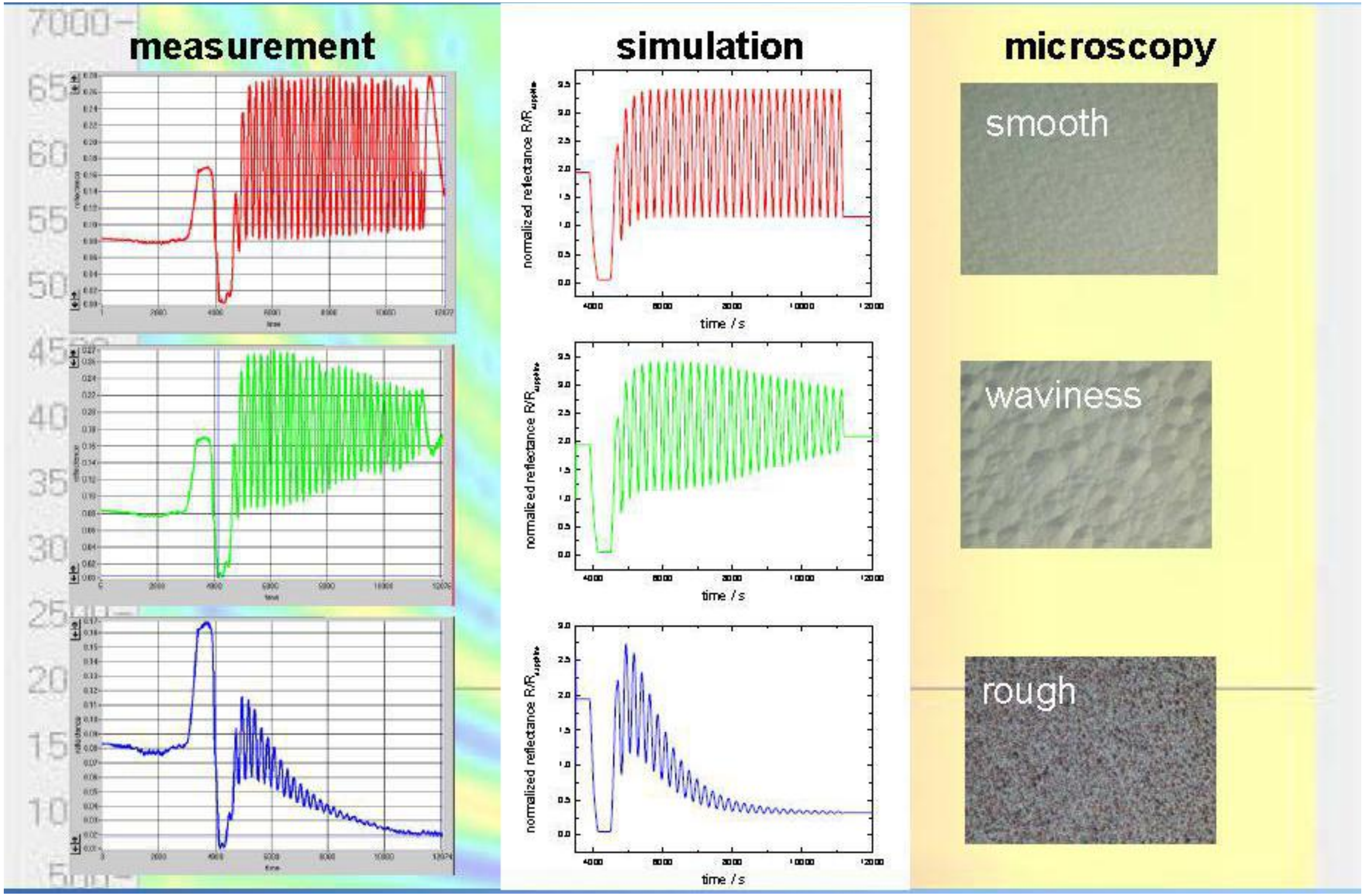


$$n\lambda = 2d\sin\theta$$

$$\Delta d = \frac{\lambda}{2n} \qquad r = \frac{\Delta d}{T}$$

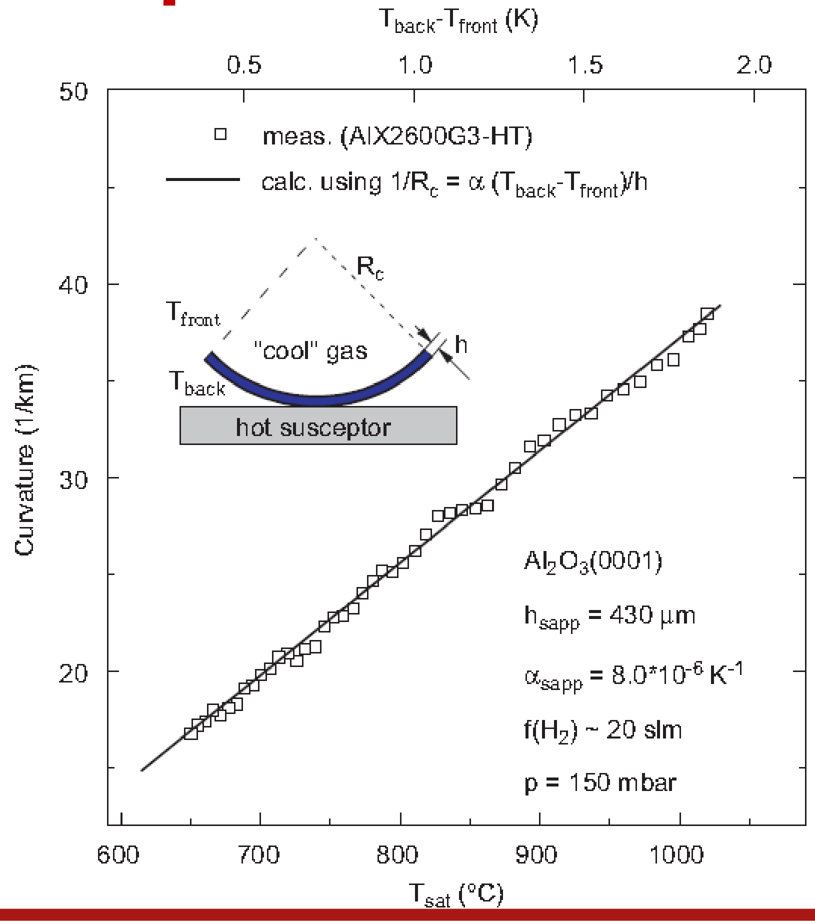
- Incident source ~ 650nm
  - Very low extinction coefficient
  - Reflectance artefacts due to physical alloy properties

Reflectivity

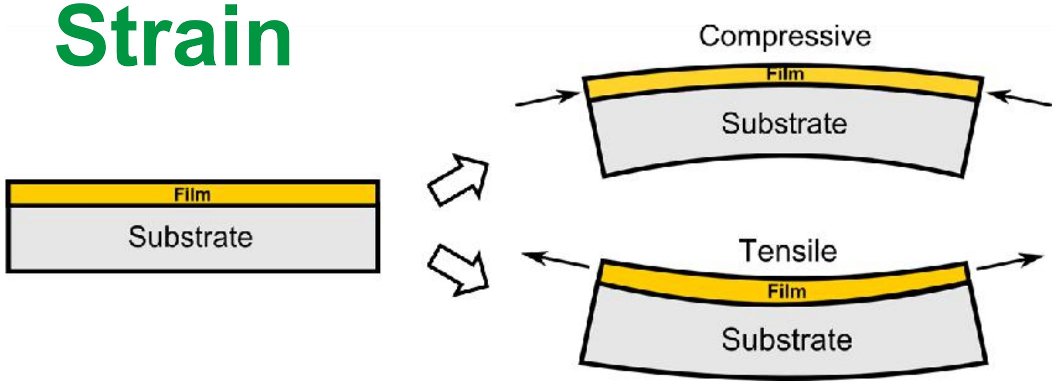


What influence wafer curvature

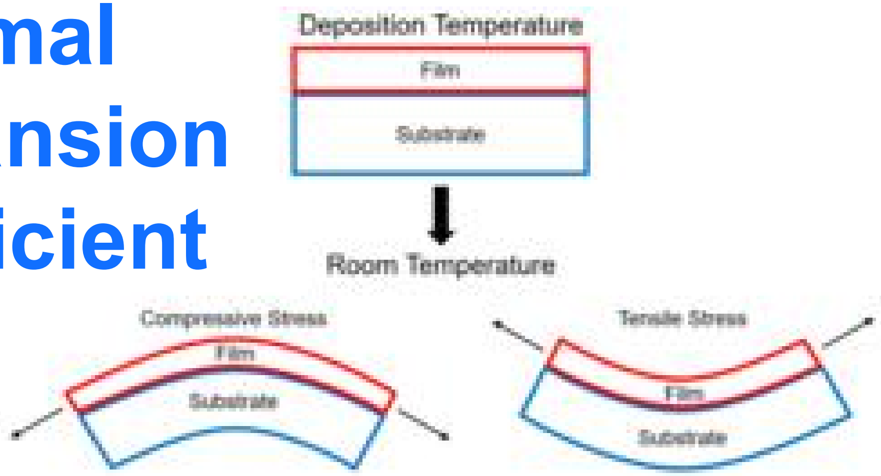
Temperature



Strain



thermal expansion coeficient



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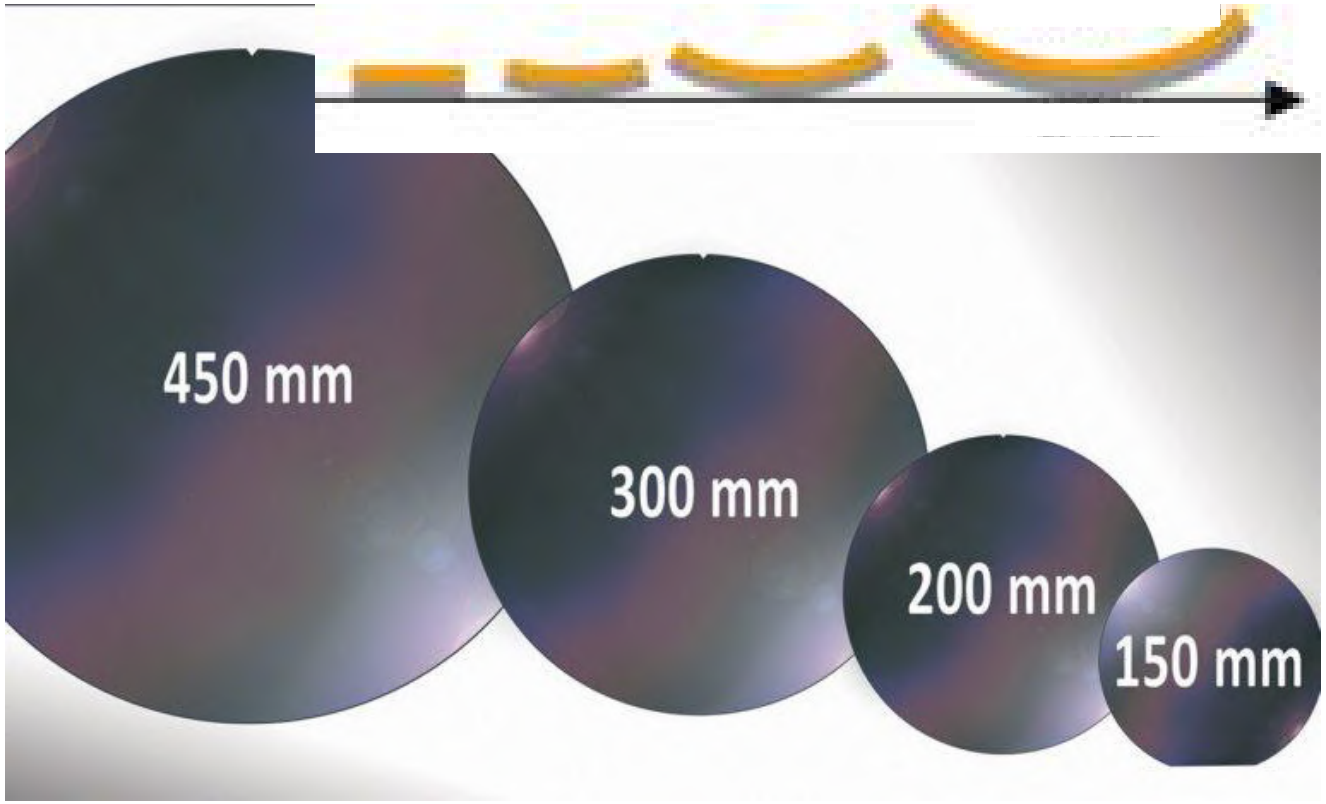
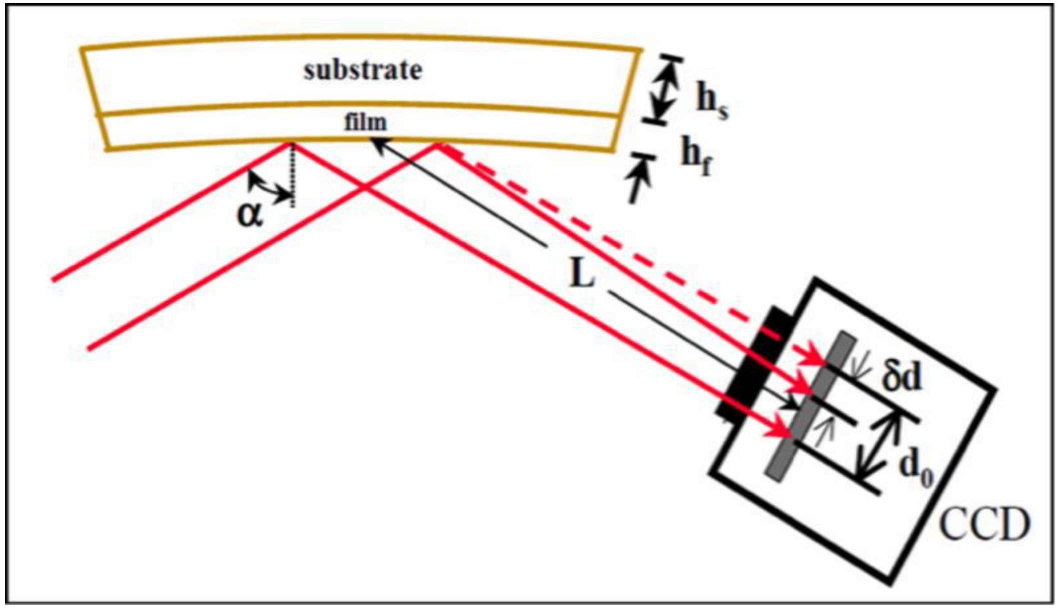
Why the wafer curvature is so important?

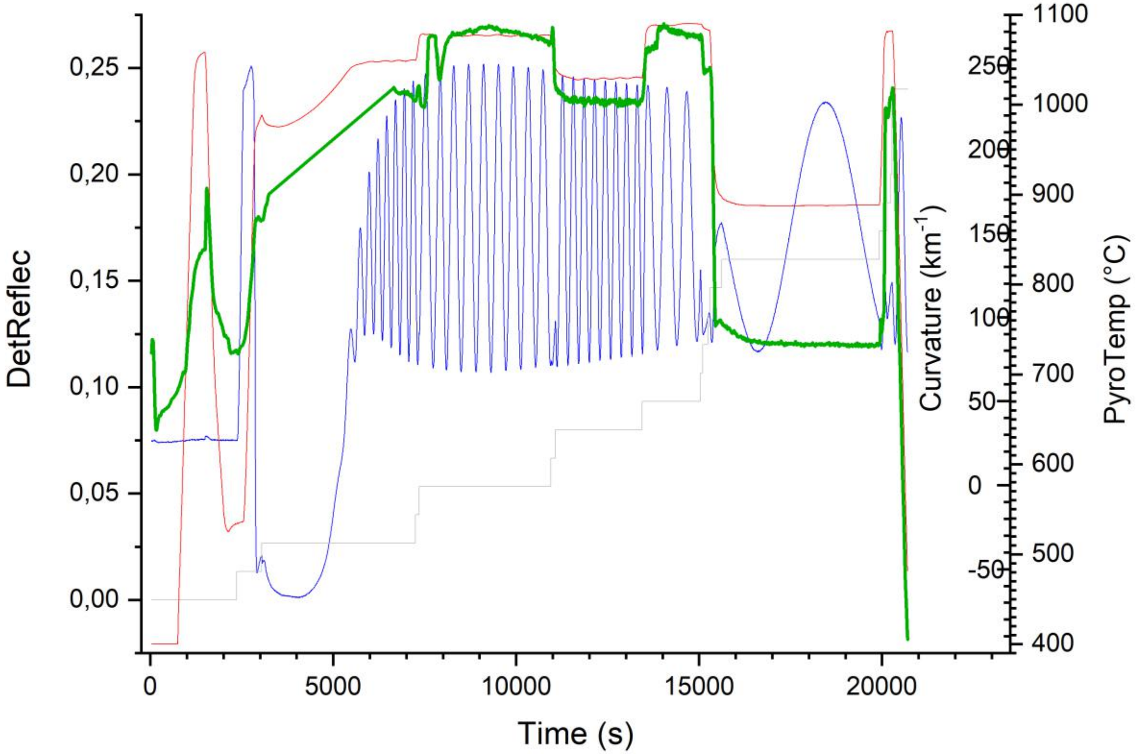


1. With increased curvature **during epitaxy** the **temperature** over the wafer is **inhomogenious**, which has impact on homogeneity of epilayer properties

2. Wafer curved **after epitaxy** complicates furthe technological steps (litography)

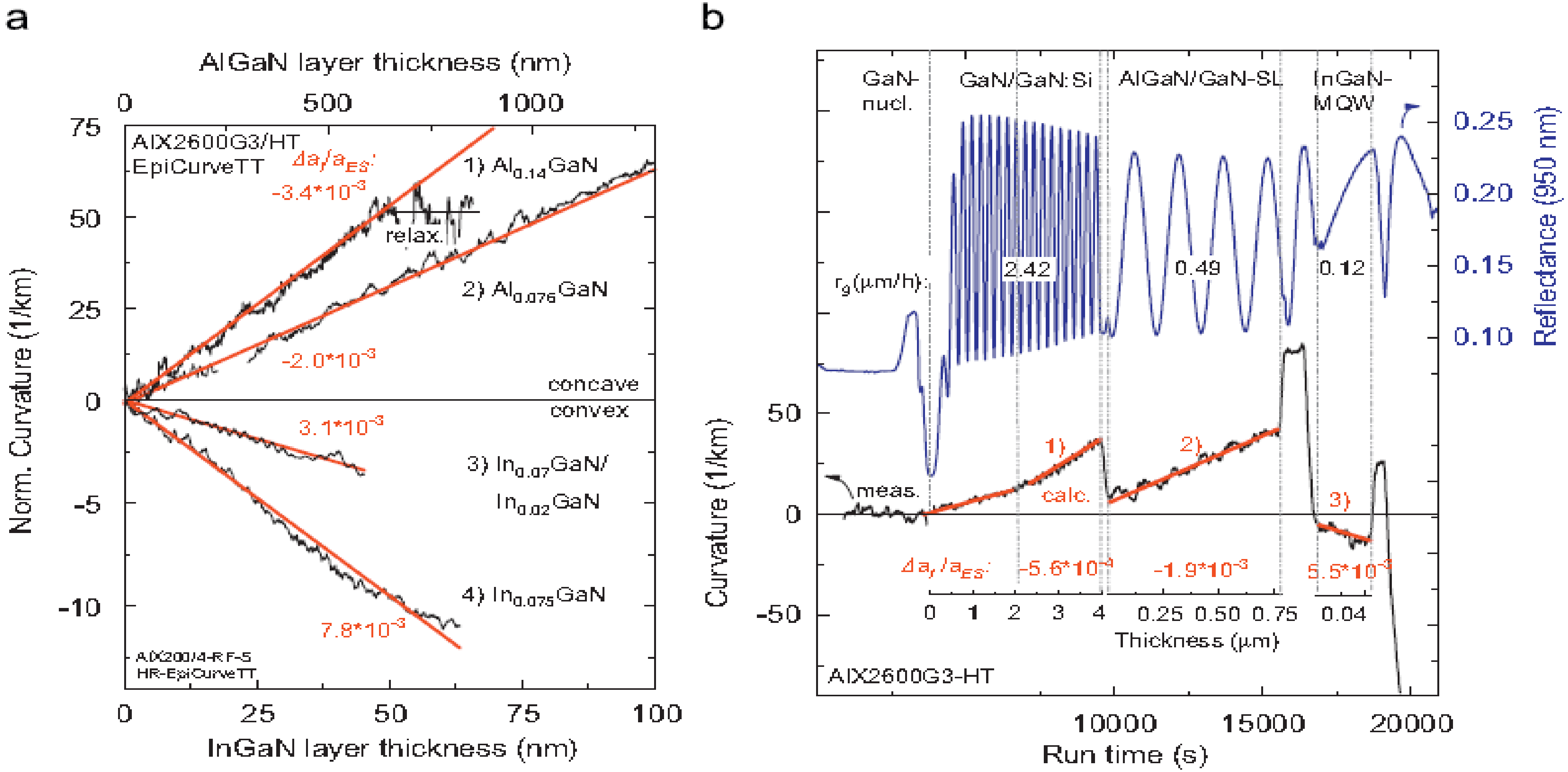
Measurement of wafer curvature - temperature





In case of non direct semiconductors, dopants with deep levels and Heisenberg relations were employed

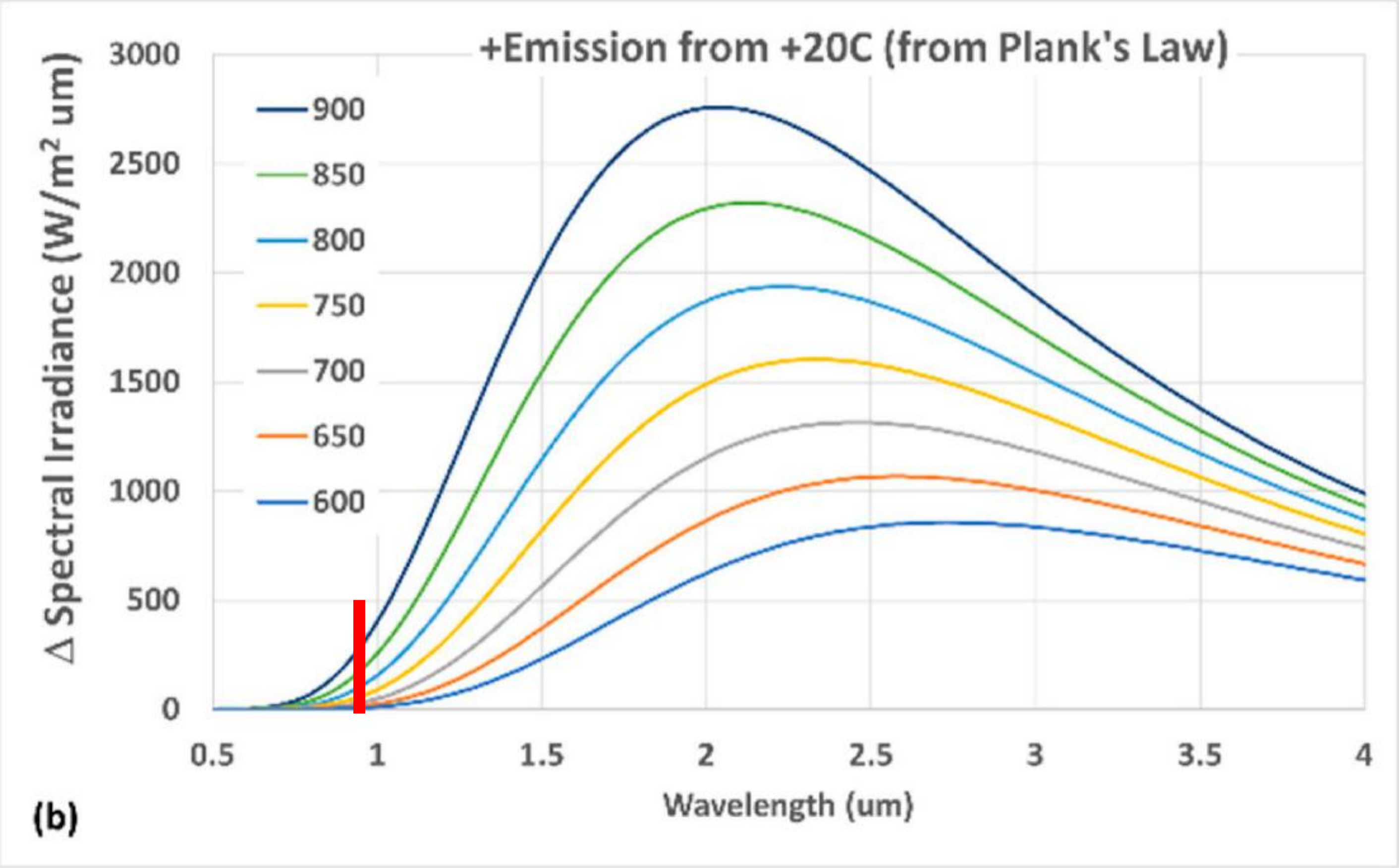
Curvature caused by strain - examples



True temperature measurement
Emisivity corrected pyrometry

Measured at 950 nm

Transparent for nitrides: susceptor temperature is measured



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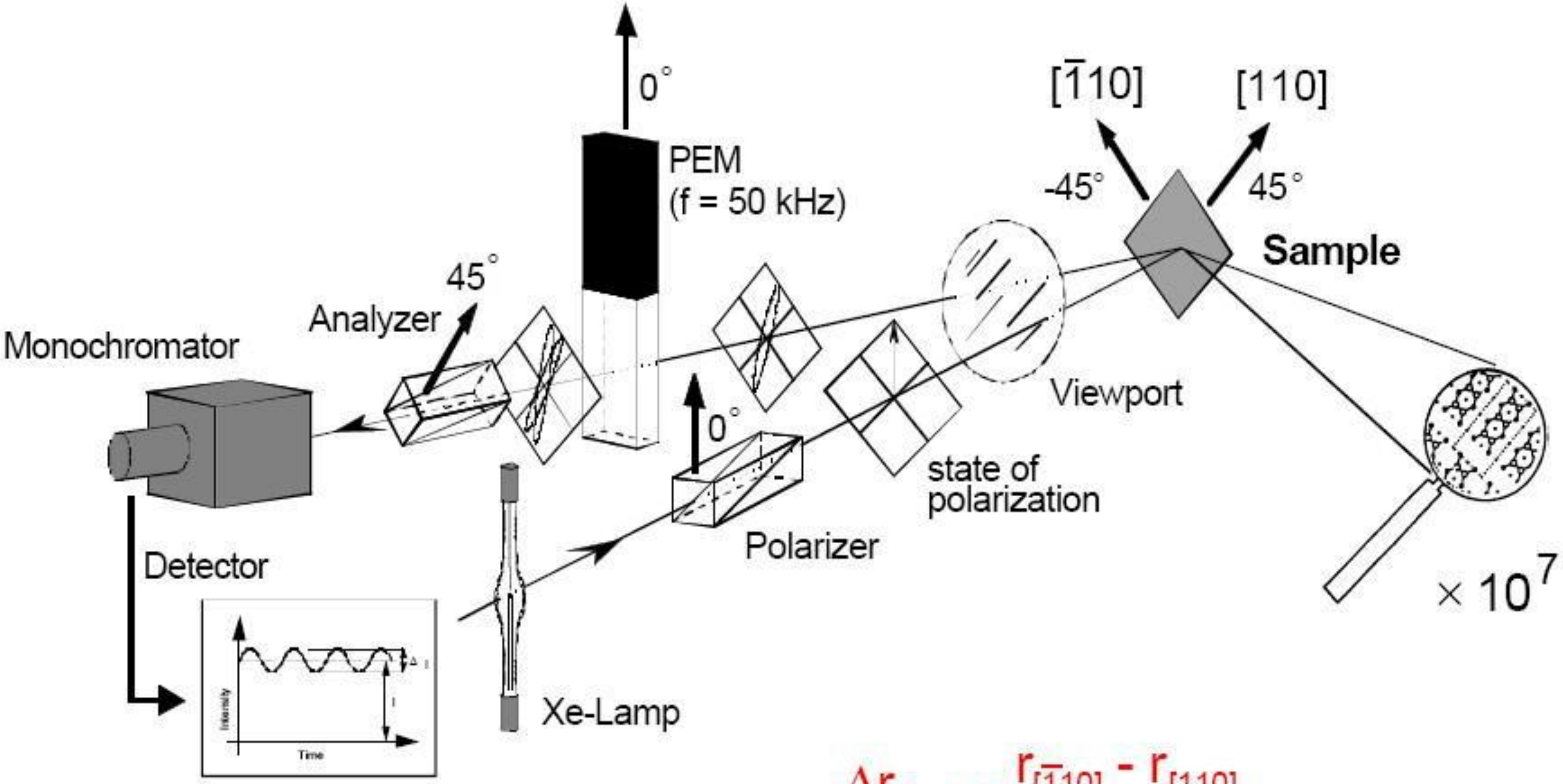
RAS – reflectance anisotropy spectroscopy



$$\frac{\Delta r}{r} = 2\,\frac{r_{[\bar{1}10]} - r_{[110]}}{r_{[\bar{1}10]} + r_{[110]}}$$

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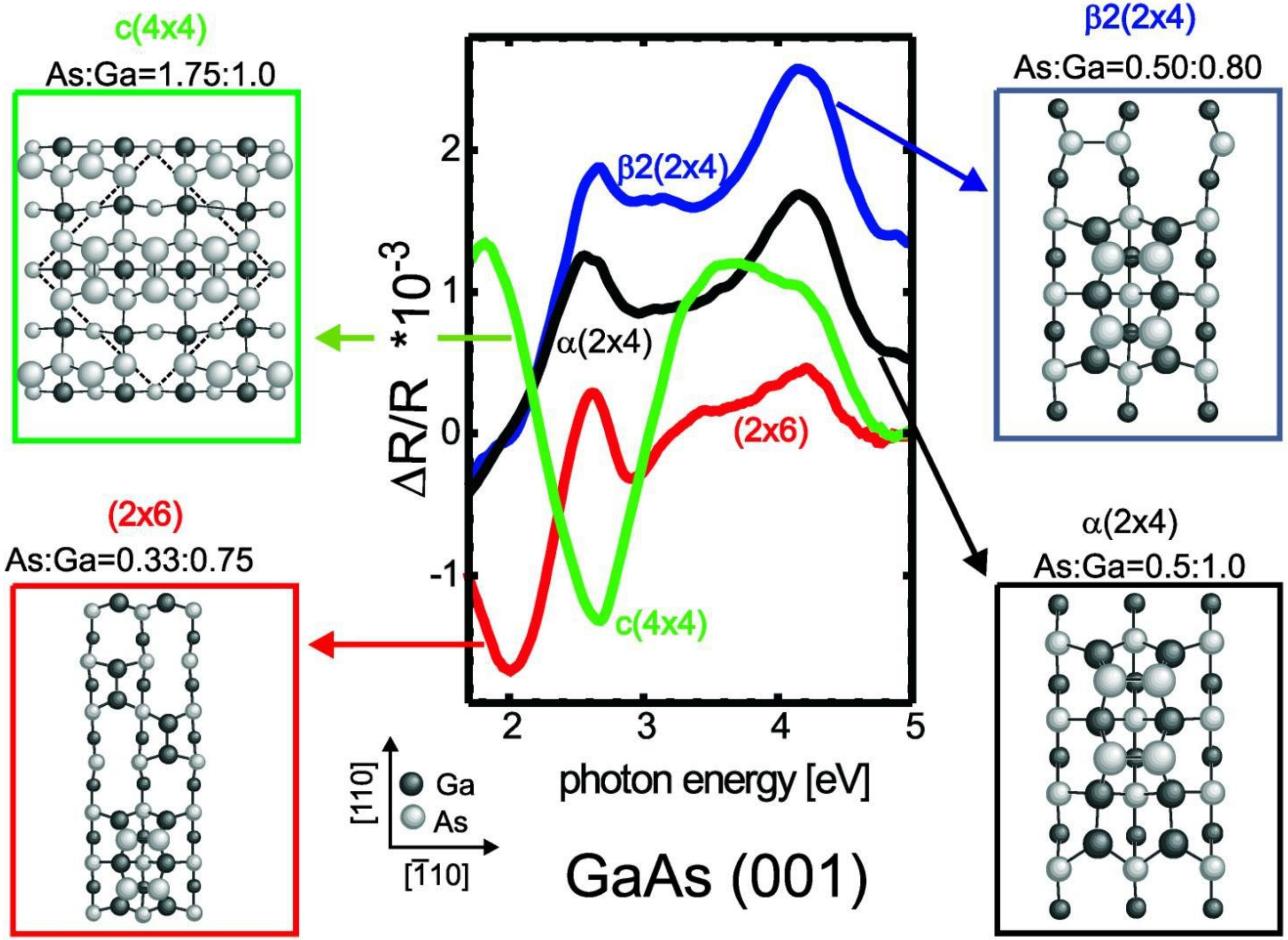
RAS – reflectance anisotropy spectroscopy

