Crystal Growth: Physics, Technology and Modeling

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MBE of nitride semiconductors

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http://www.unipress.waw.pl/~stach/cg-2024-25

Molecular beam epitaxy of nitride semiconductors

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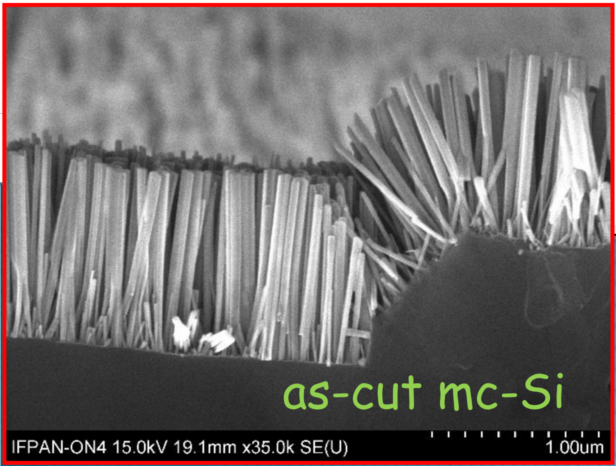
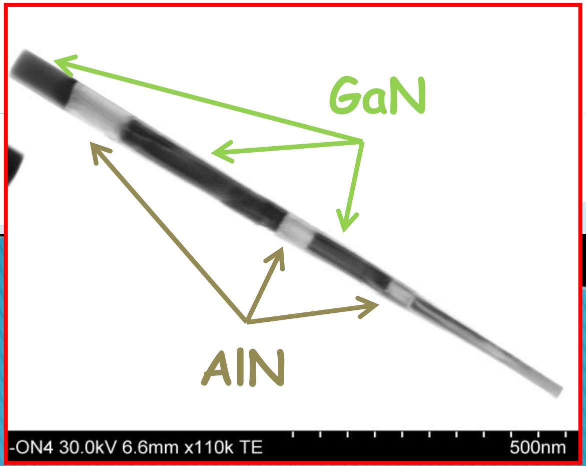
Group of MBE Growth of Nitride Nanostructures

http://info.ifpan.edu.pl/Dodatki/WordPress/mbe2en/





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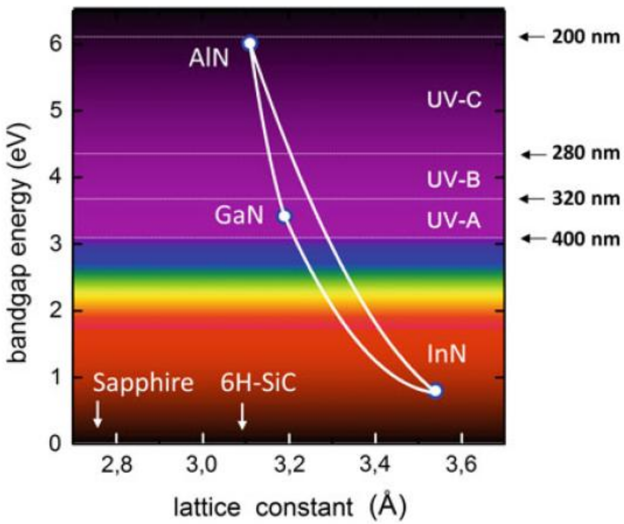
Outline

1. Introduction
2. Overview of surface processes during crystal growth
3. Specific case – MBE of nitride semiconductors,
   How surface phenomena can be observed *in situ by:*
   - Reflection High Energy Electron Diffraction (RHEED)
   - Laser Reflectometry (LR)
   - line-of-sight Quadrupole Mass Spectroscopy (QMS)

   ❖ What atoms do on the surface ?
4. PAMBE growth of GaN nanowires
5. Summary

Why nitride semiconductors ?



(Al,Ga,In)N:

- very broad range of E_g (InN 0.7 eV – AlN 6 eV)
  the only one material system that covers so large E_g range
- resistant to main chemicals and high temperature (applications in harsh environment)
- large breakdown voltage (GaN 3×10^6 V/cm) – high power electronics
- good thermal conductivity
- ...

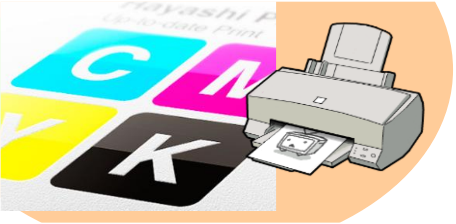
High power/RF electronics

Solid State Lighting

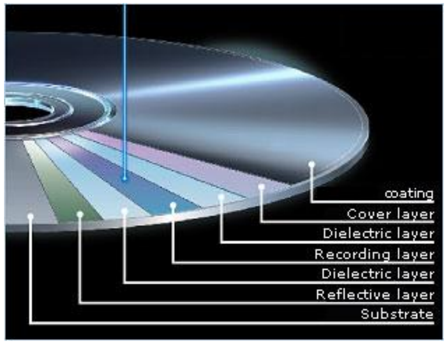
UV Lithography

Water processing

Medical treatment

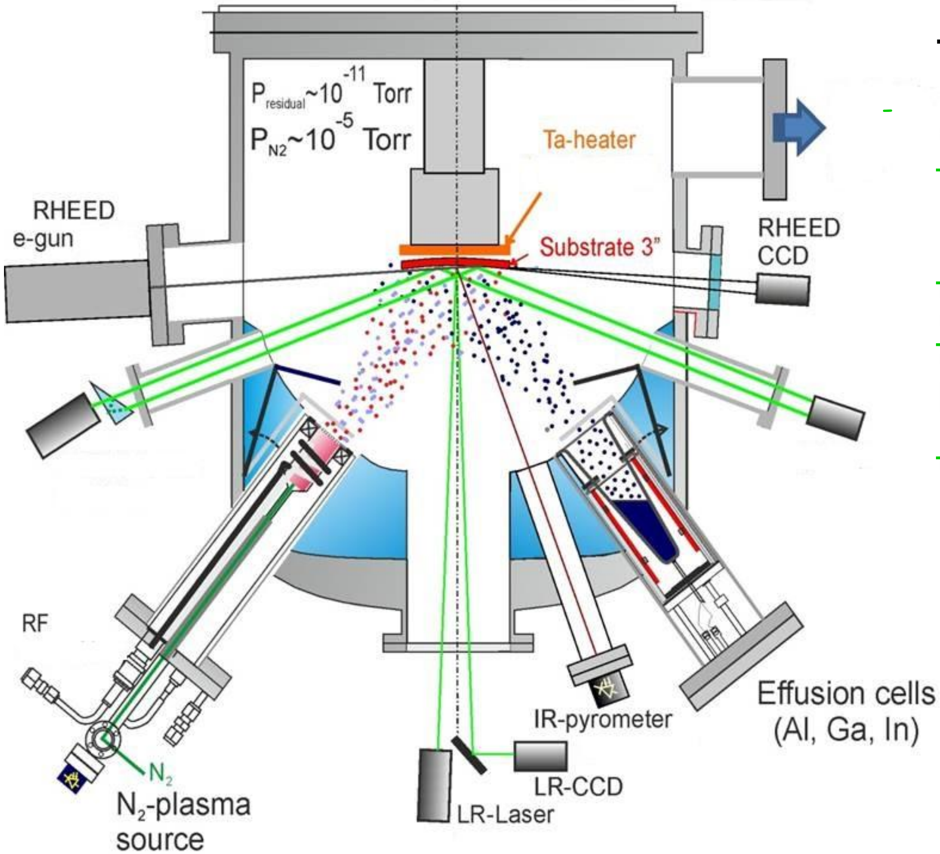


High resolution printing



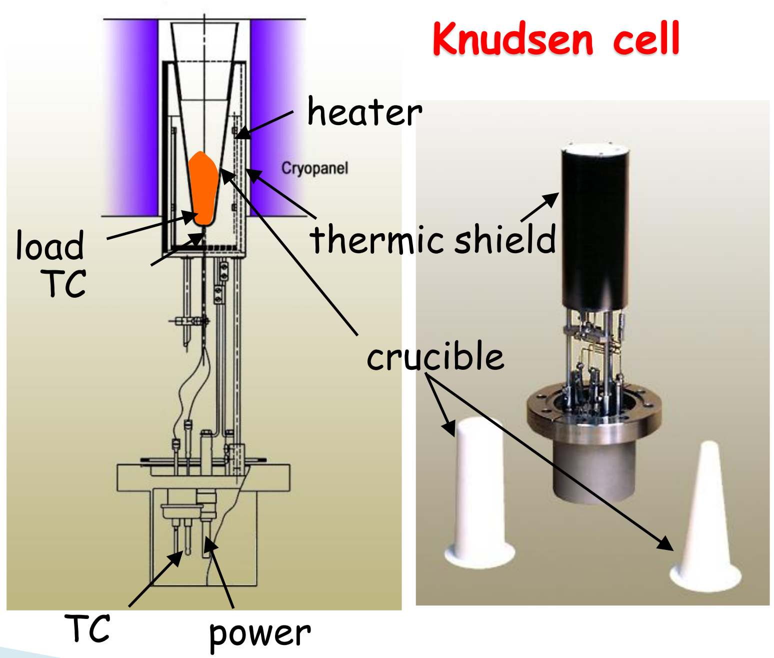
Data storage

What Molecular Beam Epitaxy (MBE) means ?



- very low residual gas pressure ~10^{-11} Tr (efficient UHV pumps and LN_2 filled cryopanel)

  → high purity of crystals (low doping)
- pressure inside the beam ~10^{-5} - 10^{-6} Tr
  - → mean free path of species inside the beam ~5 m >> source – substrate distance
  - → ballistic flow of species; shadowing effect
  - → growth environment transparent for light, X-rays, e-beam, etc.
  - → many *in-situ* diagnostic tools available



Nitrogen sources in nitride MBE

N_2 molecule very stable and chemically inactive ☹

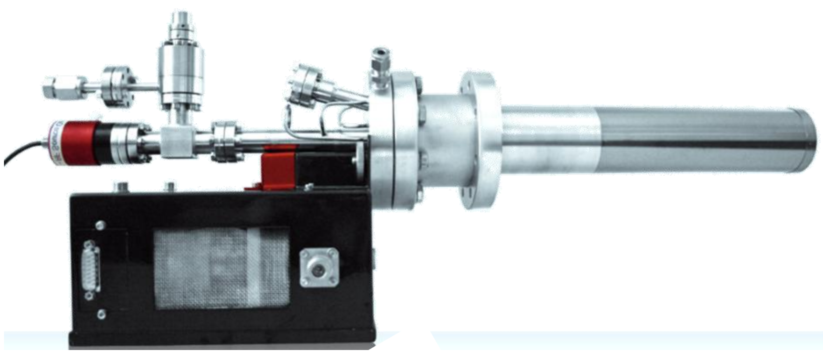
ammonia (NH_3) MBE

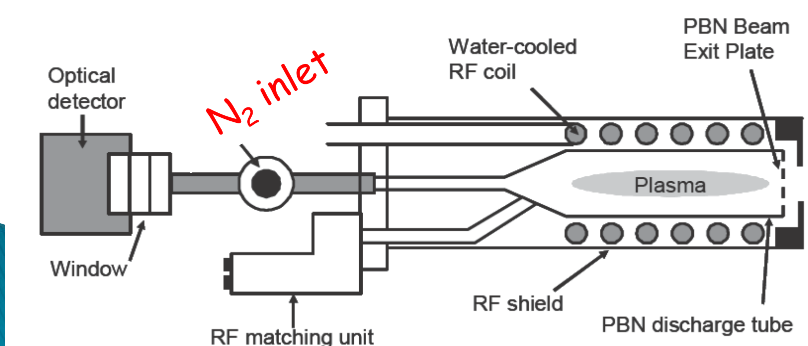
gas NH_3 injector

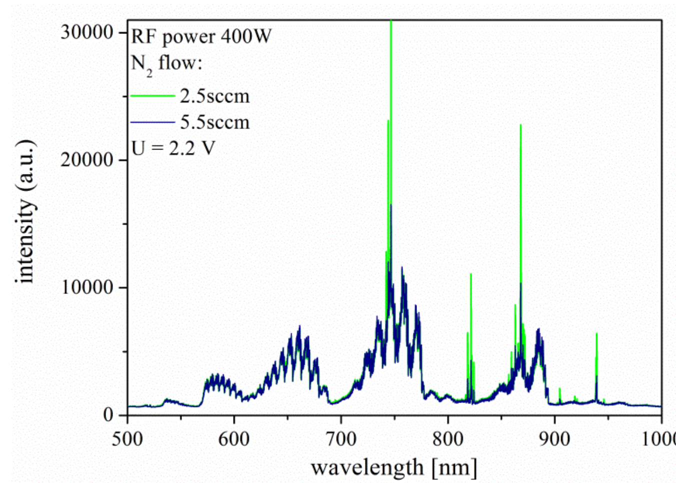
thermal cracking of NH_3 molecule at the hot substrate surface; N atoms and hydrogen released;

requires high growth temperature (usually ~900 - 1000°C); similar mechanism as in MOVPE

plasma-assisted MBE (PAMBE)







optical spectroscopy of nitrogen plasma in the RF cavity

nitrogen plasma emits atomic N and excited N_2^* species;

MBE growth at much lower T possible

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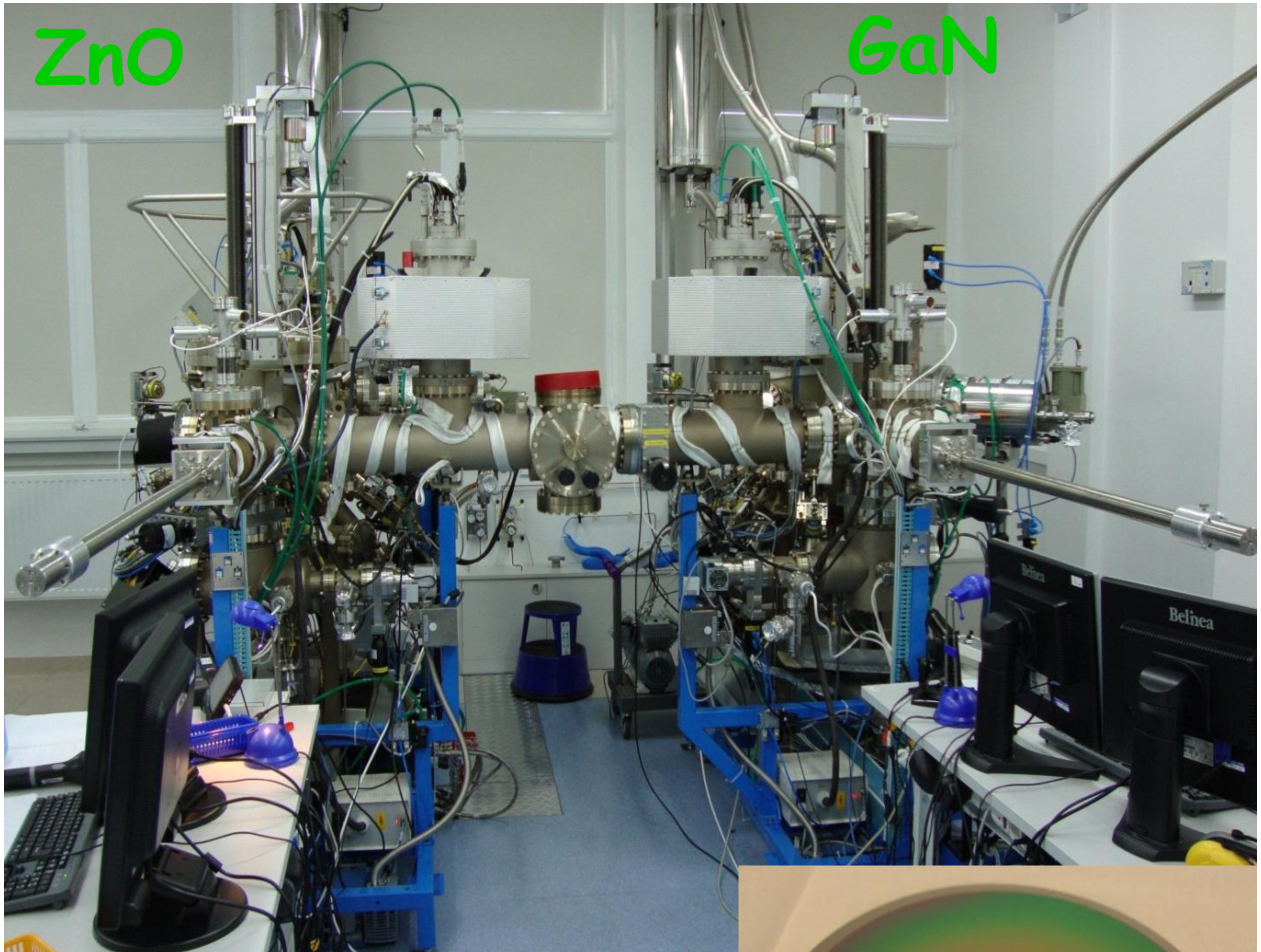
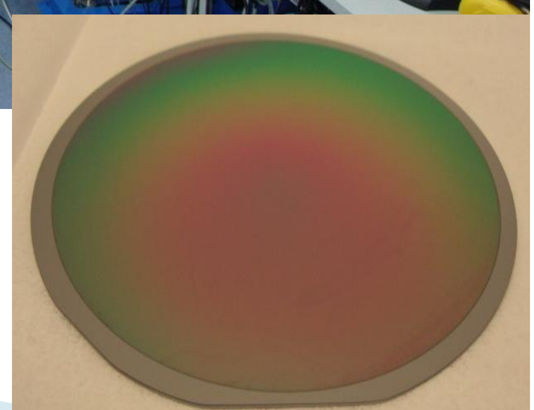
Plasma-Assisted MBE (PAMBE) Riber Compact 21



growth on
3" substrates



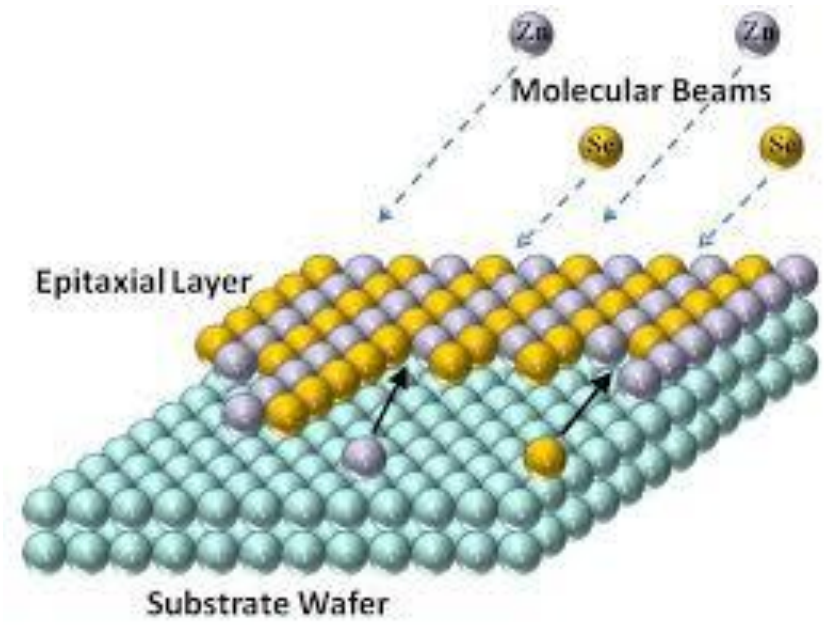
TOOLS:

- optical pyrometer
- RHEED (k-Space)
- laser reflectometry
- LayTec EpiCurve TT (temperature, wafer curvature)
- line-of-sight quadrupole mass spectrometry (QMS)

SOURCES:

- Ga x2
- Al x2
- In
- RF nitrogen source
- Si x2
- Mg
- Fe

Crystal growth by MBE



crystal growth = two step process

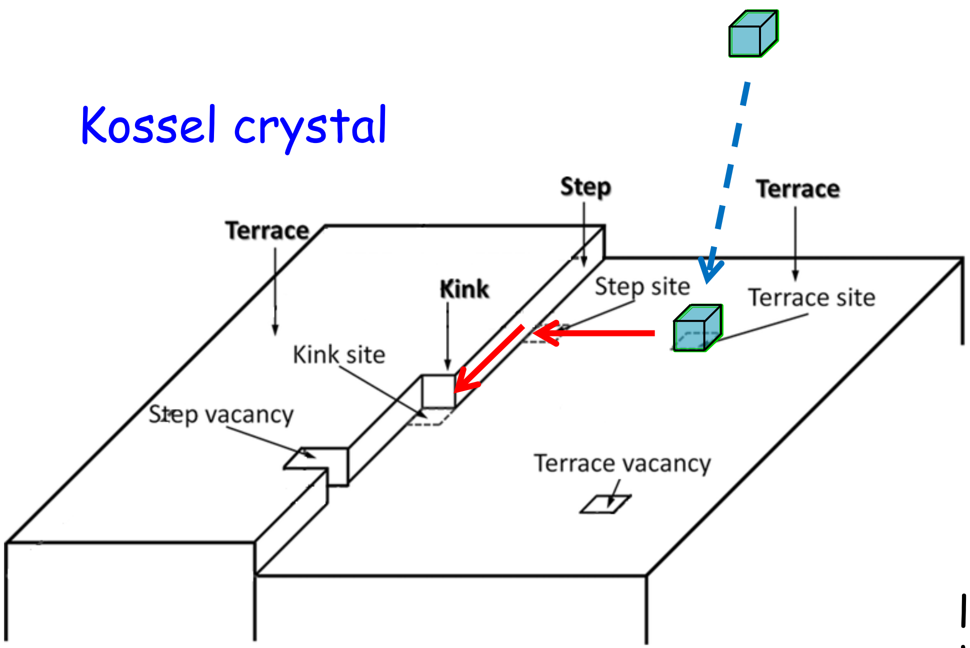
1. bulk material transport towards the growth interface
2. surface phenomena

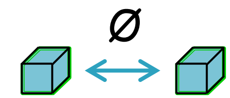
As always in two-step processes, the slowest step determines the overall growth kinetics

Usually (for sure in MBE ☺) the growth kinetics is limited by the rate of surface processes

How crystals grow ? Surface phenomena

Kossel crystal





Ø – bonding energy of two cubes

terrace site – Ø
- weakly bonded;
- high probability of desorption

step site - 2×Ø

kink at the step – 3×Ø

step vacancy – 4×Ø

terrace vacancy - 5×Ø Is it the best site ?

low concentration;
hard to create e.g. by thermal decomposition
negligible contribution to the growth !!!