RAS can be used only for cubic crystal lattice:
GaAs, GaP, GaSb, InAs…



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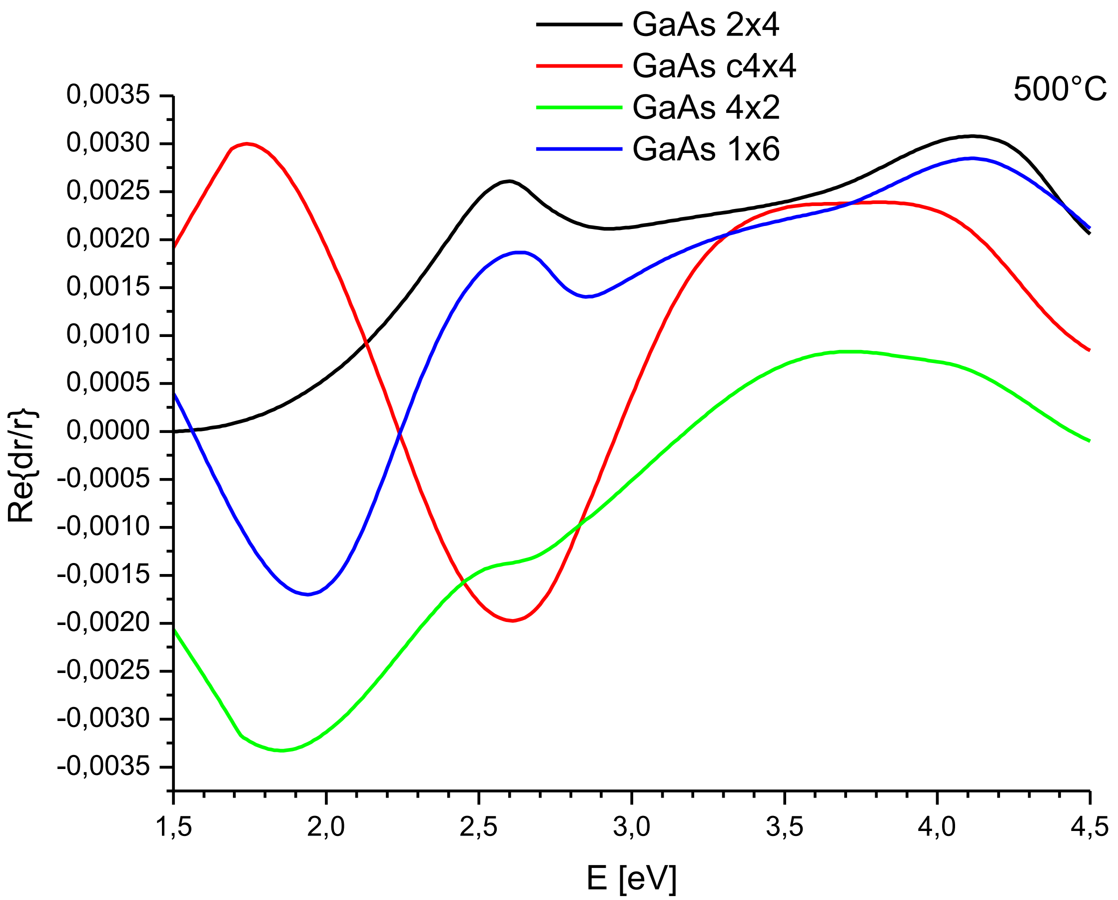
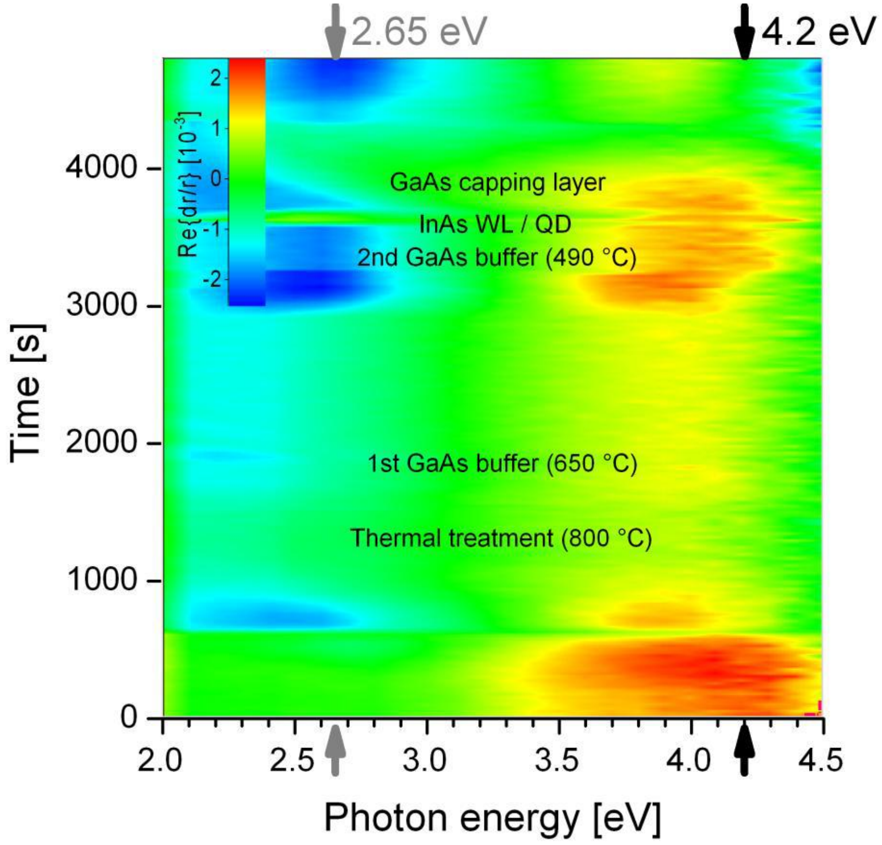
RAS – reflectance anisotropy spectroscopy





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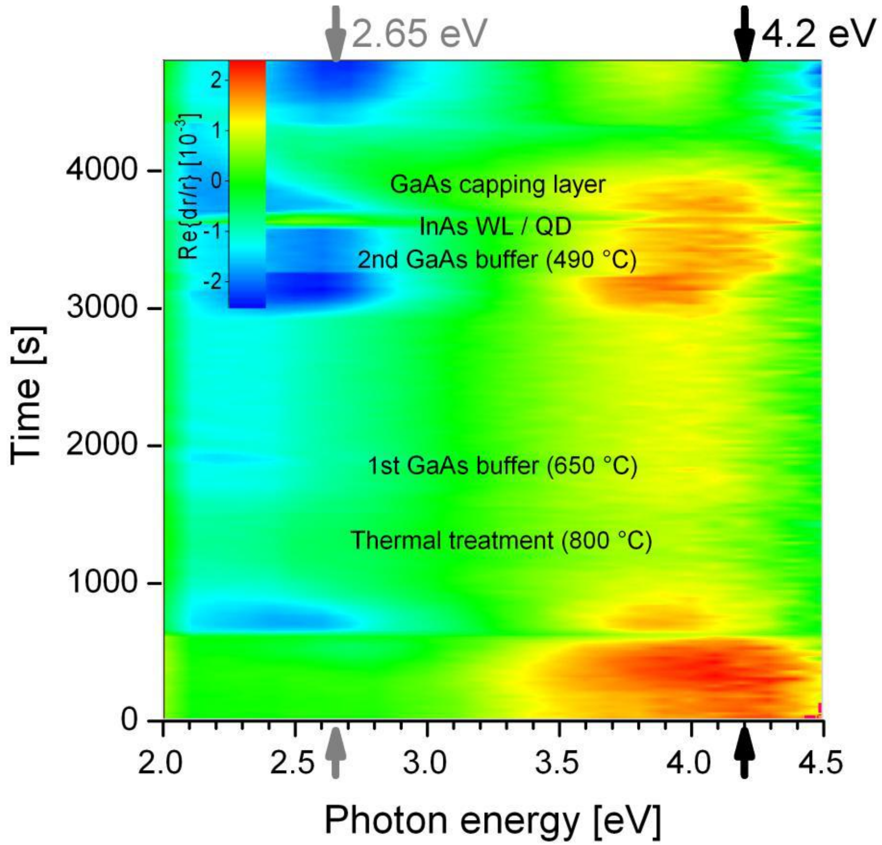
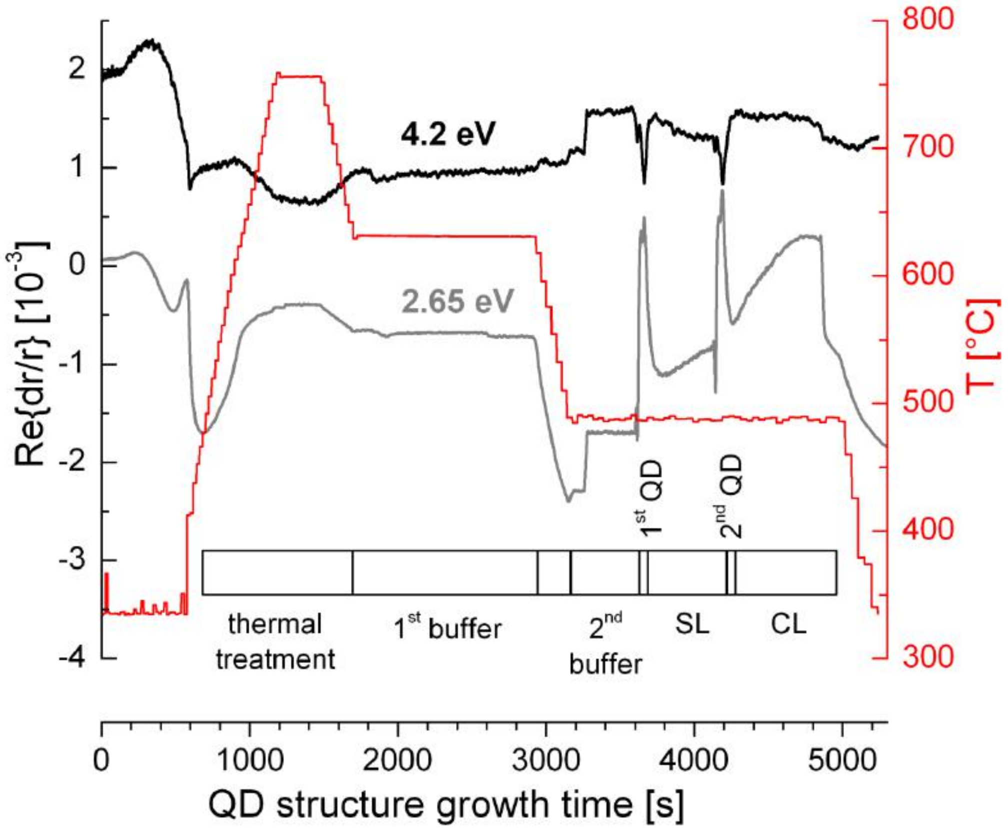
In situ growth monitoring and controling III

Quantum dot growth





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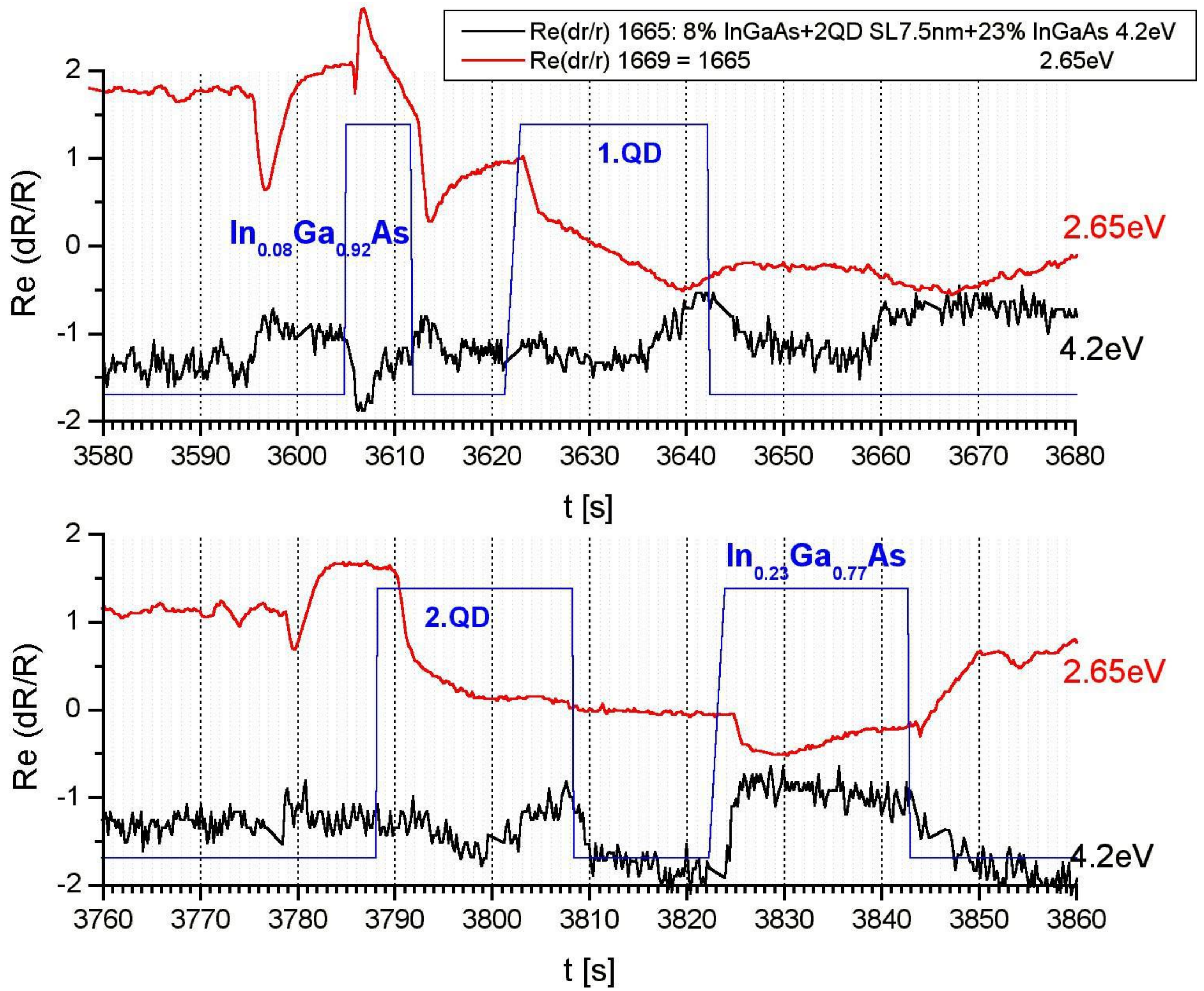
Re(dr/r) 1665: 8% InGaAs+2QD SL7.5nm+23% InGaAs 4.2eV
Re(dr/r) 1669 = 1665 2.65eV
$In_{0.08}Ga_{0.92}As$
1.QD
2.65eV
4.2eV
Re (dR/R)
t [s]
2.QD
$In_{0.23}Ga_{0.77}As$
2.65eV
4.2eV
Re (dR/R)
t [s]

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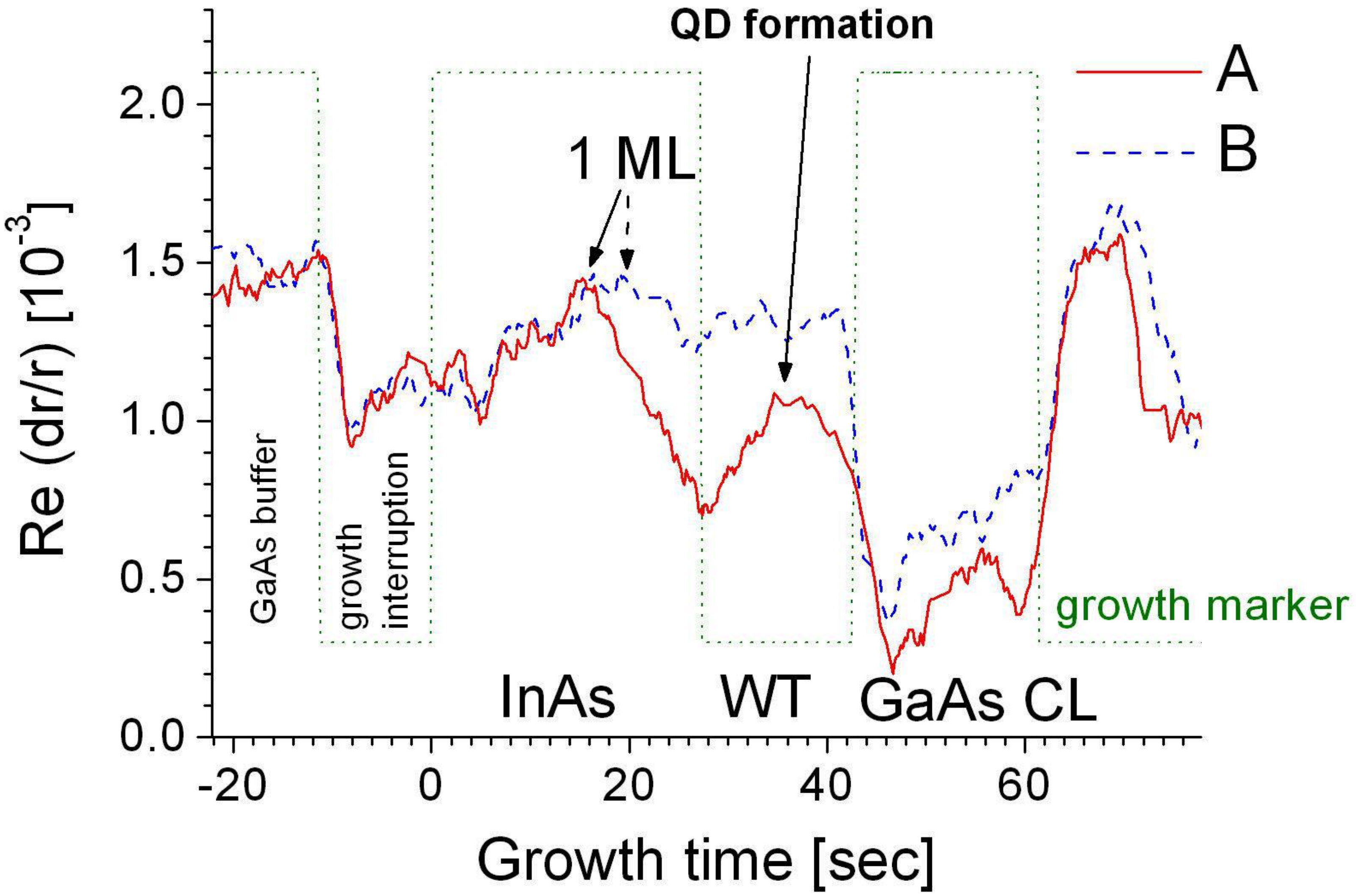
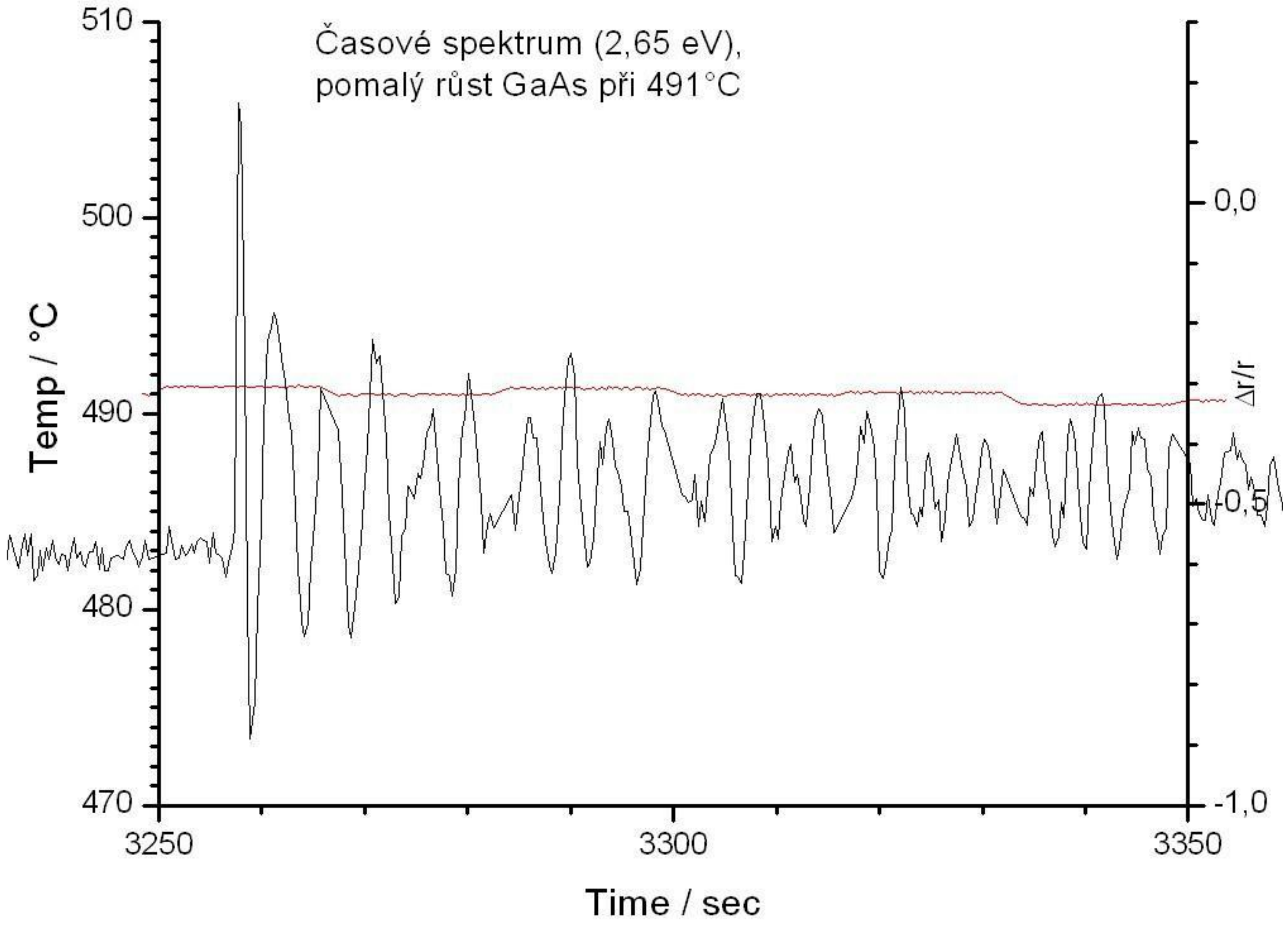

QD formation
A
B
1 ML
Re (dr/r) [10^-3]
2.0
1.5
1.0
0.5
0.0
GaAs buffer
growth
interruption
growth marker
InAs
WT
GaAs CL
-20
0
20
40
60
Growth time [sec]

Other extremely important property of the Reflection Anisotropy Spectroscopy is possibility of monolayer growth oscillations:



GaN epitaxy challenges

the first motivation: blue LEDs

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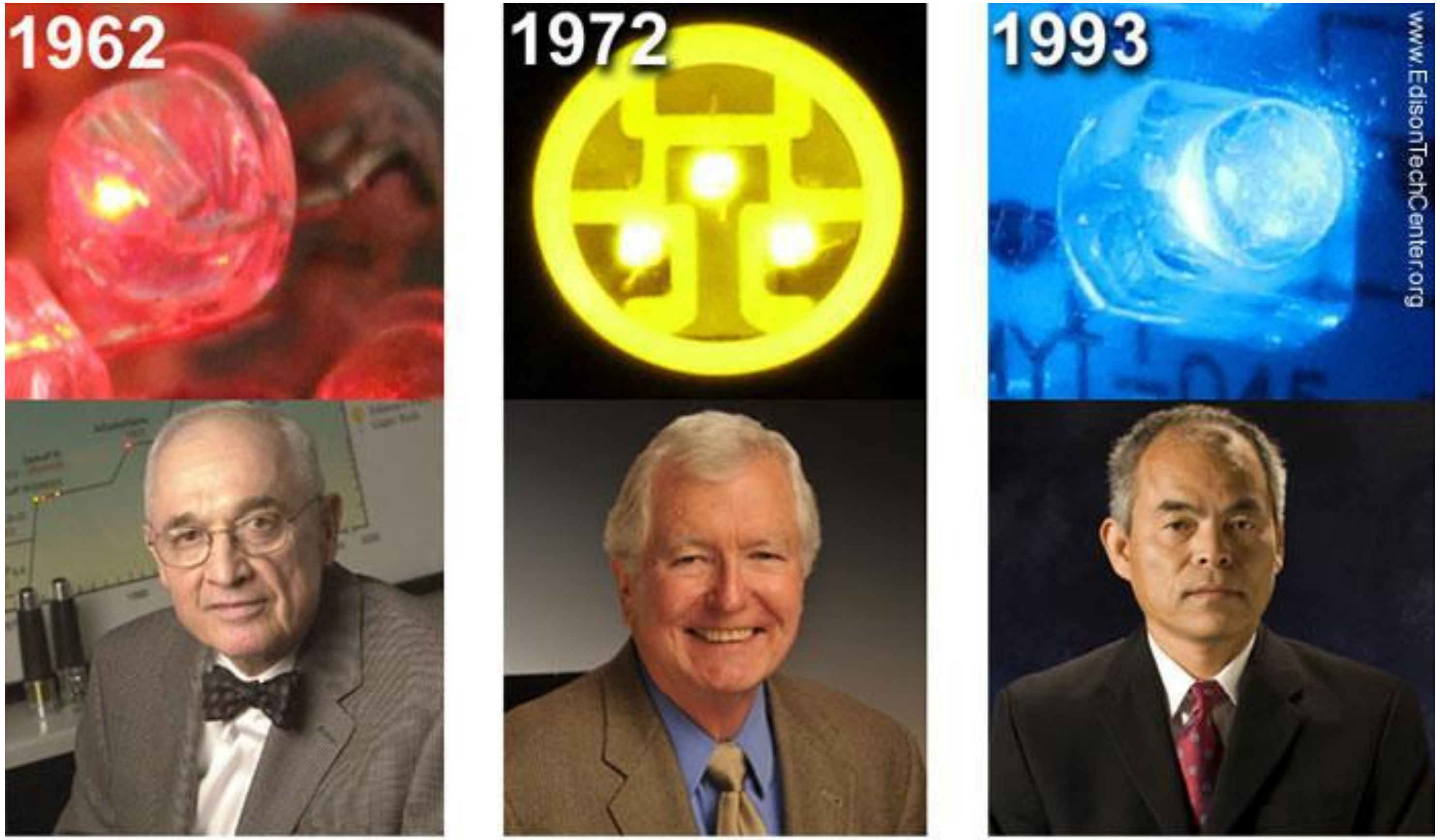
LED history



Nick Holonyak
Syracuse, NY

George Craford
St. Louis, MI

*Shuji Nakamura
Tokushima, Japan

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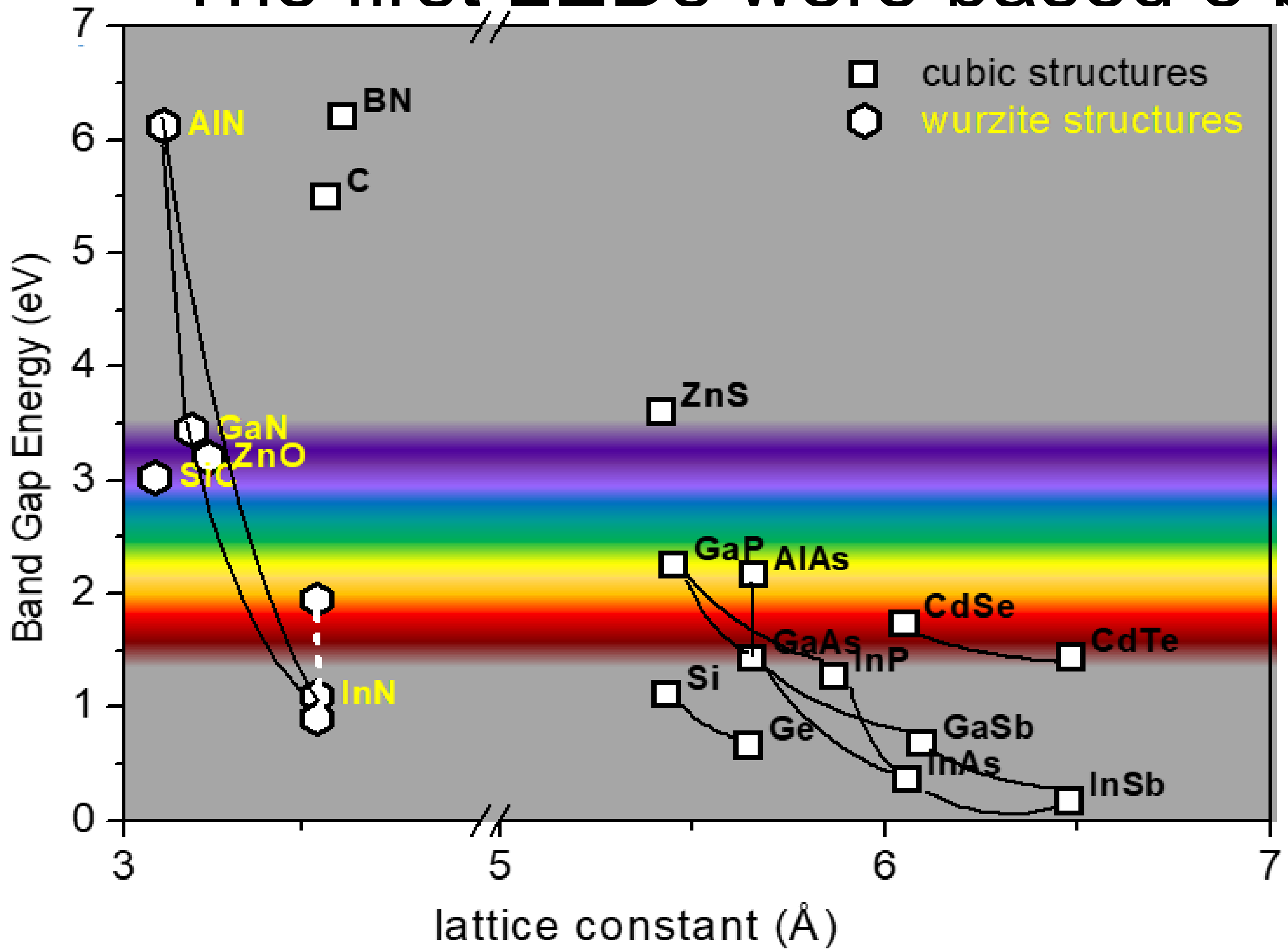
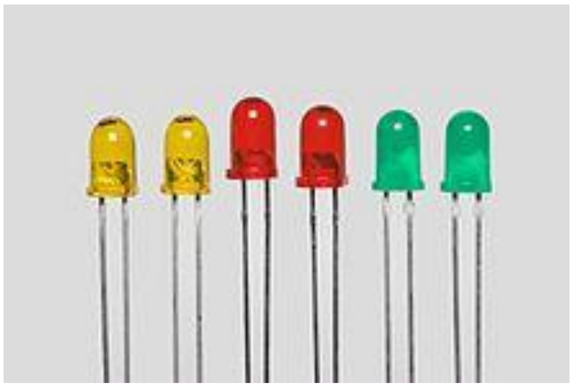
The first LEDs were based o phosphides



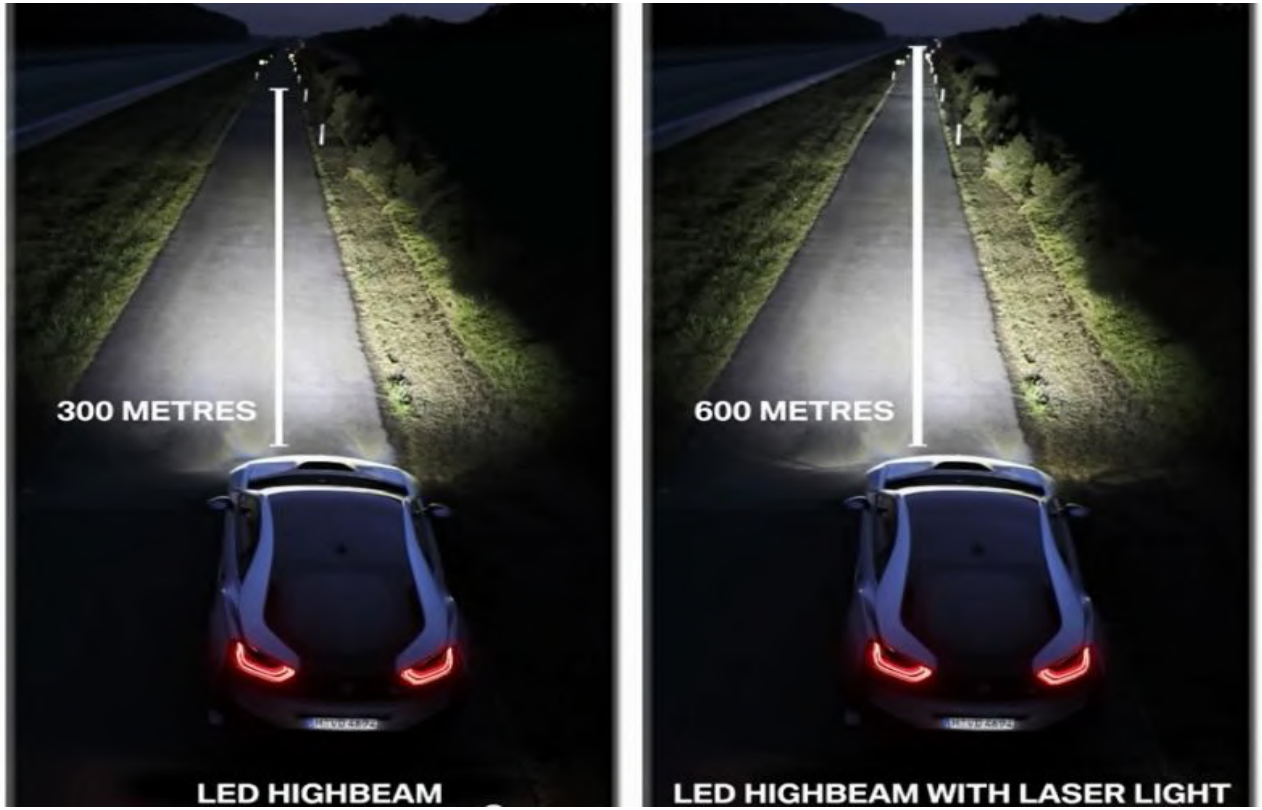


InGaP, GaAsP and GaP LED

and Heisenberg relations were

Without blue LEDs none of following applications would be possible:

LED high beam for cars



The laser light is used only in most expensive cars, since the main problem is the sufficiently efficient phosphor whith long life time which can transform the laser light.

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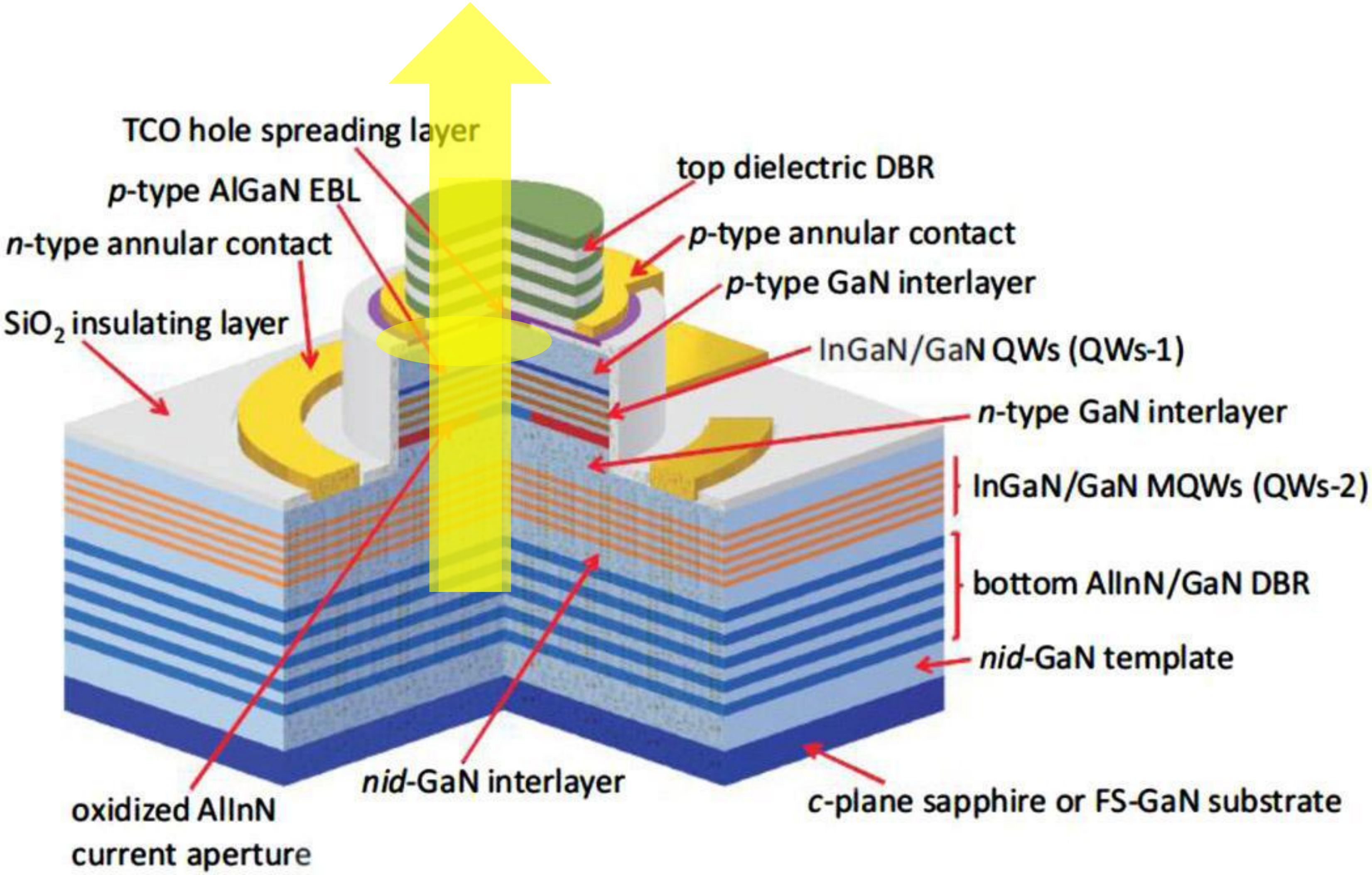
Blue VCSEL structure



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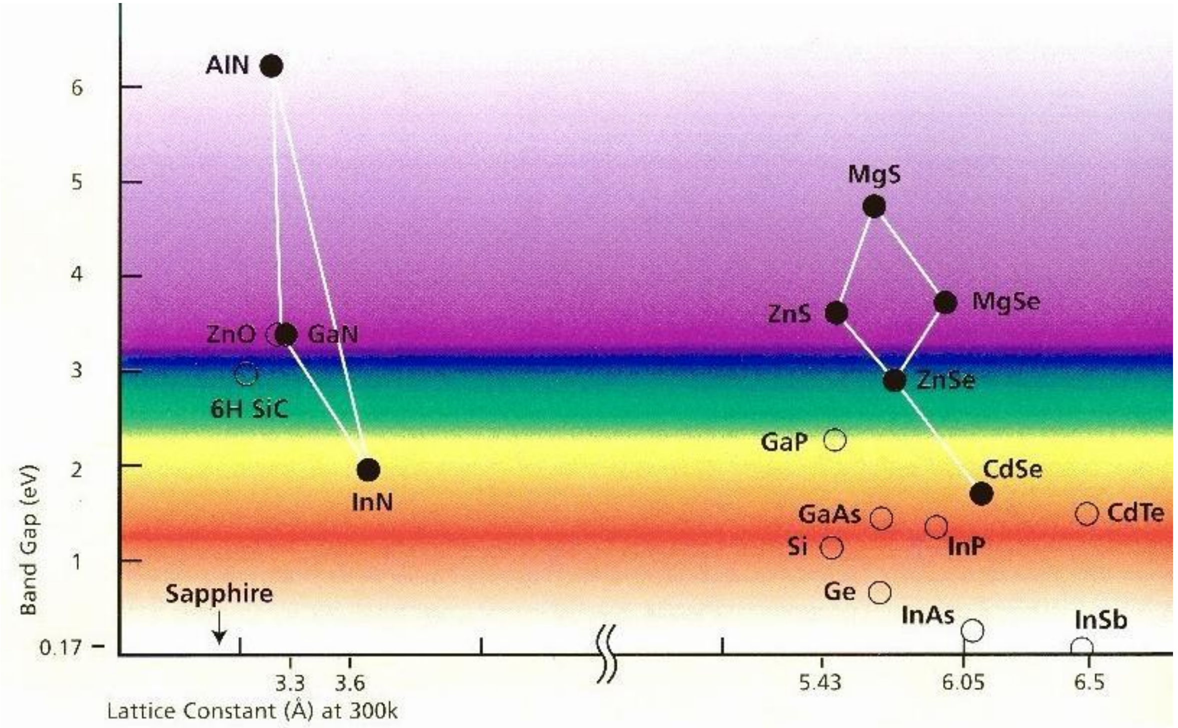
New LED application
Pink green houses ☺

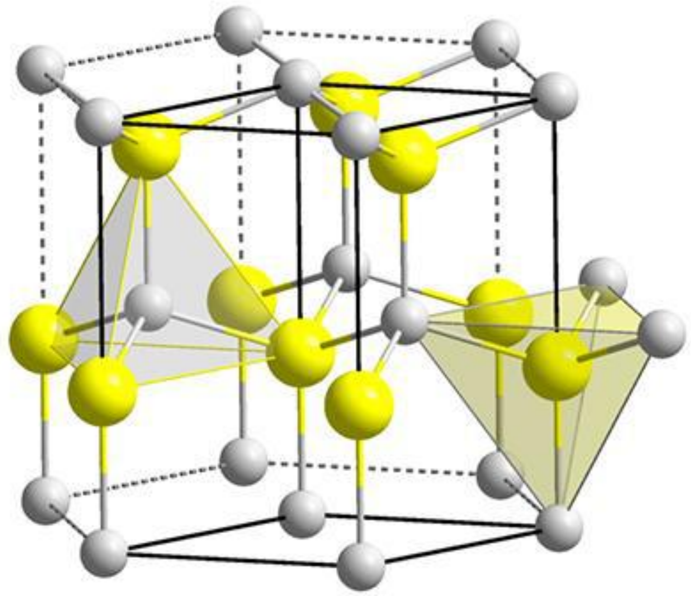
Possible semiconductors for blue LED

Sulfides-selenides, silicon carbid, ZnO or nitrides?



Sulfides-selenides have weak bonds and the lifetime of LEDs was only few hours. SiC is non direct semiconductor with very low luminescence efficiency. ZnO is dificult for doping and it cannot form heterostructures. Nitrides are very suitable, but there were no available substrates for epitaxy.

Wurzite structure of GaN



Lattice constants:

a = 3.19 Å

c = 5.10 Å

Strong binding of atoms:

- High temperature stability
- Difficult to prepare bulk semiconductor

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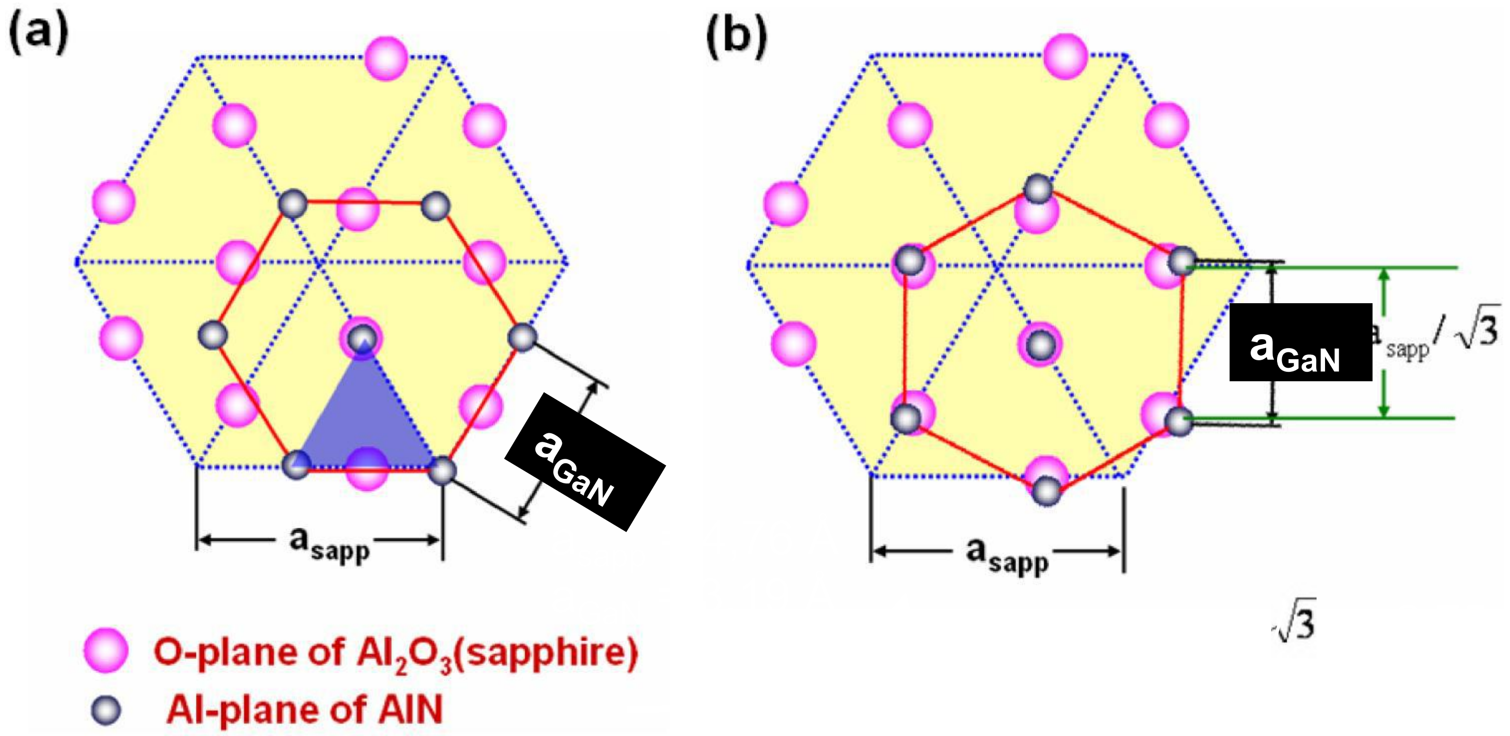
GaN on saphire substrate



V. P. Kladko et al., Appl. Phys. Lett. 95 (2009) 031907

Saphire substrates were very promissing, but not ideal.
The strain was still too high

Nobel prize laureates for physics 2014

Isamu Akasaki   Hiroshi Amano   Shuji Nakamura

Univerzity of Nagoja   Nichia

After 20years battle this 3 scientist succeded to improve the growth of GaN on sapphire and to produce the first blue LED

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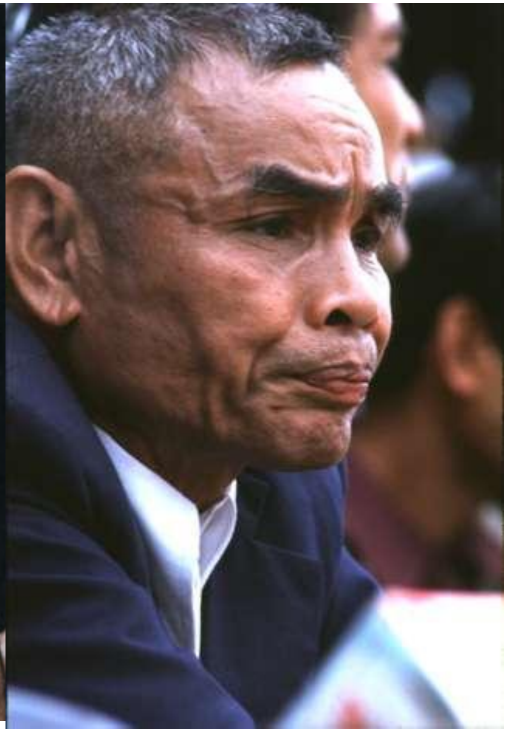
Japanies soldiers

Jokoi Shoichi
Guamo (Pacific)

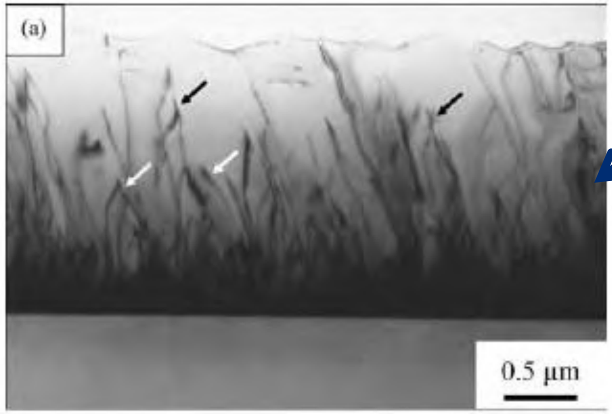
Hiroo Onoda
Philipines



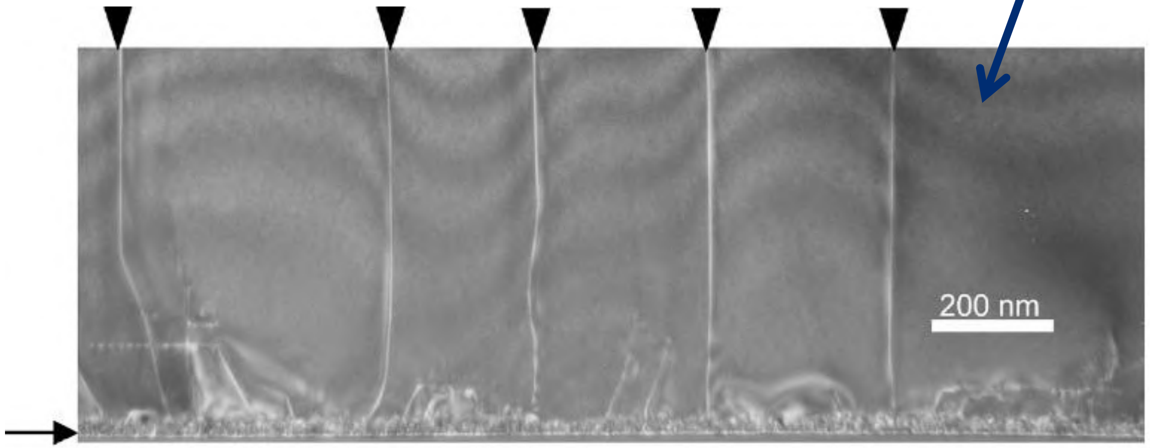
Teruo Nakamura
Indonesia

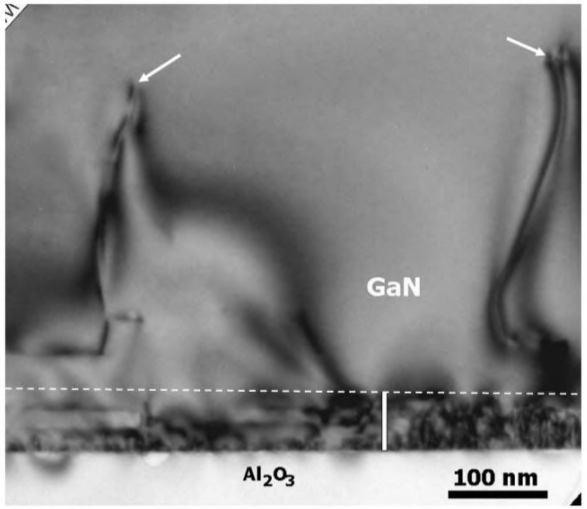
Although their fight was supposed to be as useless as the fight of these 3 Japanies soldiers who did not accept the Japan capitulation and fighted against US still in 1970.

Dislocation in GaN after epitaxy on saphire



- Growth without low temperature buffer layer
- Improvement after low temperature buffer layer





The main idea was to grow the buffer at very low temperature. It resulted in very rough surface which enable to curve the dislocation. Dislocations mutualy anihilated and only few of them penetrated into the upper layers.

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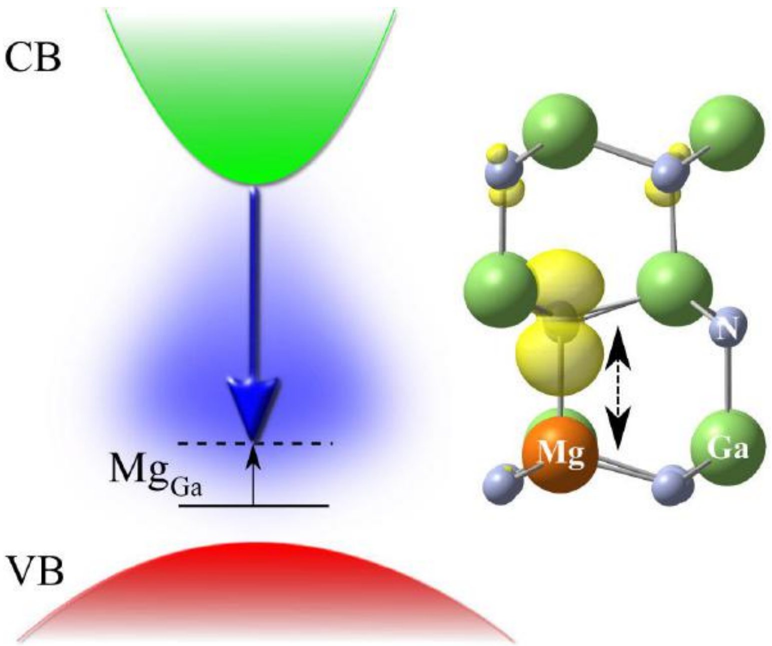
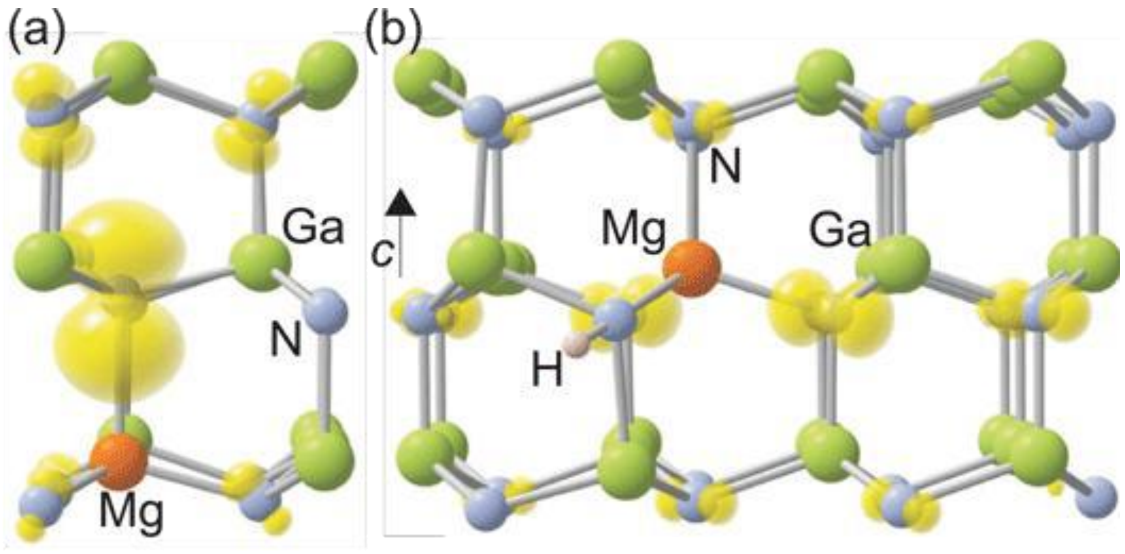
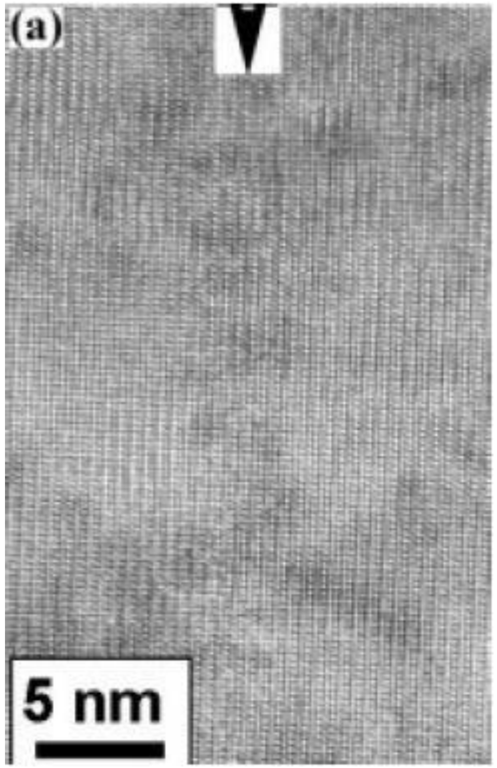
P-type doping by Mg atoms

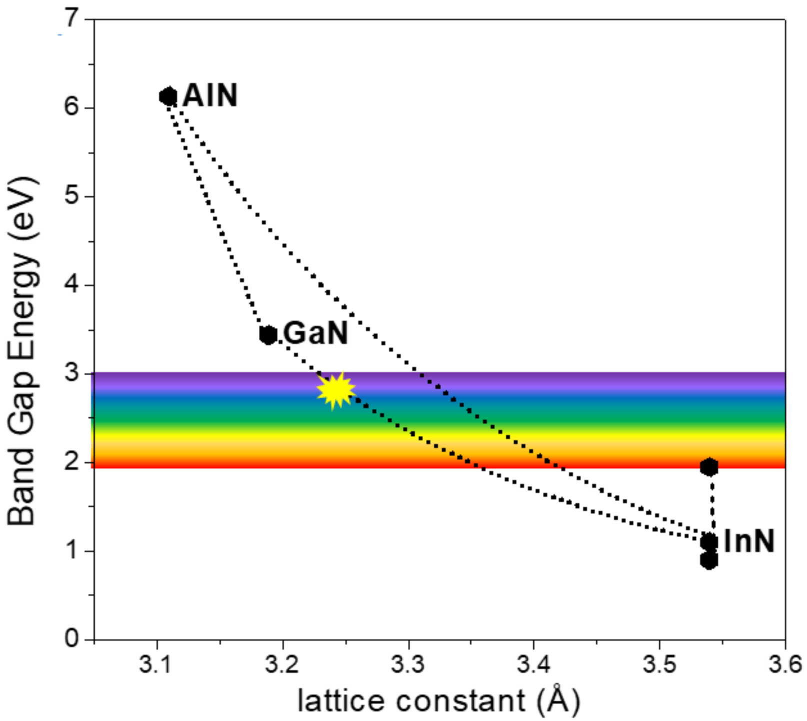




Another problem was p-type dopping. Mg was supposed to be suitable dopant, but although there was enough Mg atoms incorporated in layers, they did not have p-type conductivity. The reason was H atoms on neighbour nitrogens, which compensated effect of Mg acceptors. Annealing in N2 atmosphere helped to solve this problem.

InGaN QW – blue luminescence





GaN have luminescence in UV region. To obtain Blue light big In atoms were incorporated in GaN lattice. InGaN layers were later prepared as thin quantum well layers (QW) which signifficantly enhanced luminescence efficiency.

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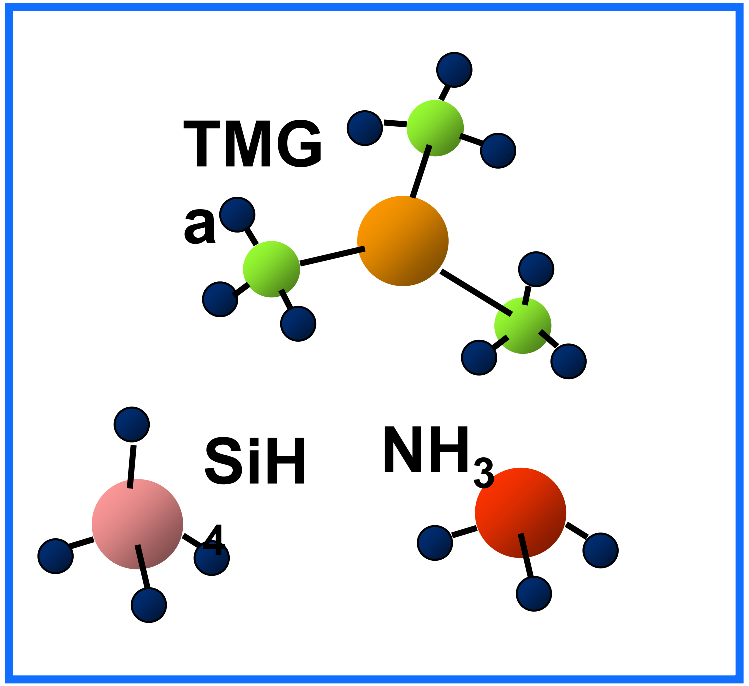
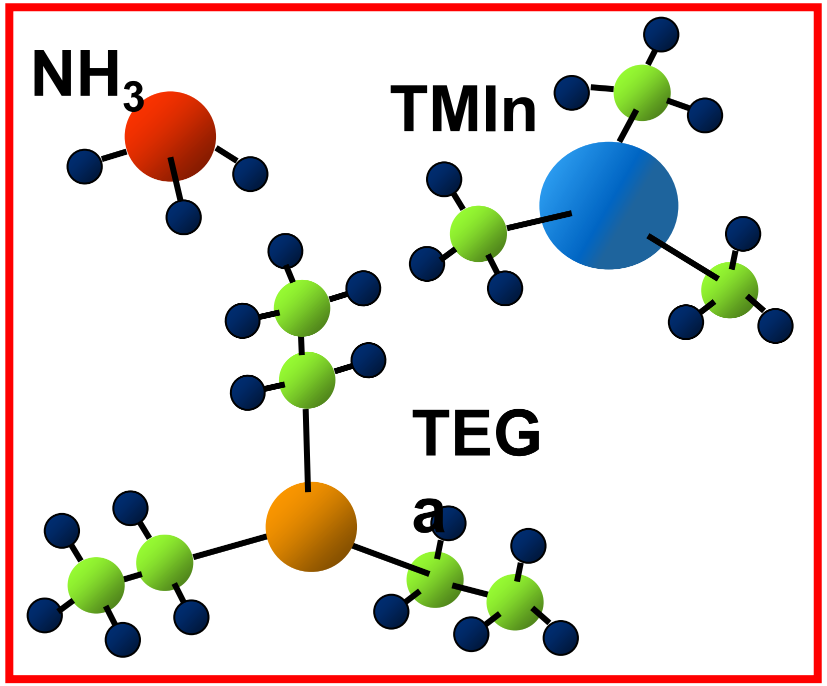
Precursor molecules

Buffer
carrier gas: H2



QW
carrier gas N2



$$TMGa + NH_3 \rightarrow GaN + 3\ CH_4$$

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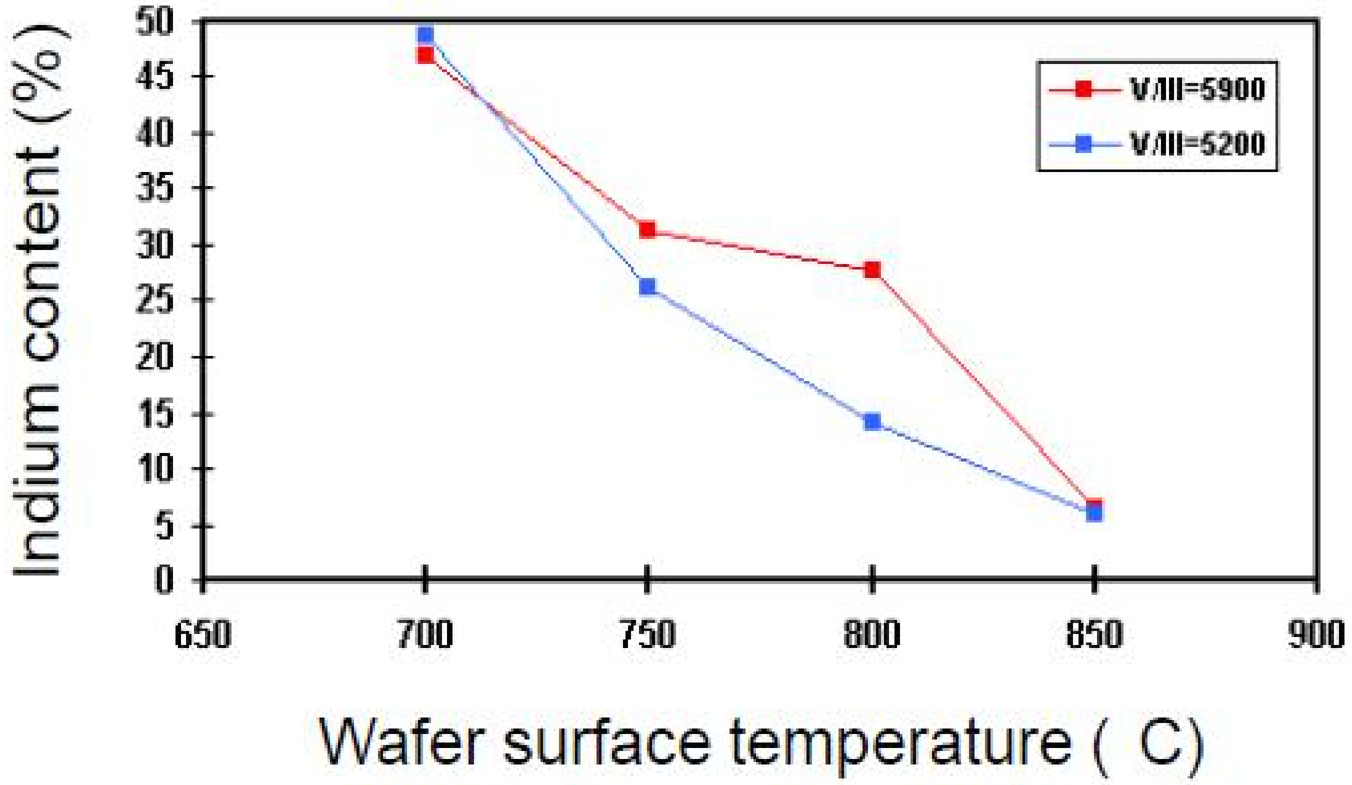
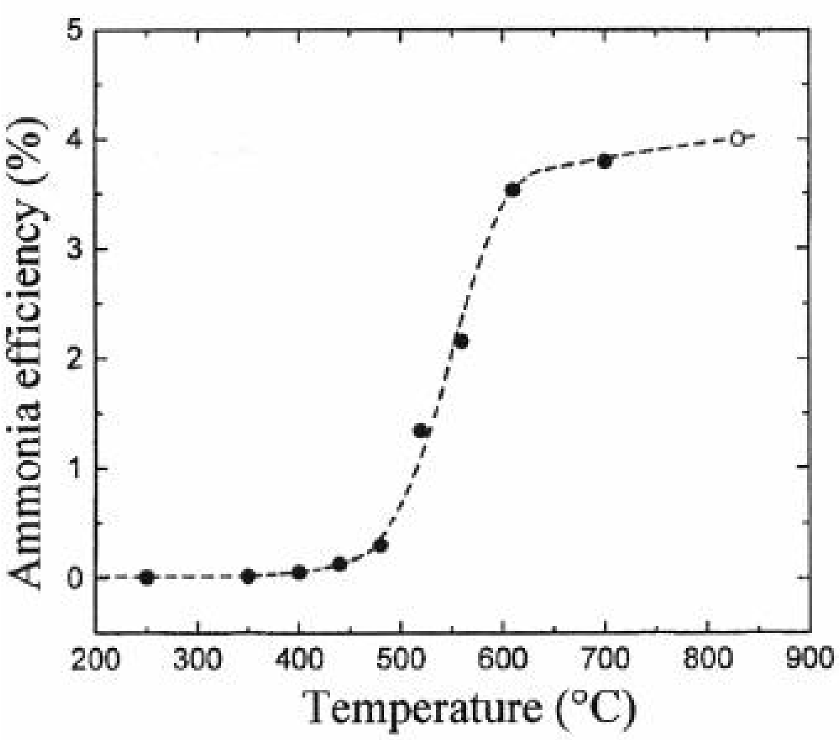
Different type of precursors has to be used for the growth of particular layers