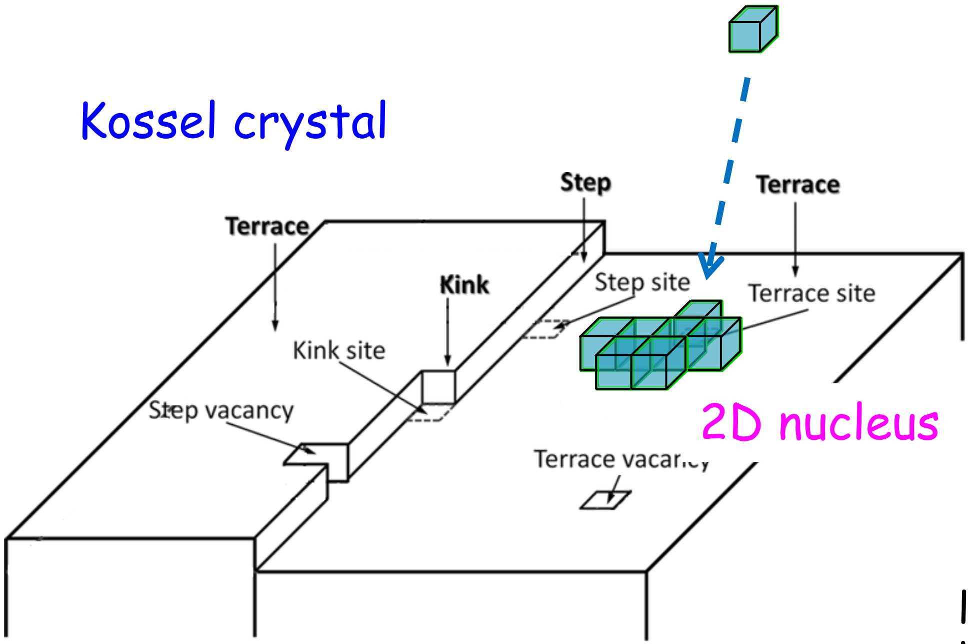
most effective – kinks at the steps
operative if atoms (adatoms) are mobile enough on the surface

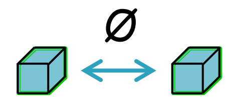
step-flow if the mean diffusion length $L_{diff} = \sqrt{D \times \tau} > terrace\ width$

diffusion coefficient   lifetime on the surface

How crystals grow ? Surface phenomena

Kossel crystal





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low concentration;

hard to create e.g. by thermal decomposition

negligible contribution to the growth !!!

most effective – kinks at the steps

operative if atoms (adatoms) are mobile on the surface

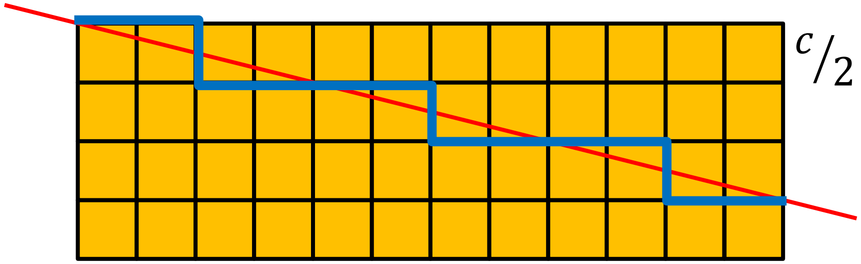
step-flow if the mean diffusion length $L_{diff} = \sqrt{D \times \tau} > terrace\ width$

otherwise – 2D nuclei form and island growth takes place

(2D nuclei stable if larger than critical size)

Sources of surface steps

surface miscut

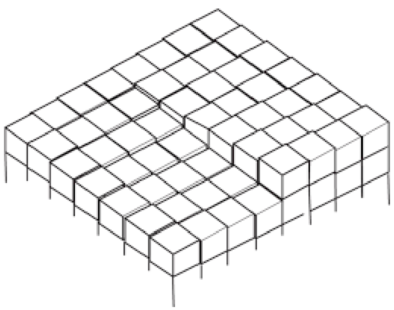


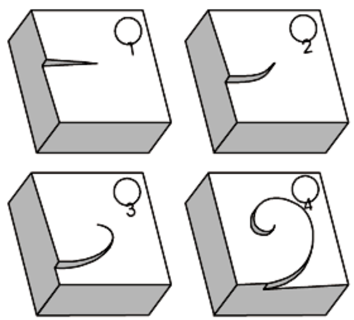
lecture #2 by prof. M. Boćkowski

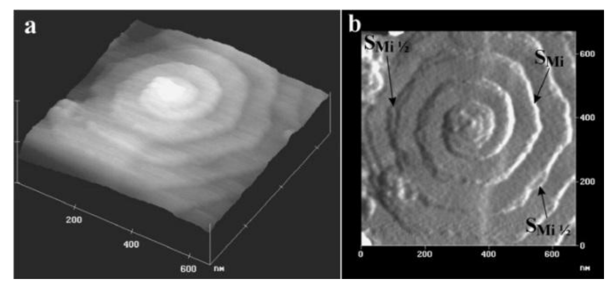
steps formed intentionally by surface miscut

$$L_{terrace} = \frac{c}{2\,tg(\alpha)}$$

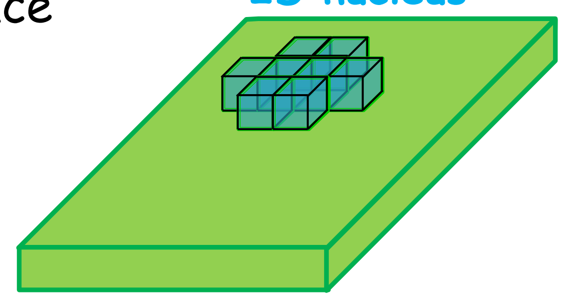
screw dislocations on flat surface

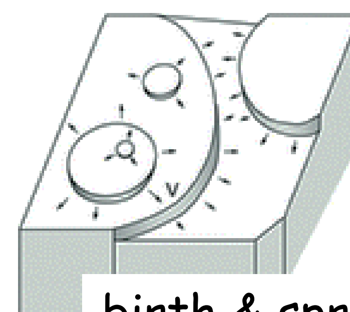






2D nuclei on perfect, flat surface



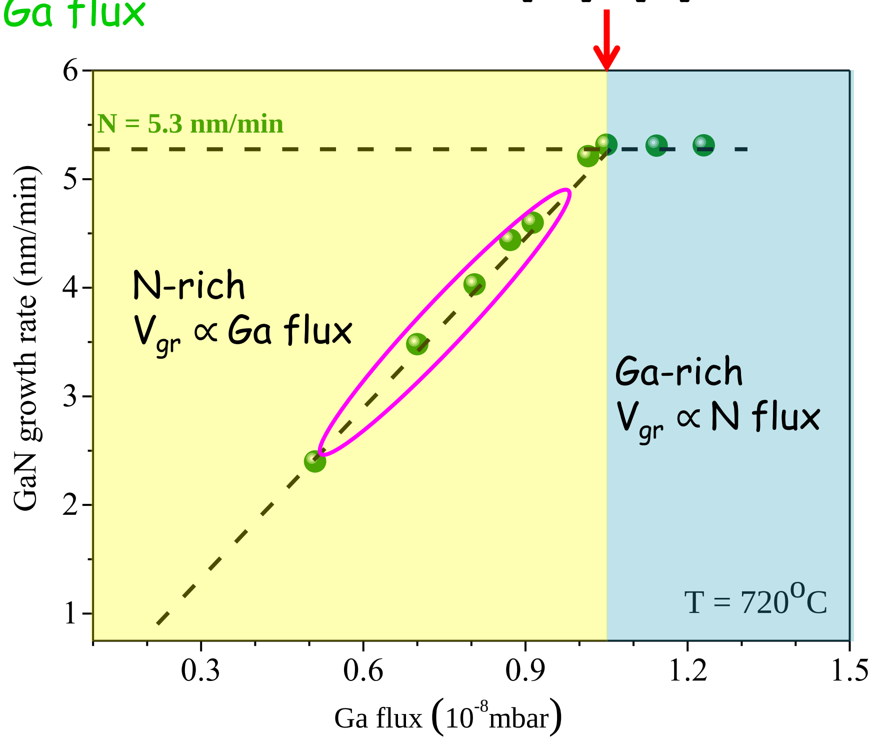


birth & spread

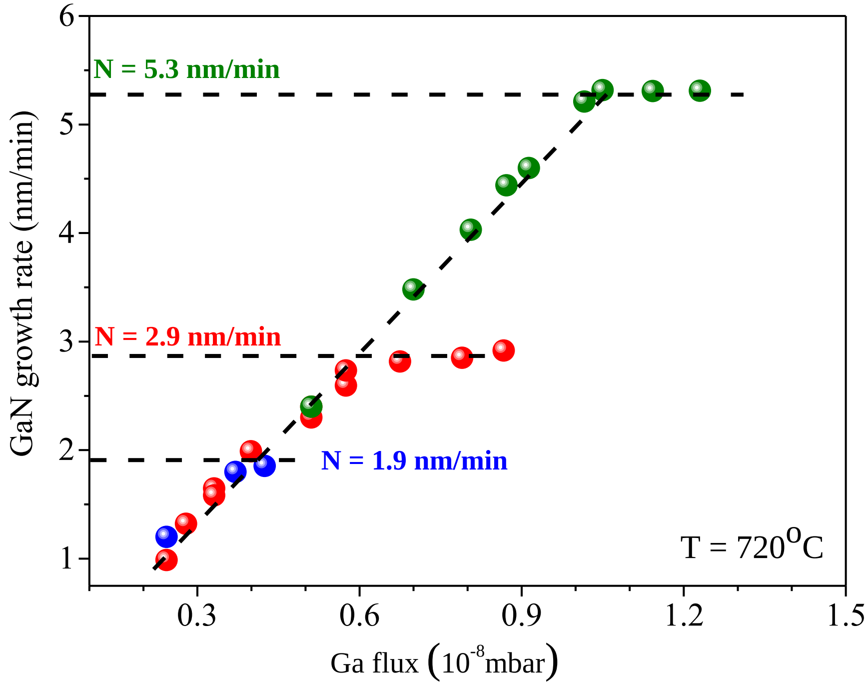
Surface steps are always present on the surface

Specific case – MBE of GaN

calibration of fluxes
Ga flux



N flux



- typical growth conditions in „classic" MBE growth of III-V's (GaAs, InAs, InP, …)
- overpressure of volatile group V species
- metal flux controls growth rate

Ga flux = 3 nm/min → Ga flux that under N-rich conditions and low T (no Ga desorption) would cause GaN growth with the rate of 3 nm/min

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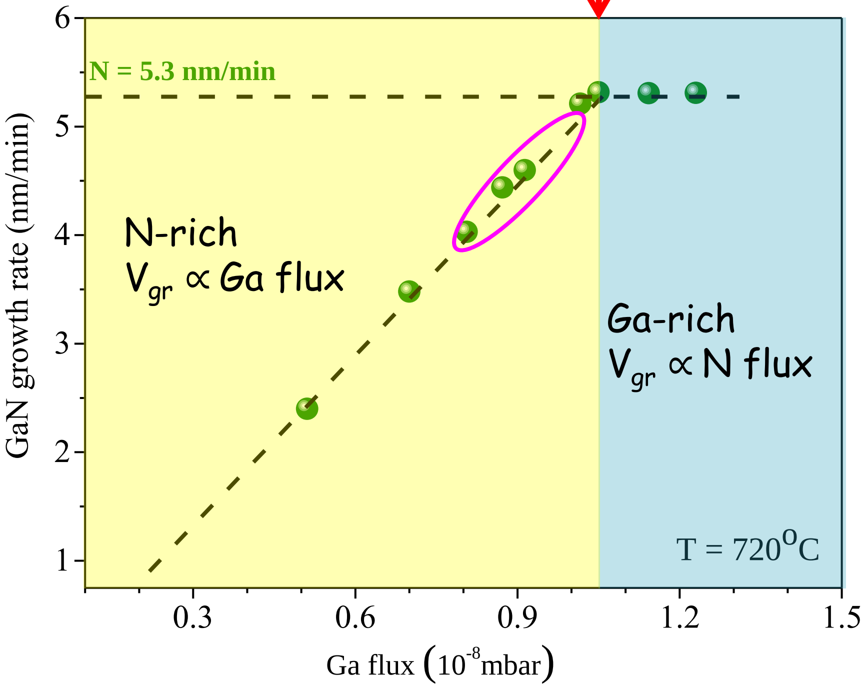
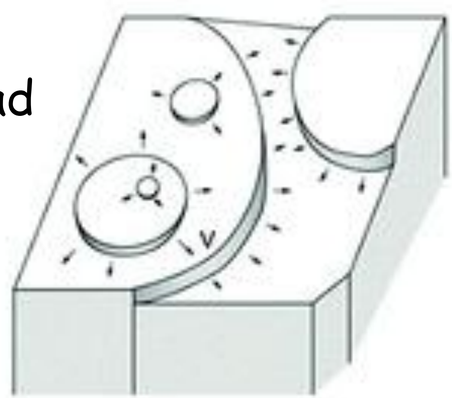
Specific case – MBE of GaN

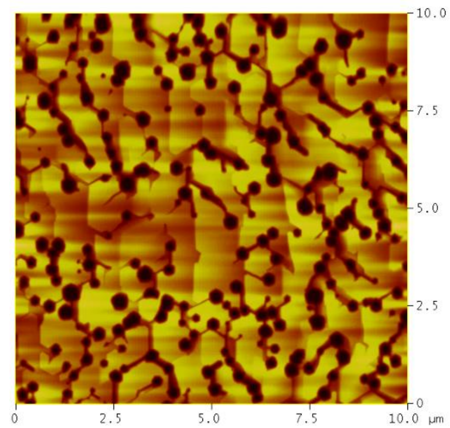
[Ga] = [N]



birth & spread

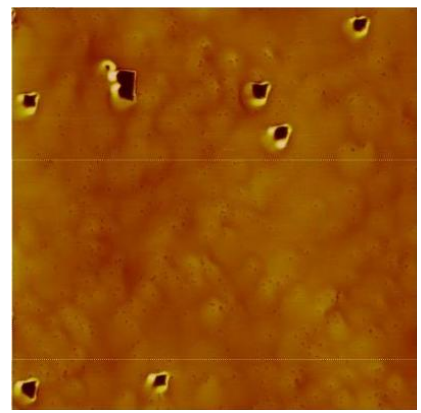


AFM image of epilayer surface
(10×10 μm^2 area)



T_{growth} = 720°C

rms = 18.3 nm



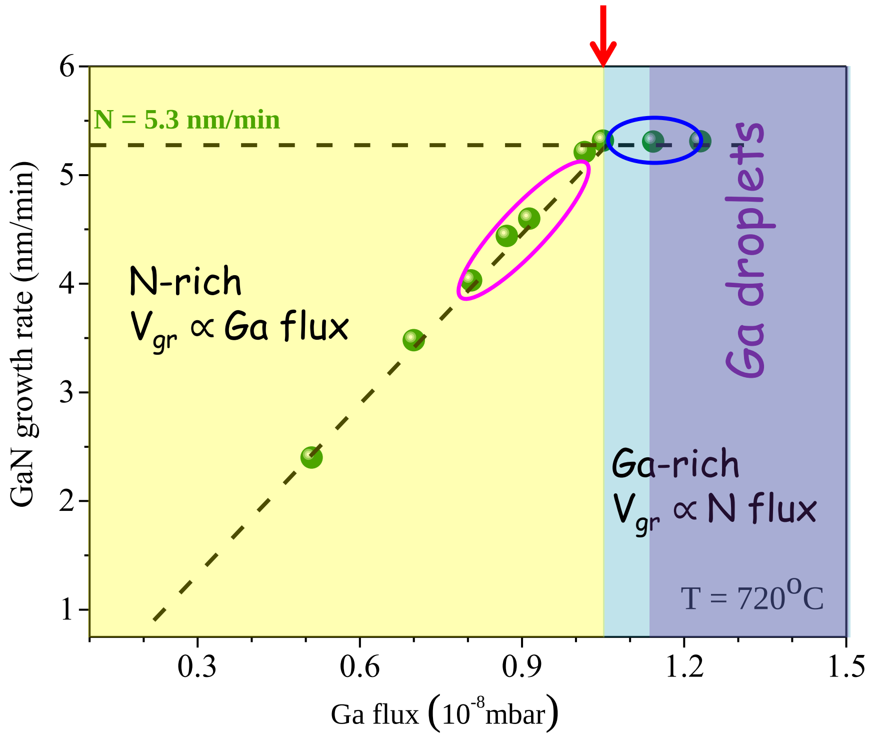
T_{growth} = 770°C

rms = 3.2 nm

T_{growth} increases -

- <u>mobility</u> of Ga adatoms increases
- more smooth surface

Specific case – MBE of GaN



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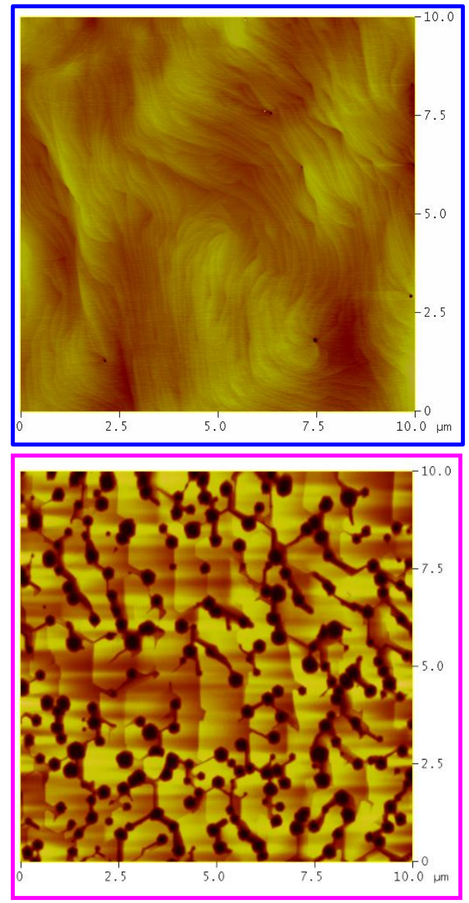
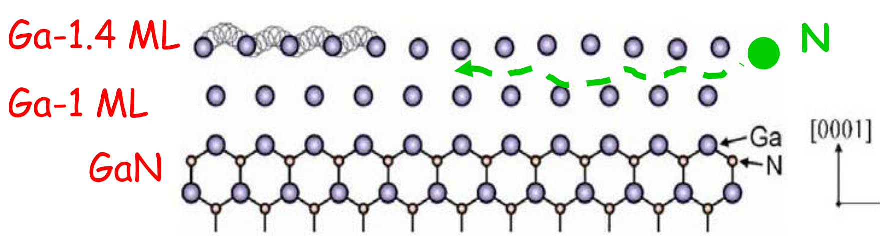