InGaN

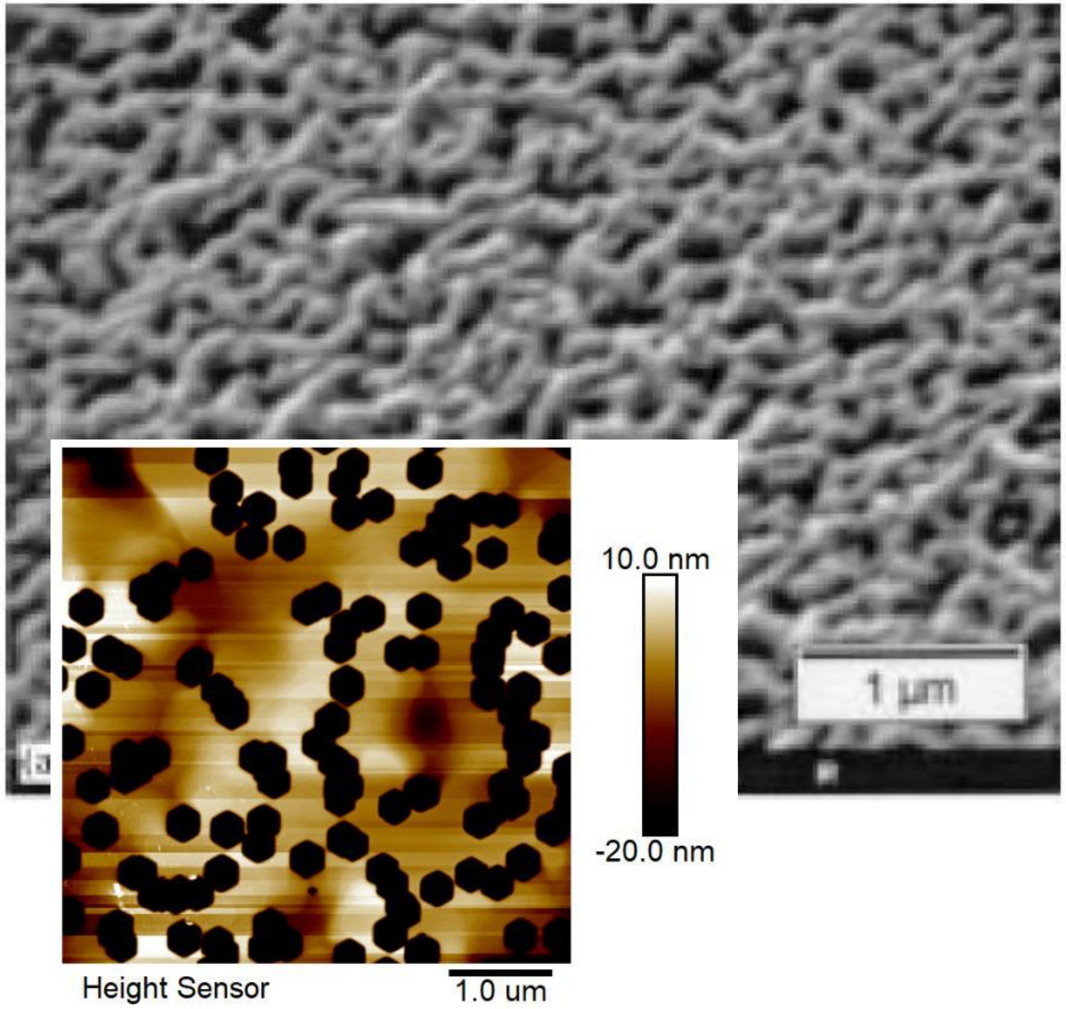


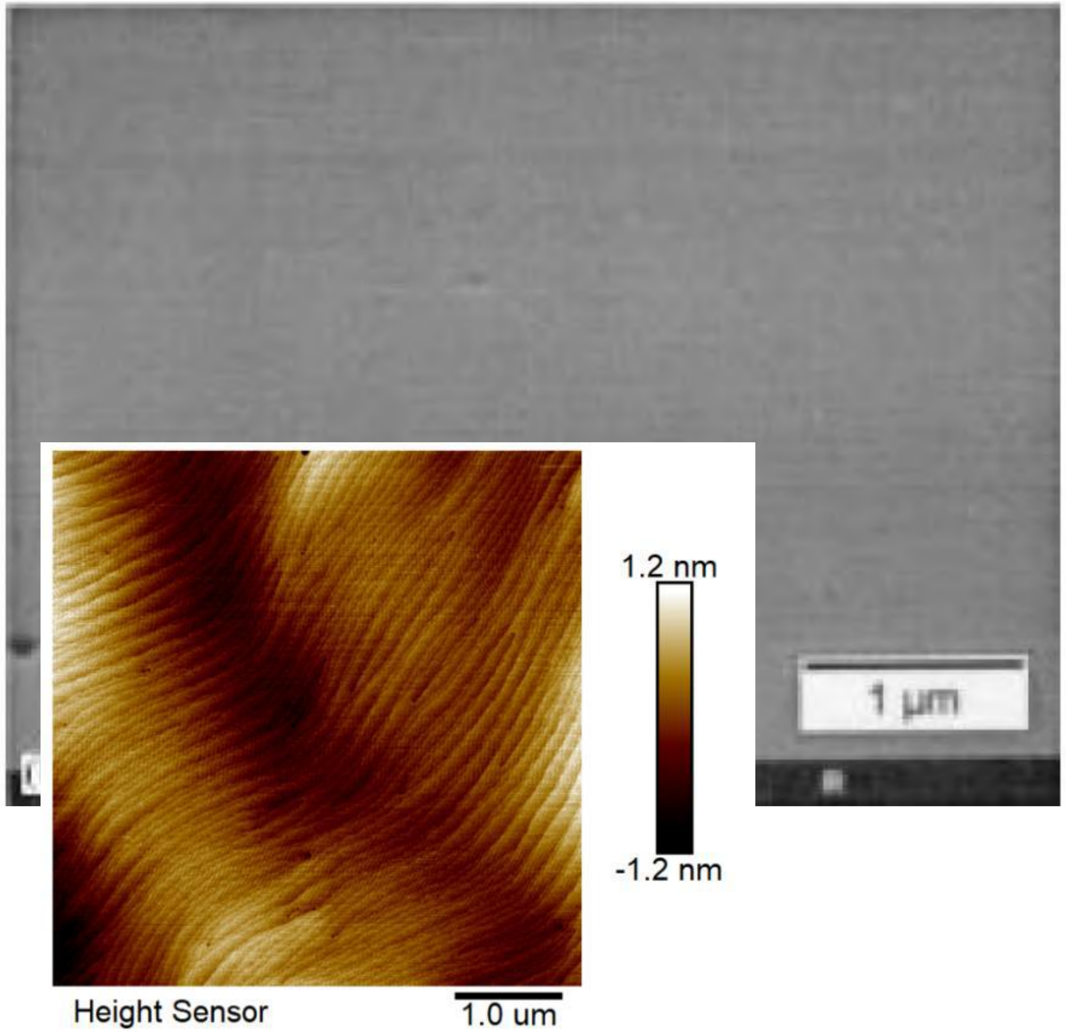
Indium content (%)
V/III=5900
V/III=5200
0
5
10
15
20
25
30
35
40
45
50
650
700
750
800
850
900
Wafer surface temperature (C)



Ammonia efficiency (%)
0
1
2
3
4
5
200
300
400
500
600
700
800
900
Temperature (°C)

Growth in N2 and H2 atmosphere





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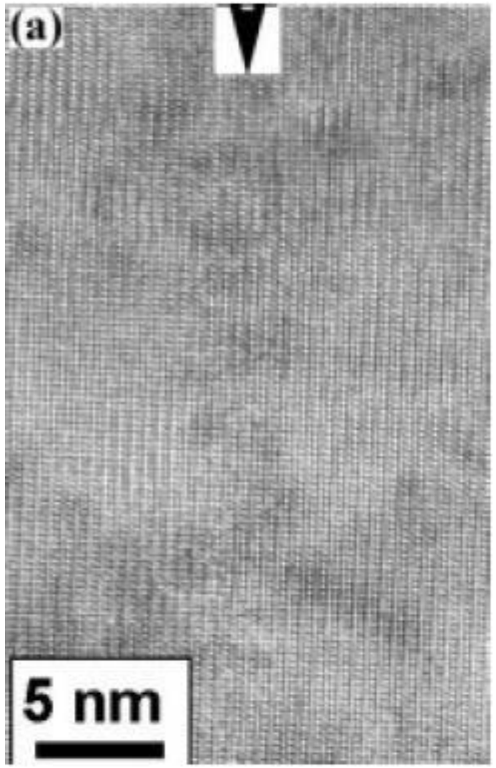
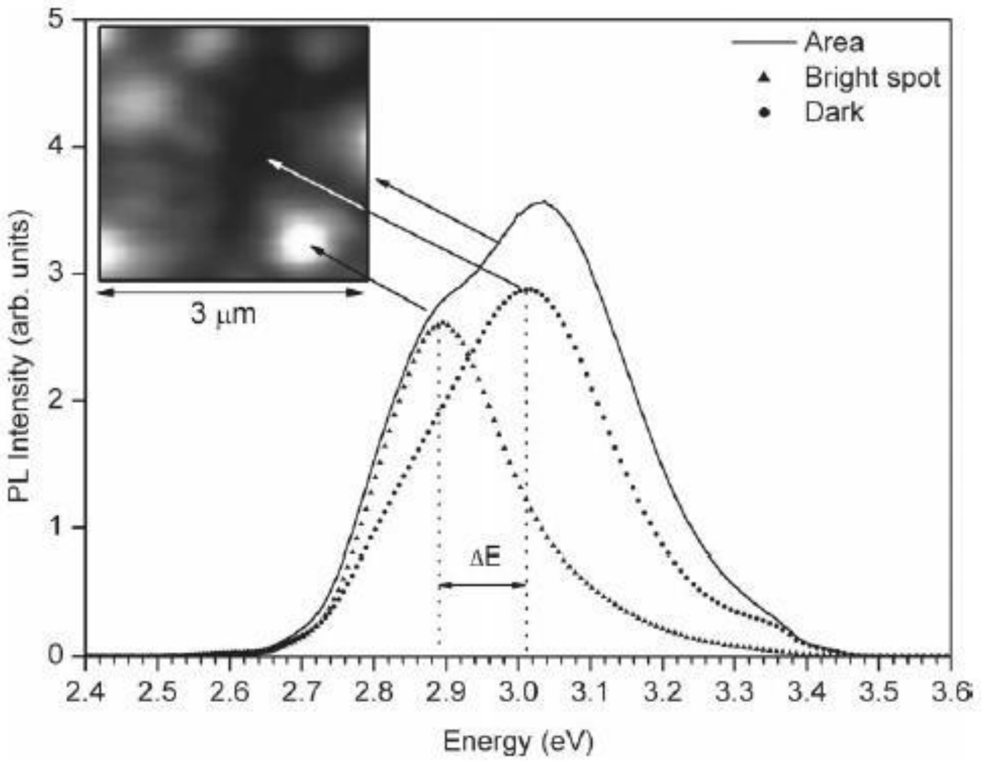
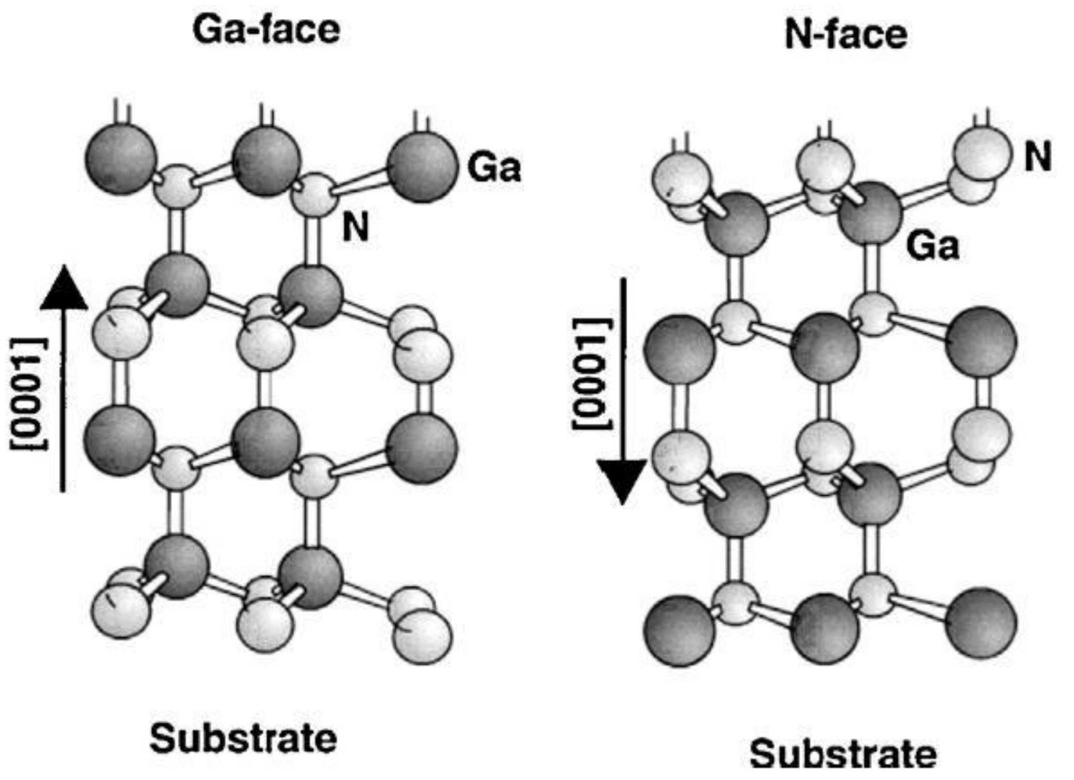
InGaN QW – increased luminescence intensity





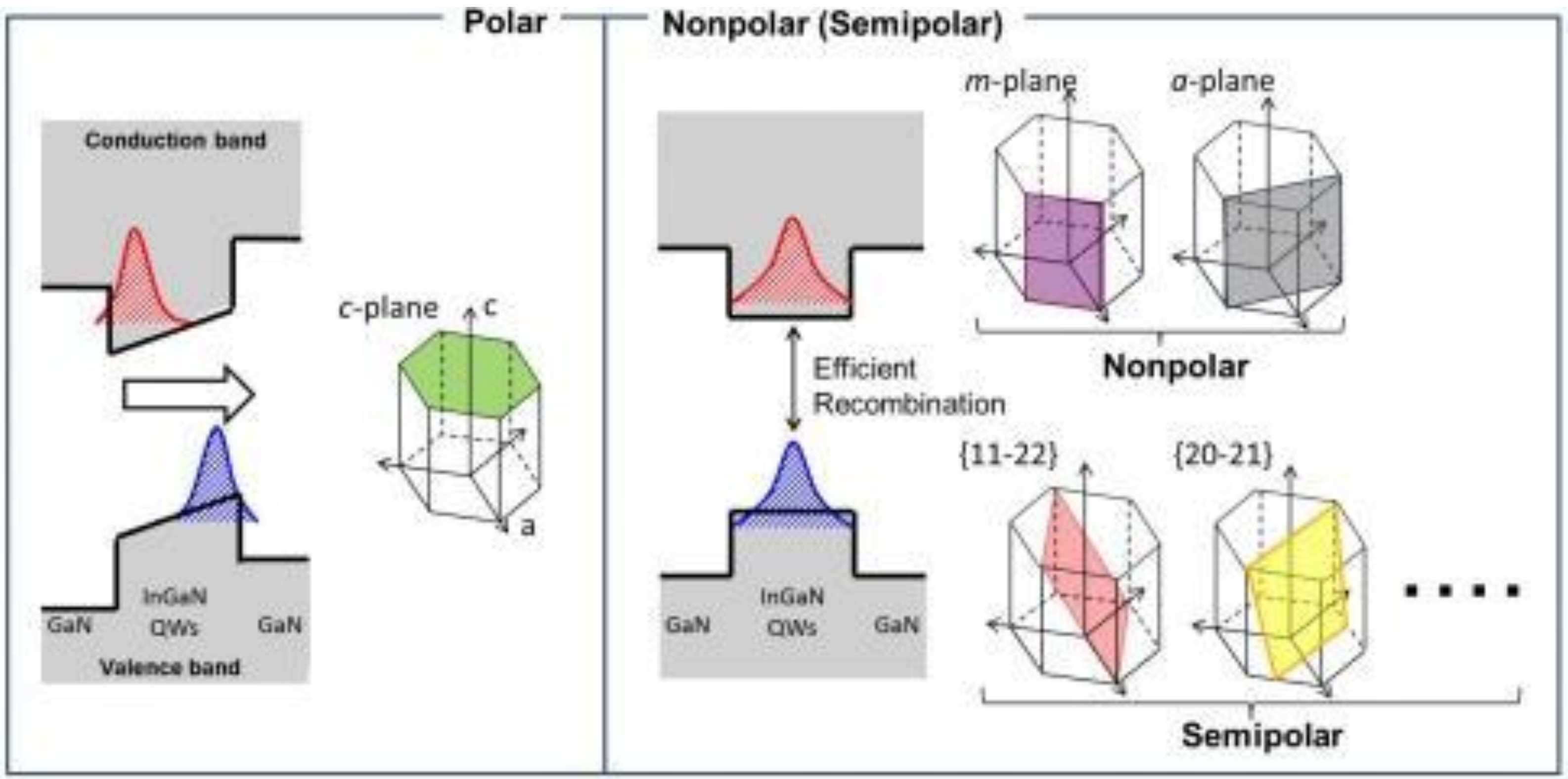
Luminescence intensity is increased in places with higher In content (potential wells for carriers)

Polar surfaces



Very important are polarization properties of nitrides which are caused by non equivalent bonds in wurzite structure. For luminescence applications the polarization is harming, but in HEMTs

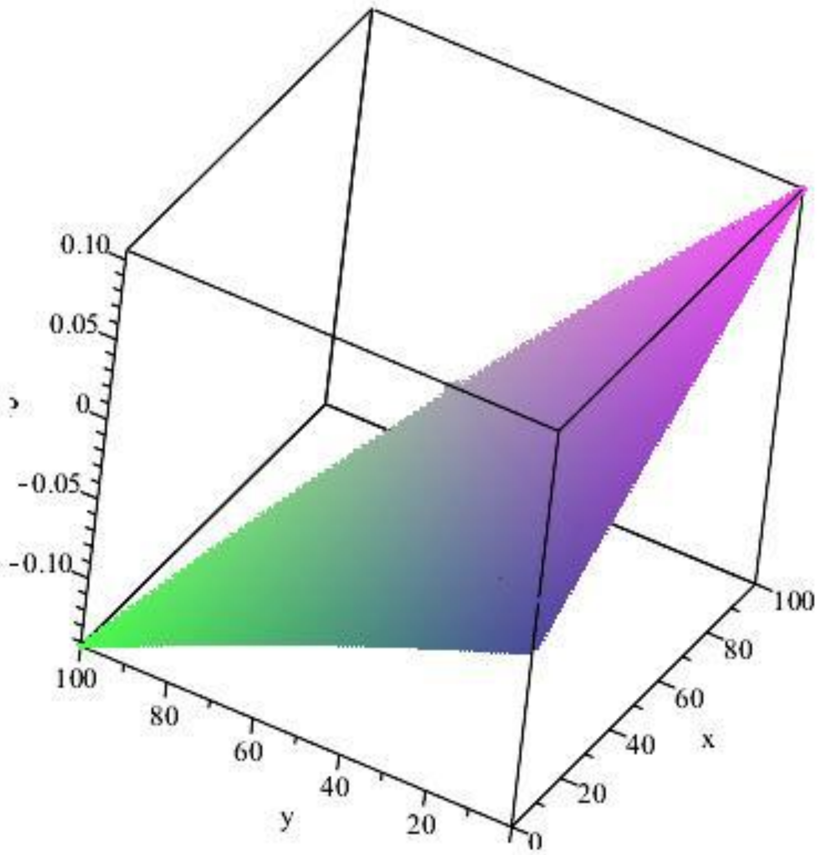
Electric field between polar and nonpolar heterojunctions



In InGaN QWs the polarization field separates spatialy electrons and hole, theirwave function overlap is lower and luminescence efficency is suppressed.

Polarization in AlInGaN layer on GaN

Polarization of $Al_yIn_xGa_{1-x-y}N$ layer with respect to the GaN as a function of Al and In content in the layer



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Substrates for nitrides

- Substrate material properties for GaN deposition:

	Coefficient of linear thermal expansion $(x10^{-6})K^{-1}$	Lattice Mismatch (%)
Al_2O_3(C)	> 8	13.8
SiC	~ 2.8	3.6
GaN	3.17	0
AlN	5.27	2.5
Si	2.6	17

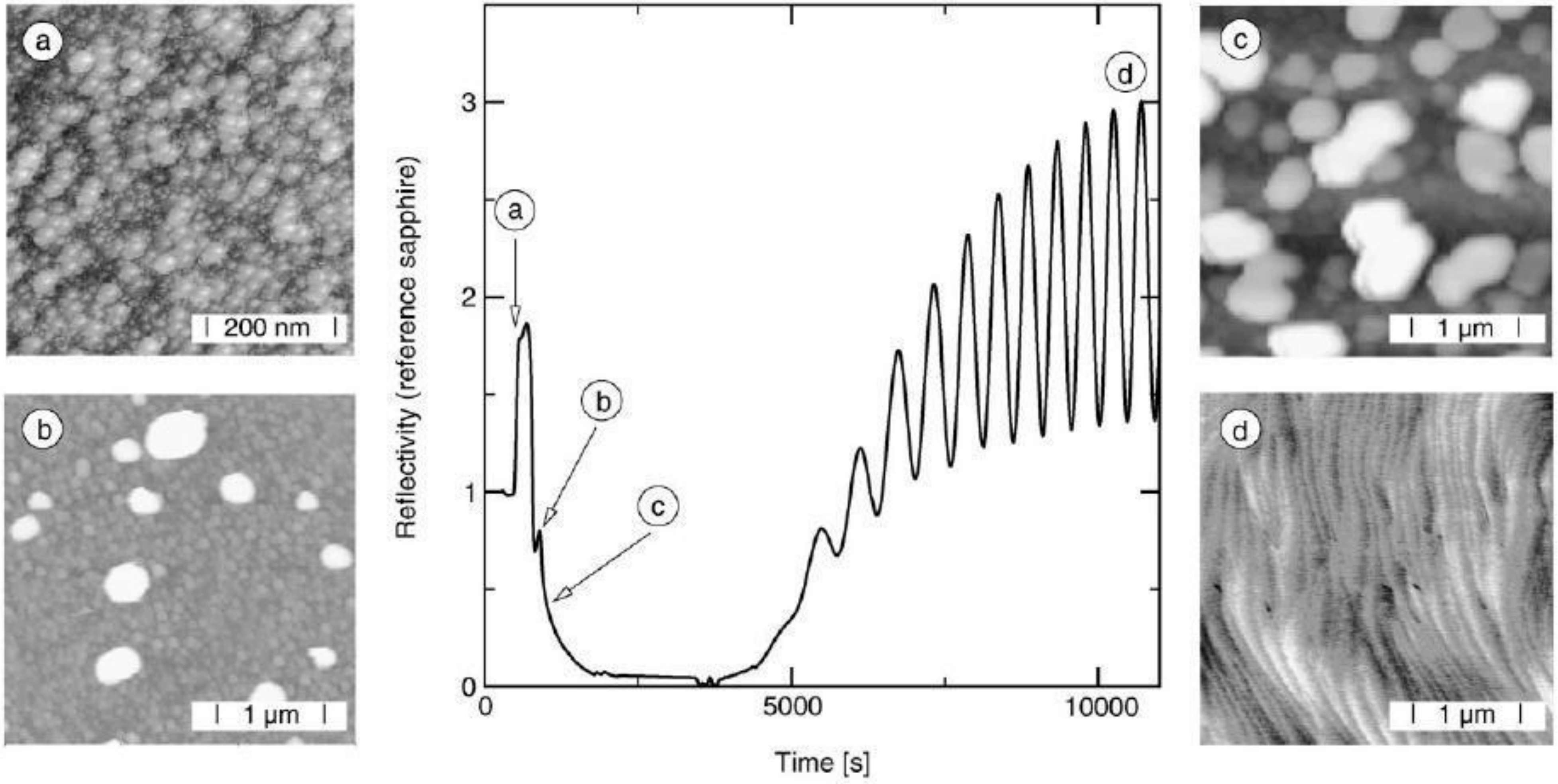
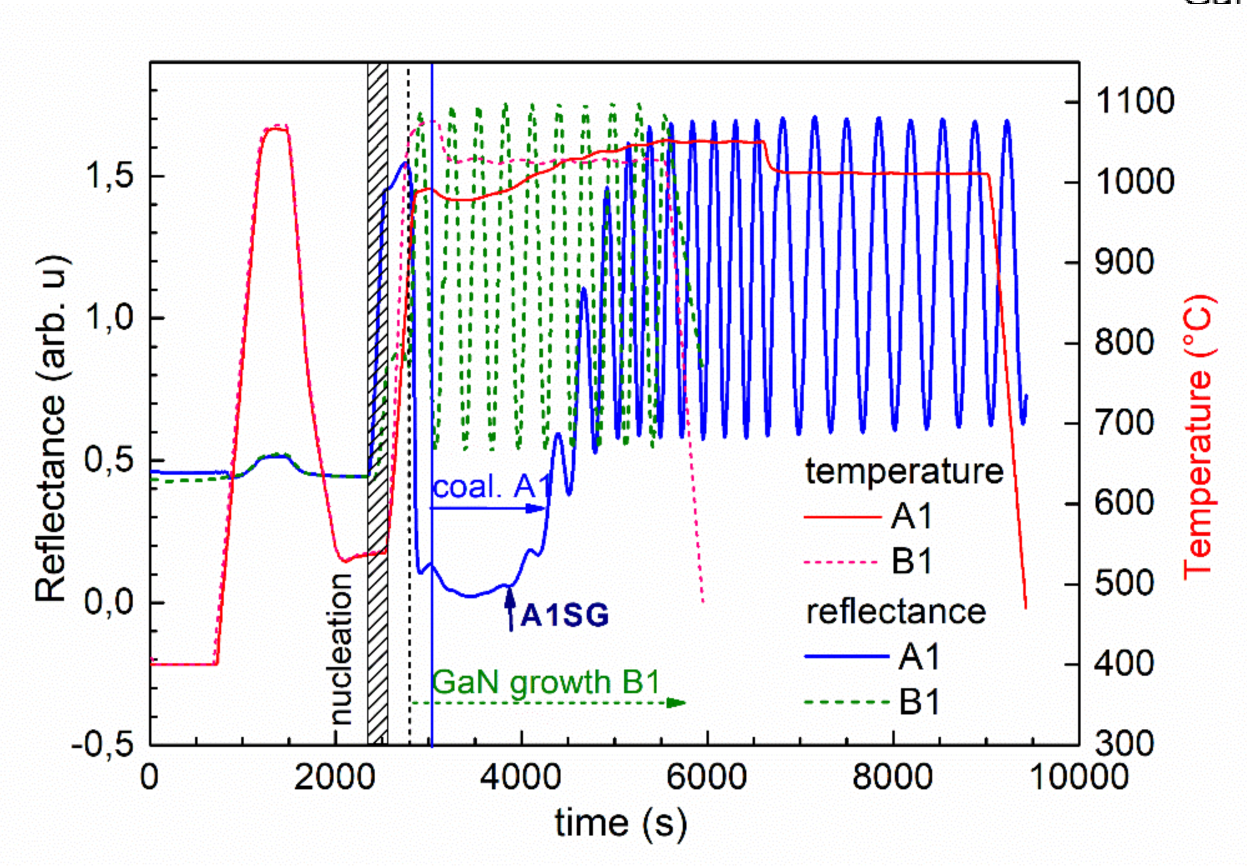
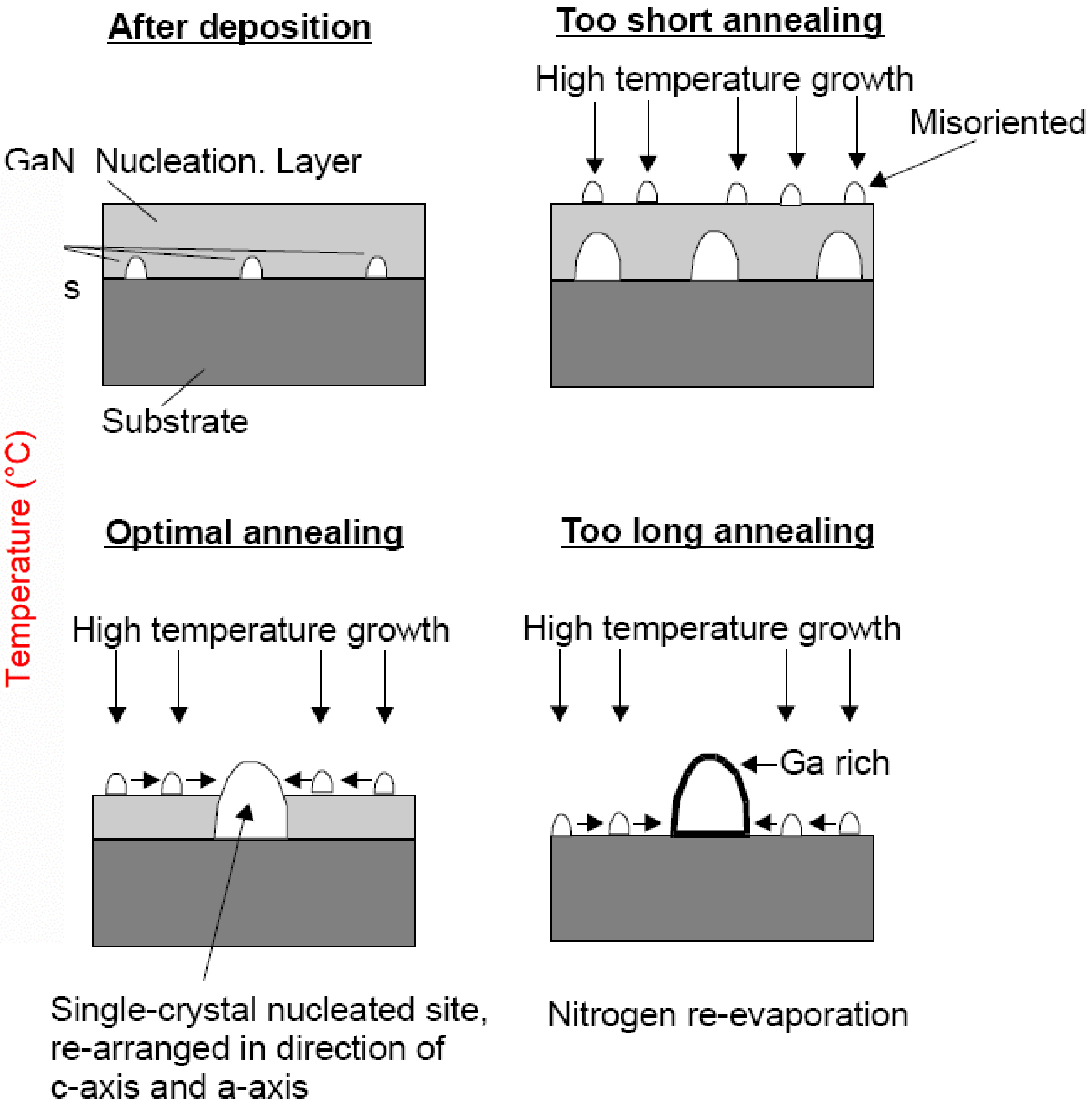


Fig. 2. Typical reflectance transient taken from a GaN growth run. AFM insets show the morphology at different stages of growth as the nucleation layer before (a) and after recrystallization (b), at the start of epilayer growth (c) and the final surface with atomic steps after coalescence (d).

O





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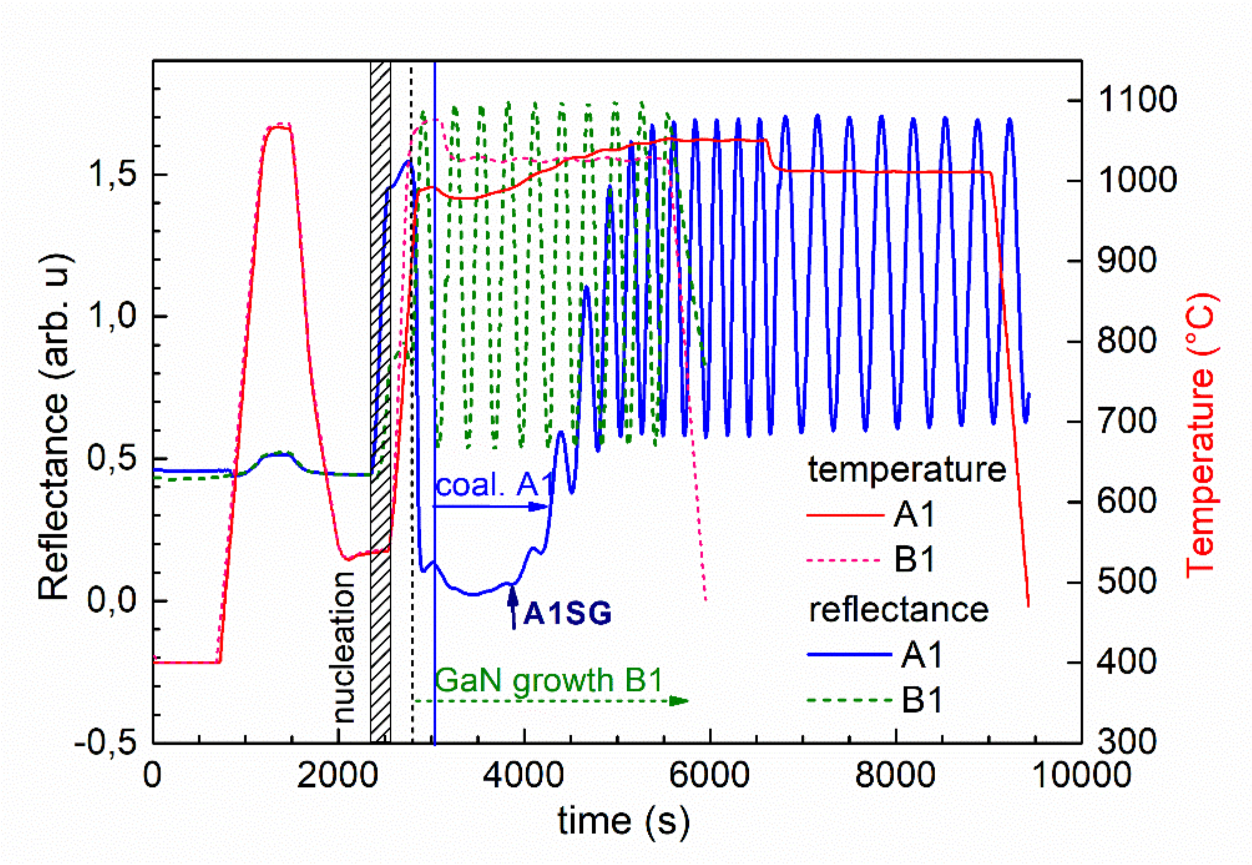
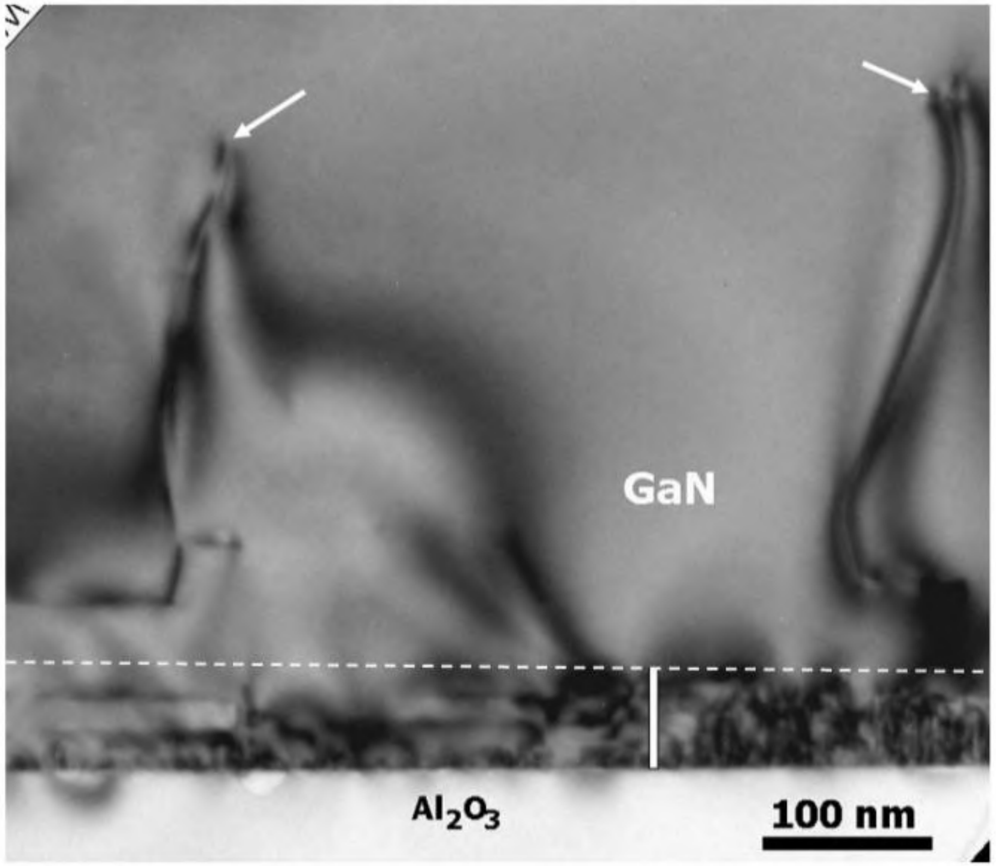
Our structures suppression od dislocation density





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Increasing the coalescence time by V/III ratio

Table 1
Growth conditions of each sample

Sample number	V/III ratio	Initial growth time (s)
S1	1760	0
S2	970	500
S3	970	940
S4	580	500
S5	580	940

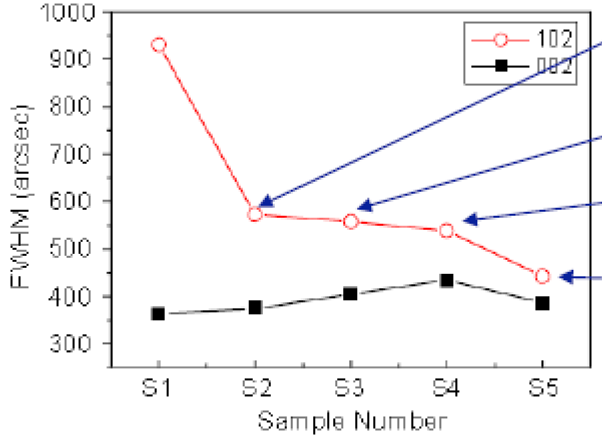

Fig. 3. **FWHM** values of X-ray rocking curves with different V/III ratios during the initial growth time.