T_{growth} = 720^{o}C

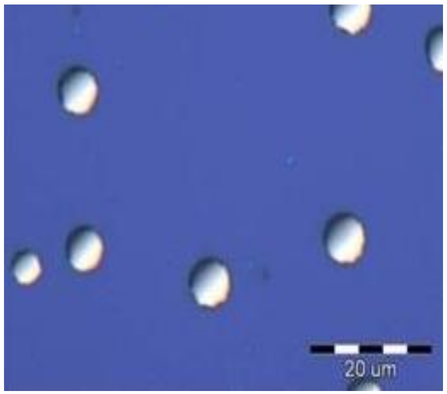
rms = 0.98 nm

rms = 18.3 nm



Northrup et al. PRB 61 (2000) 9932

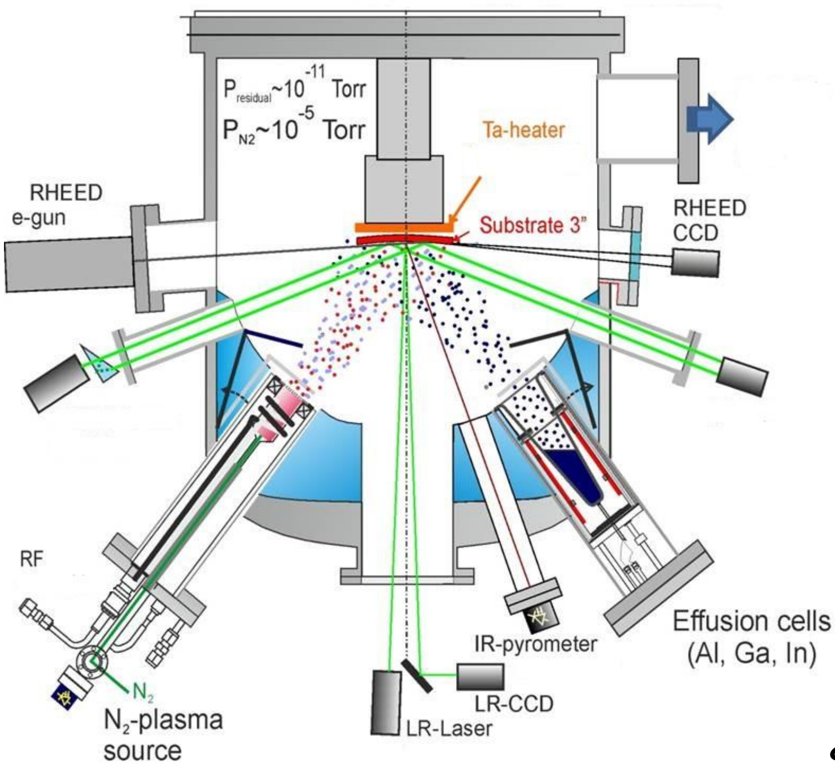
Ga droplets

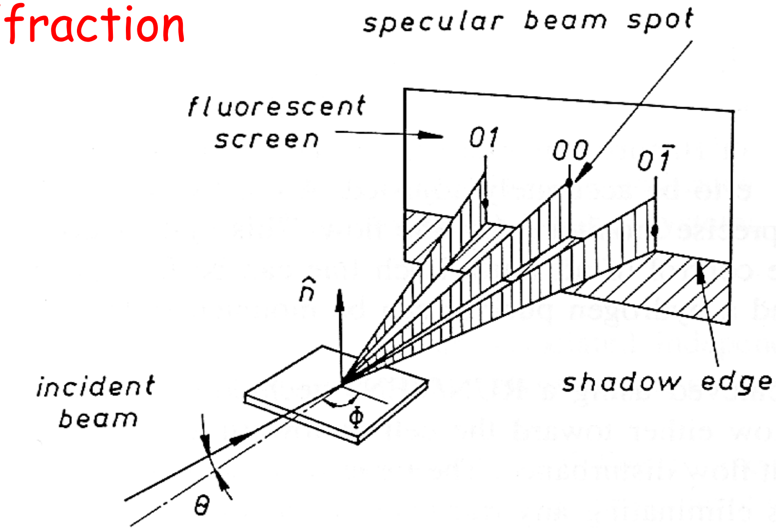


N species diffuse inside Ga-bilayer
not on GaN surface

MBE of GaN - growth rate measurements

RHEED – Reflection High Energy Electron Diffraction

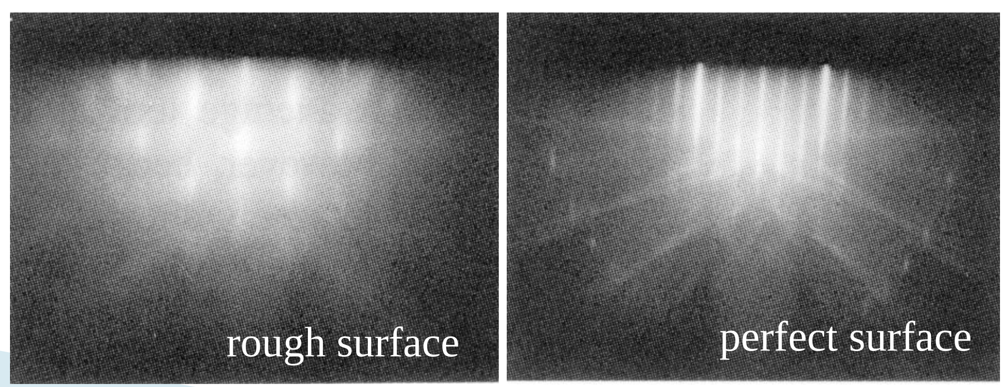




RHEED commonly used to visualize:

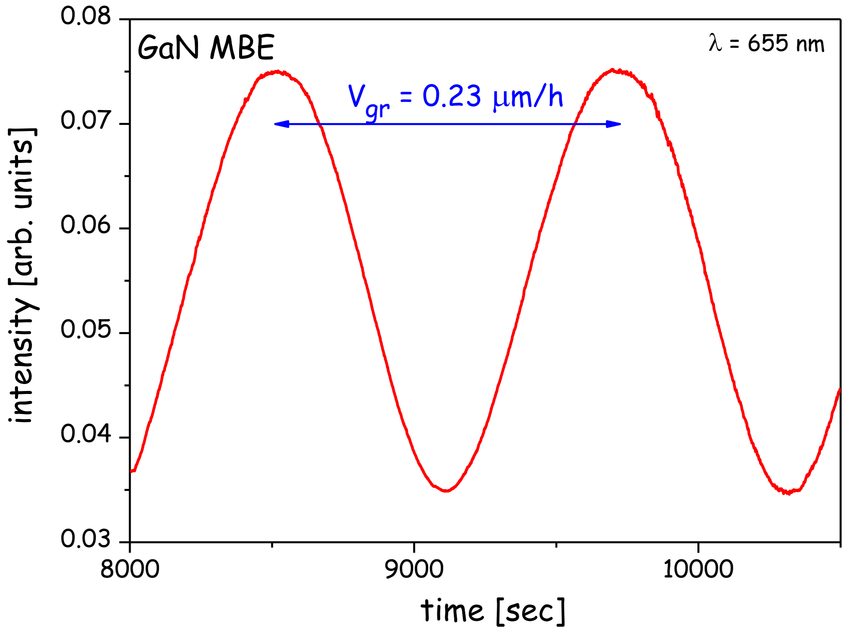
- surface reconstruction
- quality of the surface (rough/smooth)
- ....

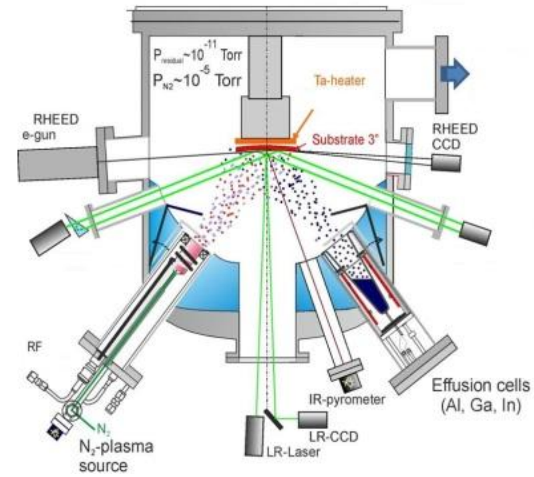
Si(001) RHEED patterns - sputter-cleaned surface

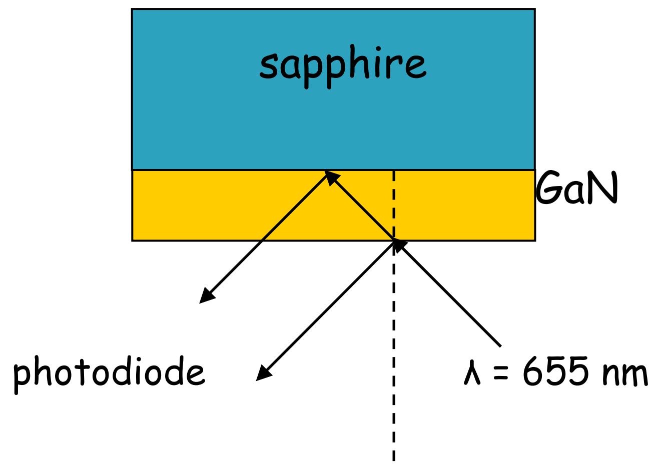


MBE of GaN - growth rate measurements

laser reflectometry





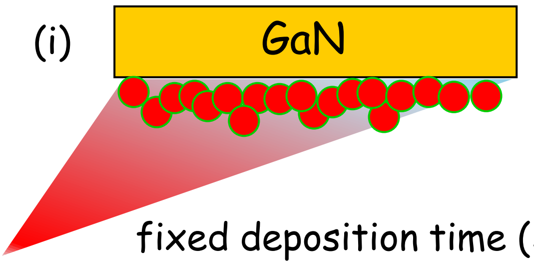


RHEED - measurement of „microscopic" growth rate
LR - measurement of „macroscopic" growth rate

Simple Ga-desorption experiment; laser reflectometry

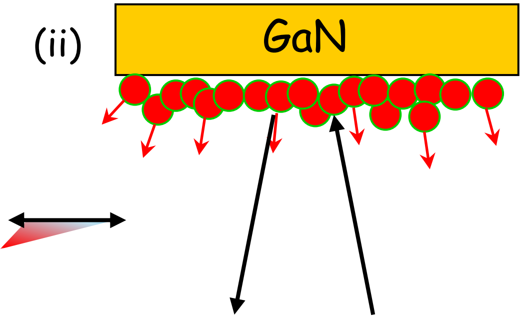
$T_{substrate}$ = 720°C; N-flux OFF

(i)



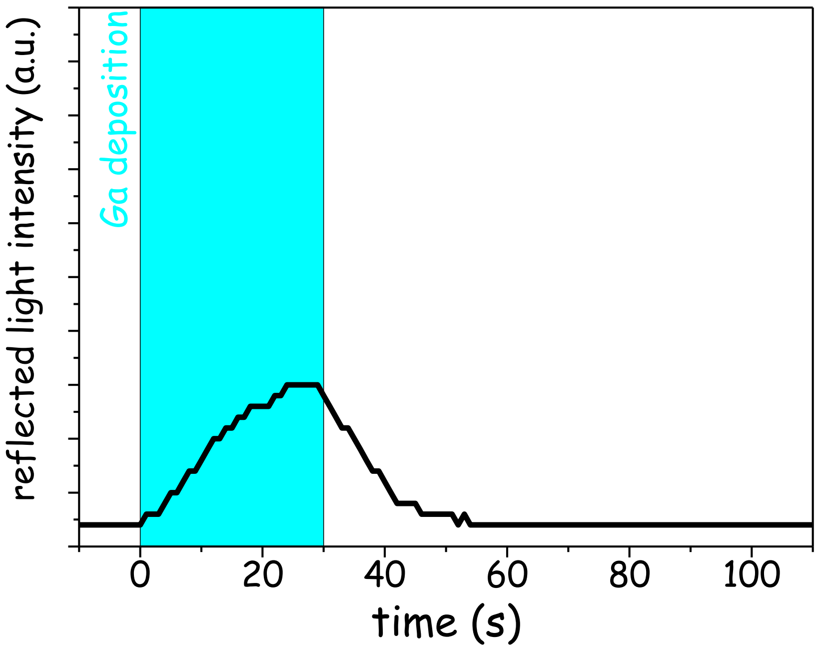
fixed deposition time (30 s)
T_{Ga} (Ga flux) varied

(ii)



photodiode λ = 655 nm

Ga desorption observed
by LR



T_{Ga} 800C

Simple Ga-desorption experiment; laser reflectometry

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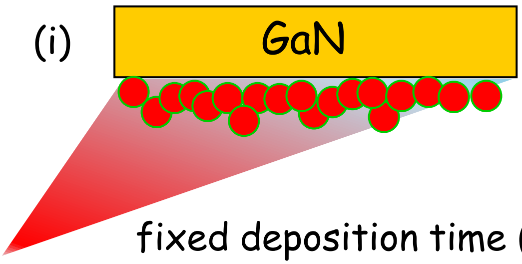

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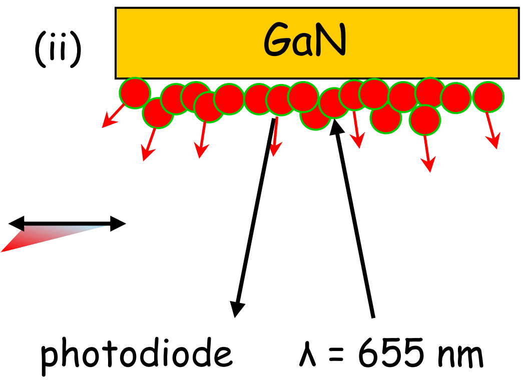
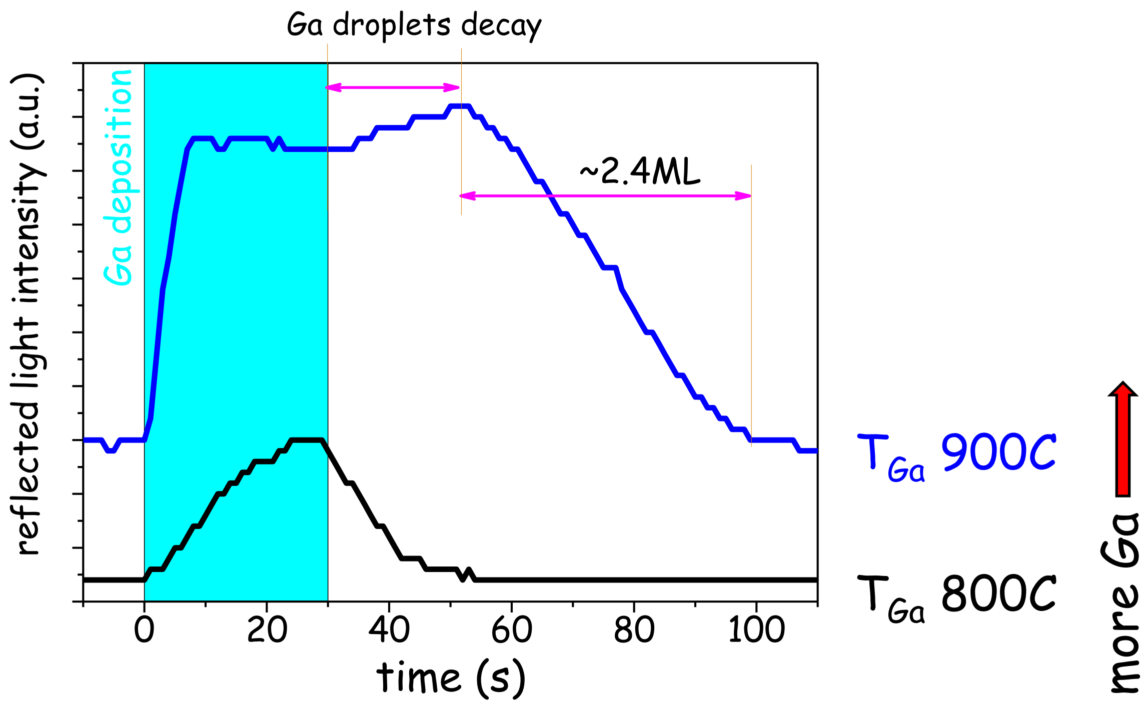


Ga desorption observed by LR



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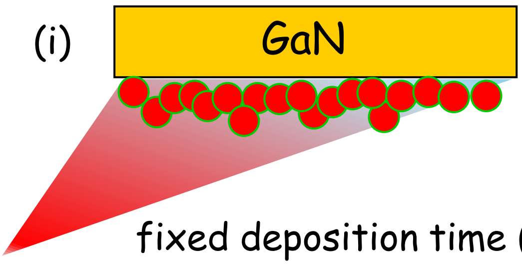

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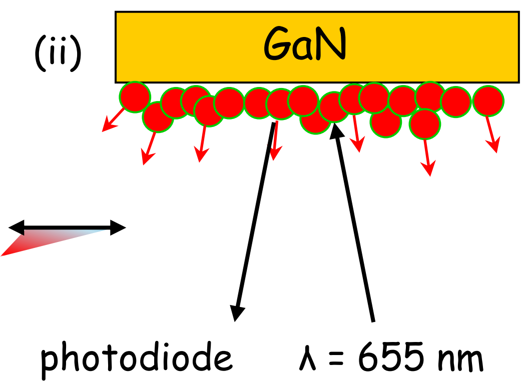
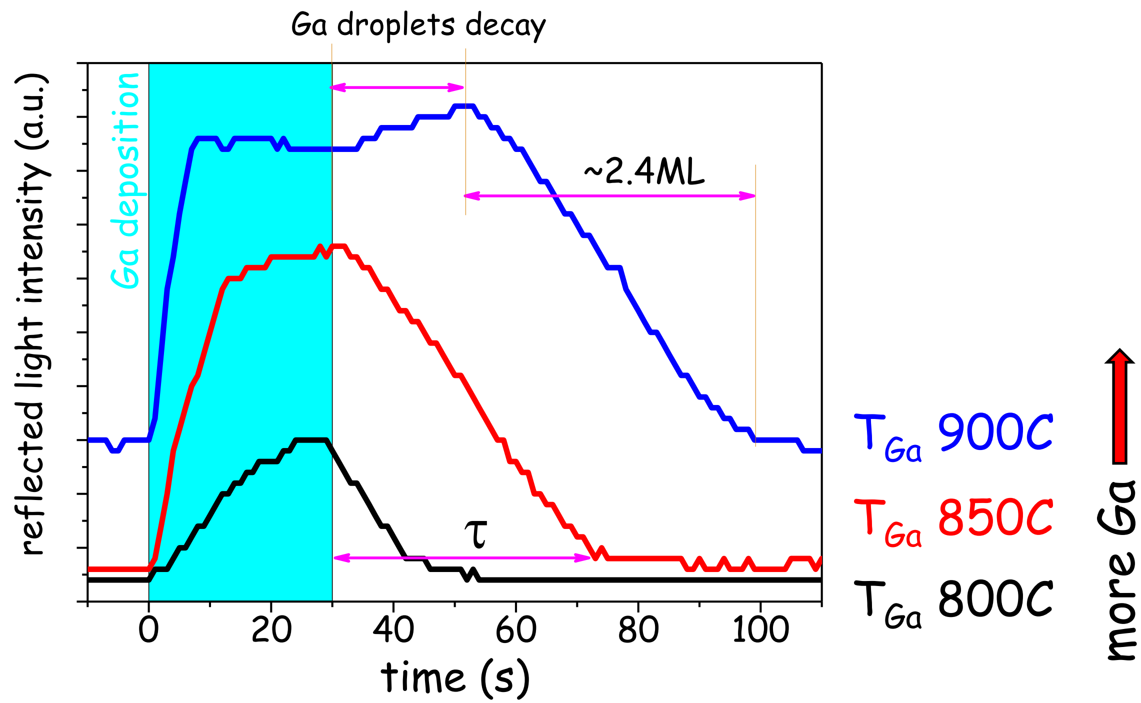
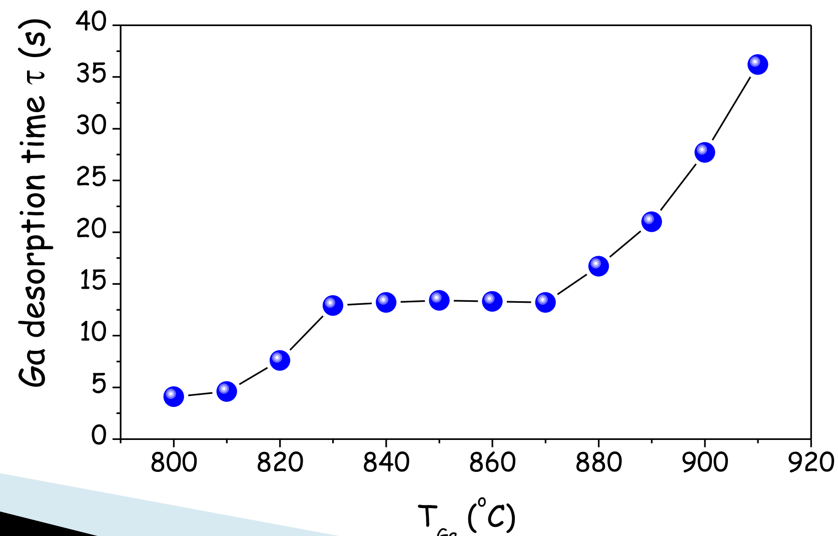


Ga desorption observed by LR

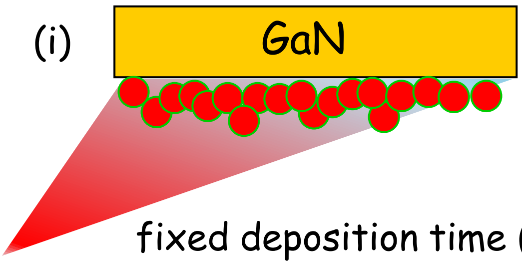




Simple Ga-desorption experiment; RHEED

$T_{substrate}$ = 720°C; N-flux OFF

(i)