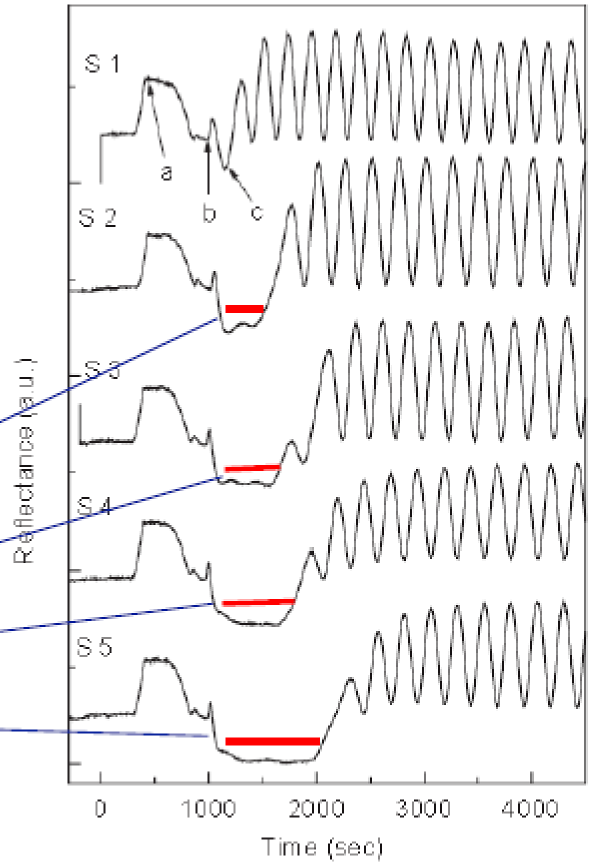

Fig. 2. Reflectance traces of five samples with different V/III ratios during the initial growth time.

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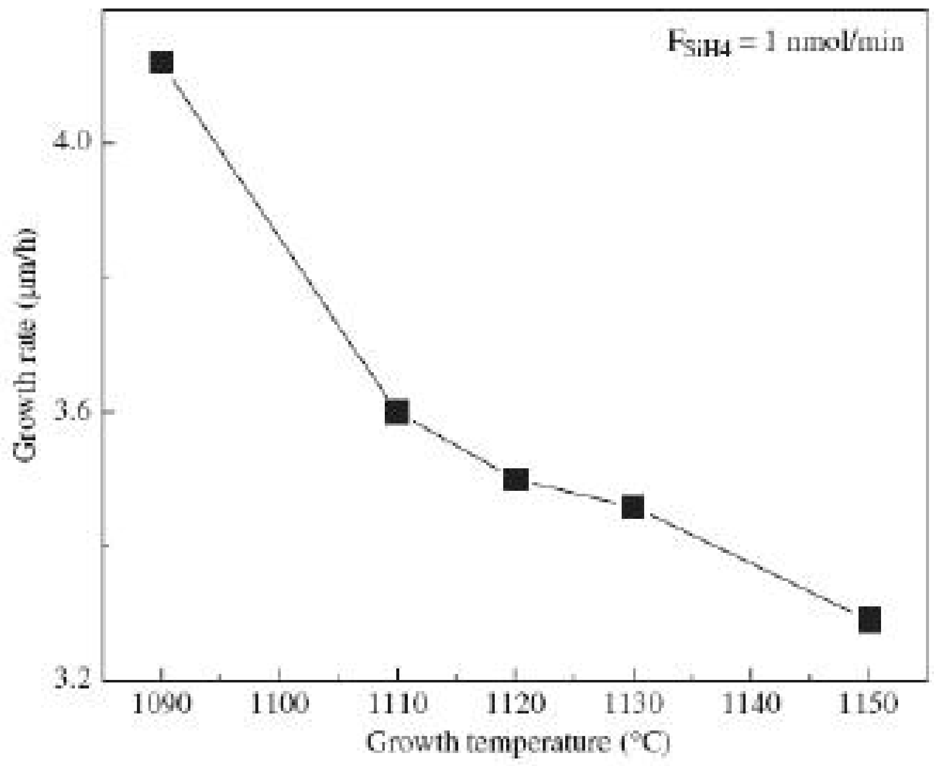
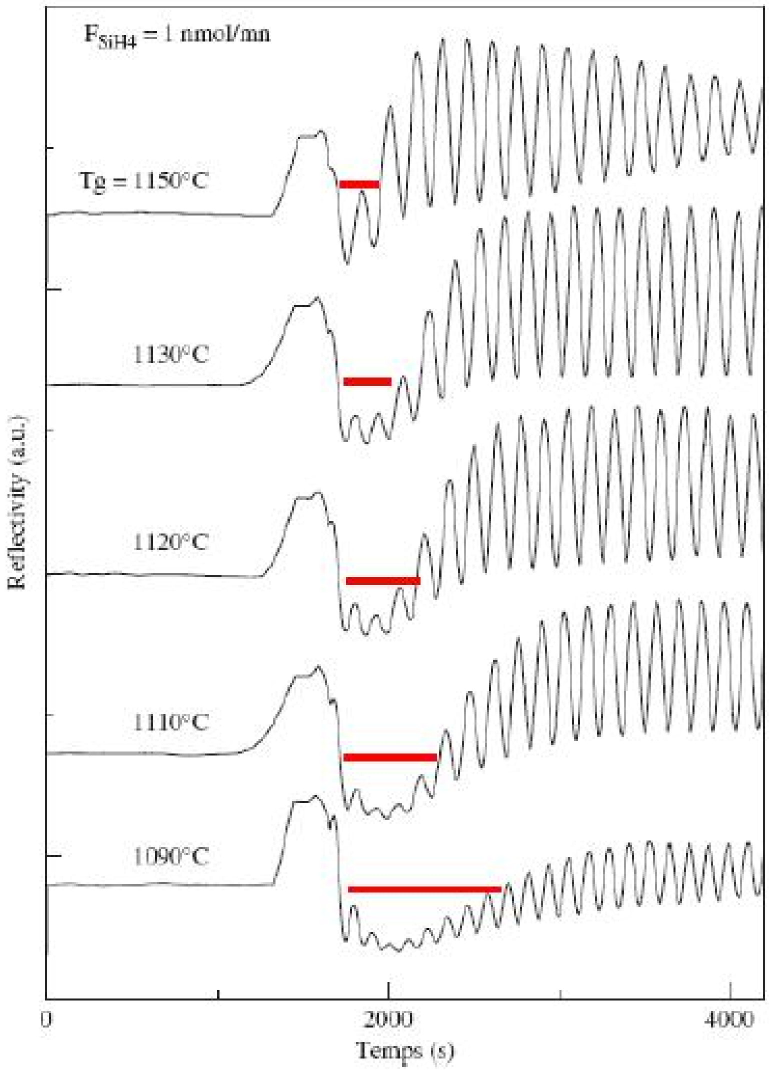
Two-step growth of high quality GaN using v/III ratio variation in the initial growth stage JCG 262 (2004) 7-13

Increasing the coalescence time by temparature





Growth temperature effect on MOVPE si-doped GaN-Thermodynamic modeling-Microelectronics journal-p363-v40-2009

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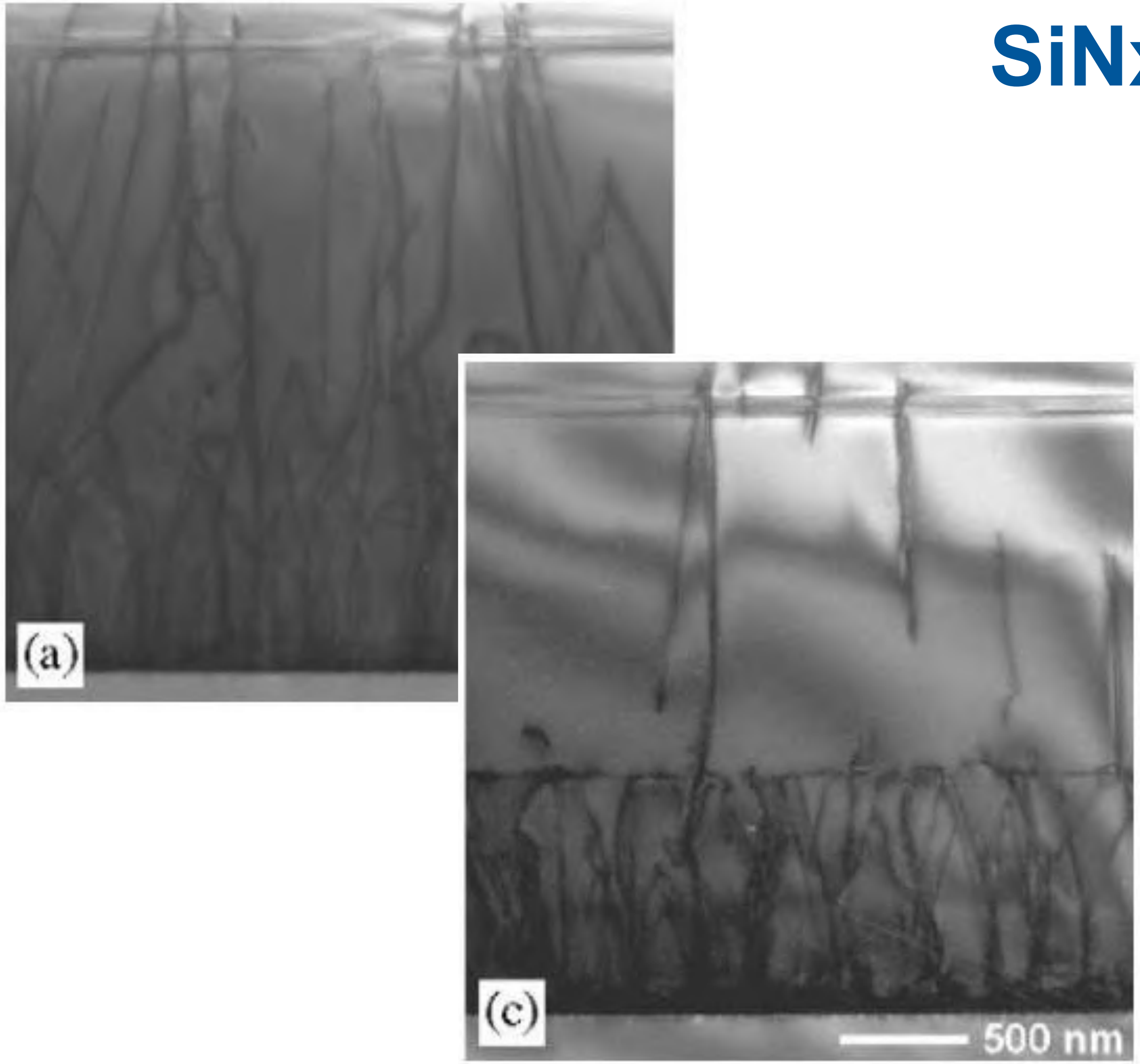
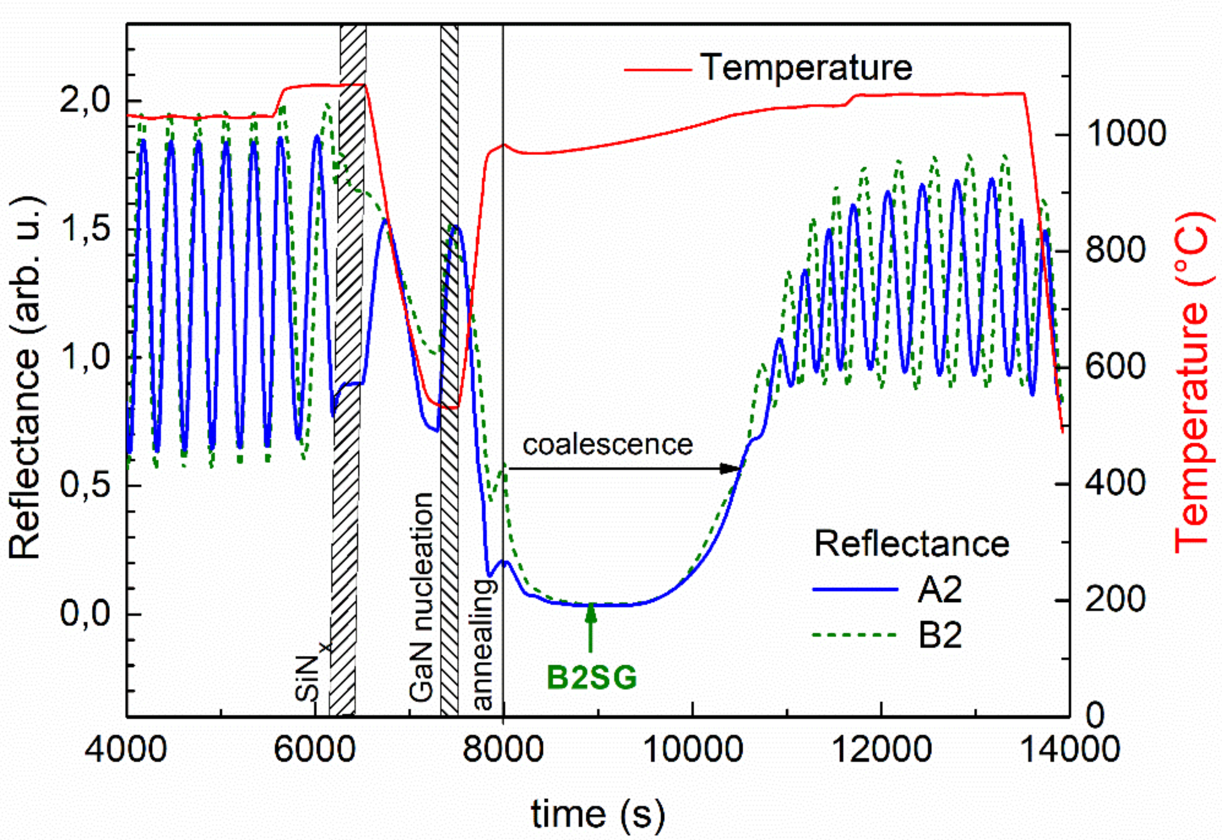
SiNx layer





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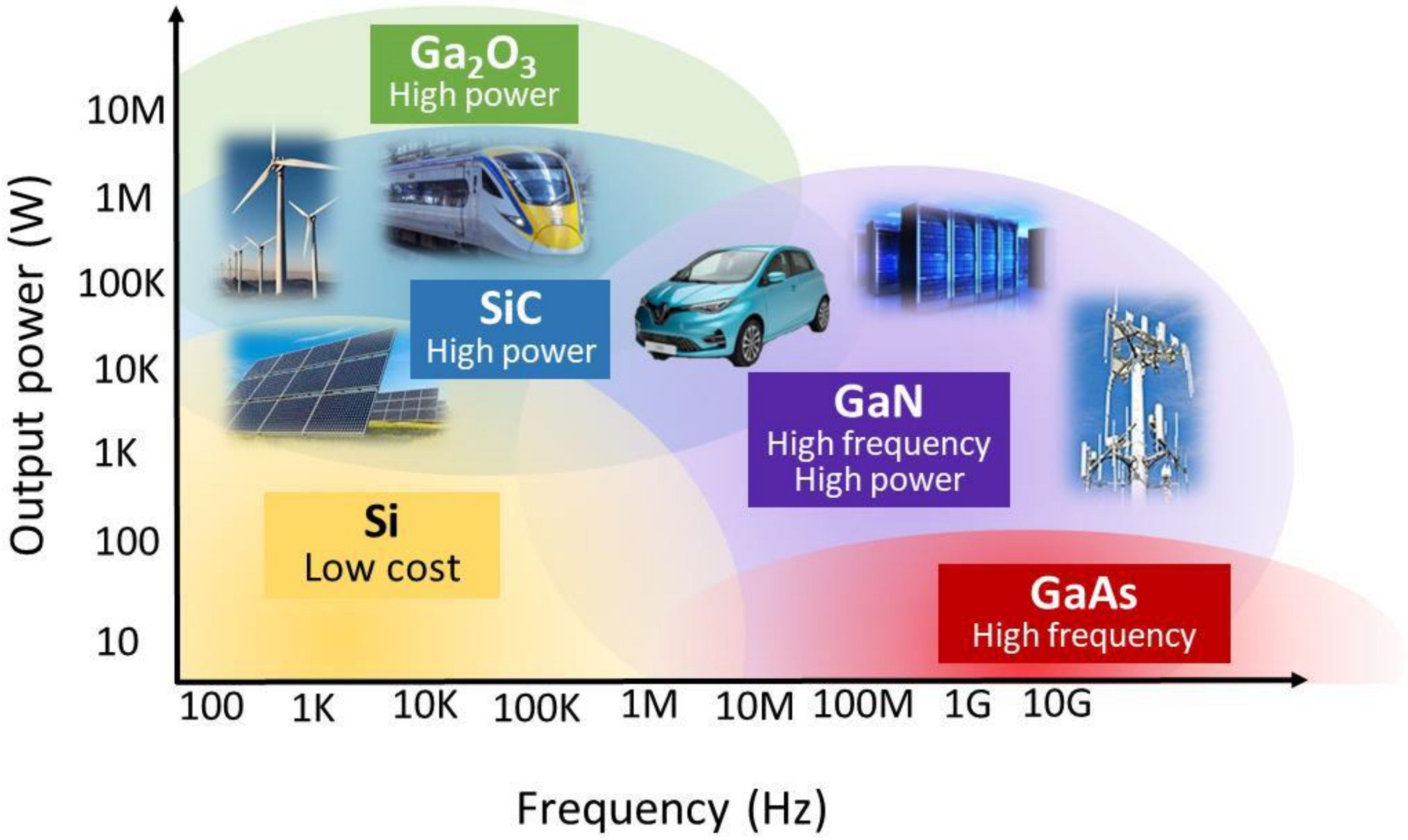
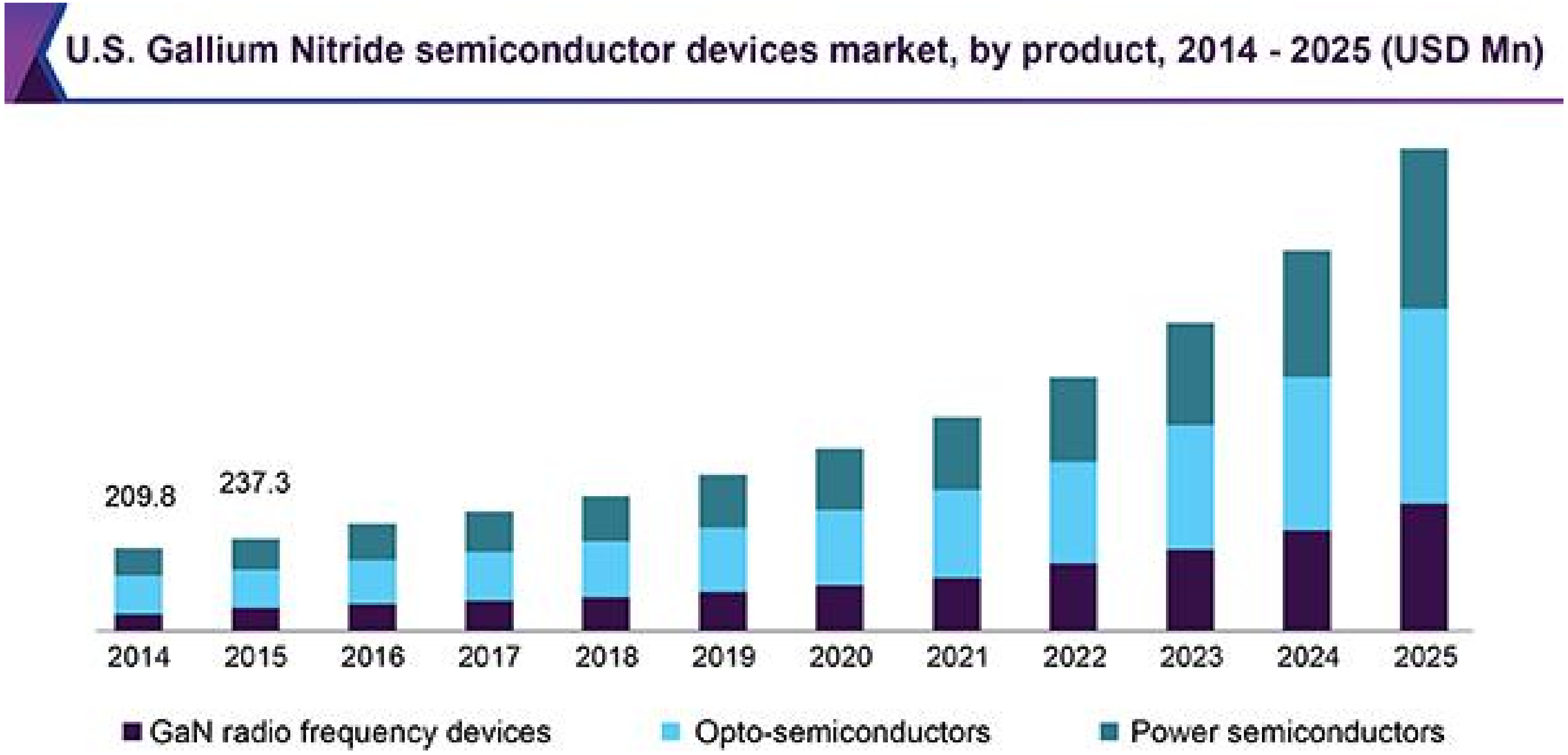
Semiconductors are not only silicon



GaN applications



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GaN RF applications
5G networks – base stations

- Higher bandwidth enable higher capacity – higher number of connected devices – higher power requirements

high power + high frequency= GaN

- Wavelengths used in 5G have shorter propagation distances – increased density of base stations

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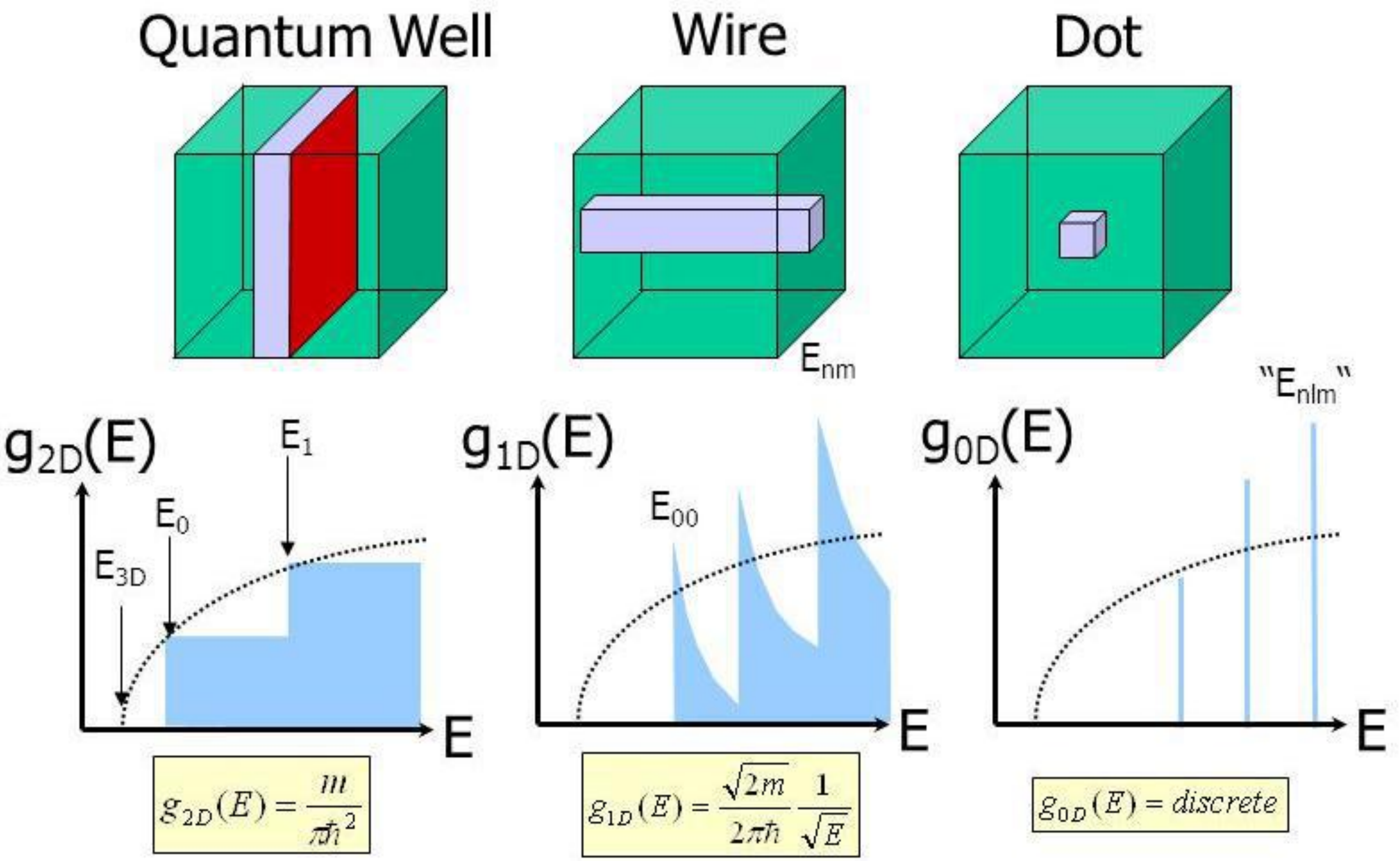
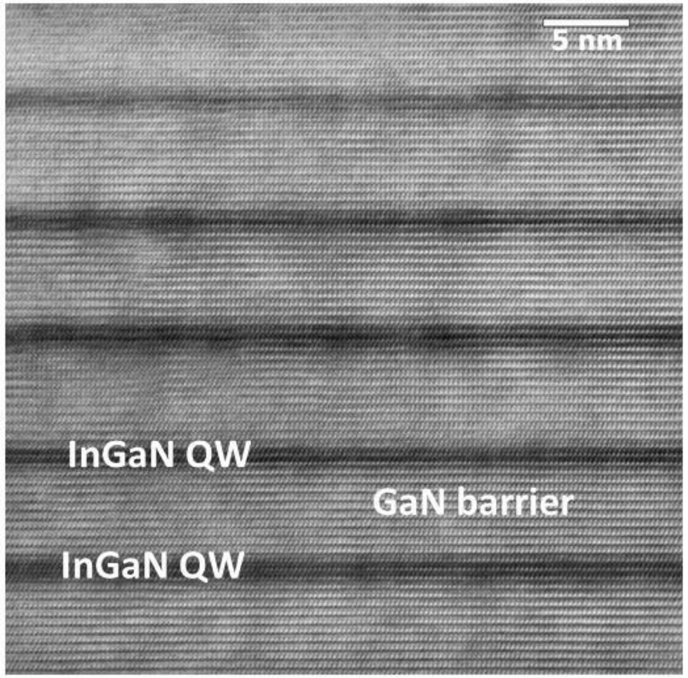
Nanoheterostructures:

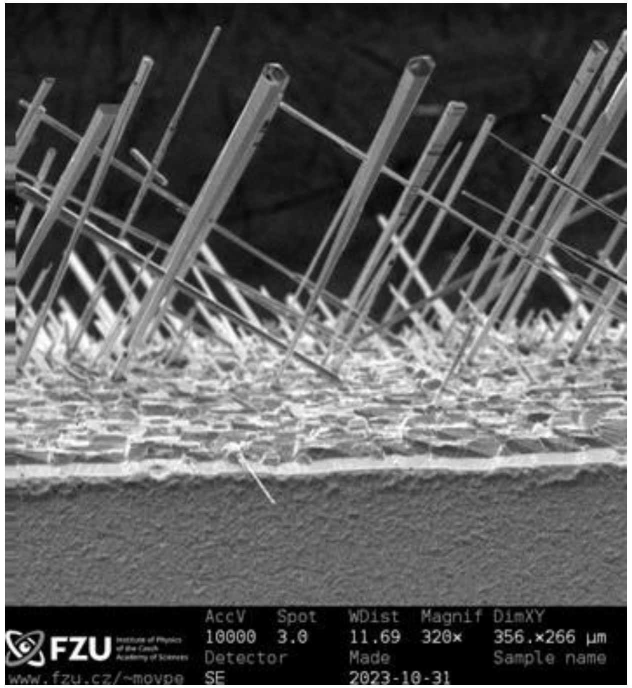


Epitaxy of nanoheterostructures:

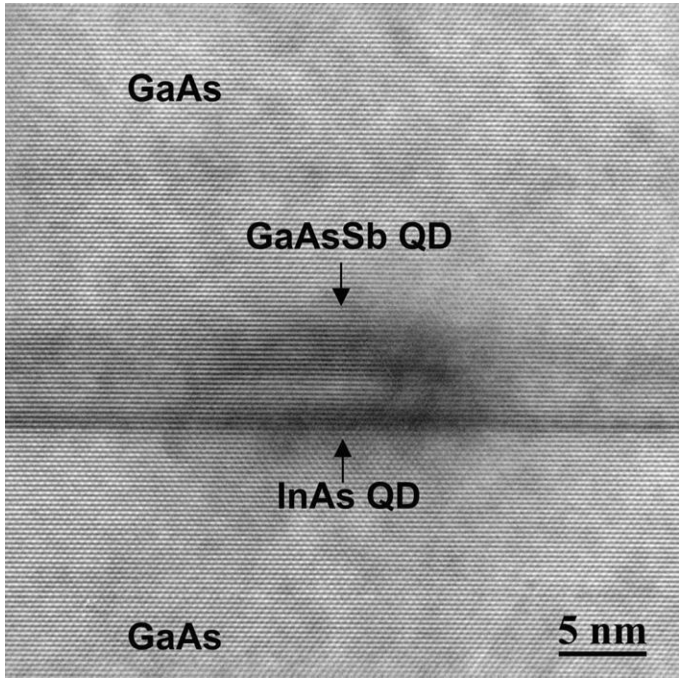
QWs



Nanorods



QDs



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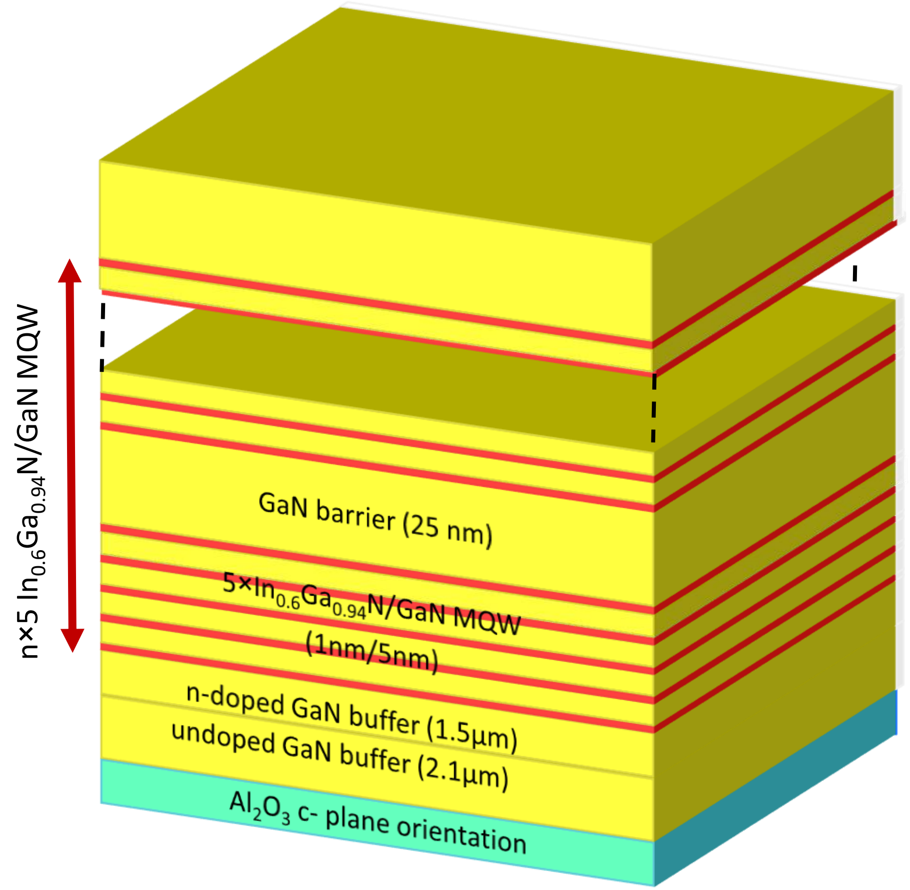
Nanoheterostructures:
QWs
For fast scintillators

Scintillator structure

In our laboratory scintillator structures are developed. They have to contain much more InGaN QWs than in LED structures, to detect bigger part of the penetrated ionizing radiation