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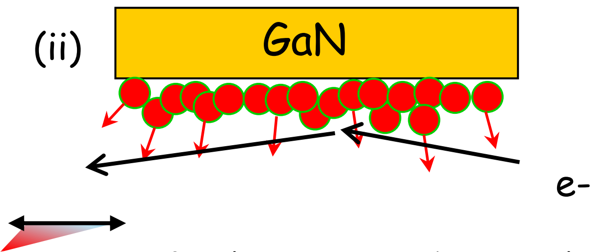
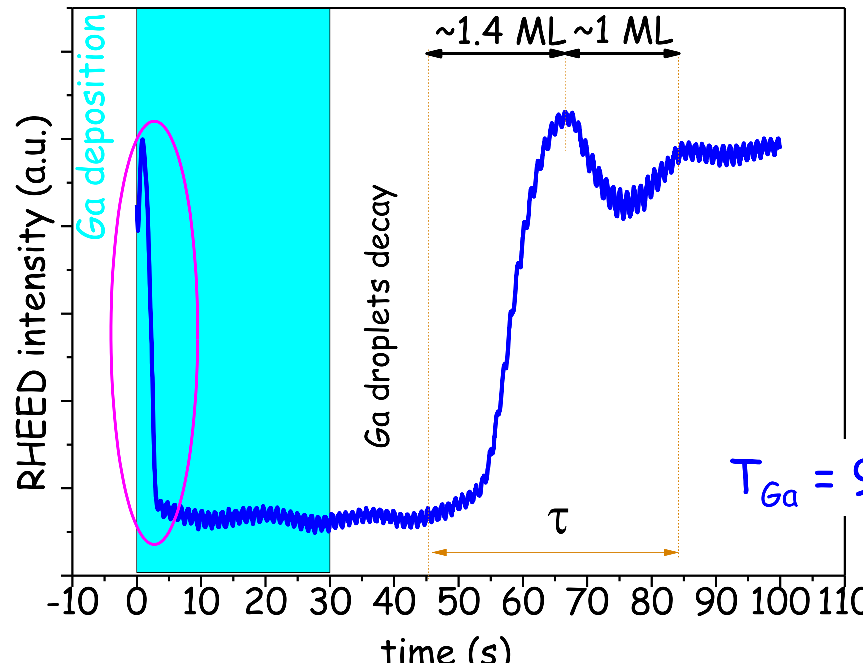
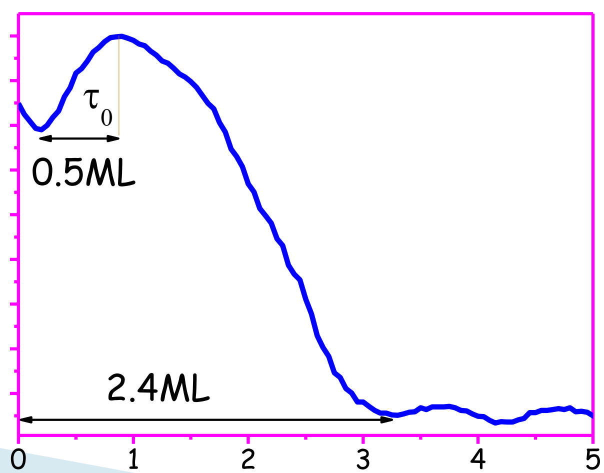


Ga desorption observed by RHEED



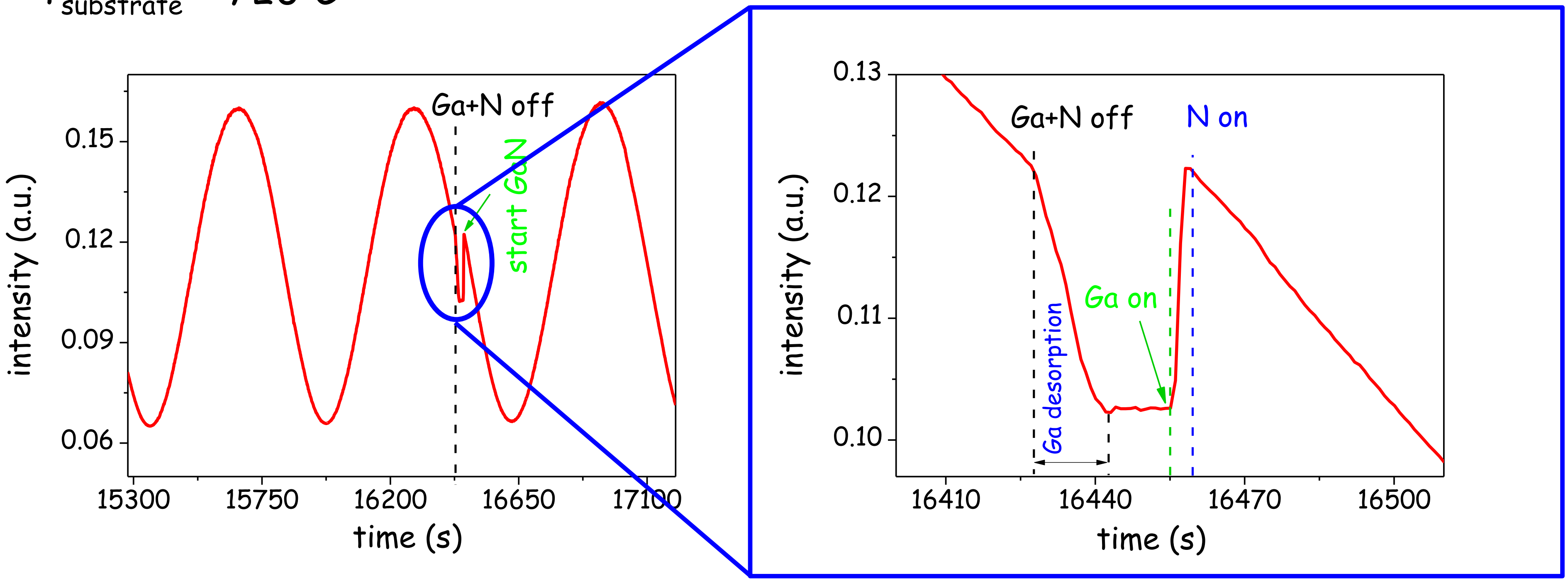
T_{Ga} = 900°C



How to control amount of Ga during growth of GaN ?

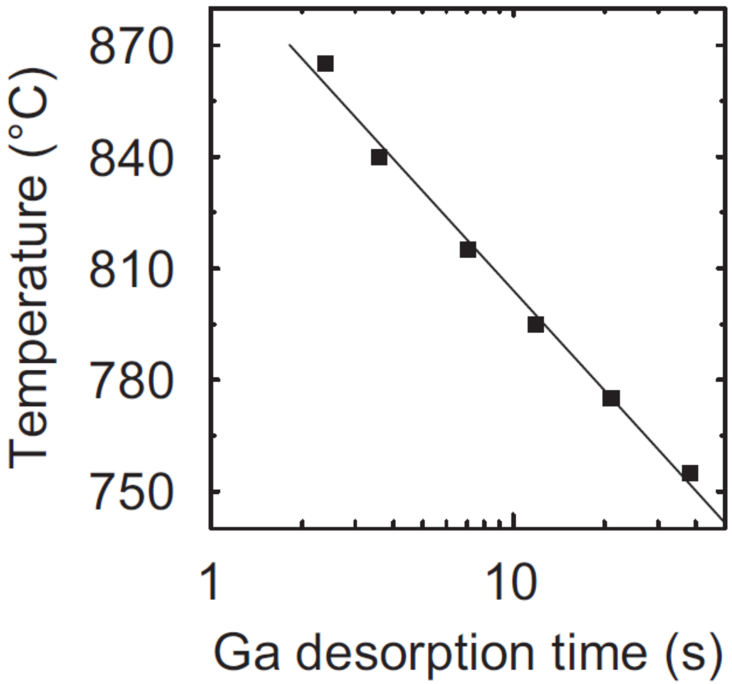
periodic growth interruptions for *in-situ* control of Ga-coverage

$T_{substrate} = 720^{o}C$



Ga flux slightly corrected (if needed) to keep 2ML of Ga on the surface

Ga desorption kinetics as surface thermometry



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1. exposure of Si(111) to 0.4 ML/s Ga flux for 10 sec
2. RHEED used to measure recovery time of 7×7 Si(111) reconstruction

in reality:

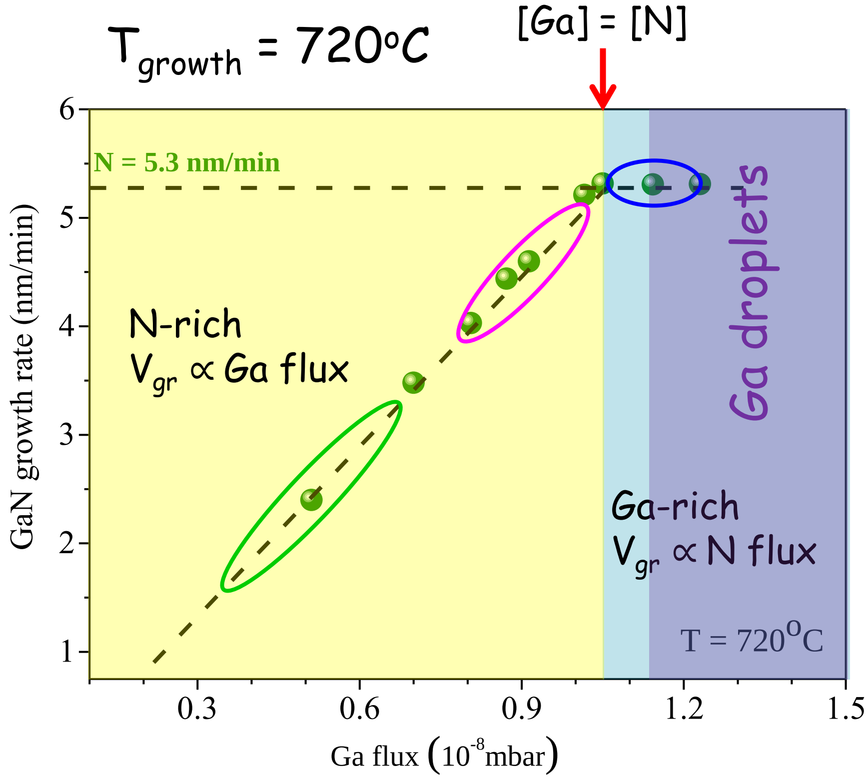
1. RHEED signal decay measured vs. heater power
2. surface T measured by a thermocouple bonded to the substrate in order to convert heater power into surface T

comments:

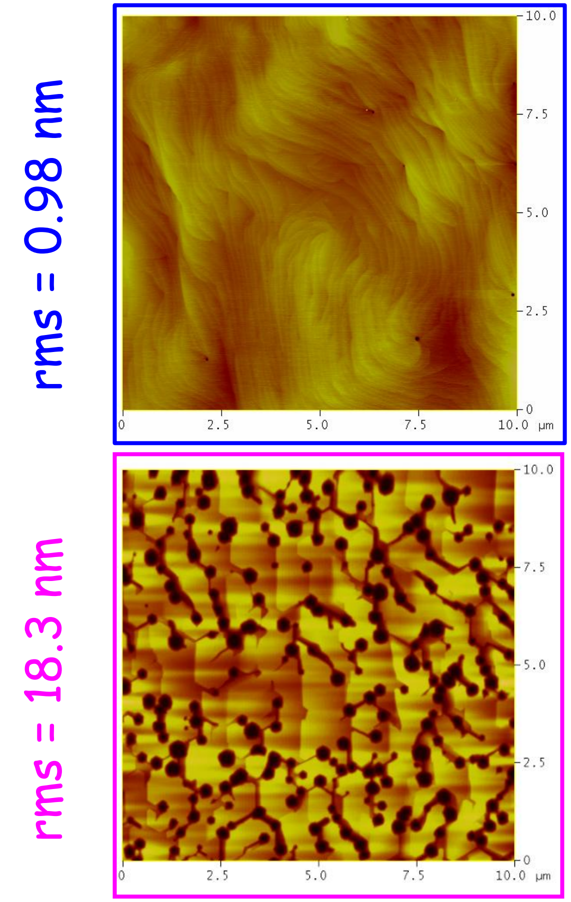
1. good tool to get run-to-run reproducibility of the surface substrate T (most important for grower)
2. absolute value of substrate surface T measured ???

Specific case – MBE of GaN

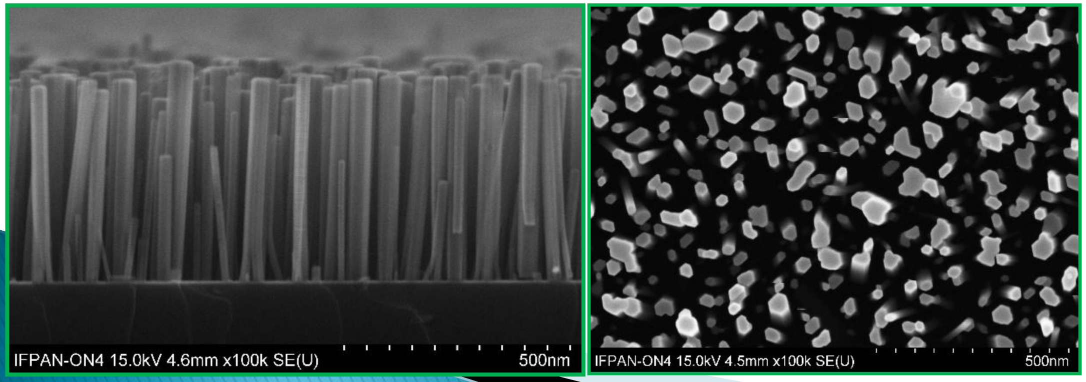
T_{growth} = 720°C



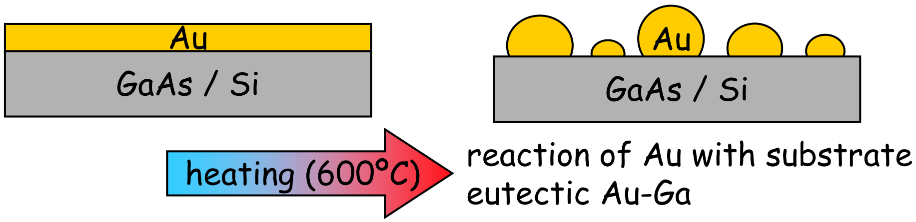
AFM image of epilayer surface
(10×10 μm² area)

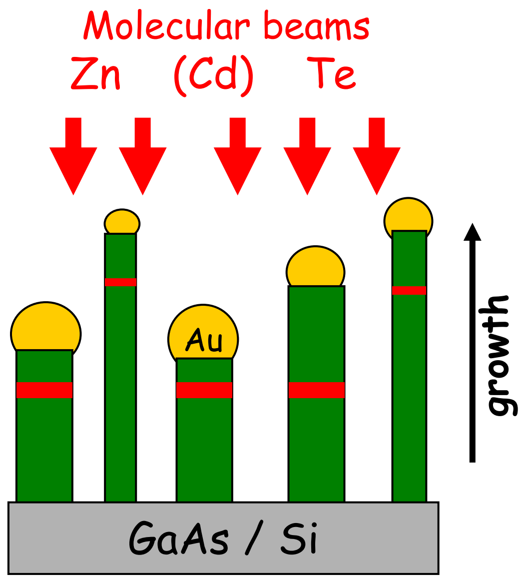


GaN nanowires (NWs)



Growth of NWs in vapor-liquid-solid (VLS) mode



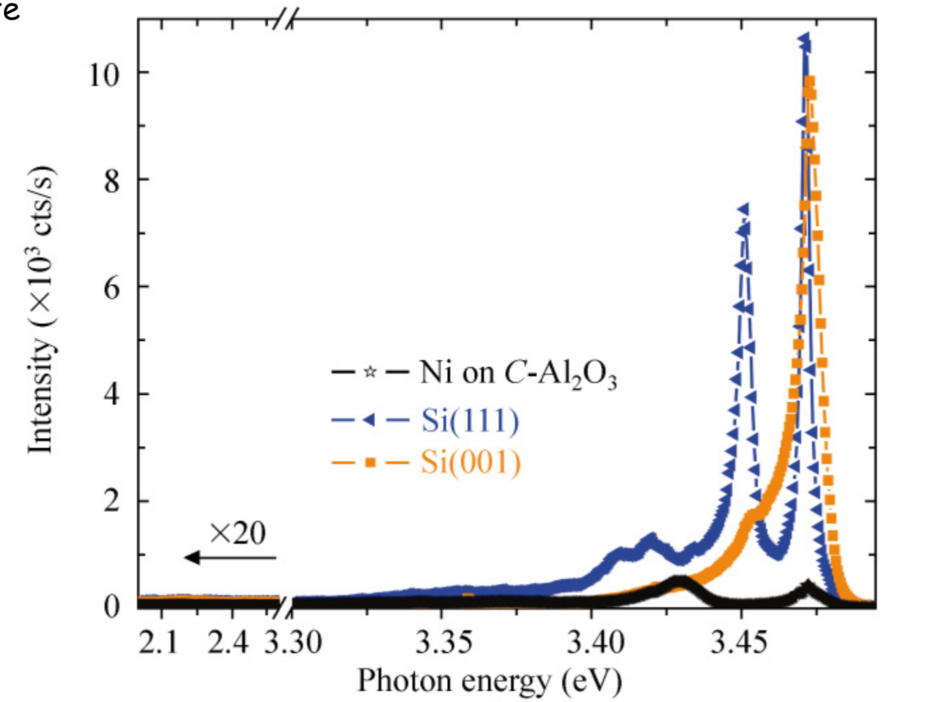


advantages:

- fast growth
- relative easy selective area growth
- size of droplet determines diameter of NW

Ni-assisted vs. catalyst-free GaN NWs

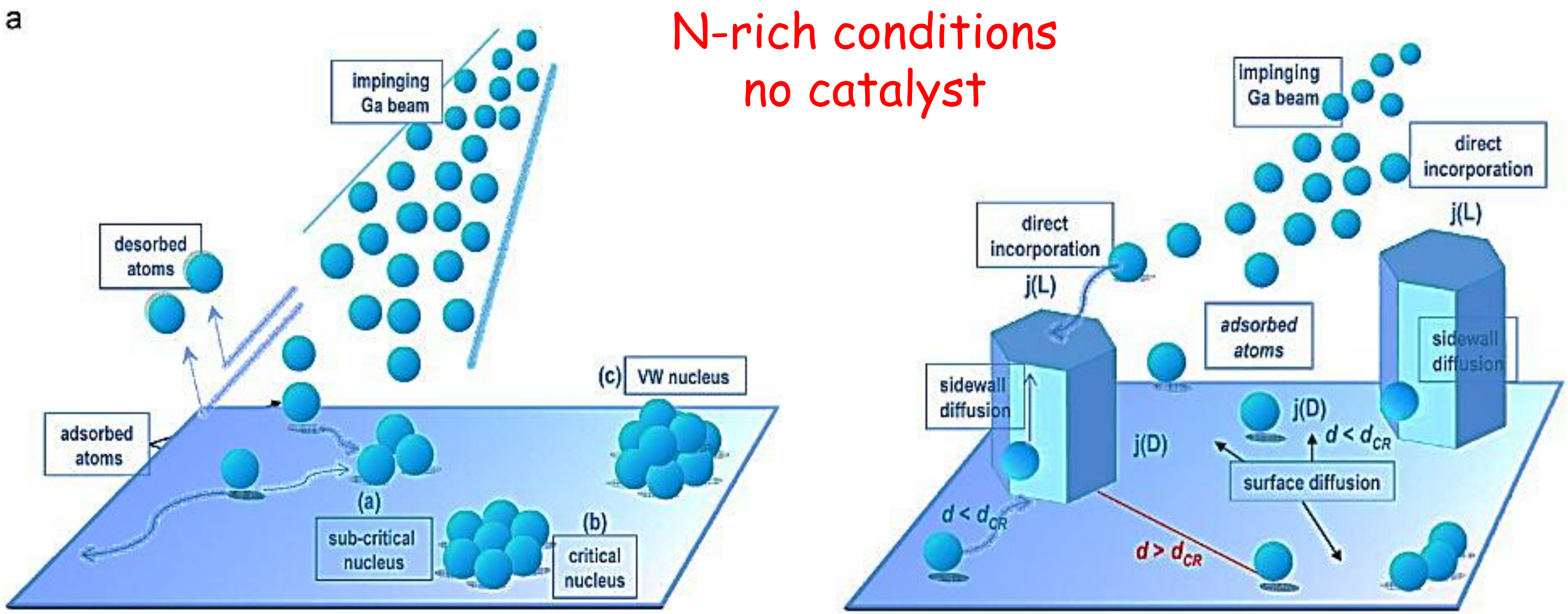
C. Cheze, et al. Nano Res 3 (2010)



- D^0X = 3.472 eV for all cases (typical for strain-free GaN layers)
- PL intensity much lower for GaN NWs grown with Ni – unintentional doping and more defects

much better optical properties of GaN NWs grown catalyst-free

How nanowires (NWs) do form ?