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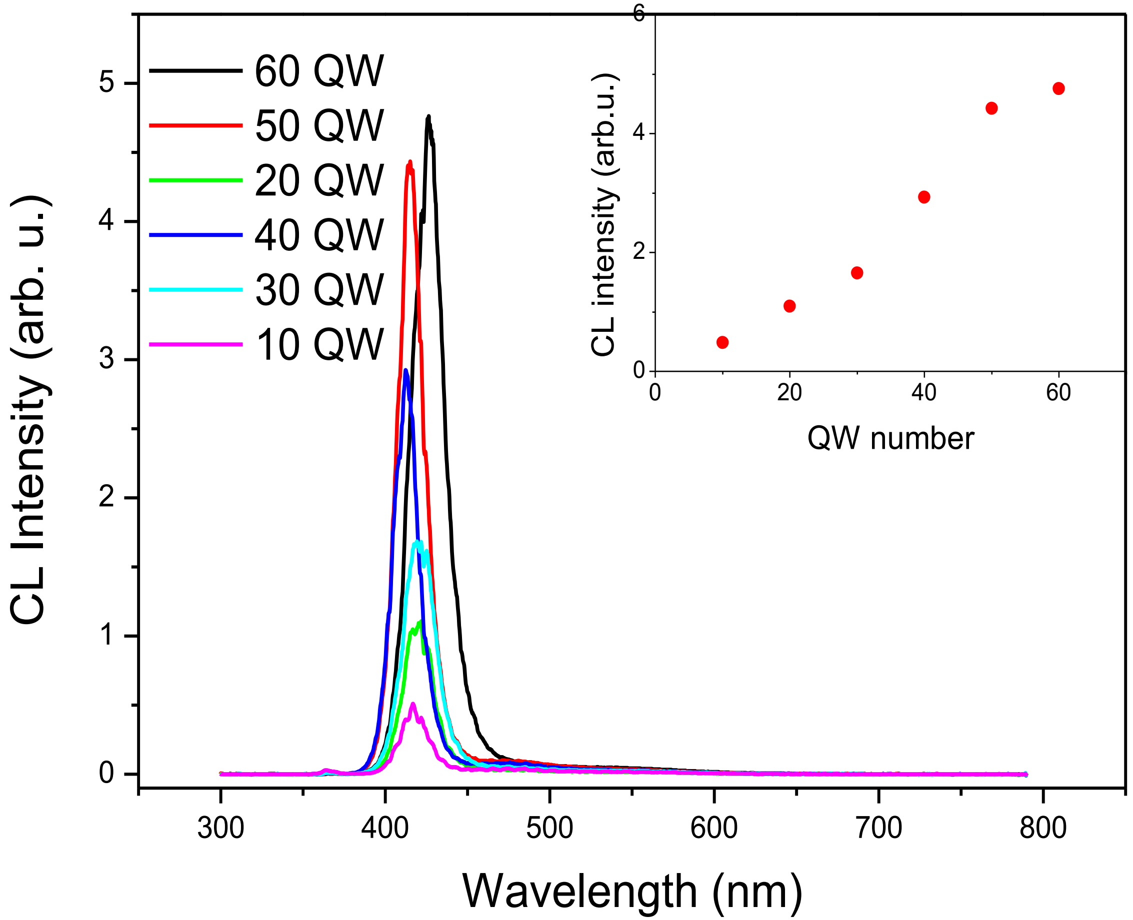
Cathodoluminescence of structures with different QW numbers



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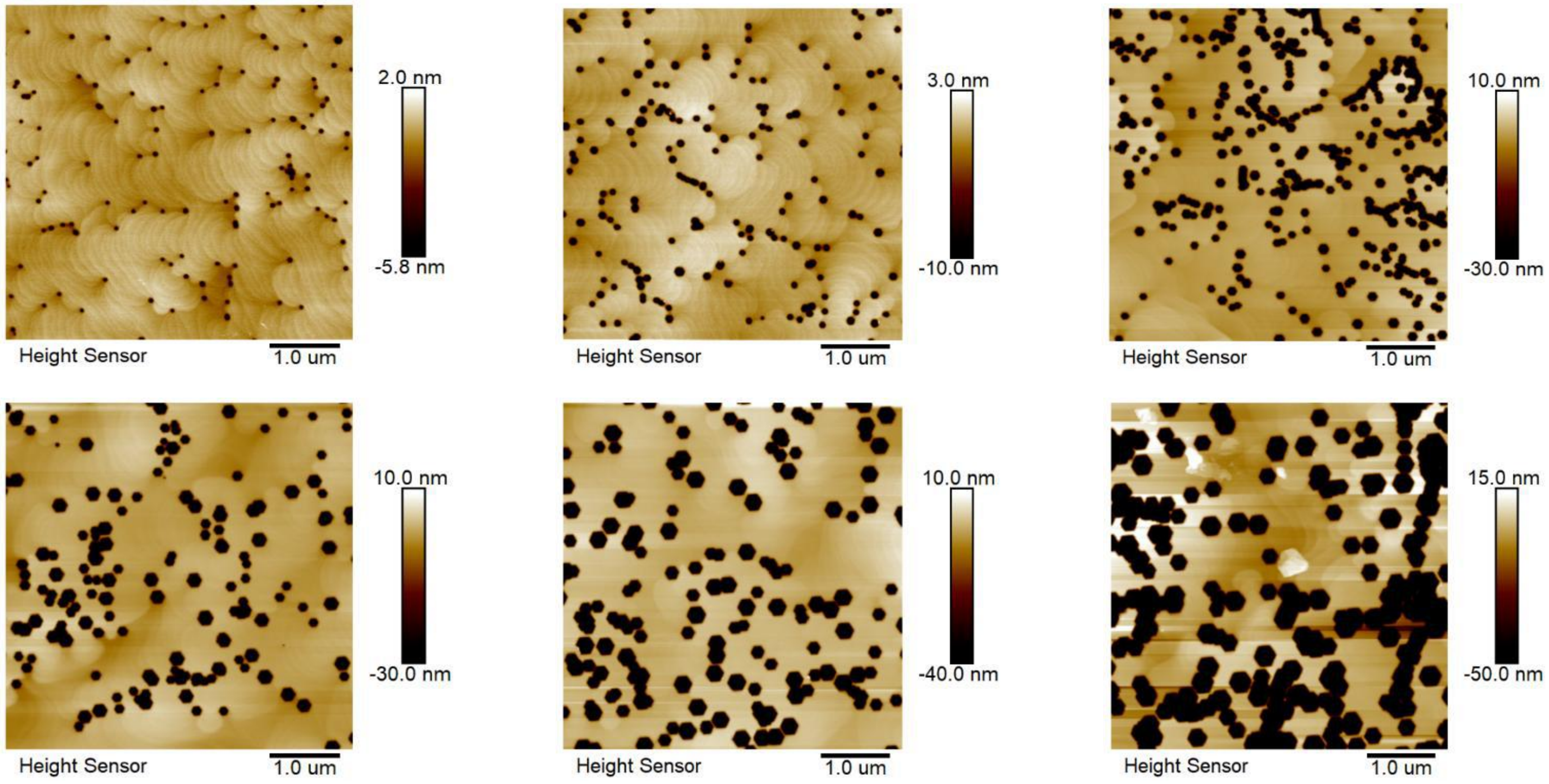
Increasing thickness of the active layer increases also V-pits



V- pits are very interesting defects in nitride semiconductors which are believed to enhance the luminescence efficiency of InGaN QWs

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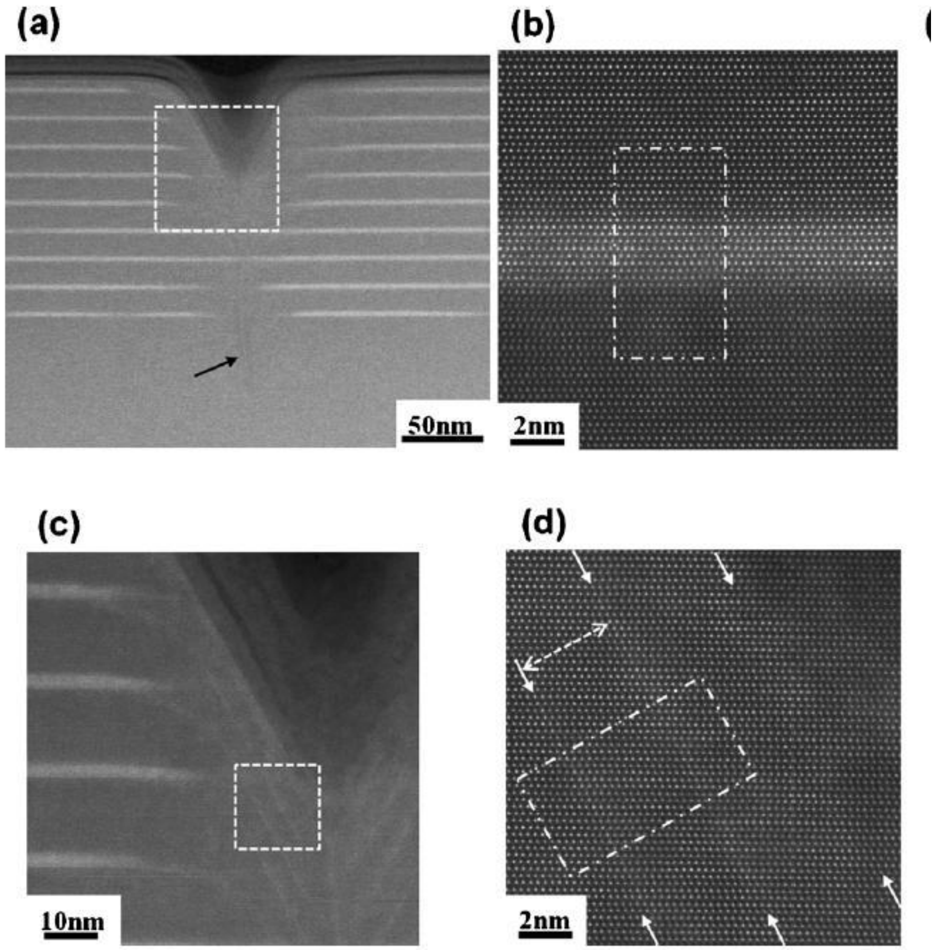
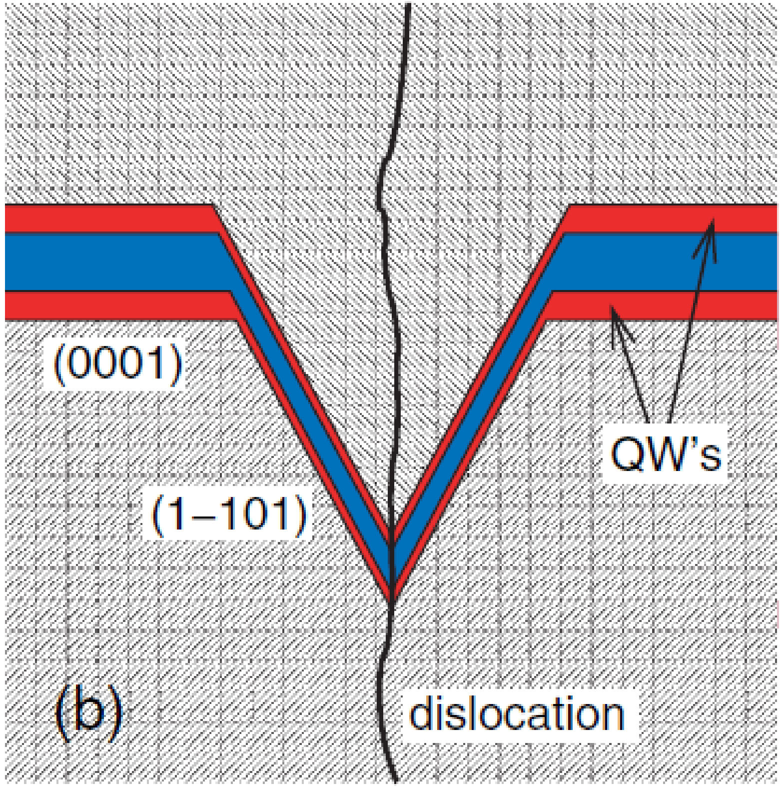
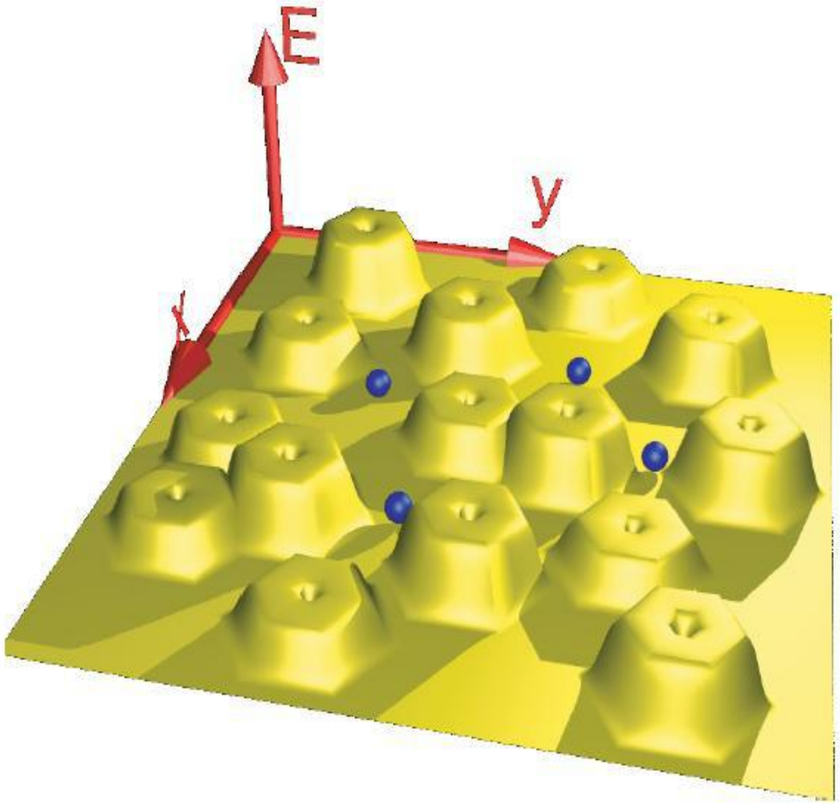
TEM and HRTEM images of V-pits

V-pits are formed arround dislocations. InGaN QWs on V-pit sides are thinner than on flat surface. The electron energy in thinner QWs is higher. That is why electrons do not penetrate into V-pit sidewalls and are effectively separated from dislocations, where non-radiative recombination takes place – see following slide.



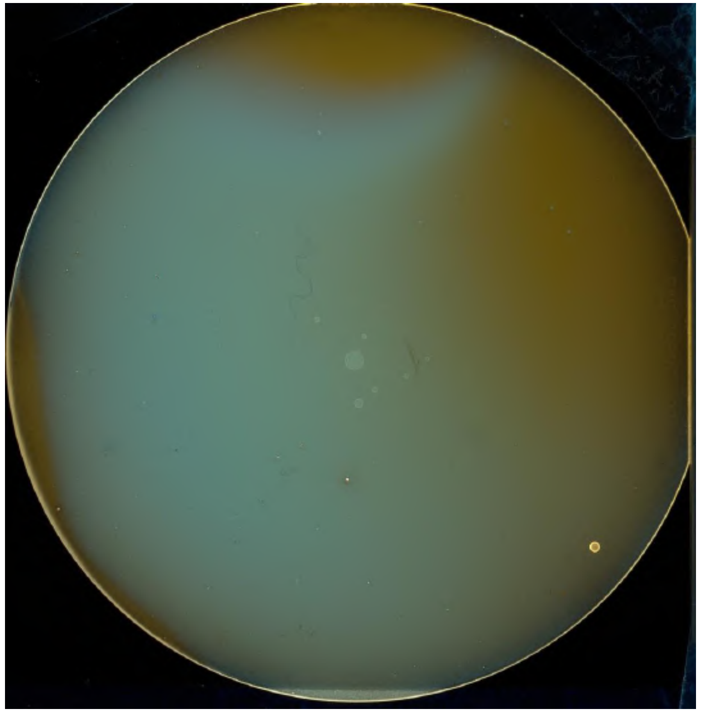
V-pits

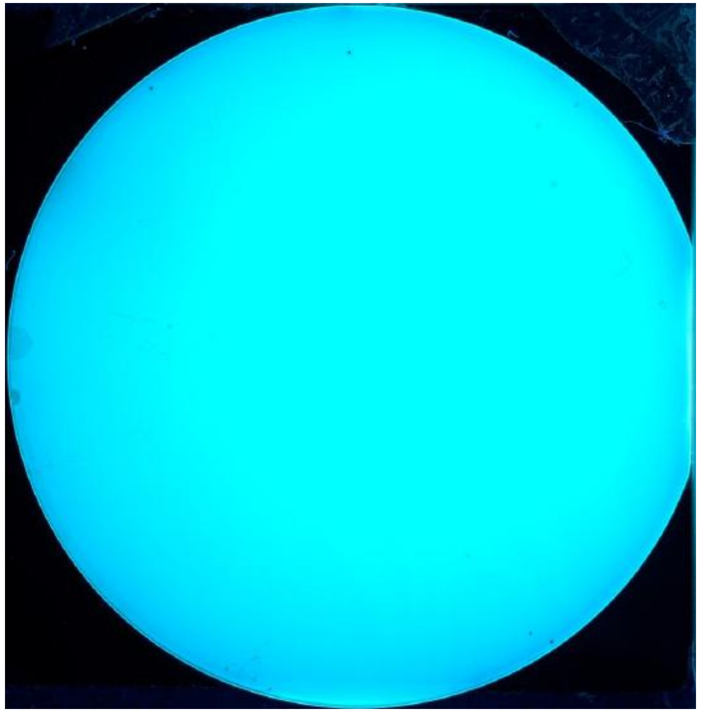




Scintillators

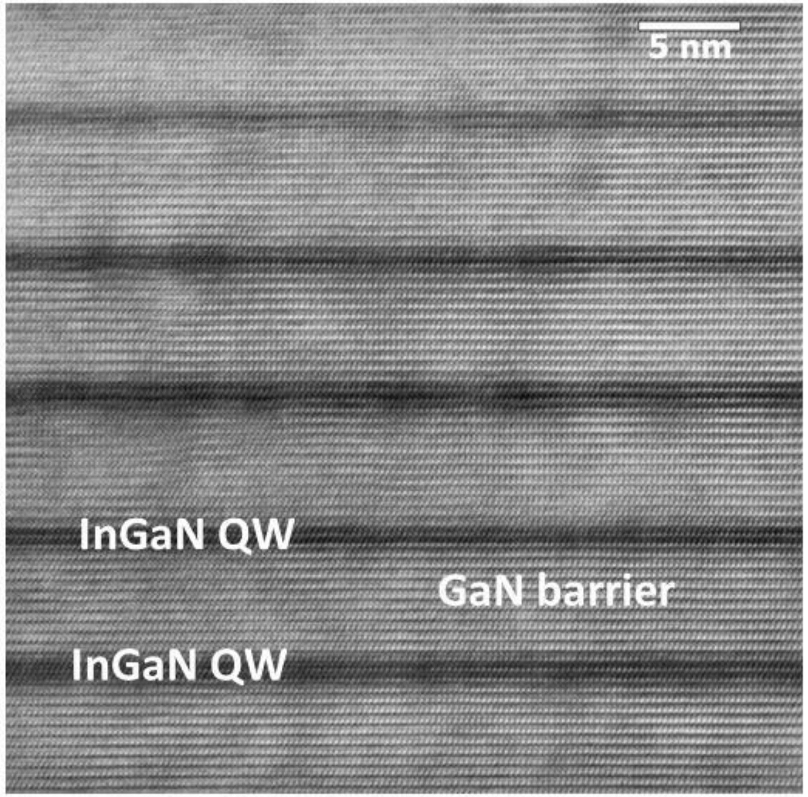
Comparisson of luminescence of scintilator structures before and after optimization

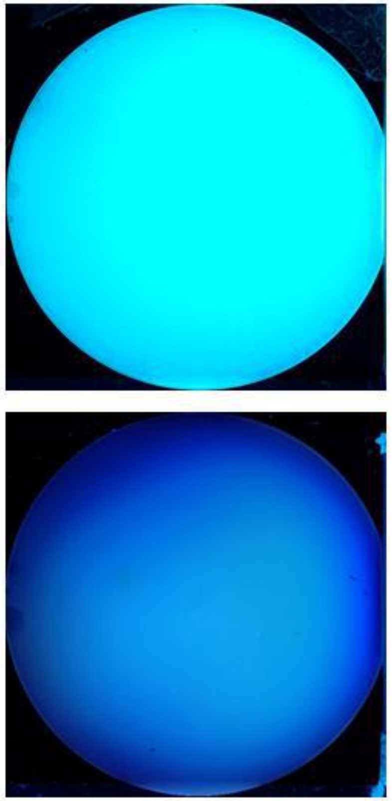




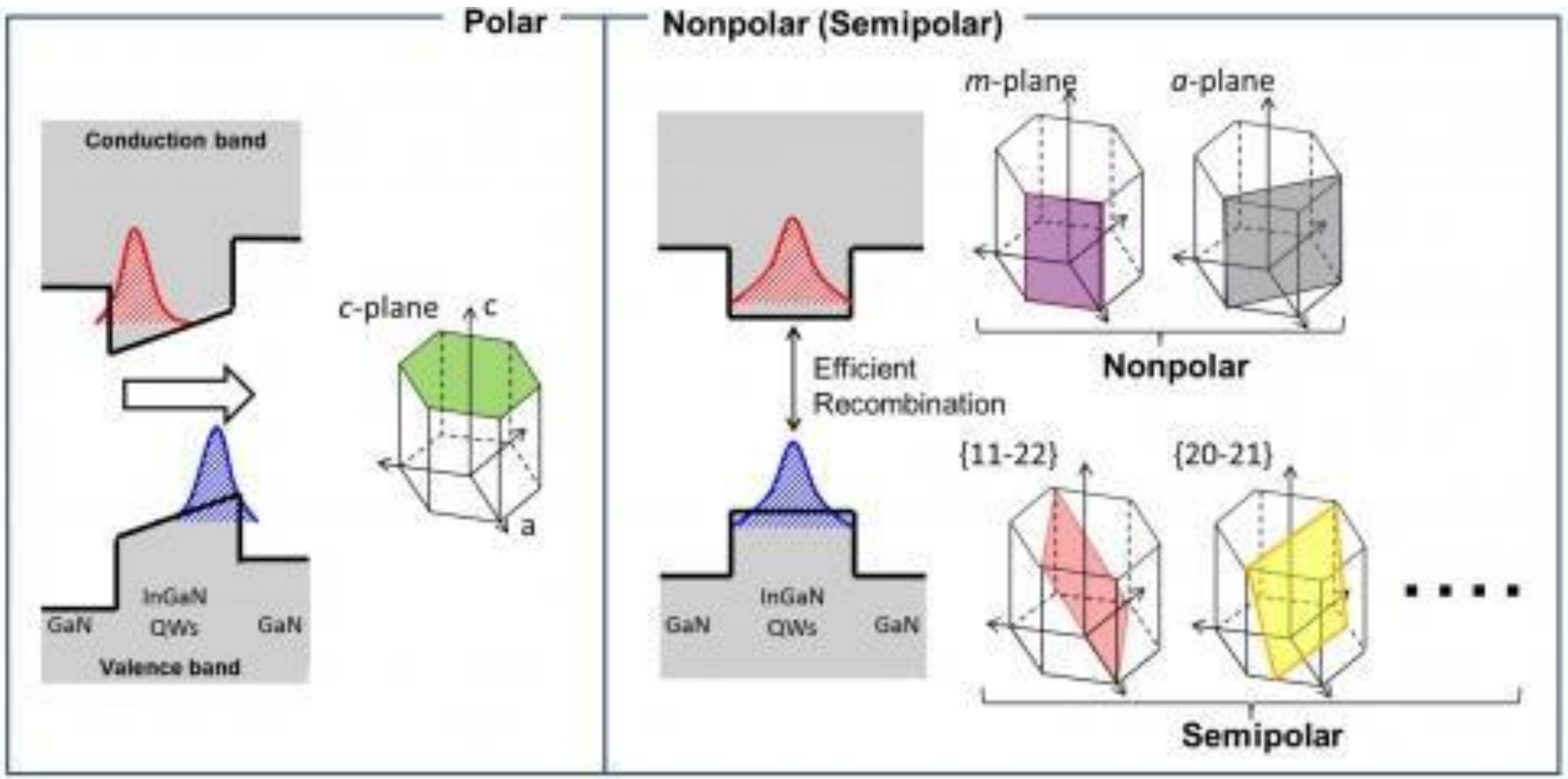
Scintillators

HR TEM image of InGaN/GaN MQW structure





Electric field between polar and nonpolar heterojunctions



In InGaN QWs the polarization field separates spatialy electrons and hole, theirwave function overlap is lower and luminescence efficency is suppressed.

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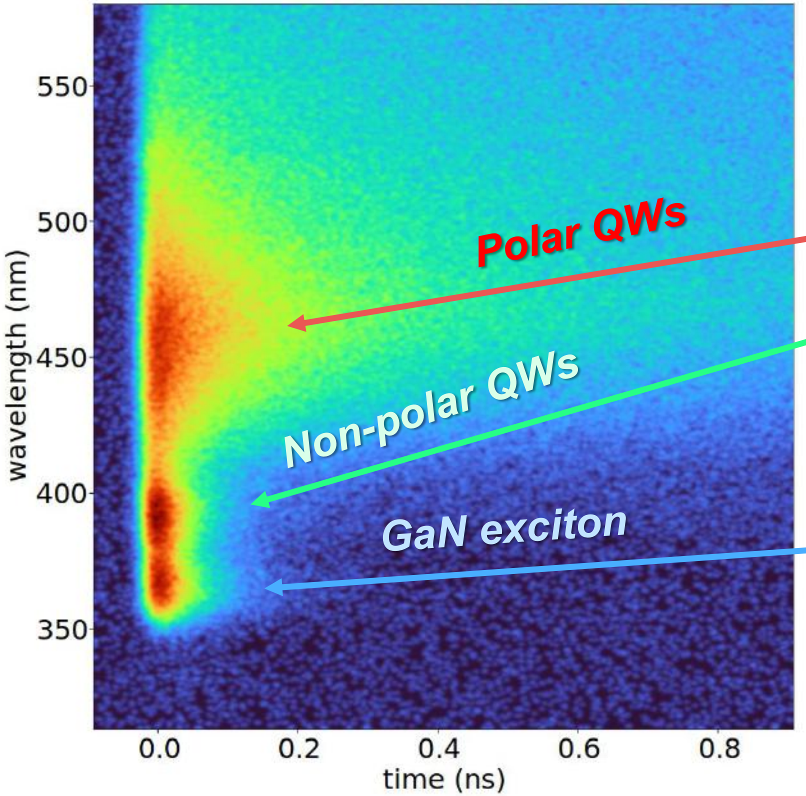
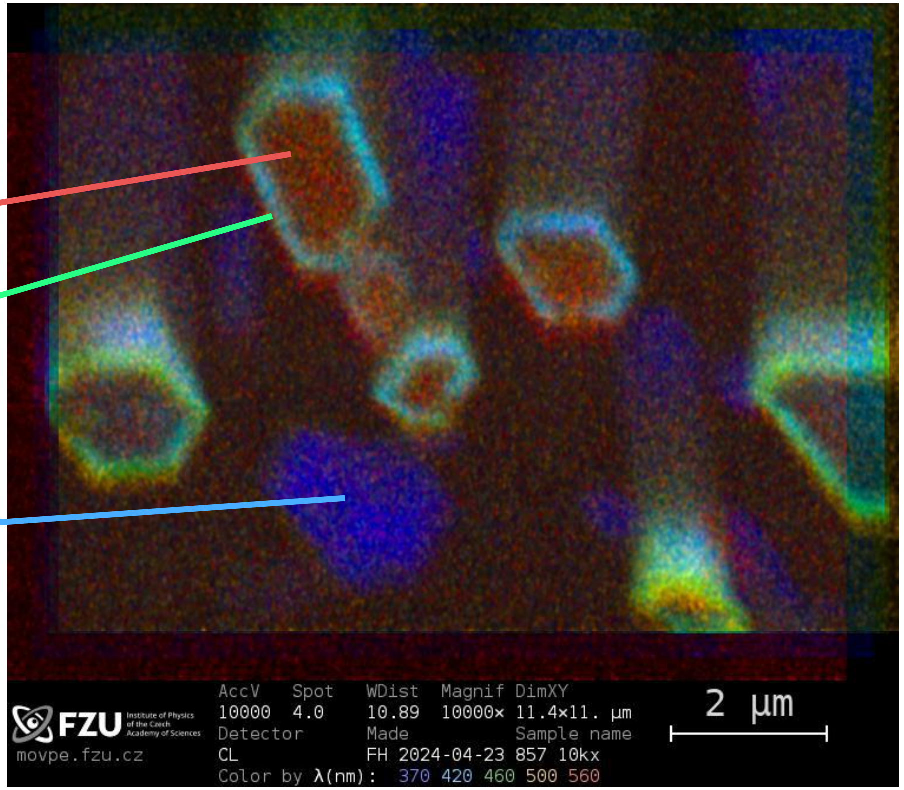
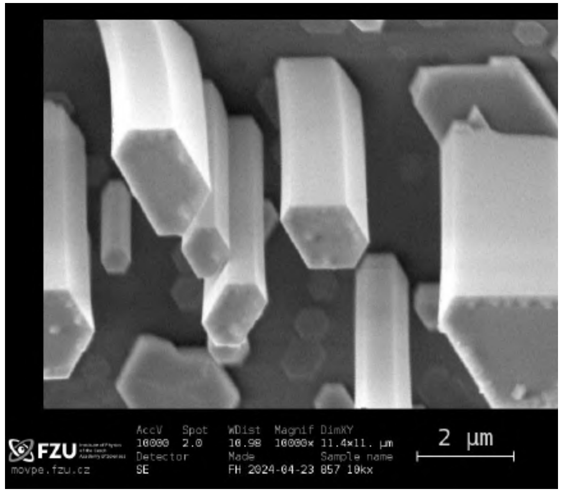
QWs on nanorods



Decay time for different parts of the InGaN/GaN nano-rod structure. PL of non-polar QWs has even faster decay than PL of GaN exciton



SEM cathodoluminescence of the InGaN/GaN nano-rods.



SEM SE mode of InGaN/GaN nano-rods. The same position.

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10×MQW of InGaN/GaN shell around the GaN rods

Nanoheterostructures:

Nanorods

For solar H_2 generation

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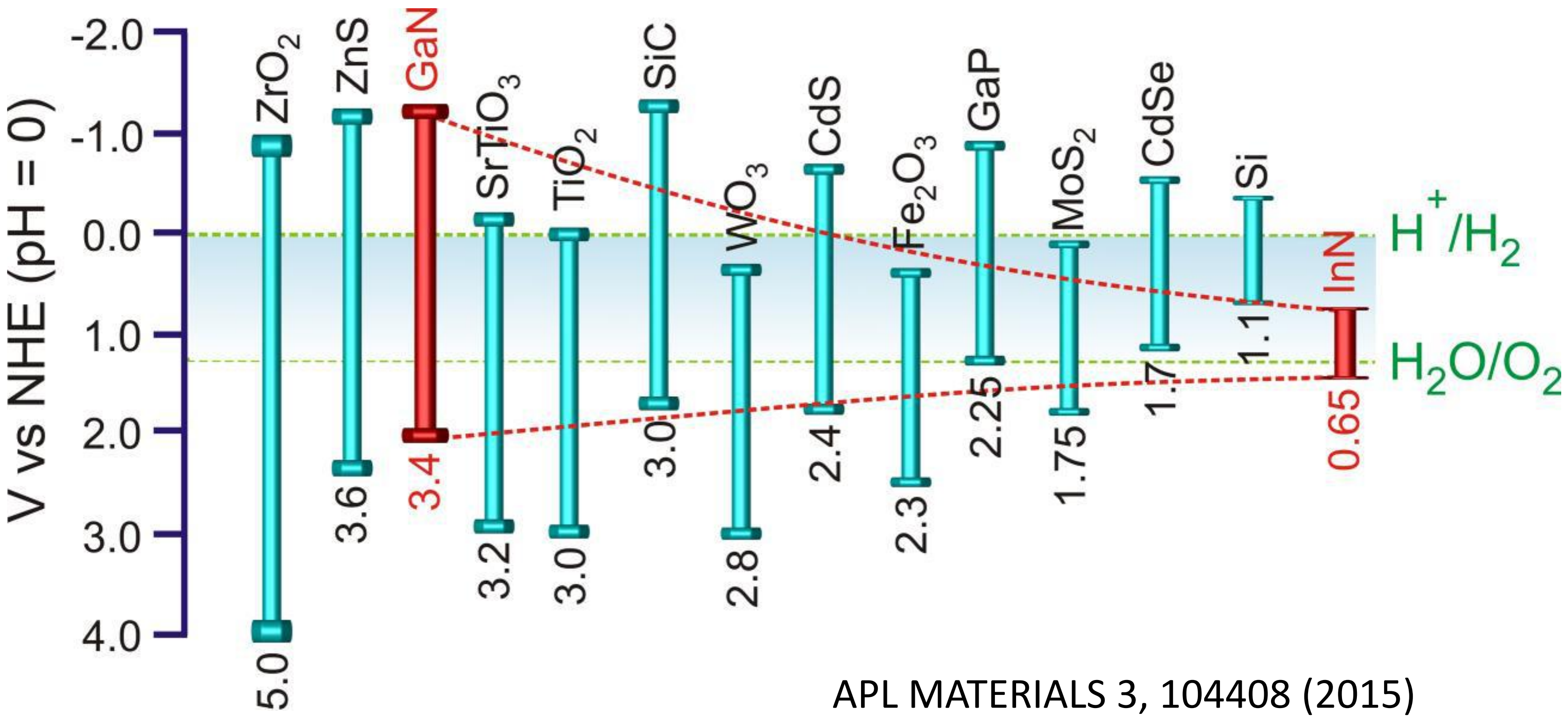
Valence and conduction band vs. redox H_2O potencials



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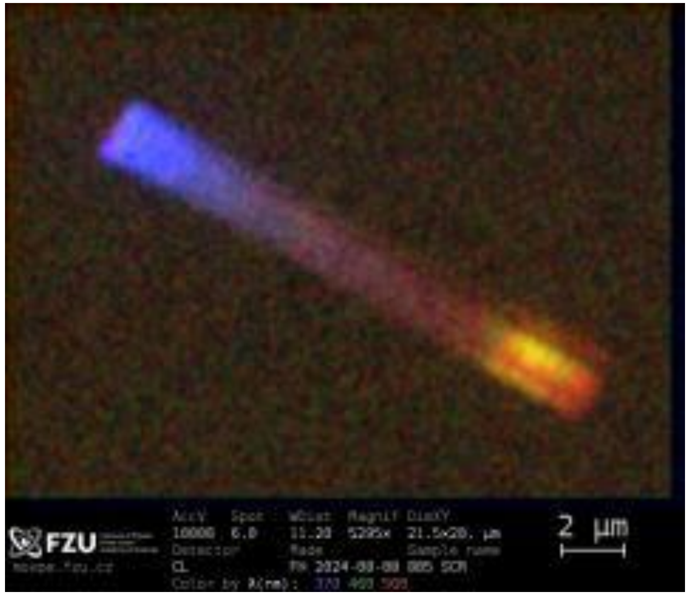
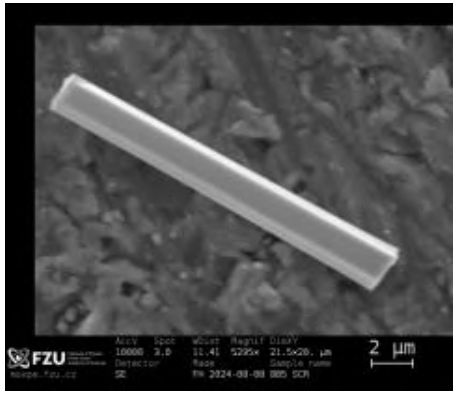
InGaN has optimal band alignement

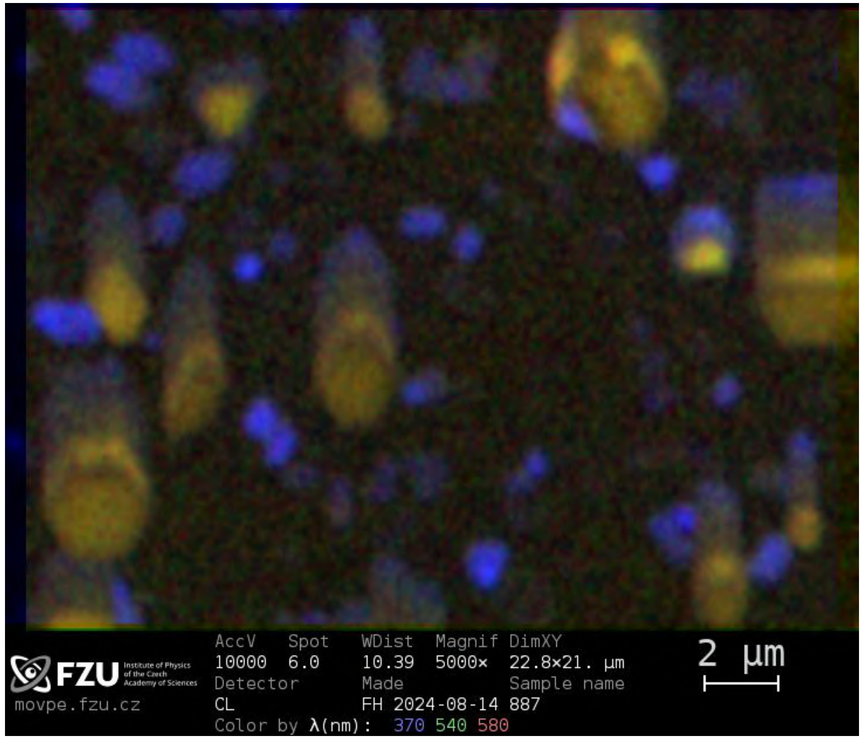
Core-shell InGaN/GaN micropillars for solar photocatalysis



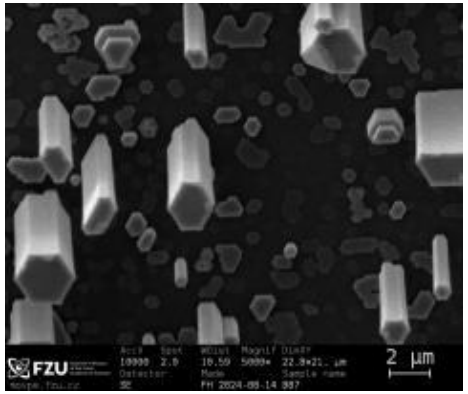
SEM cathodoluminescence of InGaN/GaN nano-rods shows different composition in polar direction, which can separate electron-hole pairs.



SEM SE mode of InGaN/GaN nano-rods.
The same rod.



SEM cathodoluminescence of InGaN/GaN nano-rods.
Blue are GaN seeds not grown to rods.



SEM SE mode of InGaN/GaN nano-rods.
The same position.

Core-shell structures - SEM

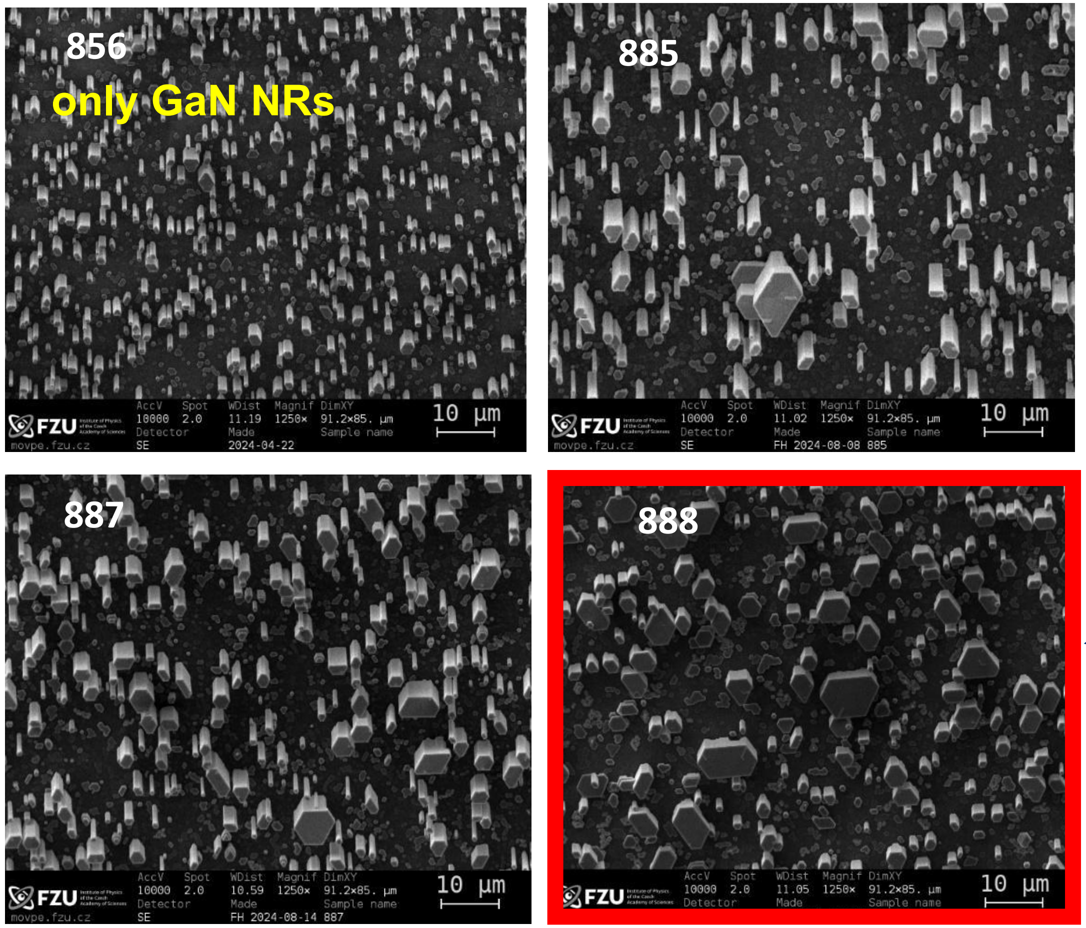
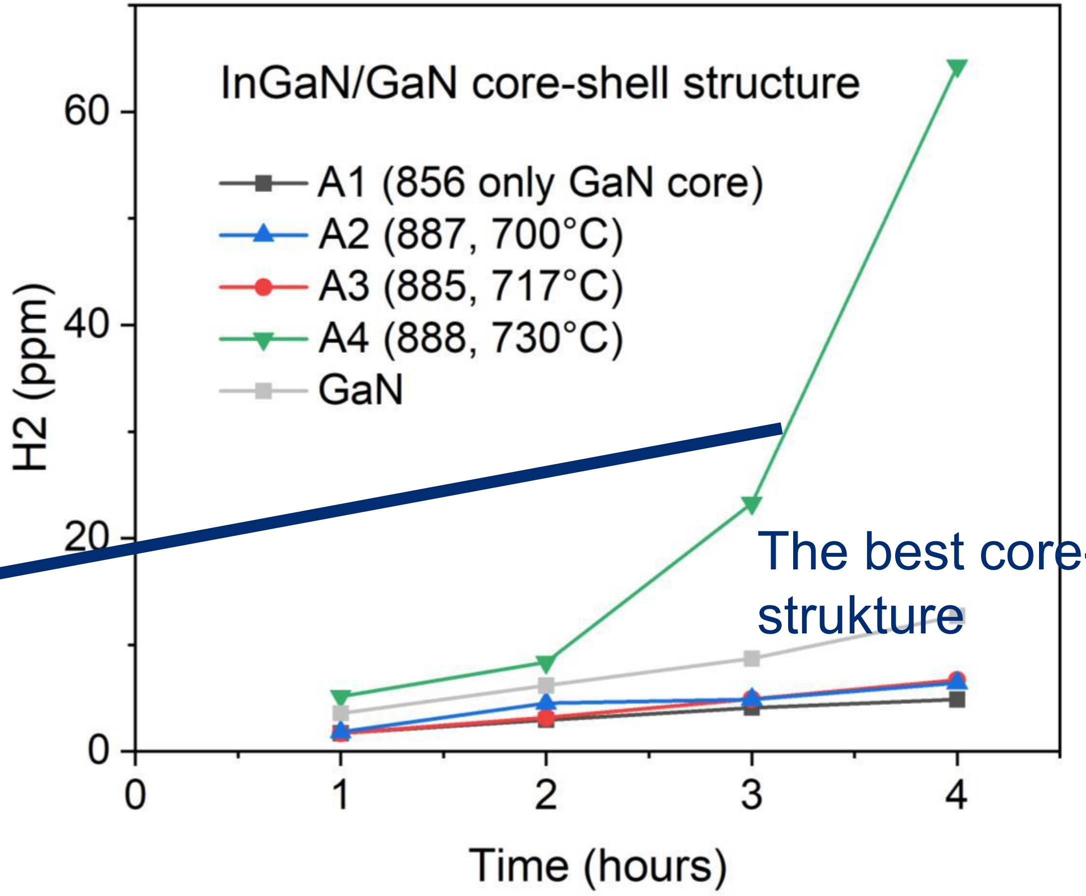


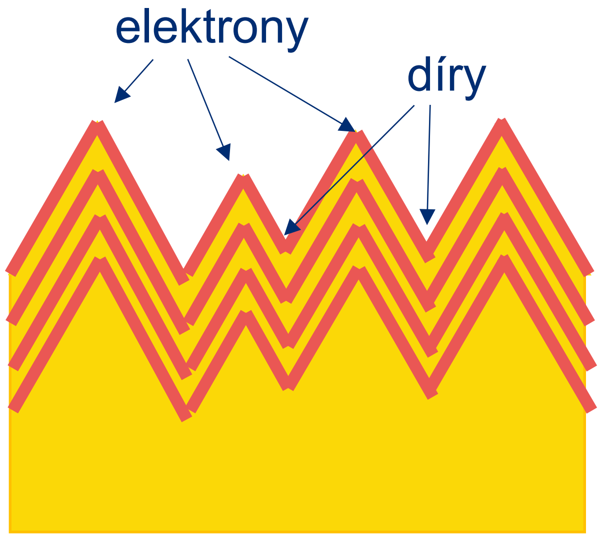
Figure 3: SEM images of nanorods in the sample centre

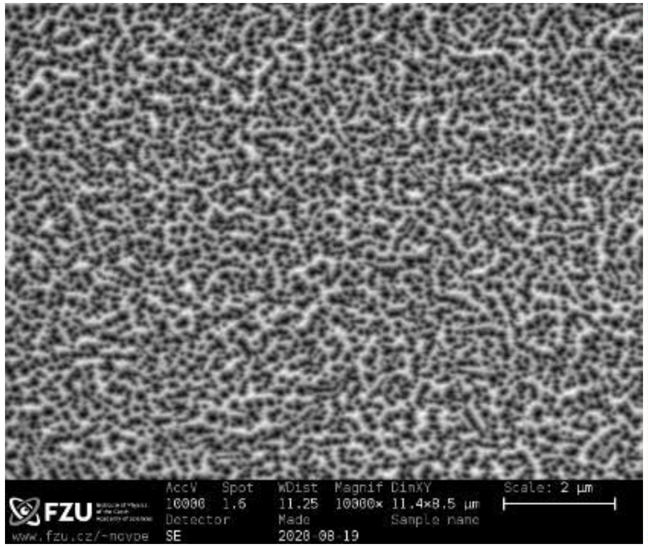


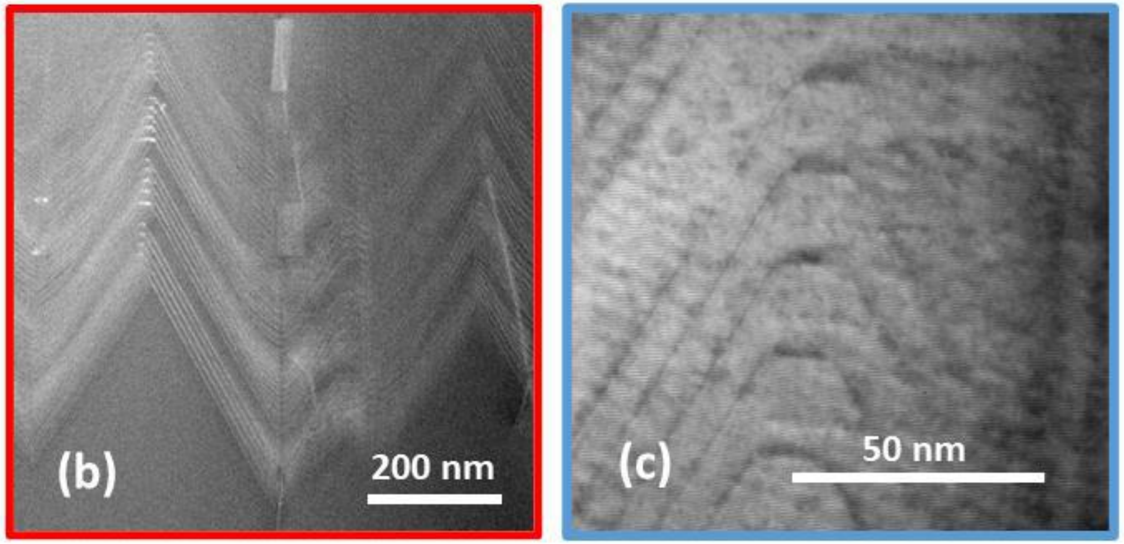
The best core-shell strukture

Semipolar InGaN/GaN MQW 3D struktures

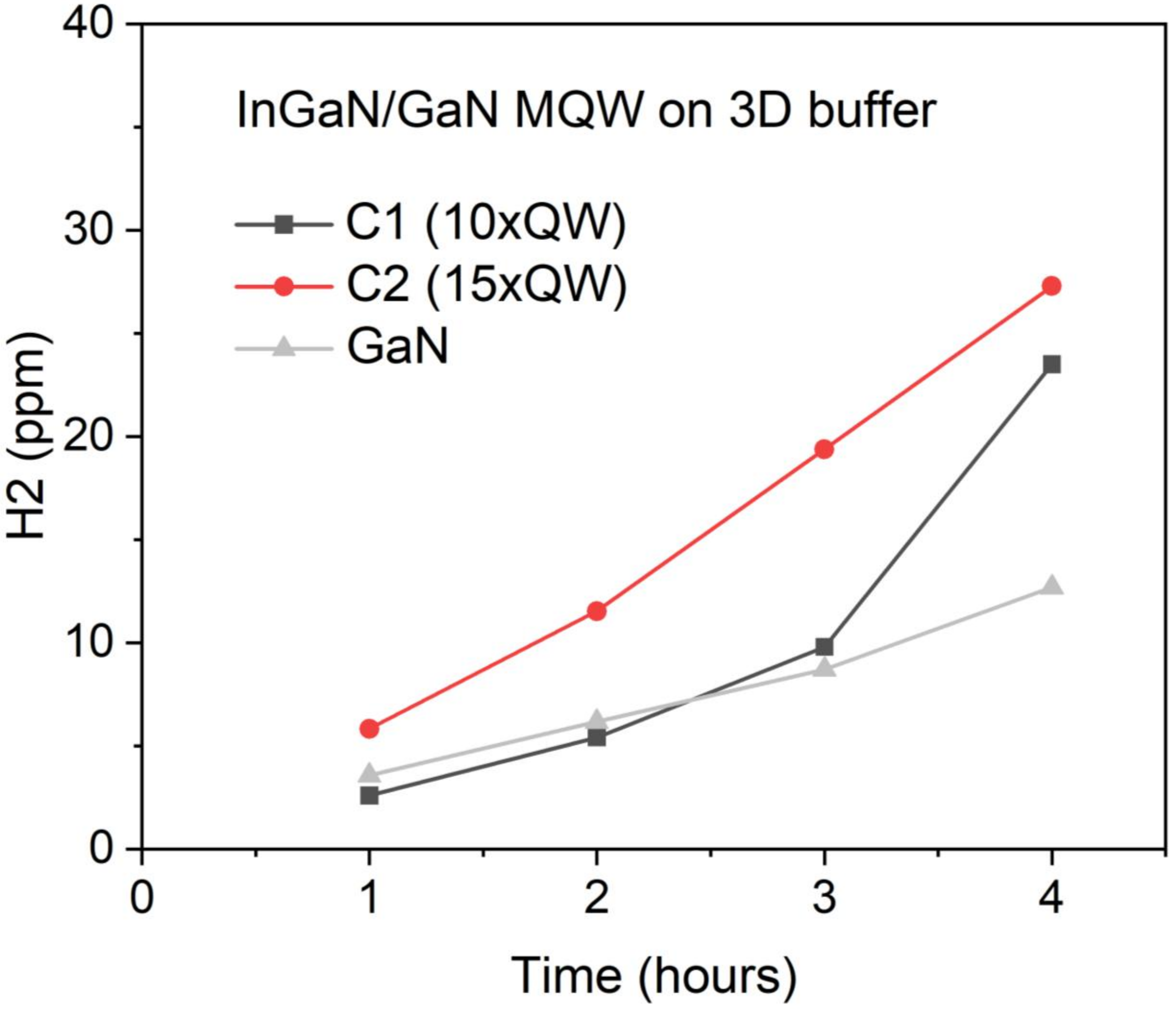
- Self assembled in nitrogen atmosphere

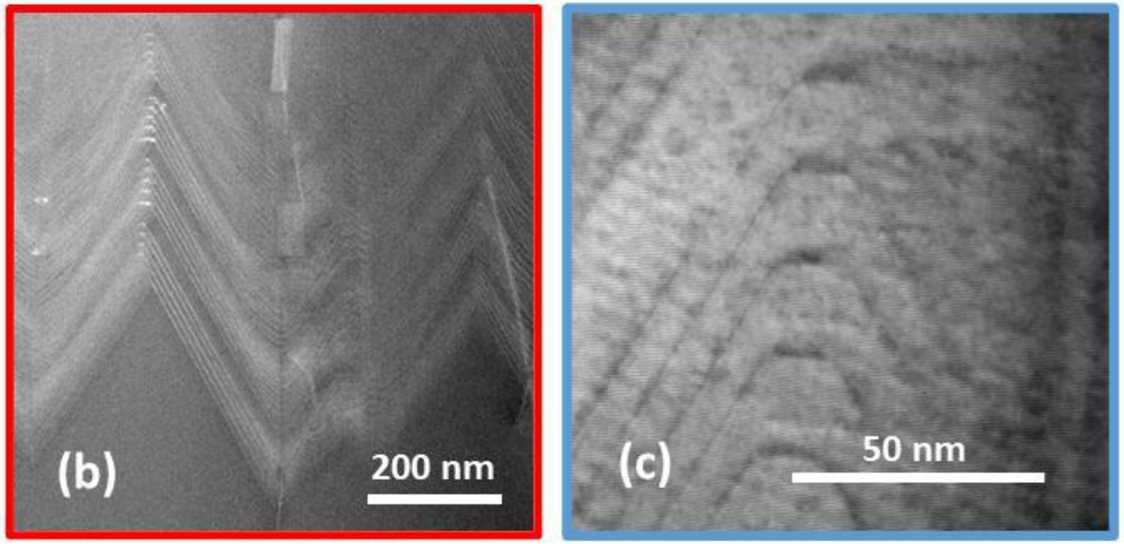




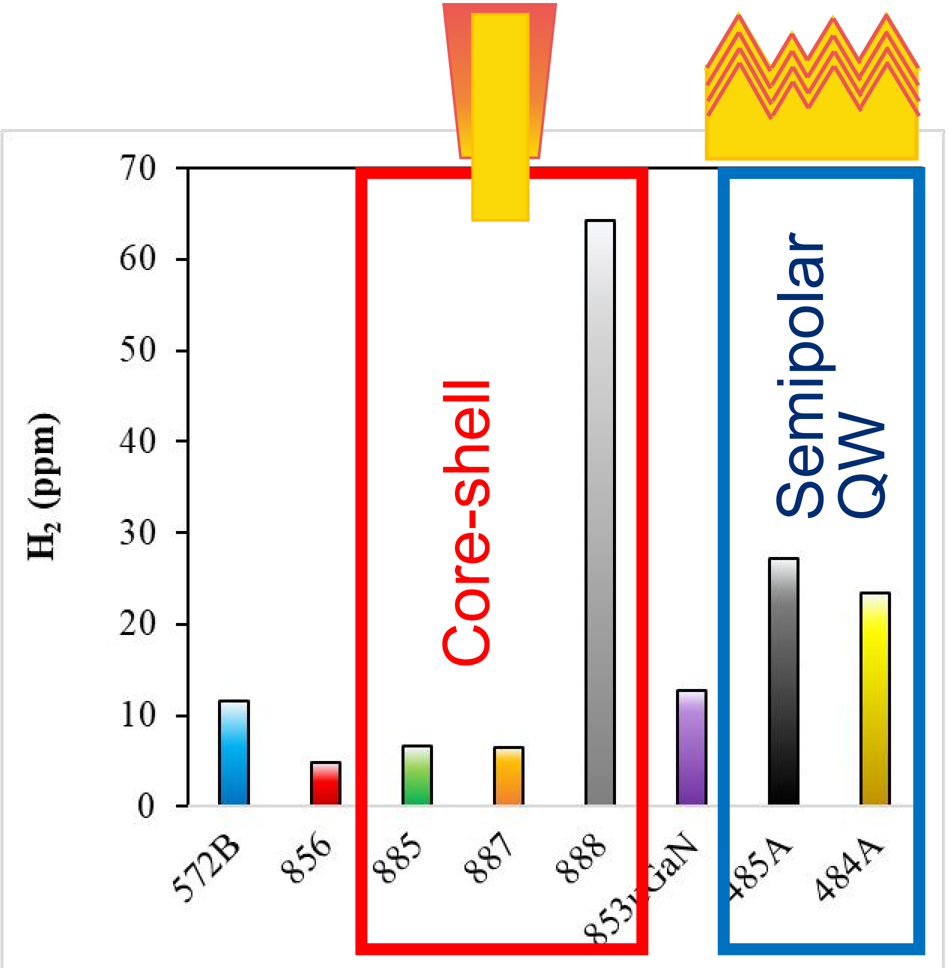


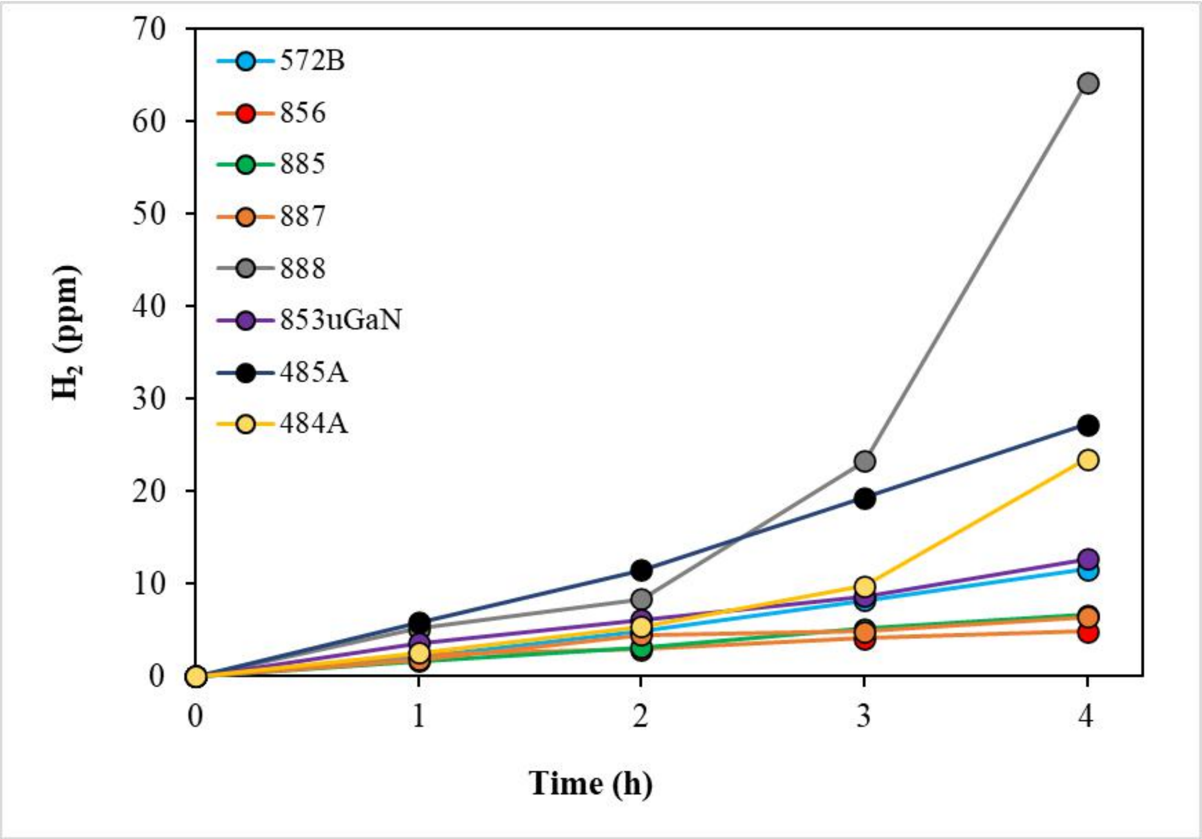
Semipolar InGaN/GaN MQW 3D struktures





First results





Měřeno s excitací 365 nm!

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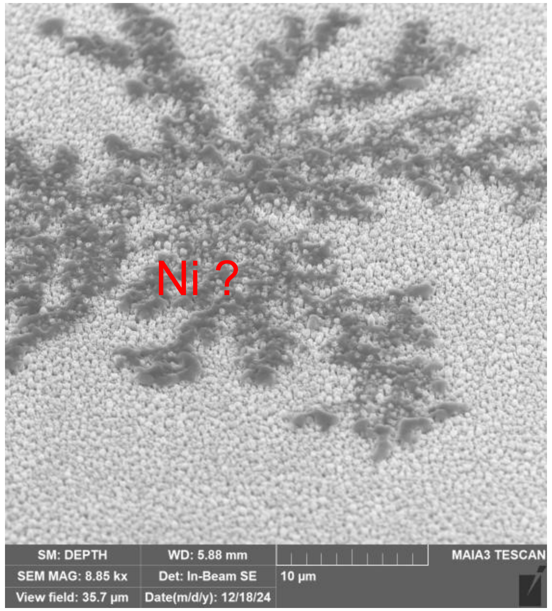
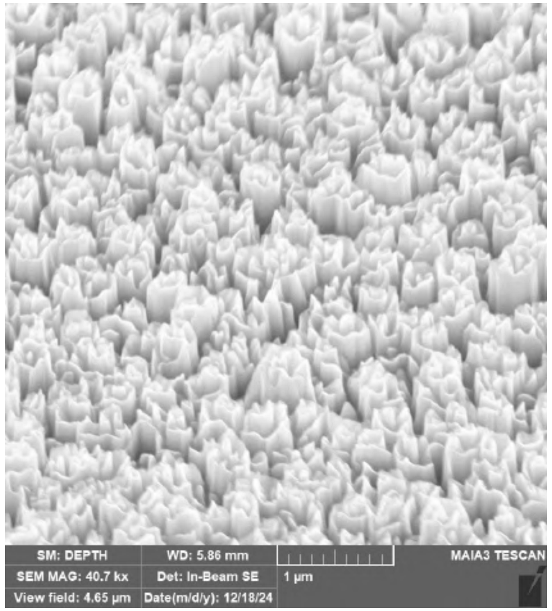
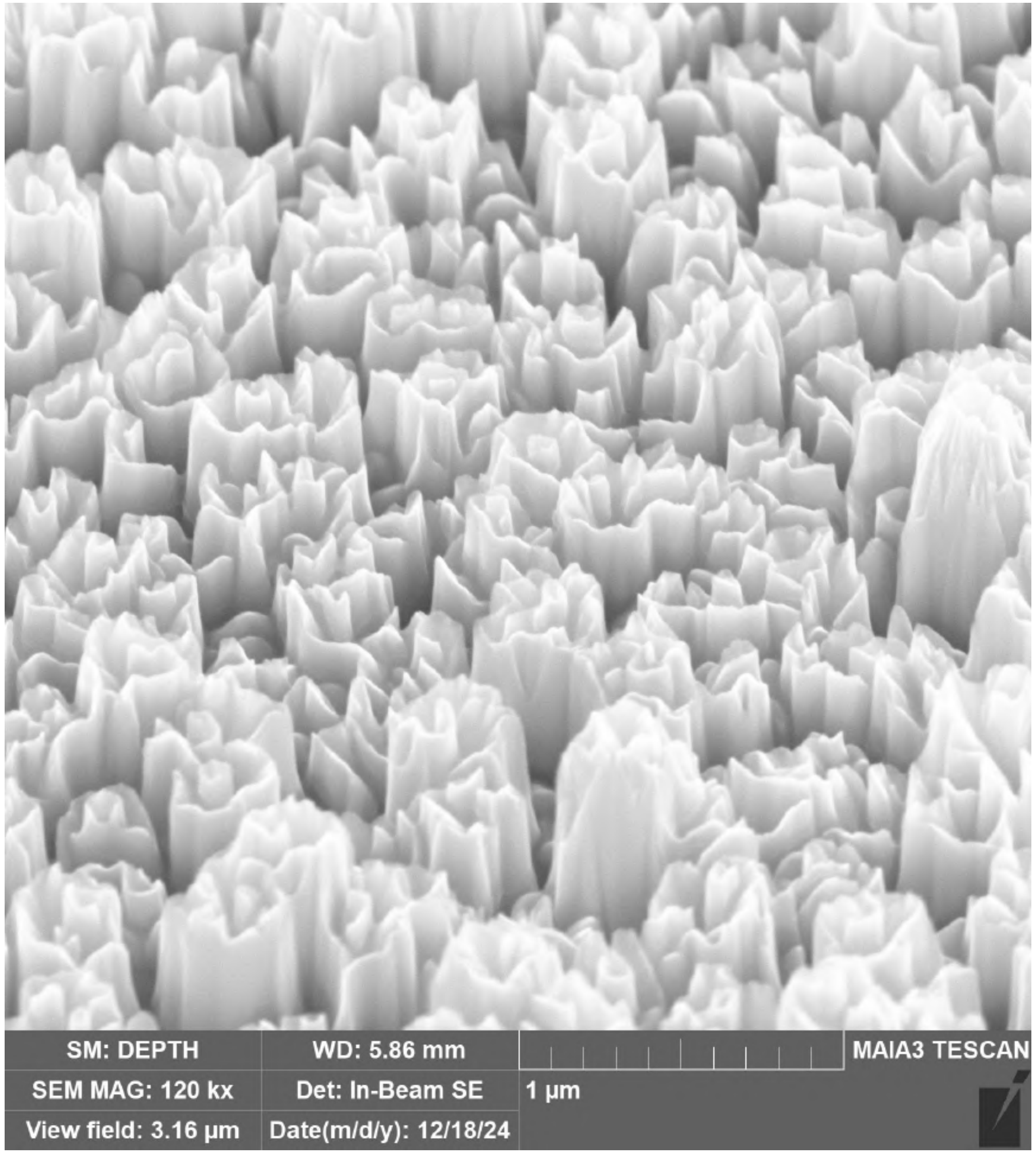
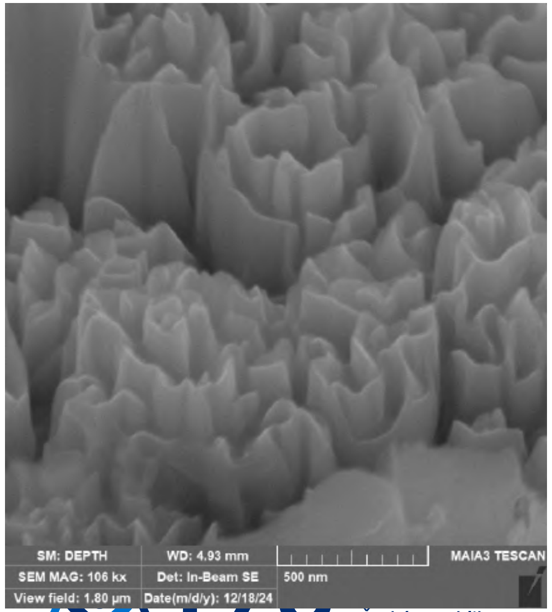
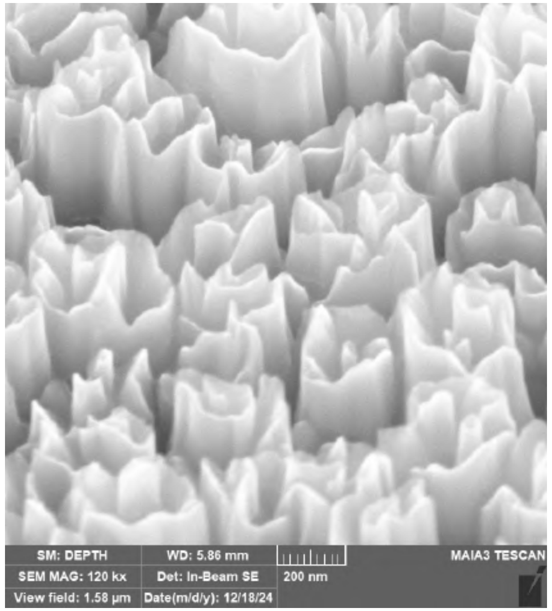
SEM (45°): RR241220_GaN_Ni mask_etching in SiCl4+Ar (30 min)