Ristic et al. JCG 310 (2008)

Two steps in growth of NWs:

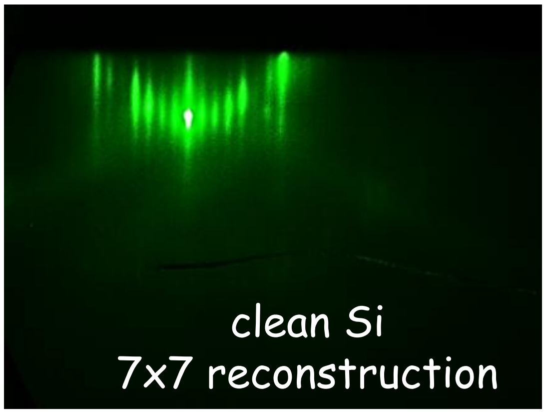
1. self-induced nucleation (Volmer-Weber mechanism): Ga adatoms migrate on the surface or desorb until stable critical nuclei are formed
2. growth of NWs by incorporation of Ga atoms from substrate surface around NW and directly from the Ga beam

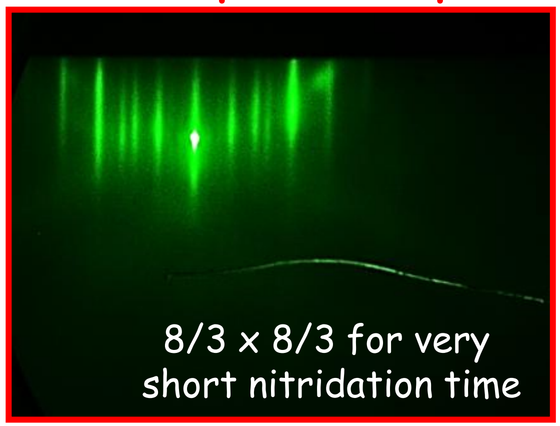
Our procedure of growth of GaN NWs on Si(111)

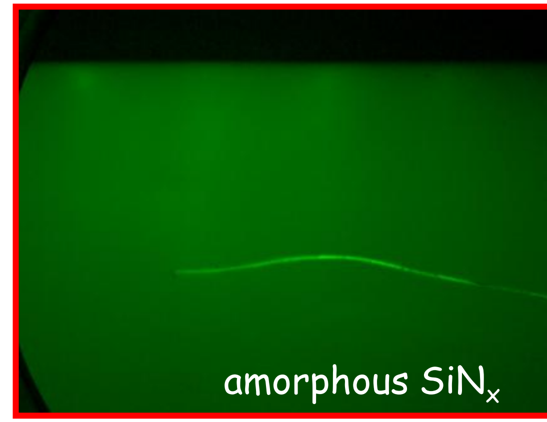
- Si-N bond 4.5 eV/bond (Ga-N bond: 2.17 eV/bond)
- competition of N bonding with Si and Ga; uncontrolled nitridation of the substrate

RHEED

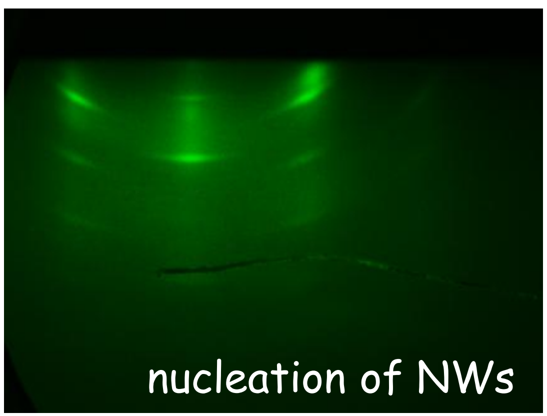
separate step of substrate nitridation

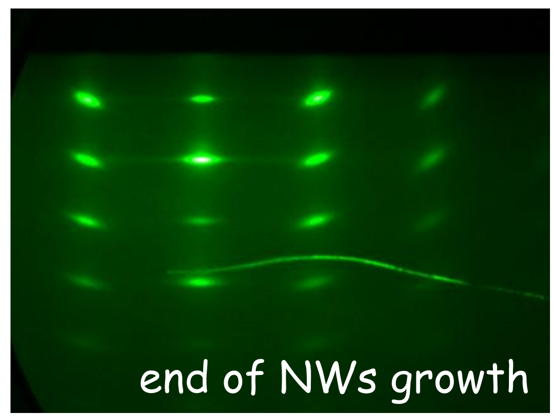






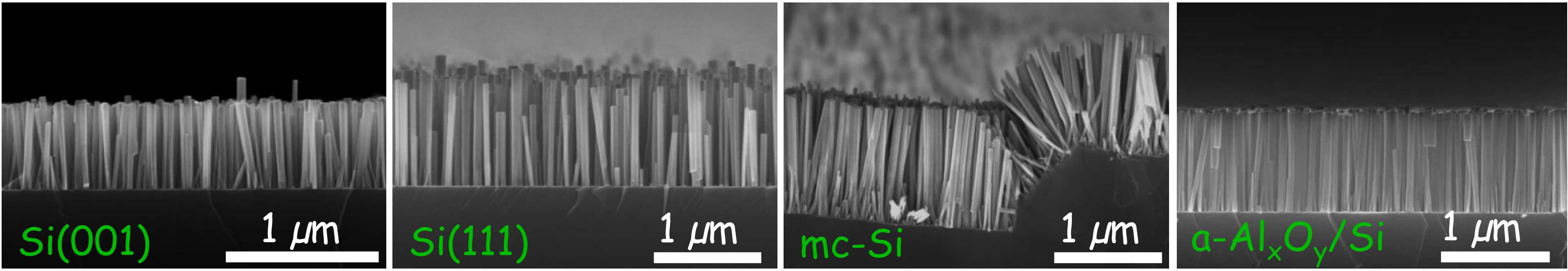
Ga+N on





A. Wierzbicka, et al. Nanotechnology 24 (2013) 035703

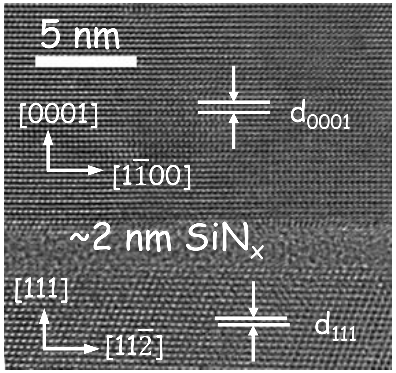
Unique feature of GaN NWs on non-crystalline substrates

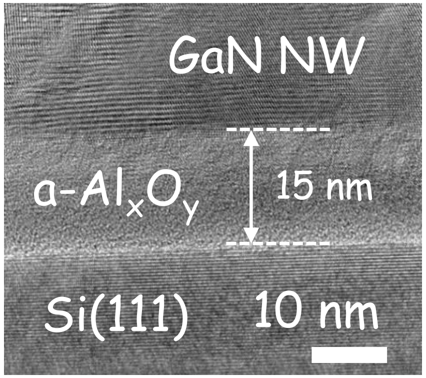


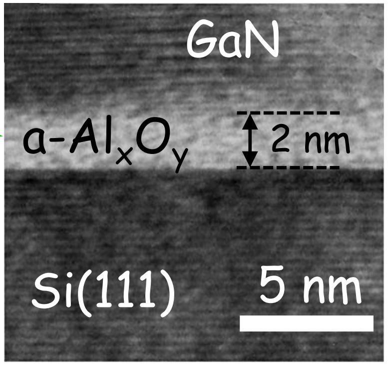
NWs always perpendicular to the surface of Si
(as opposed to VLS-grown NWs)

amorphous layer between GaN and Si

TEM





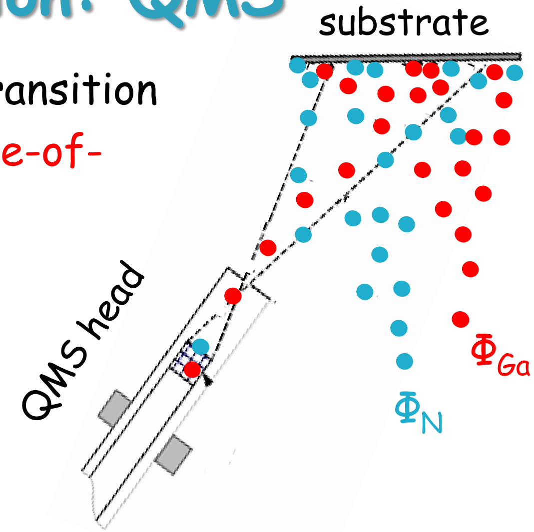


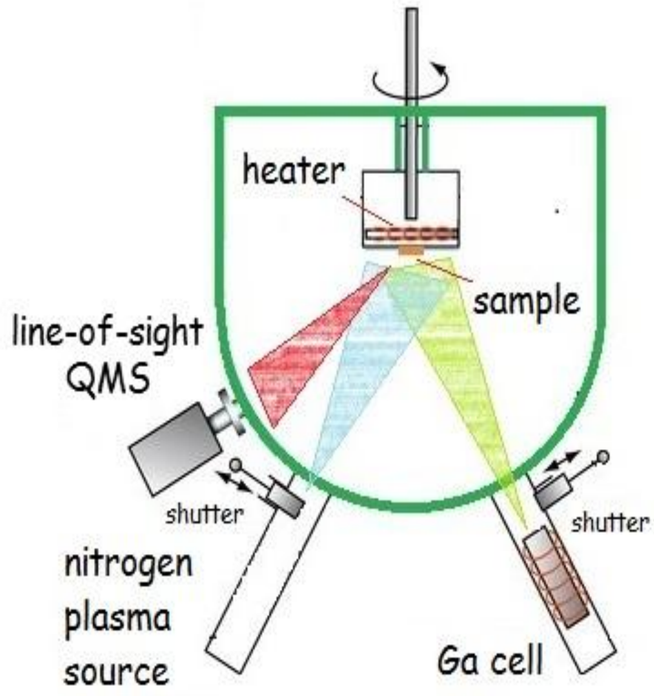
NW growth on Si ≡ NW growth on amorphous layer

A. Wierzbicka et al. Nanotechnology 24 (2013) 035703
M. Sobanska et al. J. Cryst. Growth 401 (2014) 657-660

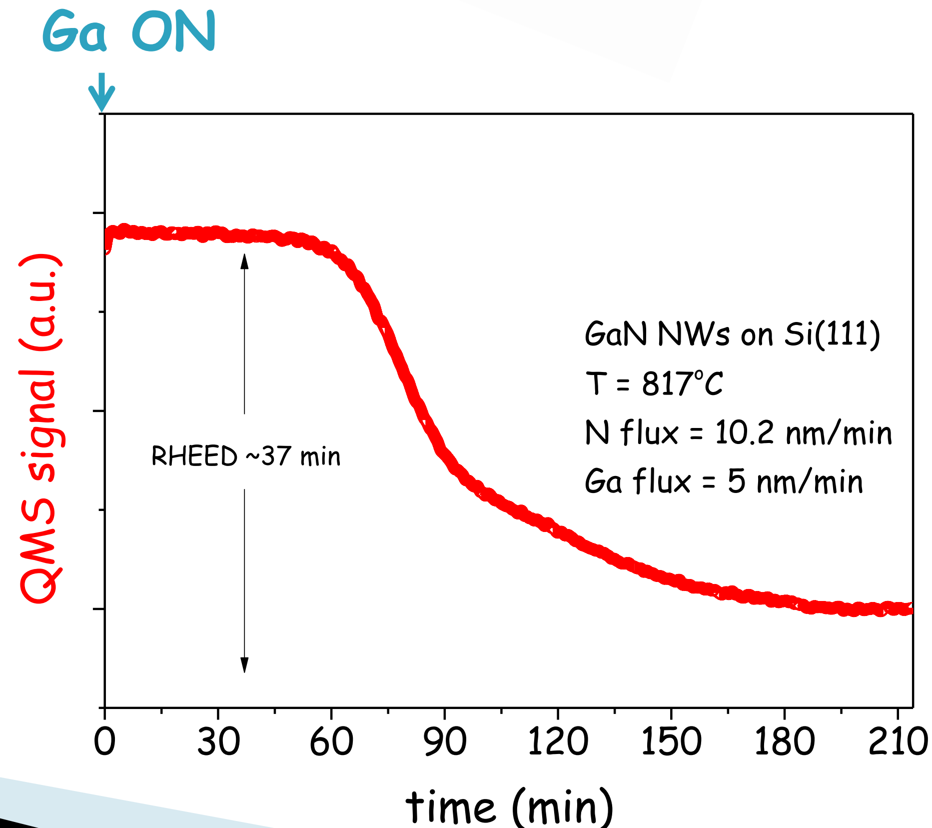
in-situ monitoring of NWs formation: QMS

- RHEED – useful for observation 2D → 3D growth transition
- a way to quantify amount of material deposited – line-of-sight quadrupole mass spectroscopy (QMS)





QMS calibrated for Ga signal installed in one of the source ports



in-situ monitoring of NWs formation: QMS

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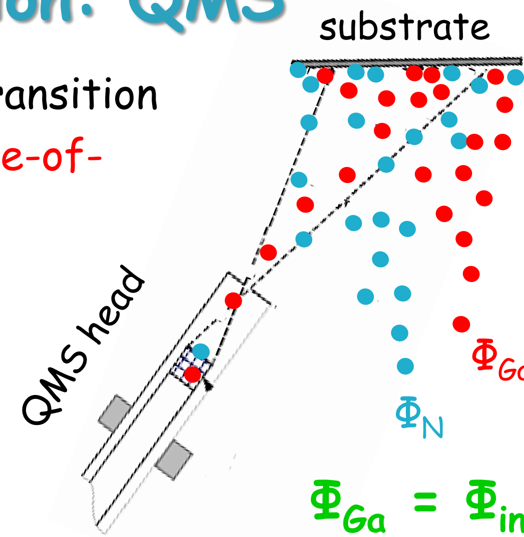
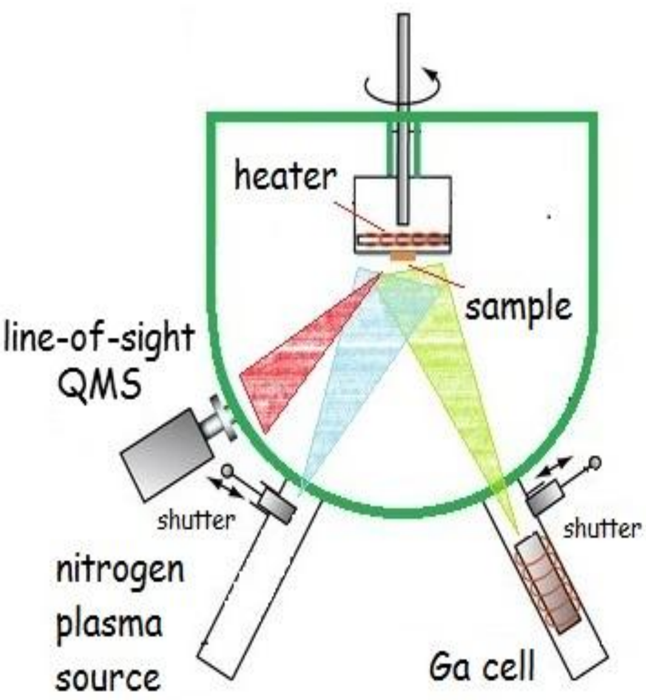


$$\Phi_{Ga} = \Phi_{incor} + \Phi_{des}$$

$$\Phi_{QMS} \sim \Phi_{des}$$



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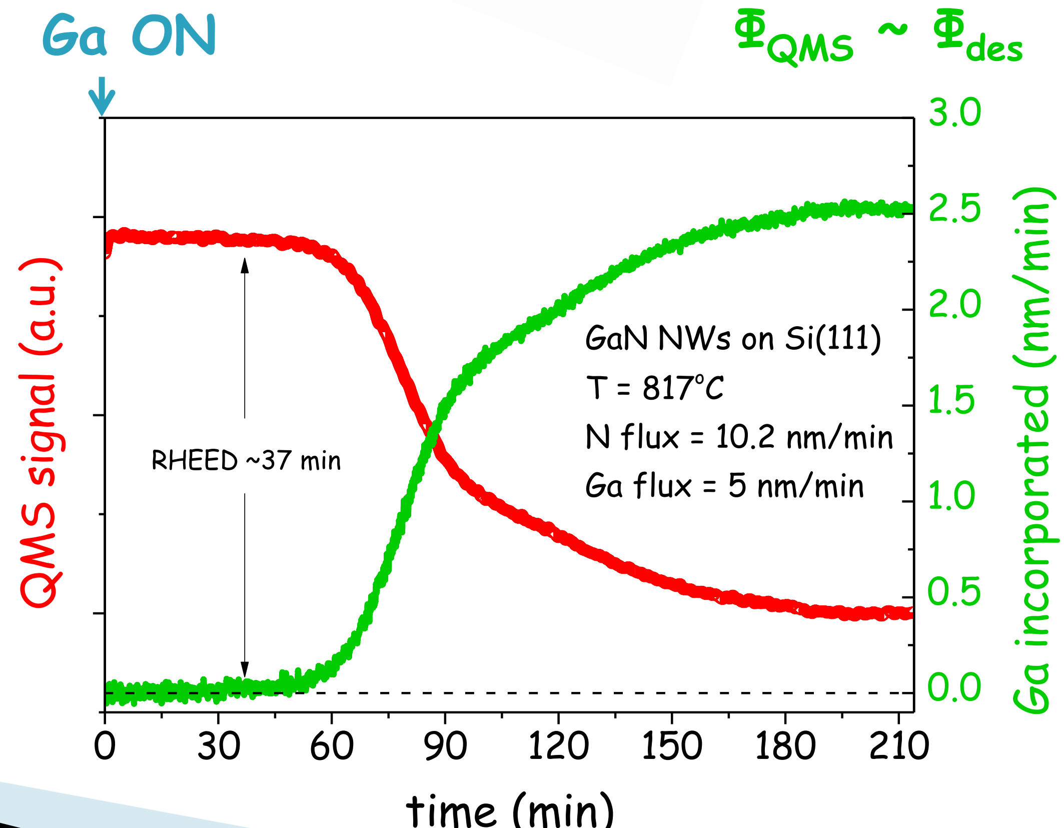
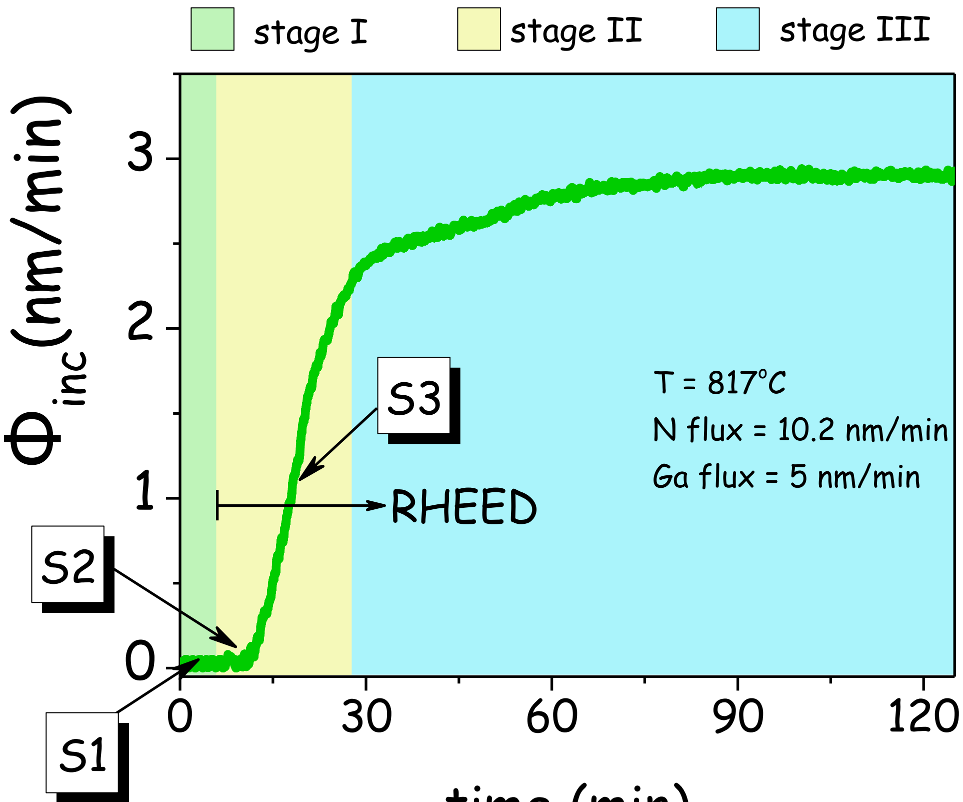
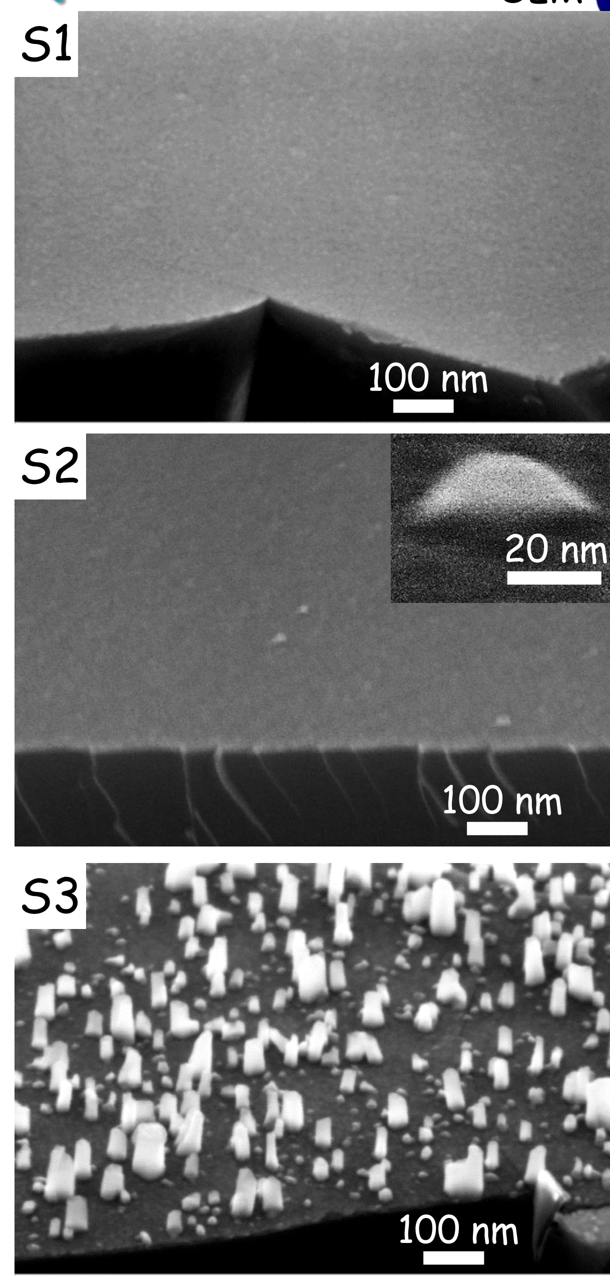


in-situ monitoring of NWs formation: QMS



SEM



stage I: incubation period (no stable nuclei formed)