$SiCl_4$/Ar (19.6/12 sccm), 20 mTorr, RF power 75 W, ICP power 45 W, 30 min

Nanoheterostructures:
QDs
For fast scintillators

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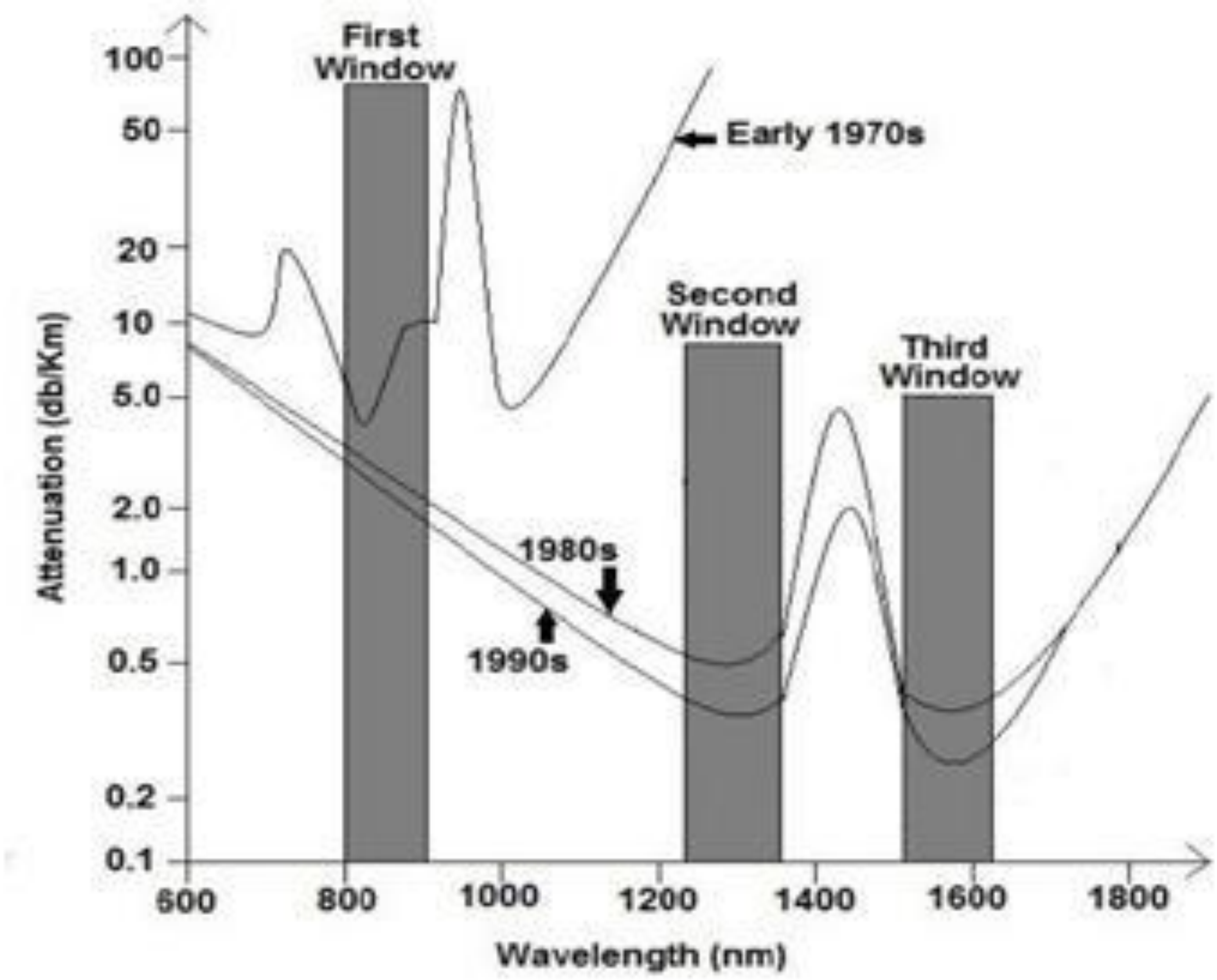
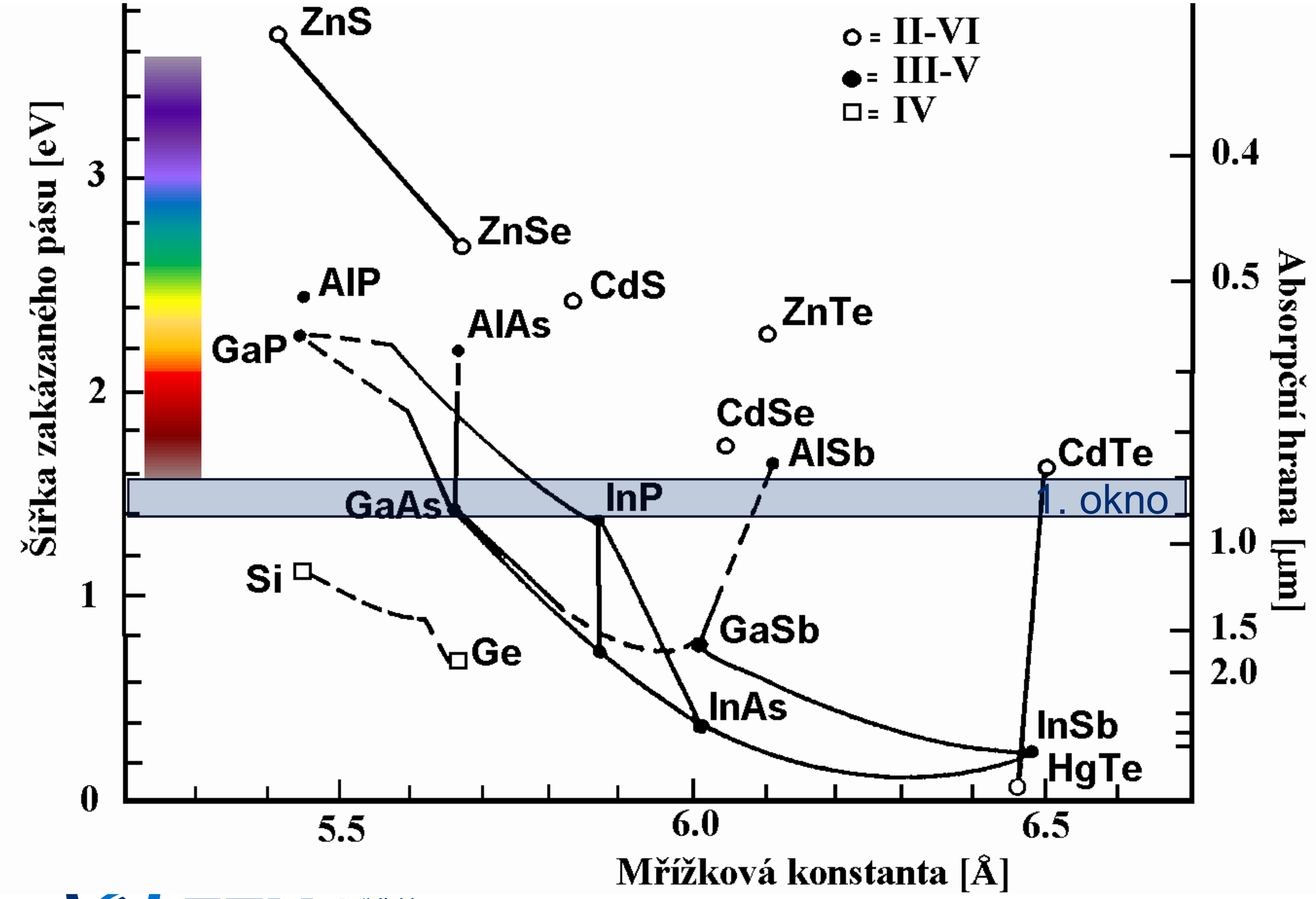
Data transfer through optical waveguides

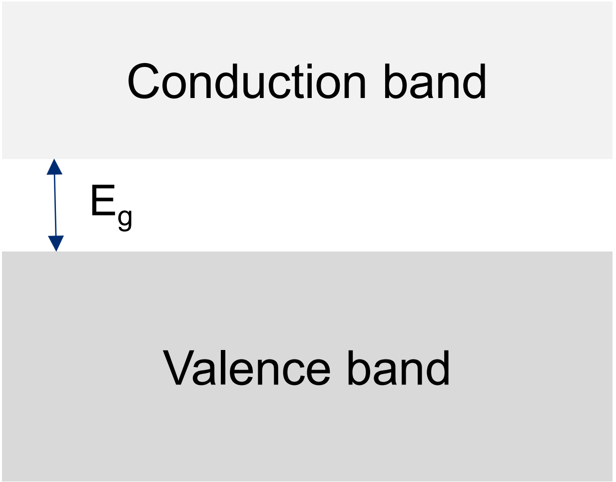
Attenuation in optical waveguides

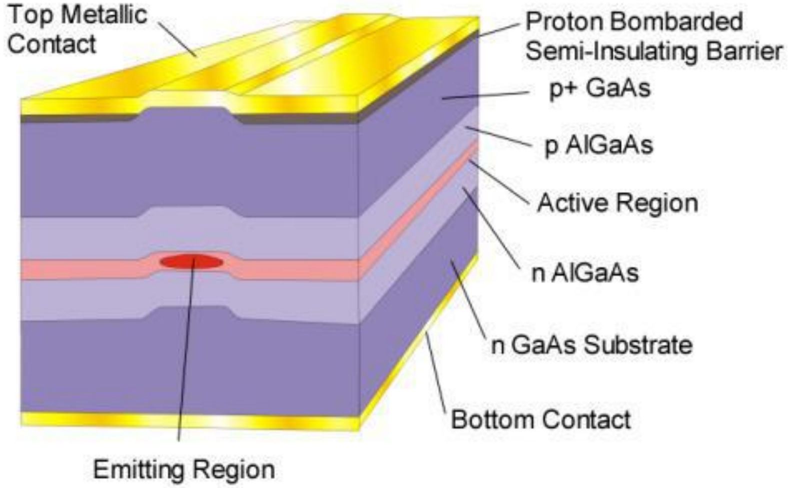
Three windows suitable for data transfer



Different semiconductor structures suitable for 4 windows







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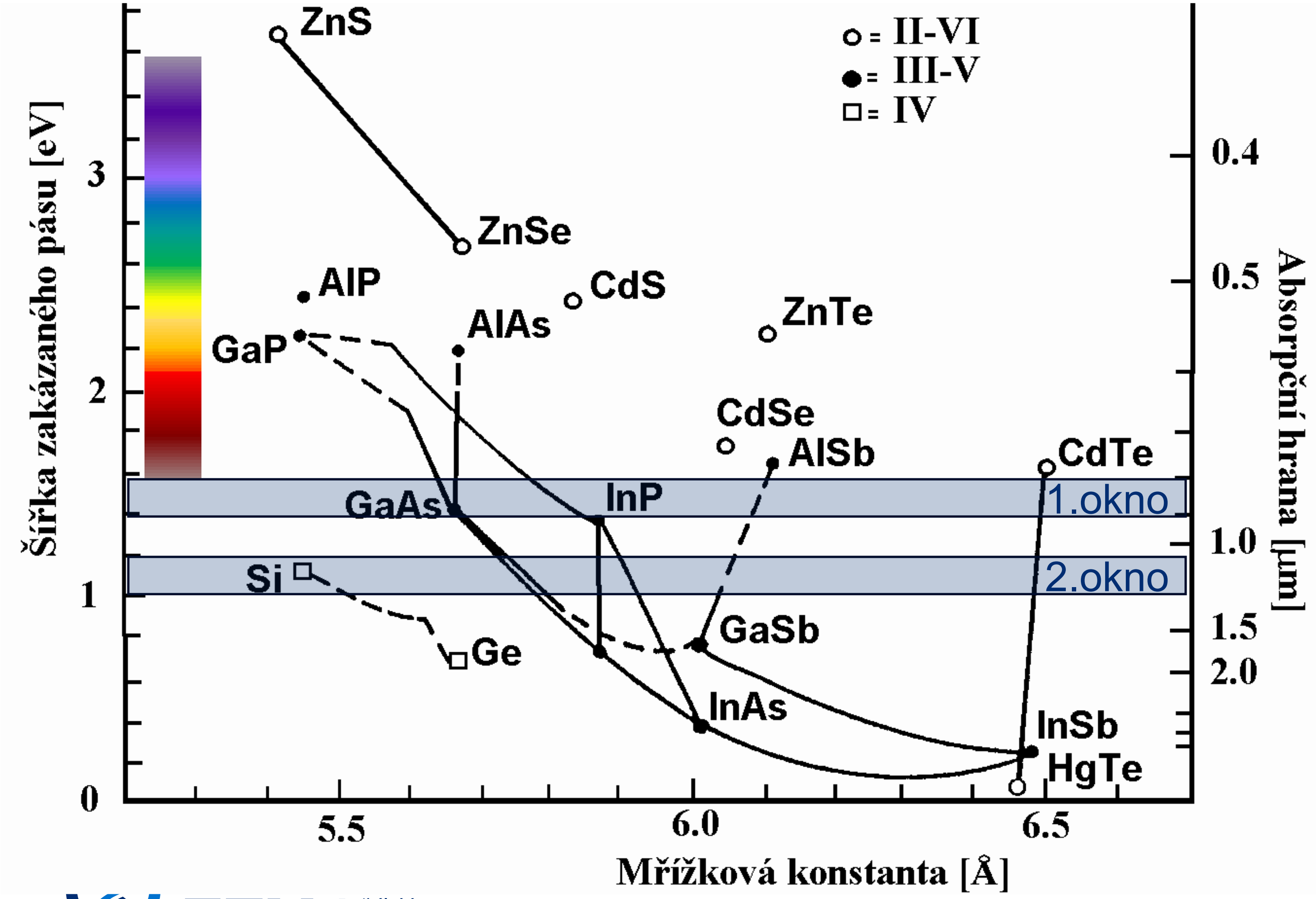
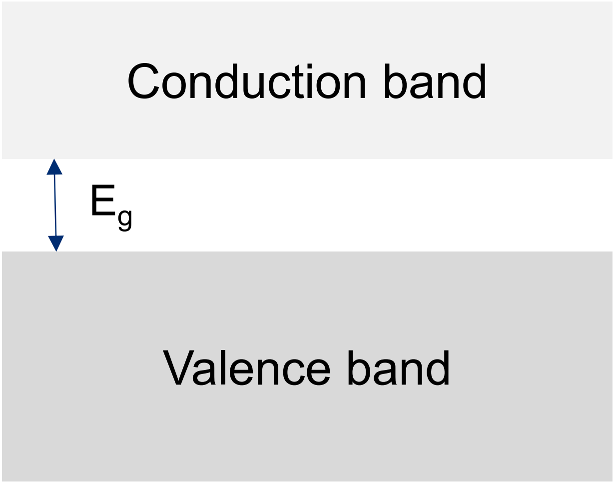
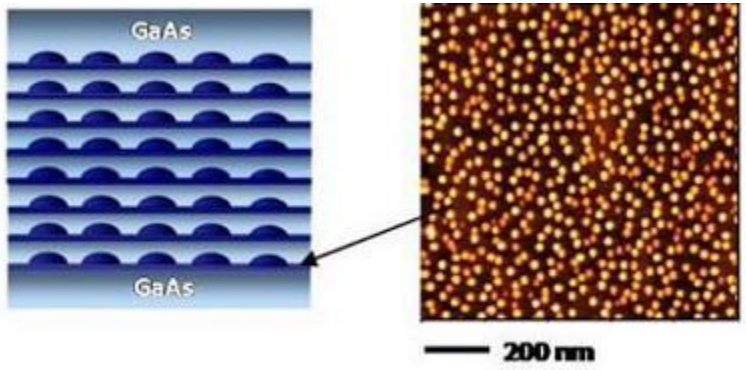
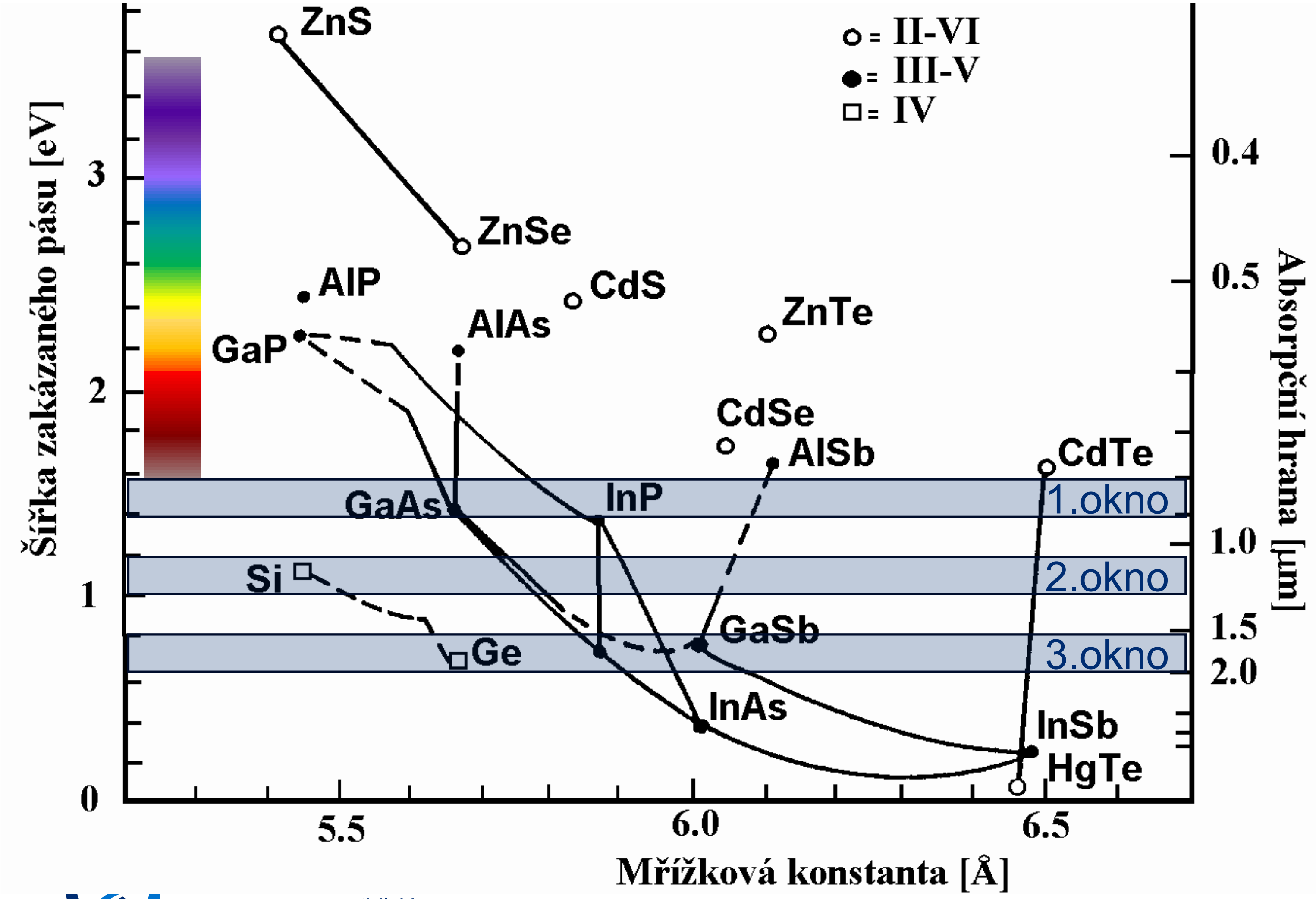
Different semiconductor structures suitable for 4 windows

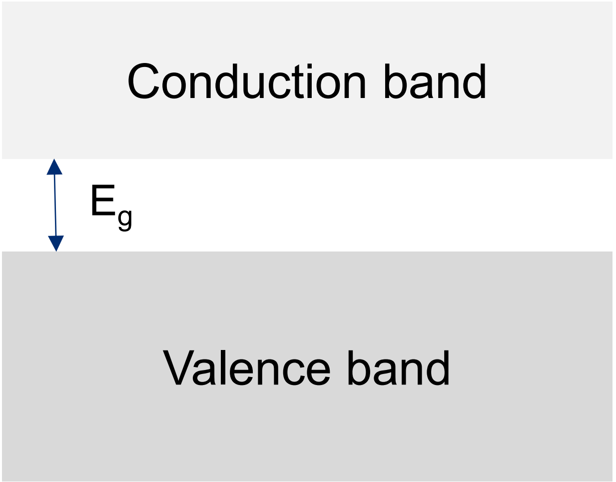


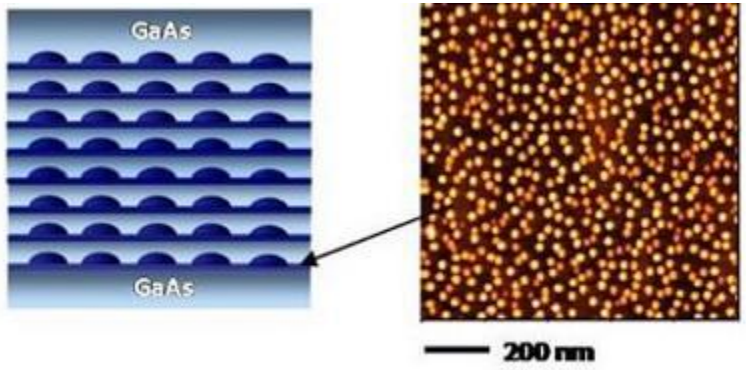




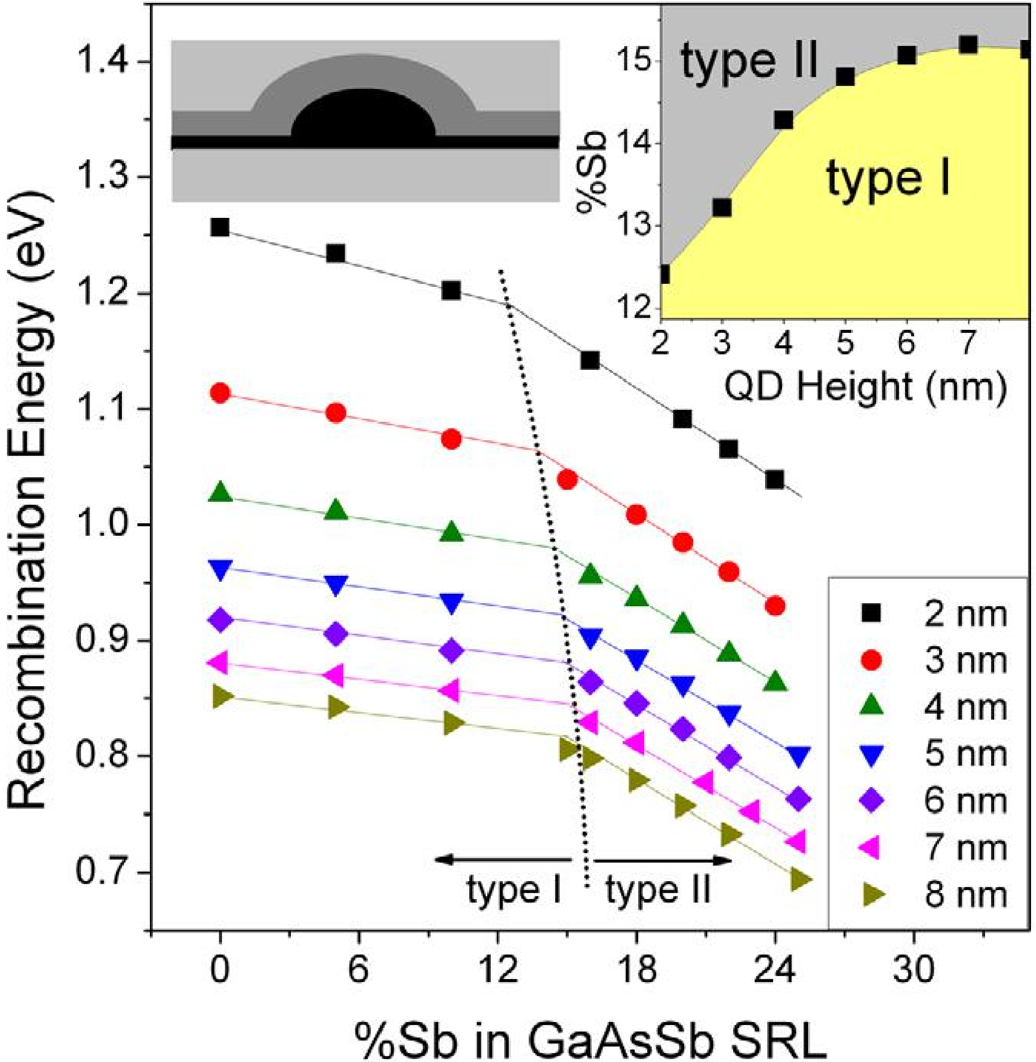
Different semiconductor structures suitable for 4 windows

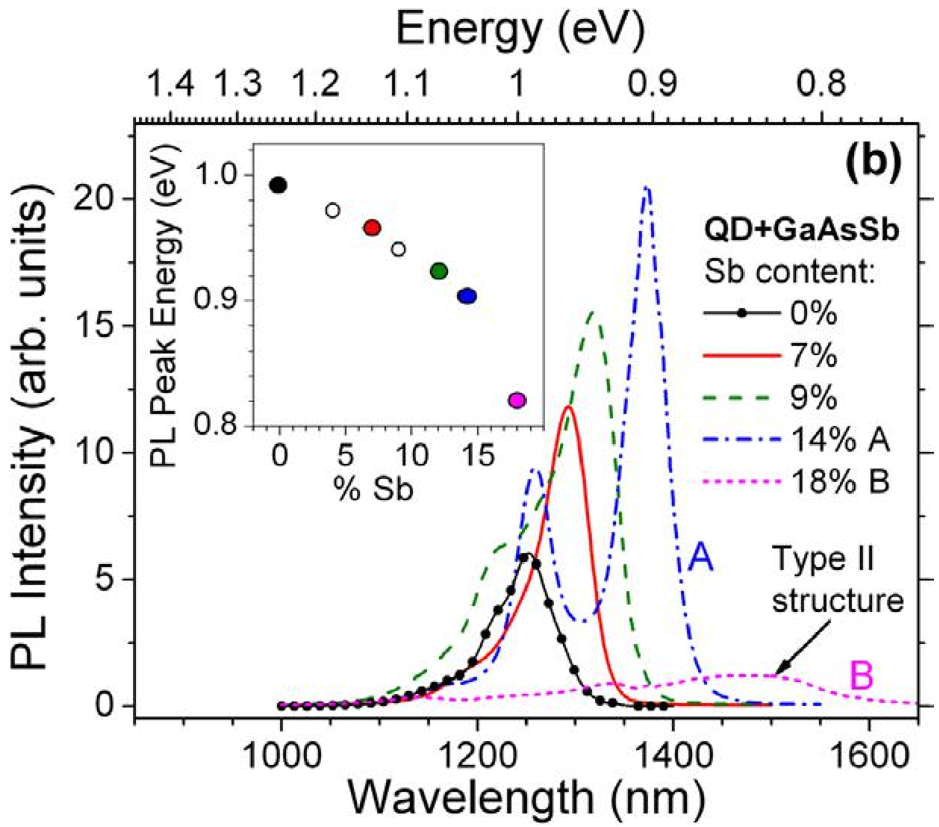


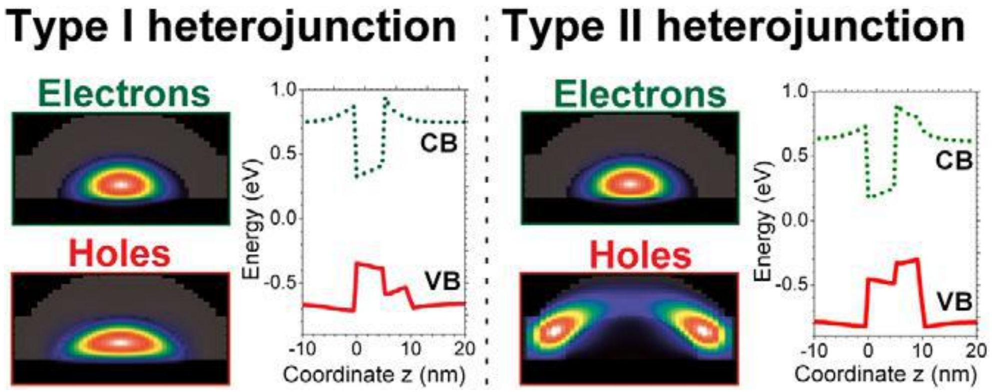




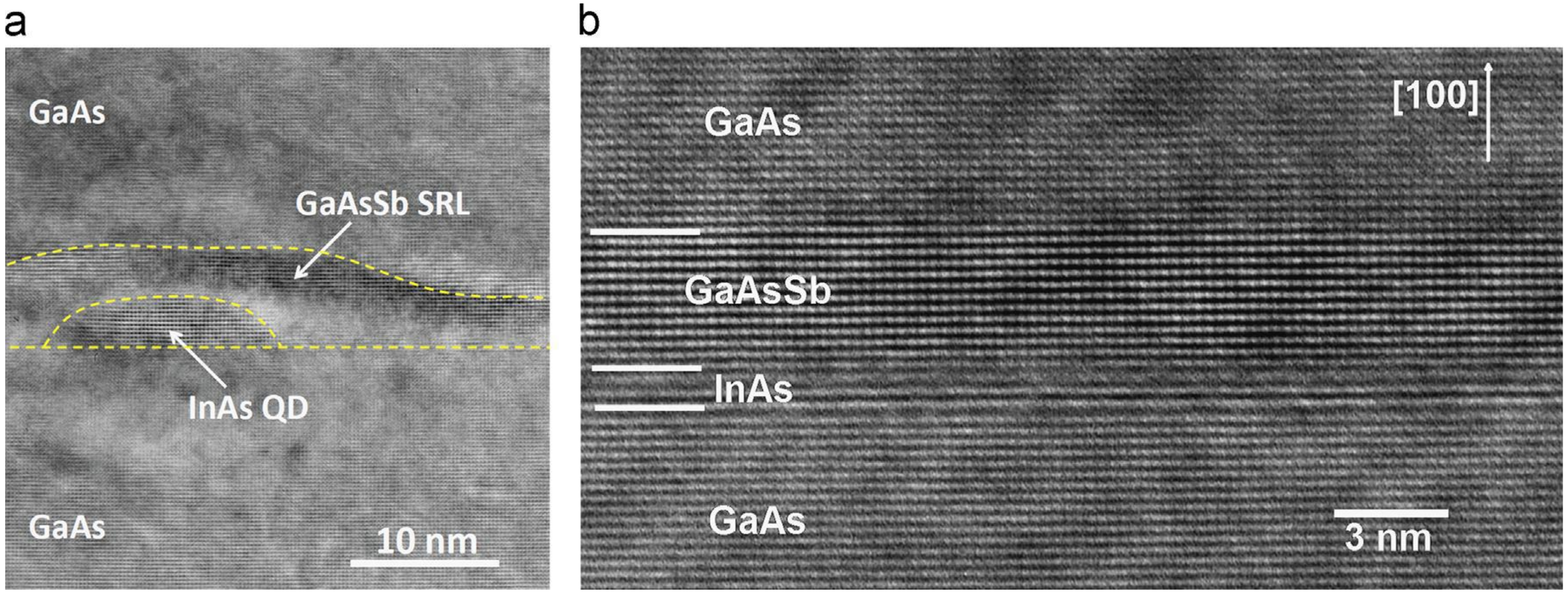
GaAsSb/InAs/GaAs QDs

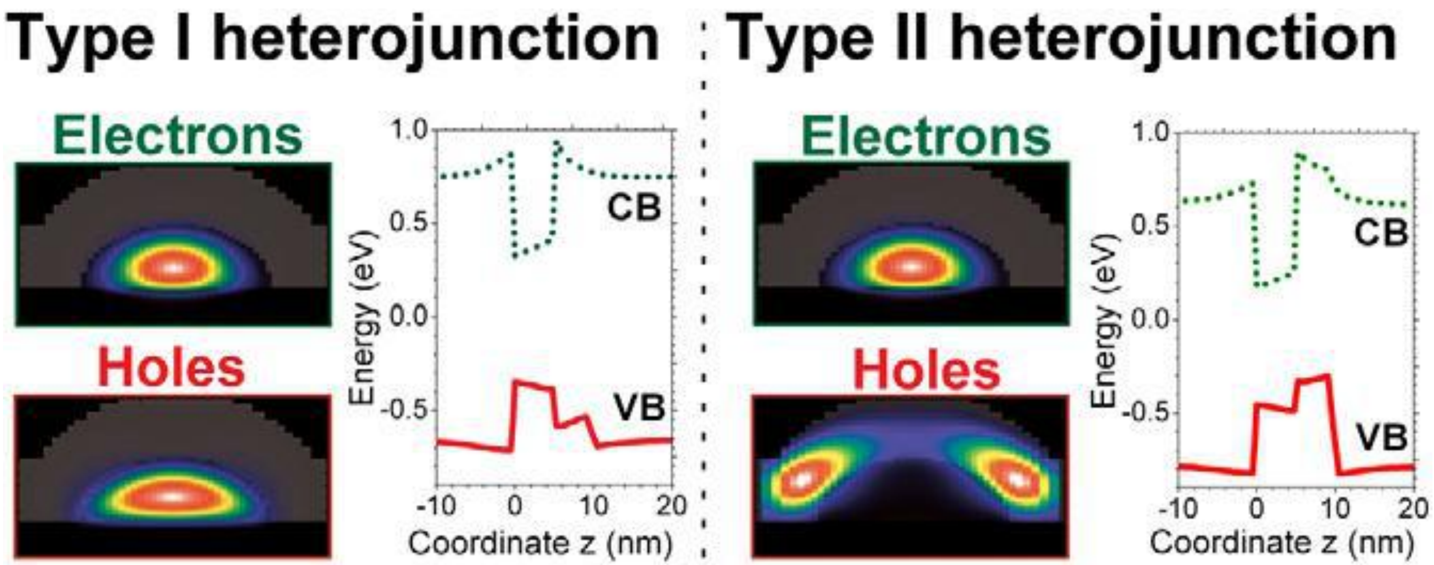


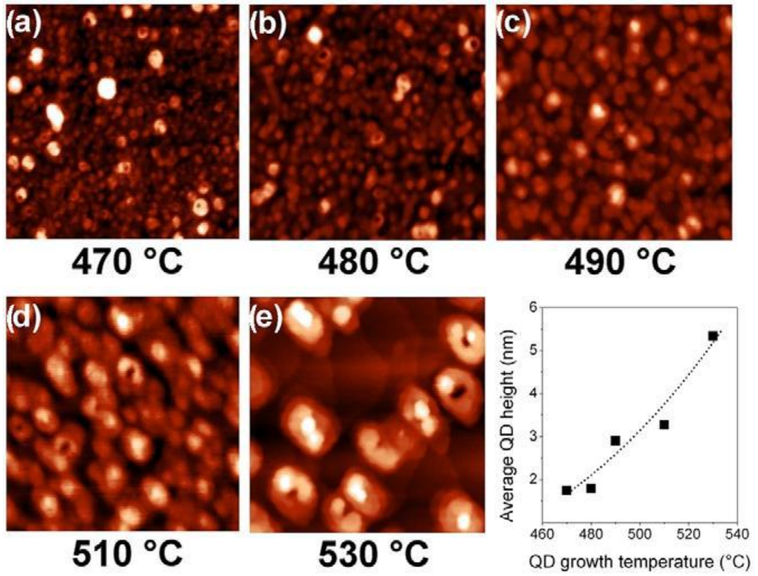




GaAsSb/InAs QDs







Summary

- Epitaxy of Heterostructures
- MOVPE – industrial epitaxy
- Reactor types: horizontal (planetary) and vertical (CCS)
- In situ monitoring (Reflectance, curvature, TT, RAS)
- GaN epitaxy challenges (substrates, doping, polarization)
- Nanoheterostructure for applications – QW, NR, QDs (in FZU)