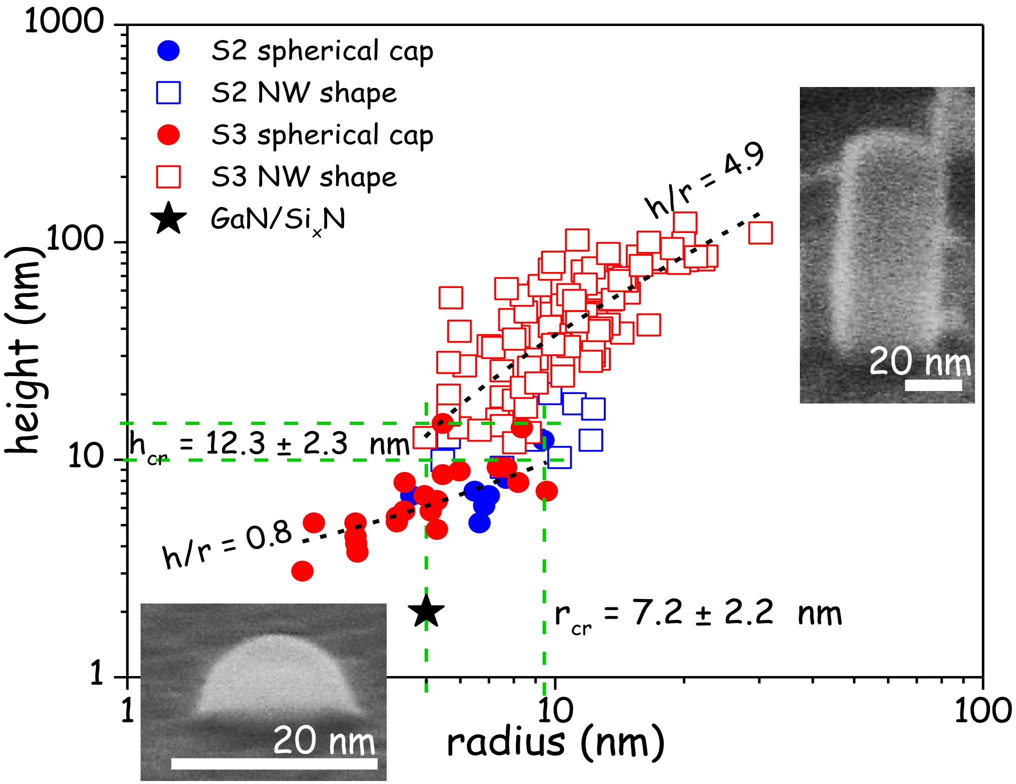
stage II: nucleation of GaN (creation of supercritical nuclei); density of stable nuclei increases

stage III: axial growth of NWs; density of NWs saturates; cooperative effects (exchange of Ga between neighboring NWs) lead to uniform lengths of NWs

M. Sobanska et al. Nanotechnology 27 (2016) 325601

Transition from spherical cap to NW shape

M. Sobanska et al. Nanotechnology 27 (2016) 325601



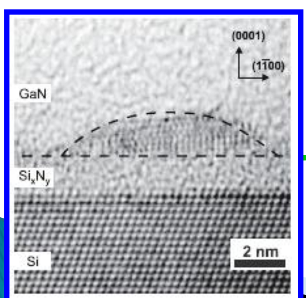
GaN NWs on a-Al_xO_y

critical size of shape change on a-Al_xO_y:

r = 7.2±2.2 nm

h = 12.3±2.3 nm

larger critical size for shape transition on a-Al_xO_y that on Si



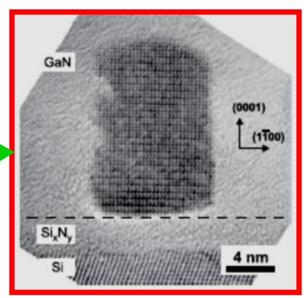
spherical cap

shape change

critical size:

r = 5 nm

h = 2 nm



NW shape

GaN NWs on nitridated Si

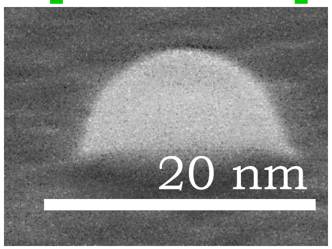
anisotropy of surface energy is the driving force for shape transition

V. Consonni et al. PRB 83 (2011)

GaN NWs: non-crystalline vs. crystalline substrate

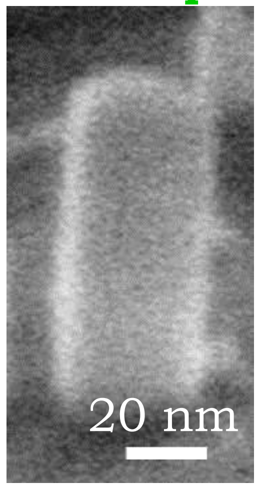
on a-Al_xO_y/Si

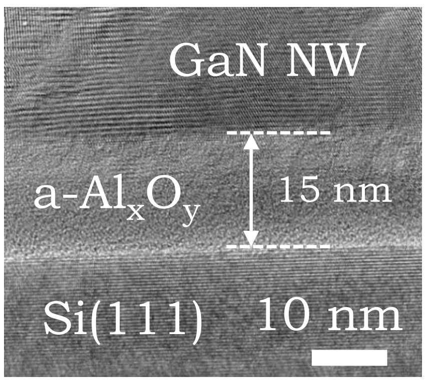
spherical cap



shape change

NW shape





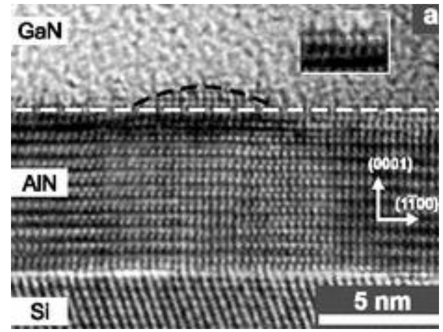
GaN weakly bonded to the substrate
(very weak epitaxial constraints)

on AlN/Si

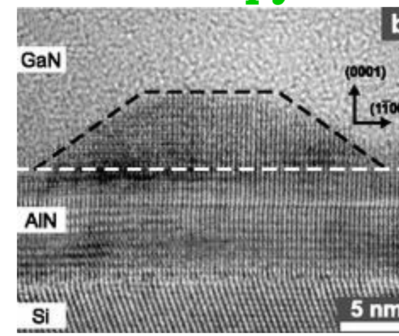
V. Consonni et al. PRB 81 (2010)

shape change

cap-shape island

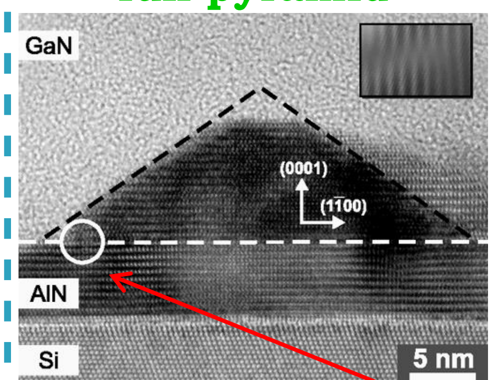


truncated pyramid

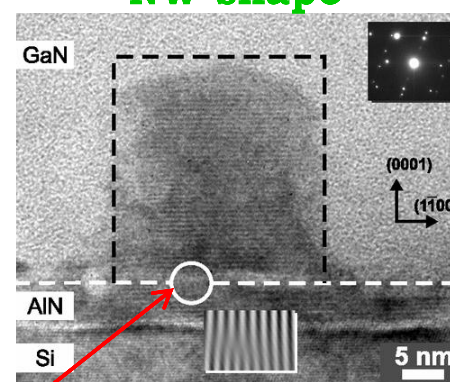


dislocation generation + shape change

full pyramid



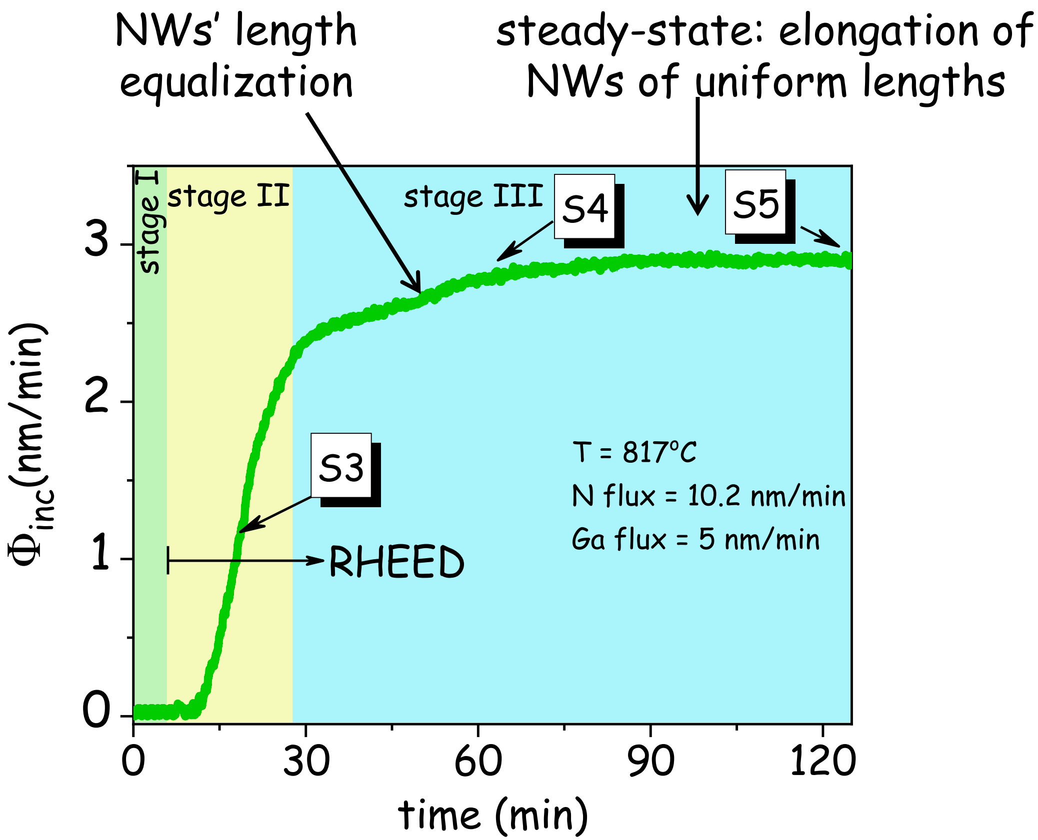
NW shape



misfit dislocation

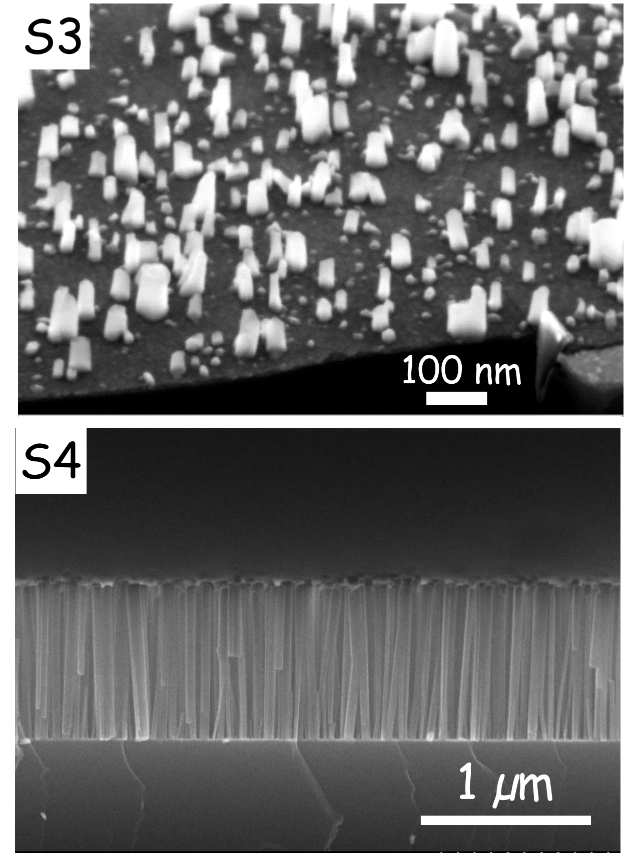
GaN strongly bonded to the substrate
(strong epitaxial constraints)

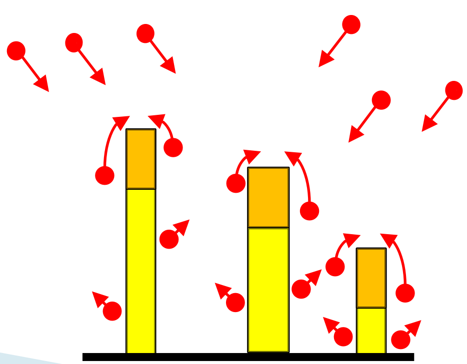
in-situ monitoring of NWs formation: QMS



stage III

elongation period; density of NWs saturates; collective phenomena



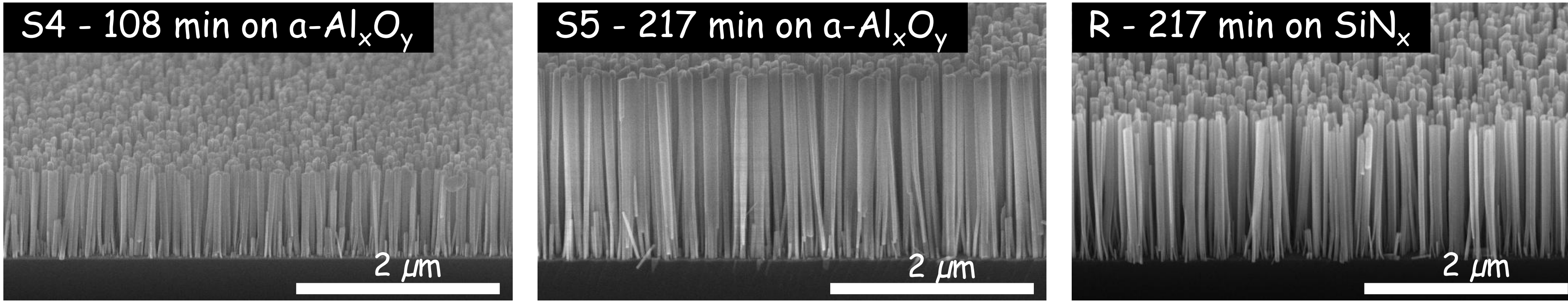


collective effects: exchange of Ga between NWs (desorption from sidewalls of longer NWs, capture by shorter ones) leading to uniform lengths of NWs

Sabelfeld et al. APL 103 (2013) 133105

Growth of GaN NWs: N- or Ga-limited?

growth parameters: Φ_N = 10.2 nm/min; Φ_{Ga} = 5.0 nm/min

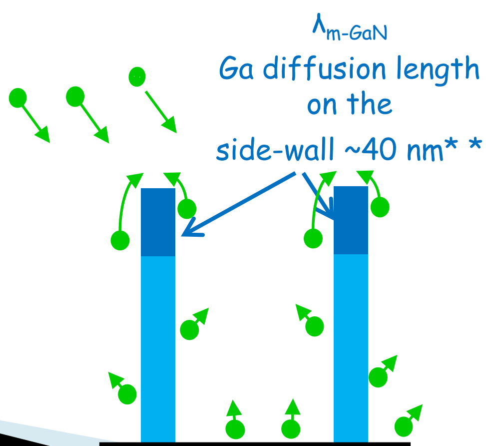


V_{gr} ~ 10.5±0.5 nm/min | V_{gr} ~ 10.3±0.5 nm/min | V_{gr} ~ 10.7±0.5 nm/min

→ growth rate limited by N flux

→ the same conclusion reported for GaN NWs grown on Si(111)*

*S. Fernández-Garrido, et al. Nano Lett. 15 (2015) 1930



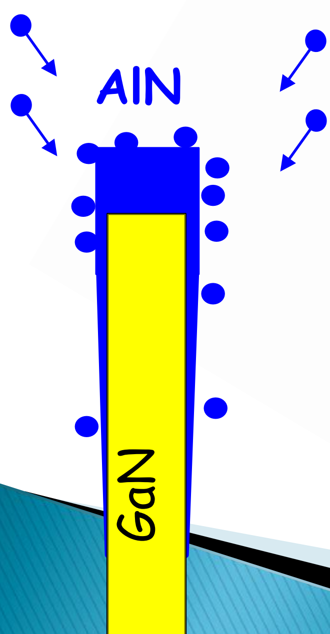
* * L. Galopin et al. Nanotechnology 22 (2011) 245606

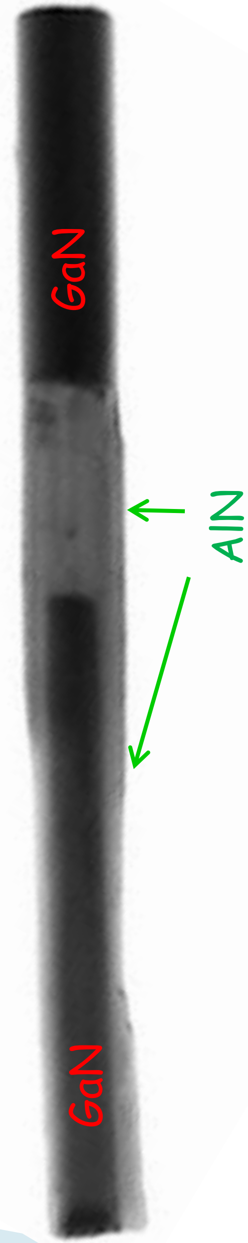
- Ga adatoms being closer to the NW top than their diffusion length $\lambda_{m\text{-}GaN}$ contribute to the axial growth
- locally Ga-rich conditions may be created at the NW top facet despite overall N-rich conditions
- at this stage diffusive Ga flux from the substrate not important

M. Sobanska et al. Nanotechnology 27 (2016) 325601

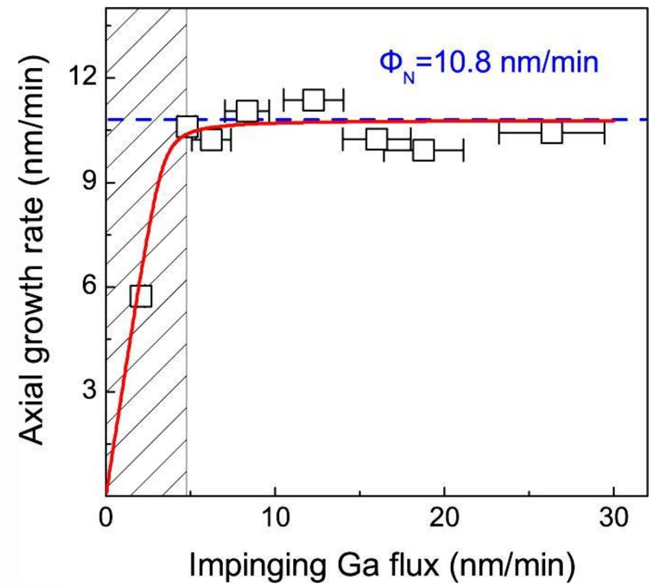
PAMBE growth of GaN NWs: N- or Ga-rich?

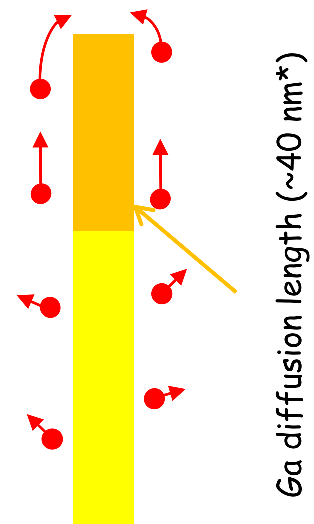
- Al much less mobile
- core-shell structures (AlN covers GaN, but NO GaN shell on AlN)





Fernandez-Garrido et al. Nano Lett 13 (2013) 3274





- overall N-rich conditions
- locally (at the NW top facet) Ga-rich conditions due to diffusion of Ga along the NW sidewalls

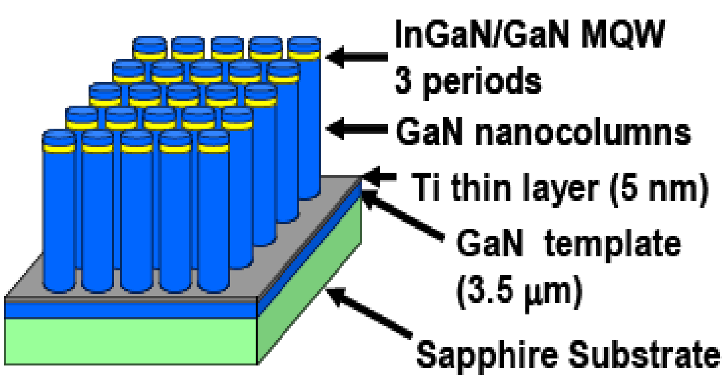
Selective area growth (SAG) of GaN NWs

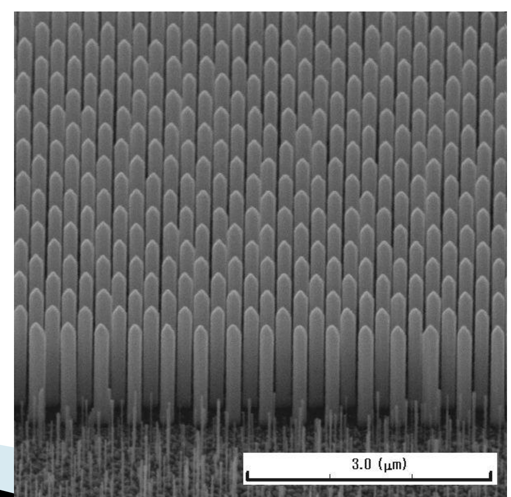
disadvantages of self-assembled NW growth:

1. control of NW density difficult
   - easier in VLS growth mode if positions of Au (or Ga) droplets from which NW grow can be ordered
2. random positions of the NWs on the substrate (due to a random nature of the nucleation process)

in SAG:

- masked substrate with a pattern created (by lithography and etching) to open the mask-free areas with exposed nucleation layer
- growth conditions needed to nucleate NWs in the openings in the mask, while nucleation on the mask surface is prohibited
- proper choice of substrate and mask material needed

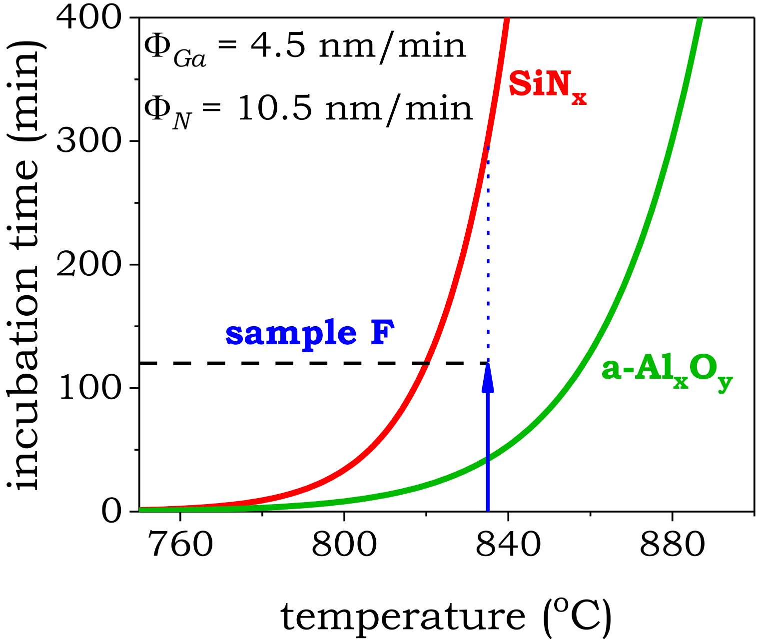




H. Sekiguchi et al., IWNS 2008 Montreux, Switzerland

How to adjust the growth conditions for SAG?

study nucleation kinetics of NWs on various materials to find the best suitable mask/substrate pair



on a-Al_xO_y/Si

T_{gr} = 835°C

t_{inc} = 42 min

on SiN_x/Si

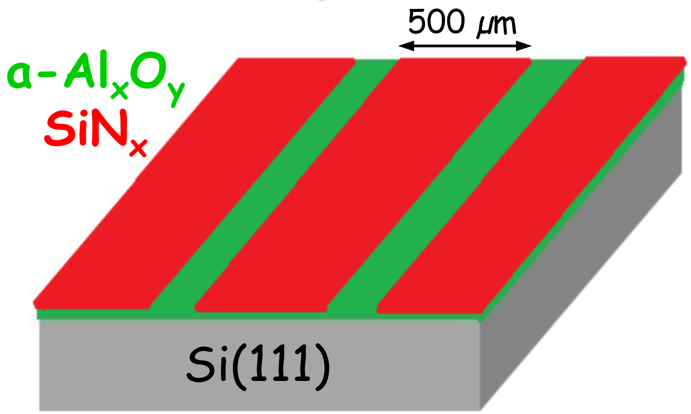
T_{gr} = 835°C

t_{inc} = 295 min

→ much more efficient nucleation of GaN NWs on a-Al_xO_y than on SiN_x

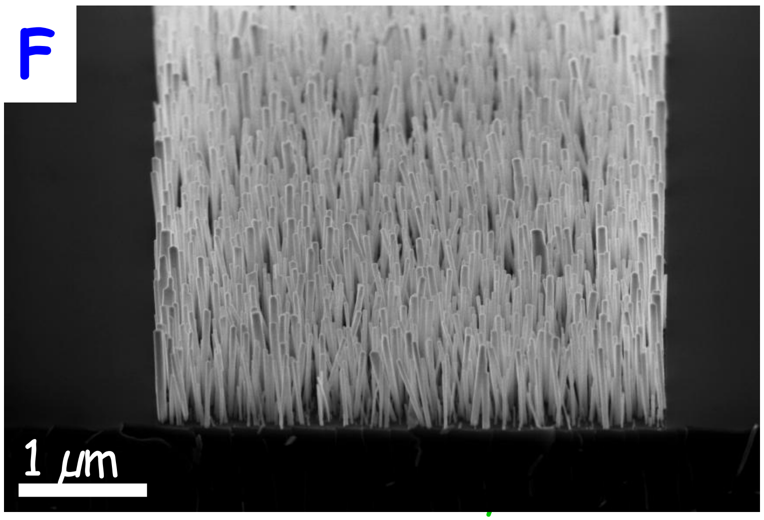
M. Sobanska, et al. Cryst. Growth Des. 16 (2016) 7205–7211

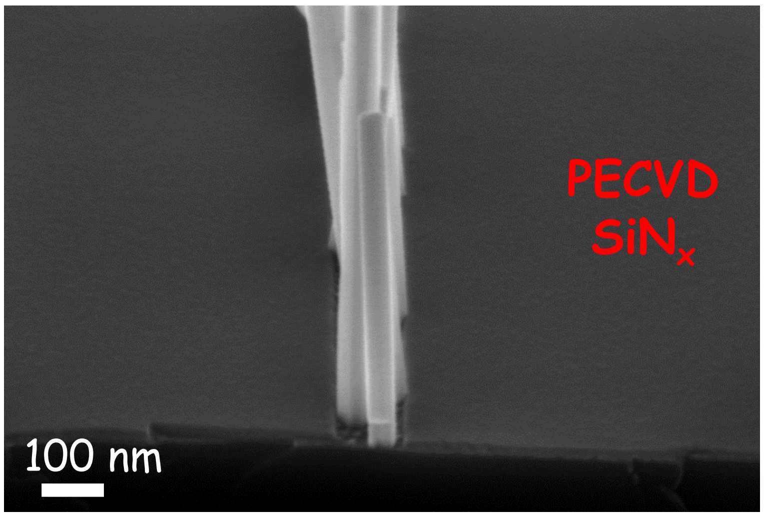
Growth of GaN on Si with SiN_x mask and a-Al_xO_y stripes



- Si substrates covered by 15 nm thick a-Al_xO_y film deposited at low temperature by ALD
- ~15 nm thick SiN_x deposited by PECVD @ T = 300°C
- e-beam lithography + RIE etching to open windows in the SiN_x mask

T_{gr} = 835°C; t_{gr} = 120 min





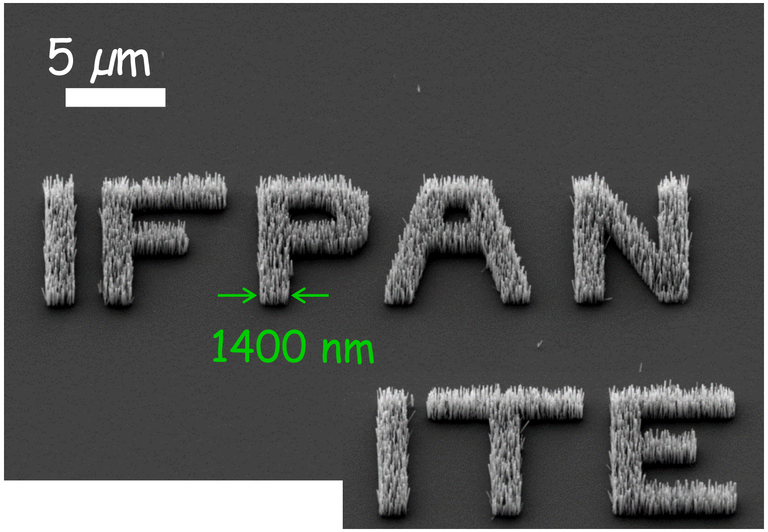
pure Selective Area Growth in the SiN_x/a-Al_xO_y system

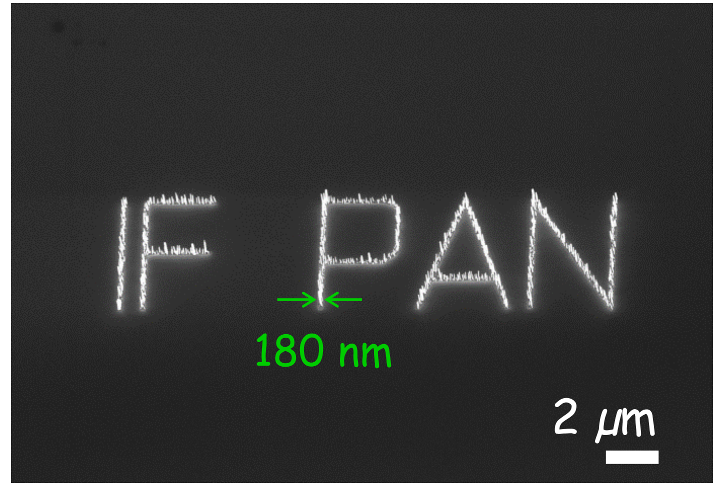
- GaN NWs formed selectively on a-Al_xO_y stripes
- no GaN nucleation on SiN_x

M. Sobanska, et al. Cryst. Growth Des. 20 (2020) 4770–4778

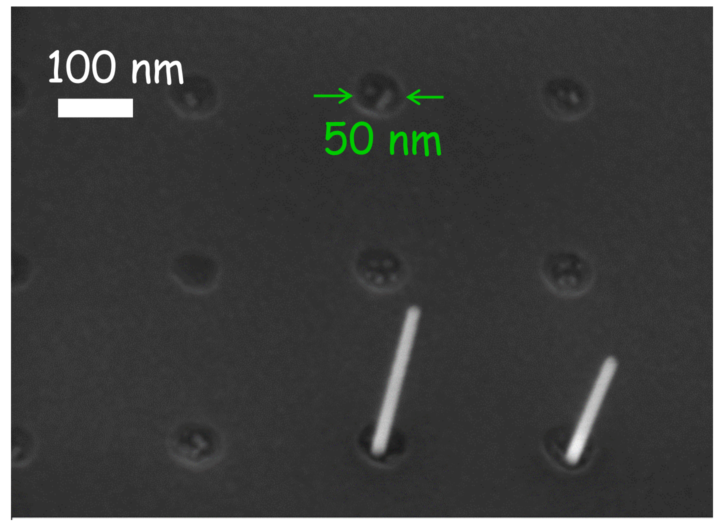
Some results of GaN NW SAG growth experiments

SEM



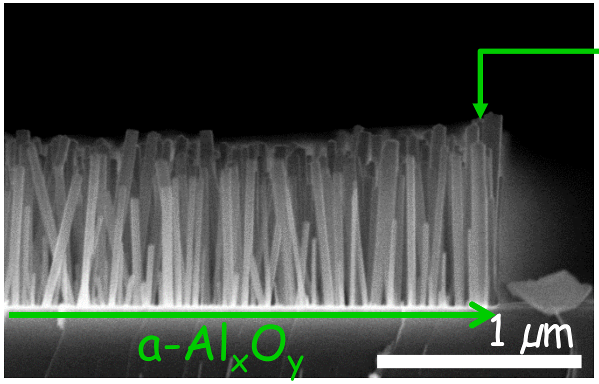


CL @ RT (A. Pieniążek)

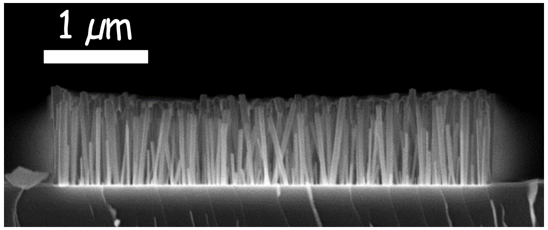


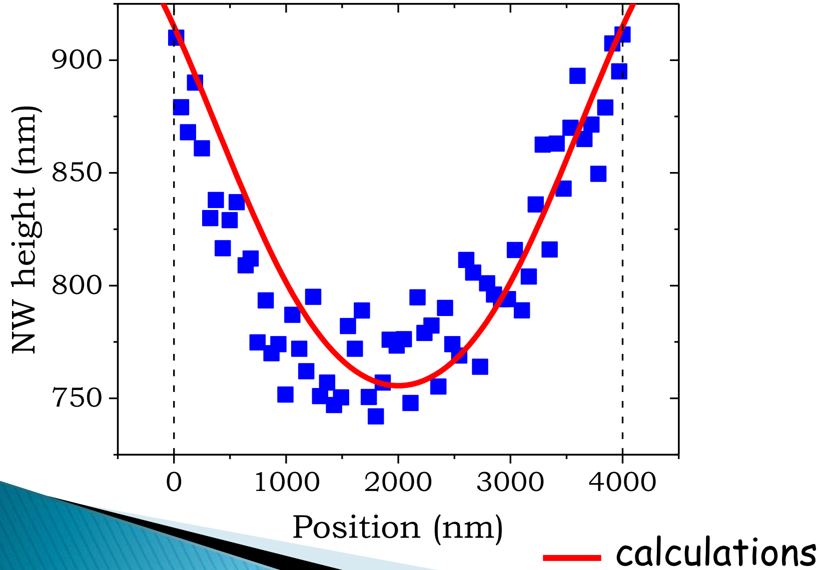
- yield on e-beam processed substrate still too low
- processing of the substrates by e-beam lithography and RIE etching must be improved

... and edge growth in SAG



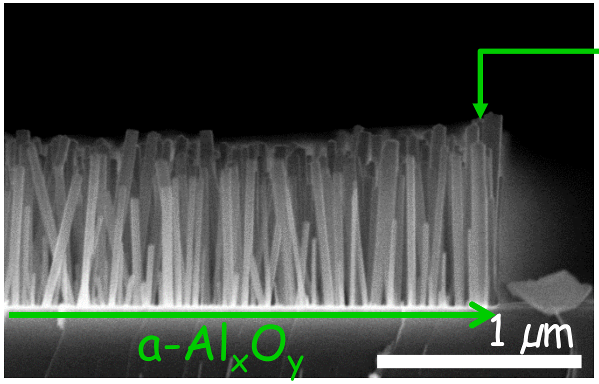
longer GaN NWs close to the edge of the stripe



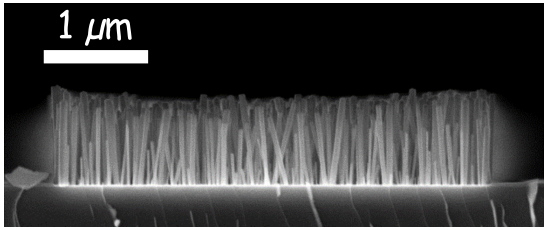


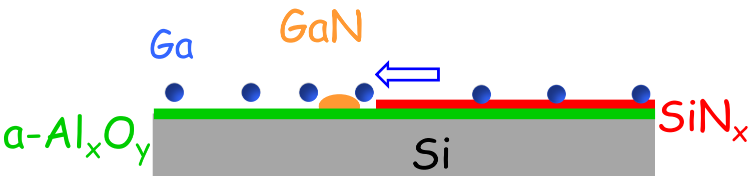
M. Sobanska, et al. Cryst. Growth Des. 20 (2020) 4770–4778

Surface Ga diffusion and edge growth in SAG

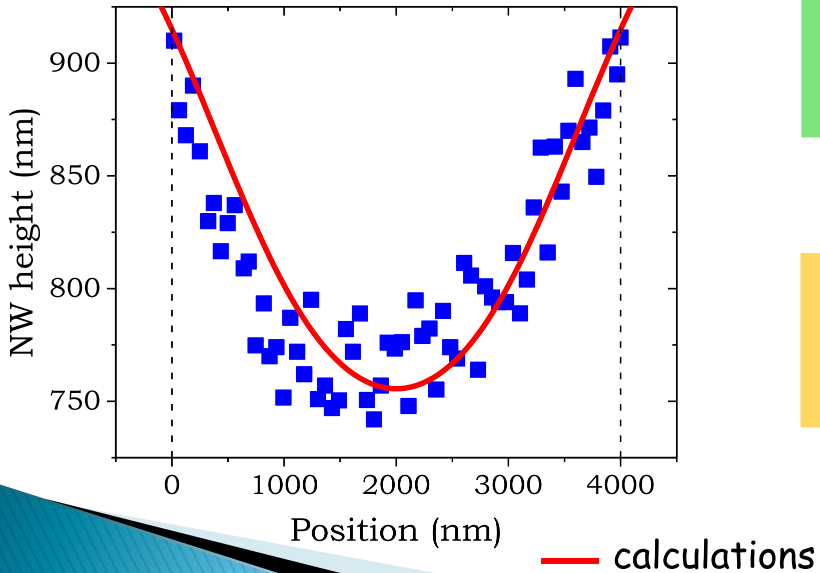


longer GaN NWs close to the edge of the stripe





Ga diffuses into the a-Al_xO_y stripe during NW nucleation period → faster GaN growth during nucleation stage → longer NWs close to the edge of the a-Al_xO_y stripe

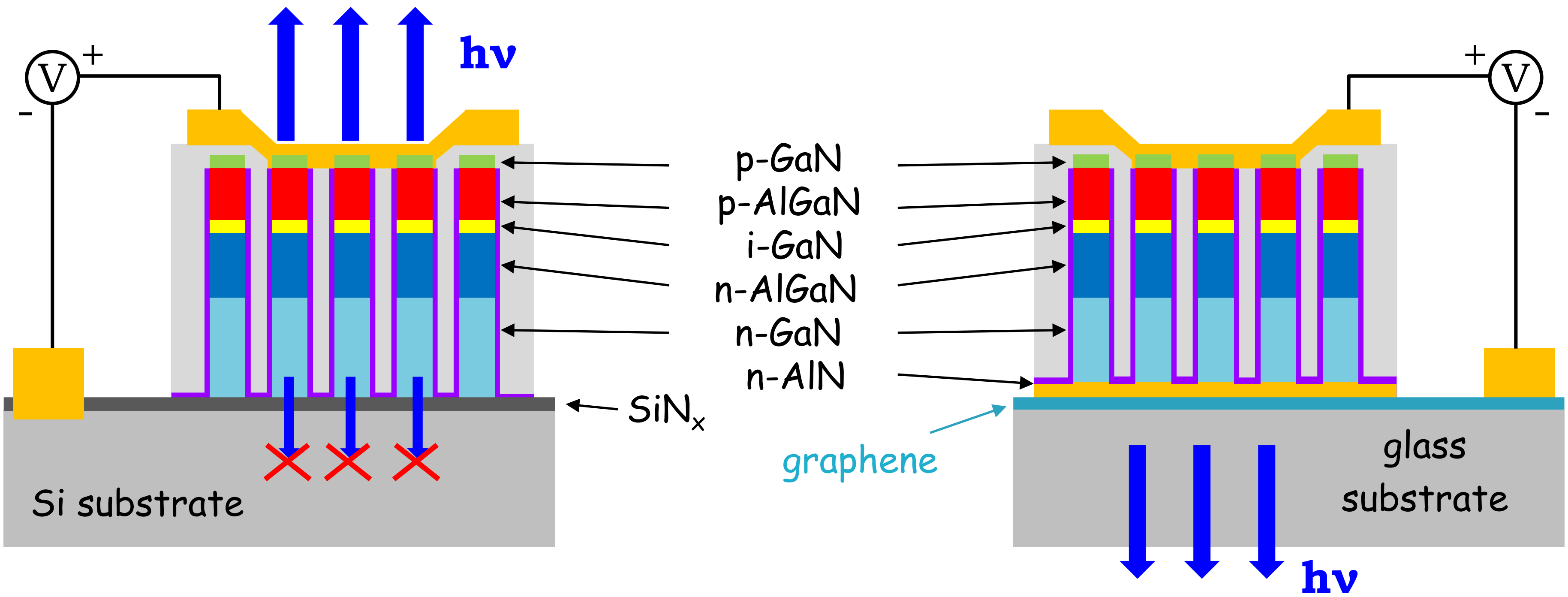


general comment: nucleation kinetics in SAG depends on the size of the substrate pattern due to significant surface diffusion of adatoms

M. Sobanska, et al. Cryst. Growth Des. 20 (2020) 4770–4778

NW LED design

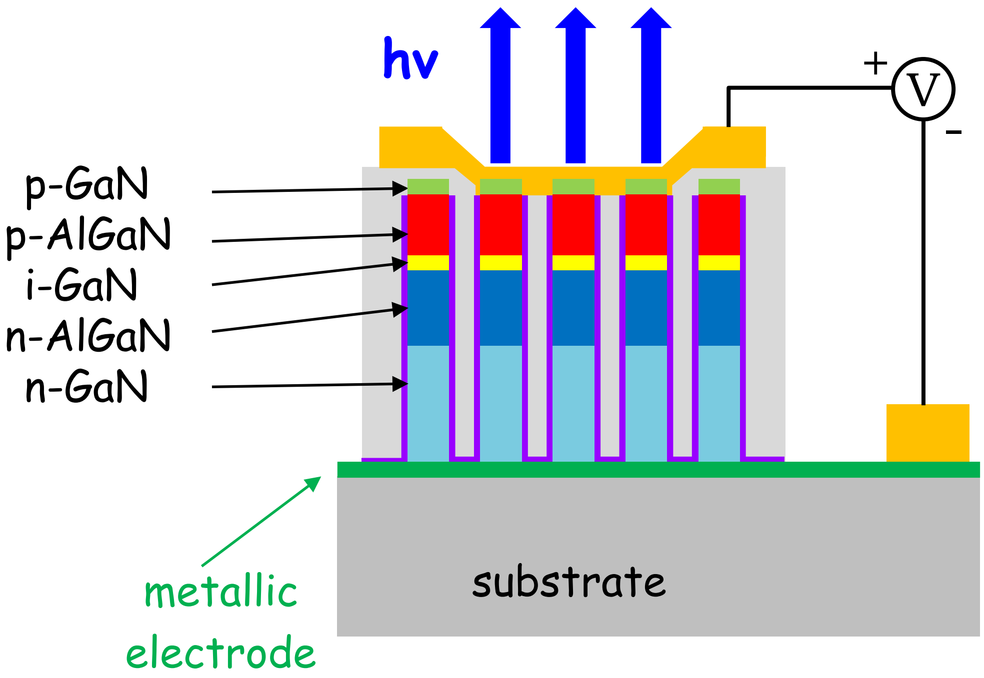
Hoiaas, et al. Nano Lett. (2019) 1649



- part of emitted light lost by absorption in the substrate
- nonlinear electrical GaN/SiN_x/Si junction

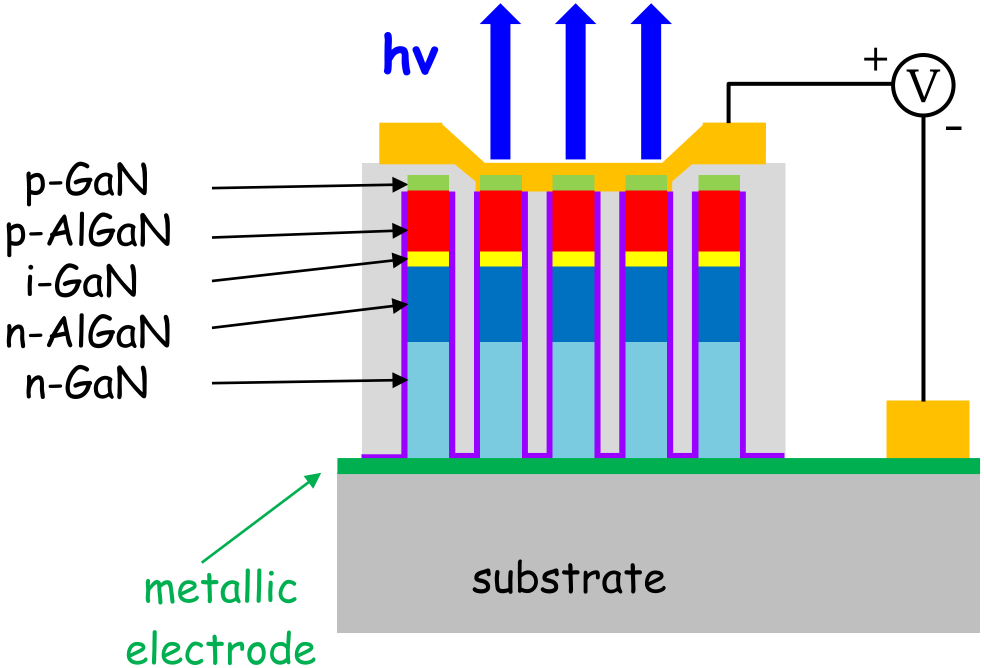
- graphene transfer from the host substrate complicated; small area - single cm^2
- nucleation on graphene very difficult
- AlN nucleation layer needed – high series resistance

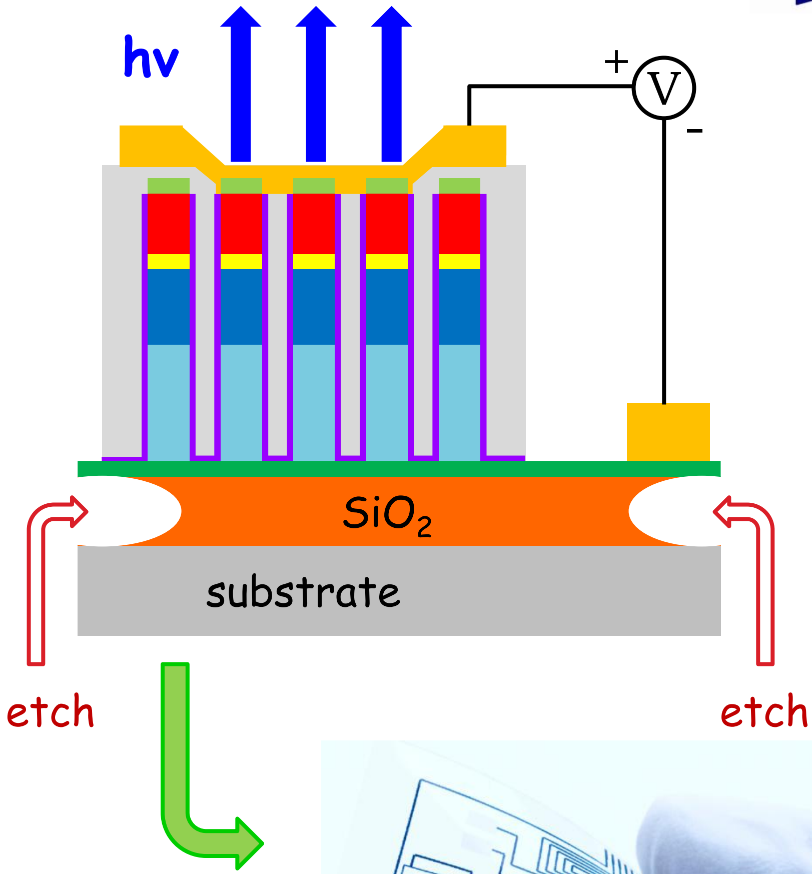
NW LED with bottom electrode



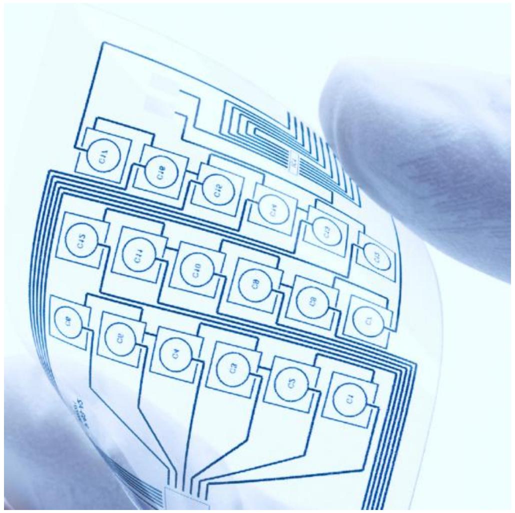
- high electrical conductivity and ohmic contact to GaN required
- high optical reflectivity desirable
- stable at MBE growth conditions
- pure metals (W, Mo, Ti, …) react with Ga
- ZrN, TiN, …

NW LED with bottom electrode – flexible electronics

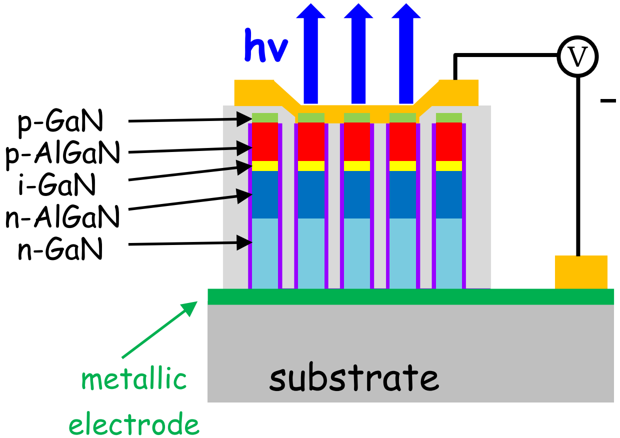


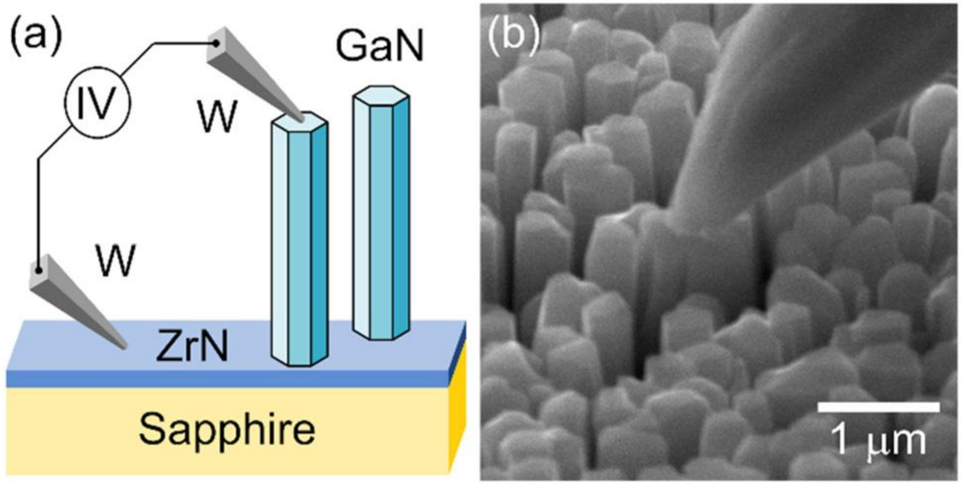


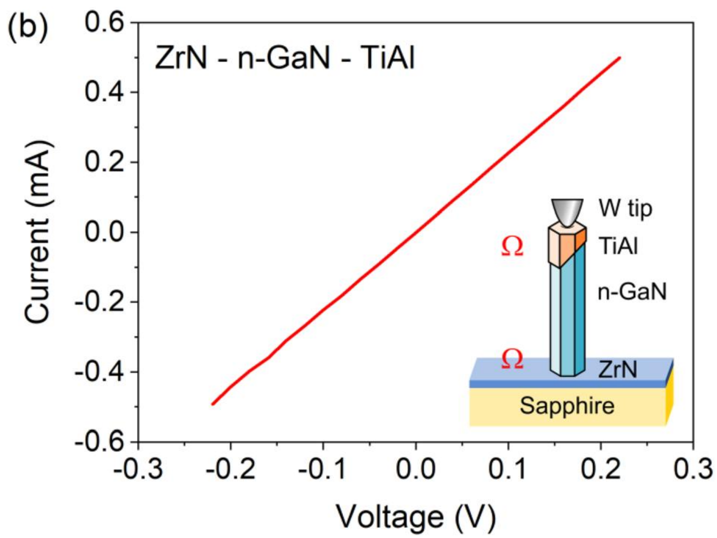
- high electrical conductivity and ohmic contact to GaN required
- high optical reflectivity desirable
- stable at MBE growth conditions
- …

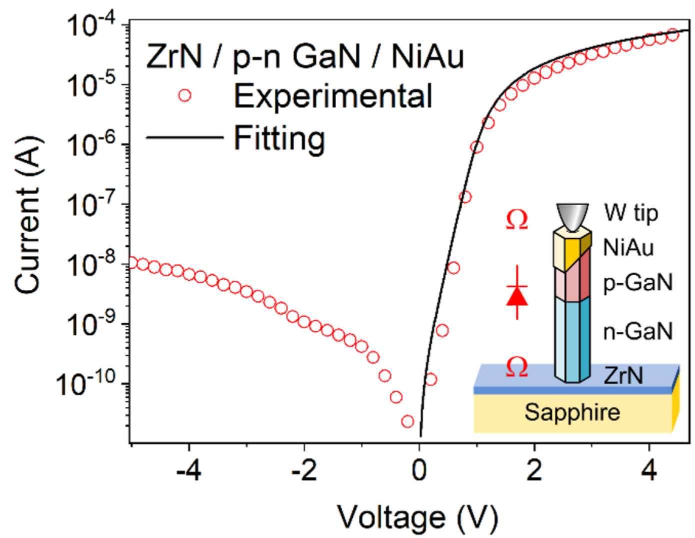

buhlergroup.com

NW LED with bottom electrode









S. Tiagulsky, et al. Nanoscale 2025

Conclusion

***in-situ* observation of the growth interface is crucial for understanding the growth processes and finding efficient ways of their control**

Many thanks to my co-workers

dr hab. Marta Sobańska

dr Ola Wierzbicka

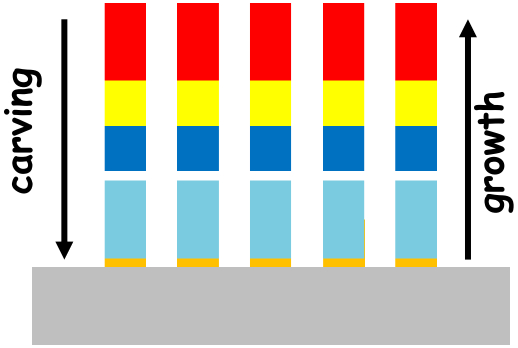
mgr Kamil Kłosek

mgr Karol Olszewski

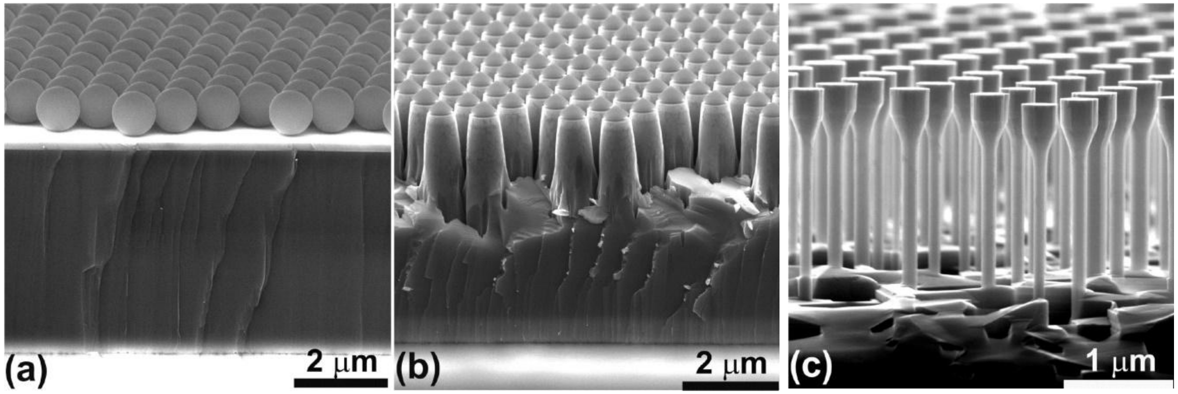
mgr Giorgi Tchutchulashvili

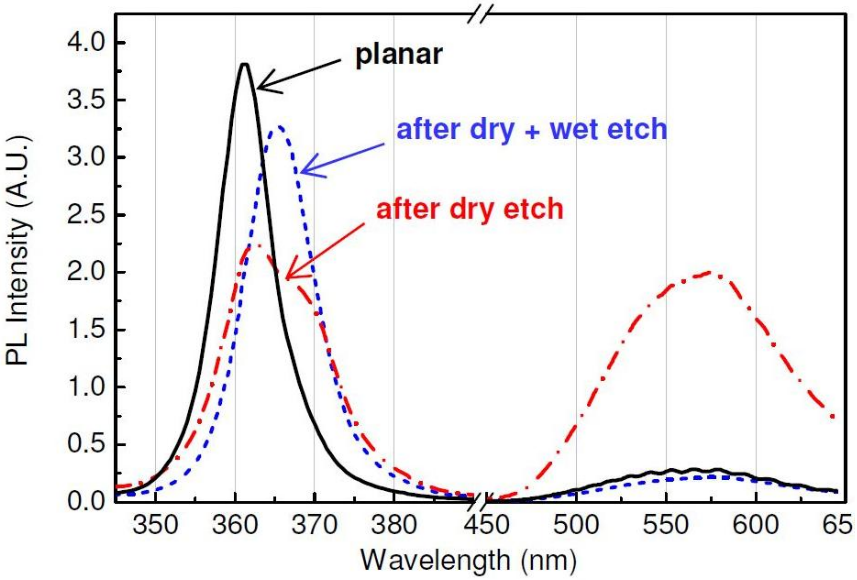
and many others …

Top-down or bottom-up (growth) ?



Q. Li, et al. Optics Expr. 19 (2011)



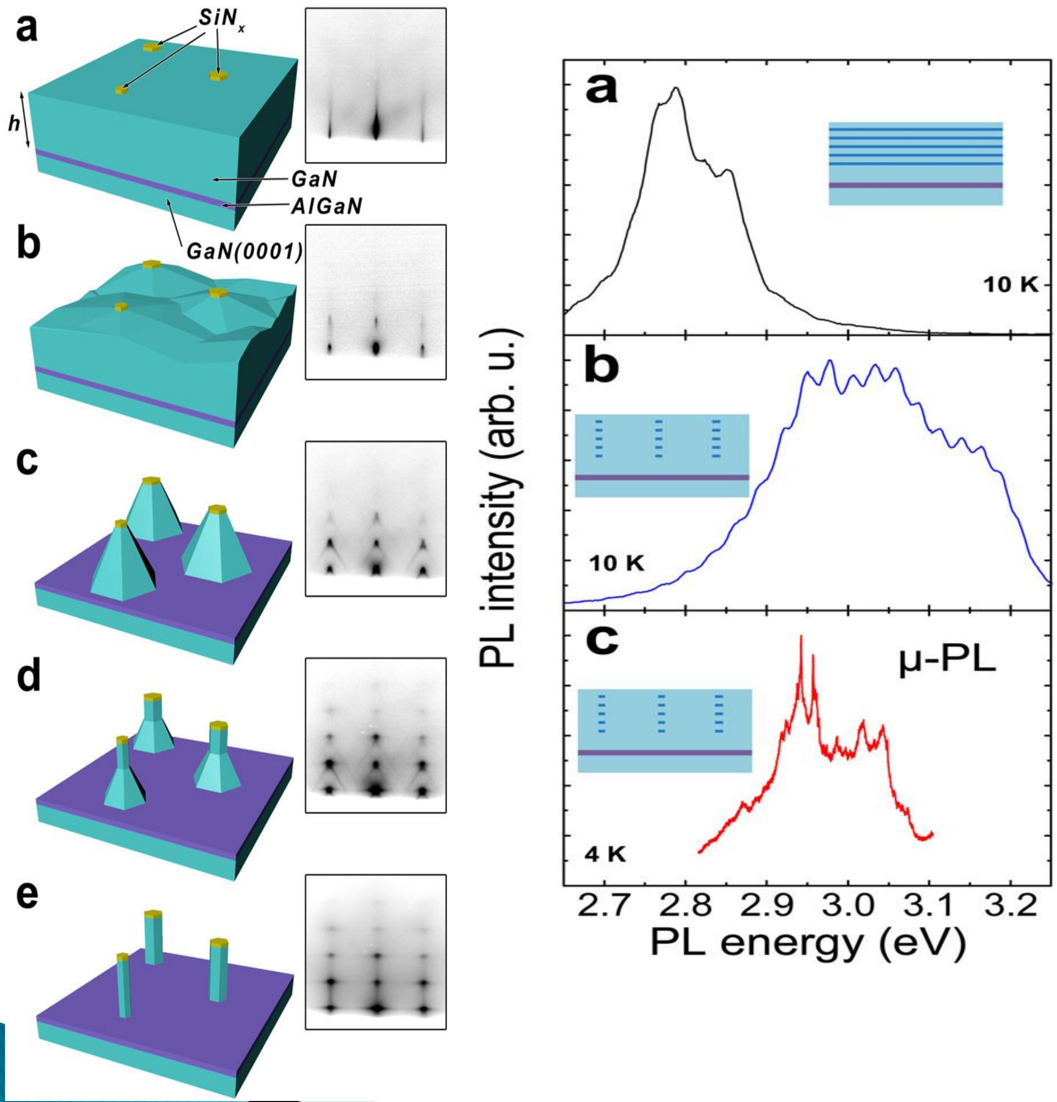


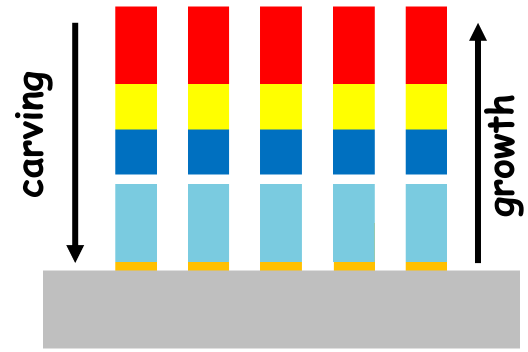
1. planar epitaxial growth of p-GaN/n-GaN
2. 1 µm diameter silica spheres mask
3. plasma etching (b)
4. very long wet etching in KOH-based solution

- significant damage after RIE (strong YL luminescence)
- PL redshift due to strain release
- wet etching rate dependent on composition

Top-down or bottom-up (growth) ?

B. Damiliano, et al. Nano Lett. 16 (2016) 1863





1. planar epitaxial growth of GaN/InGaN
2. SiN mask deposition (in-situ)
3. Selective Area Sublimation @ 900°C (b - e)

- high-quality planar growth still required
- In–Ga interdiffusion during the SAS process
- role of threading dislocations ? only a few % of NWs with TDs (geometrical factor)