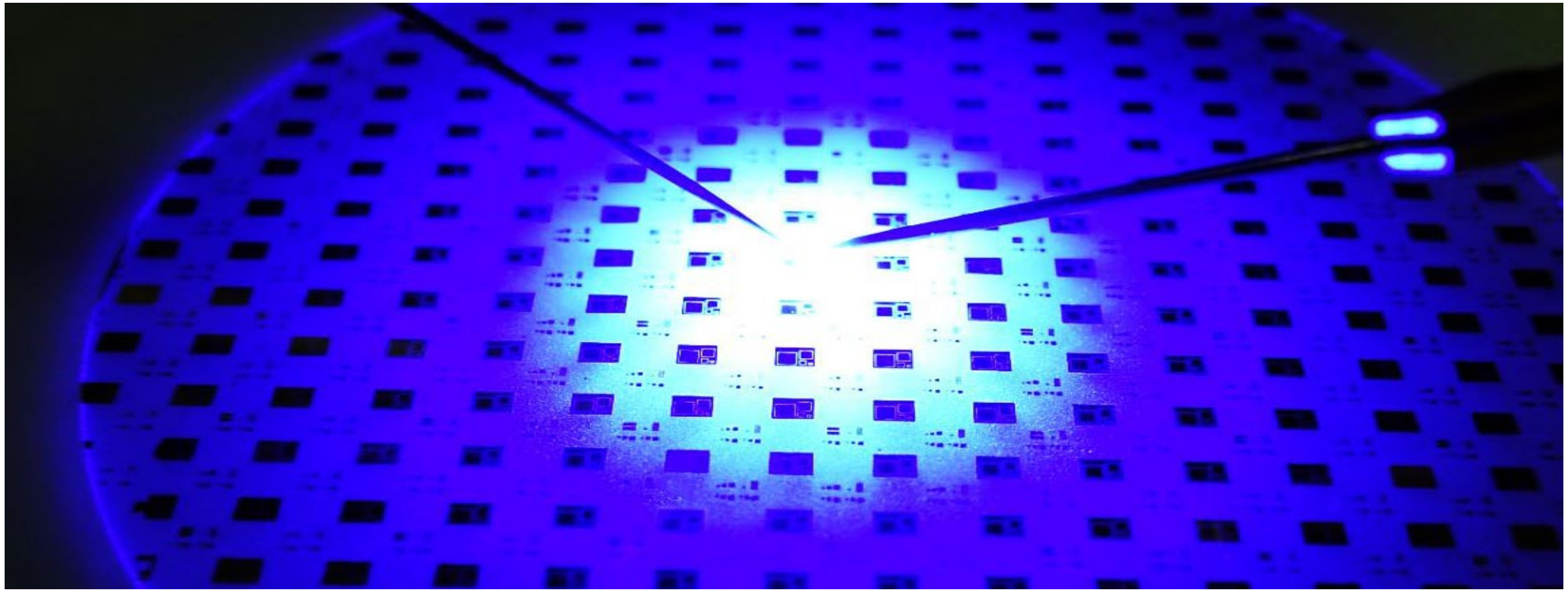
Advanced III-nitride semiconductor devices



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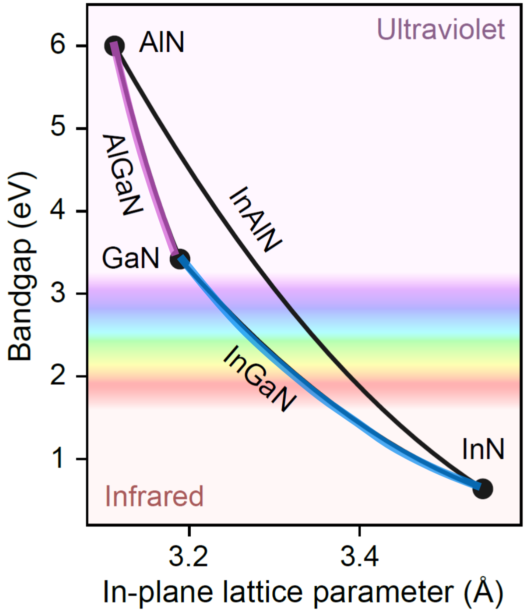
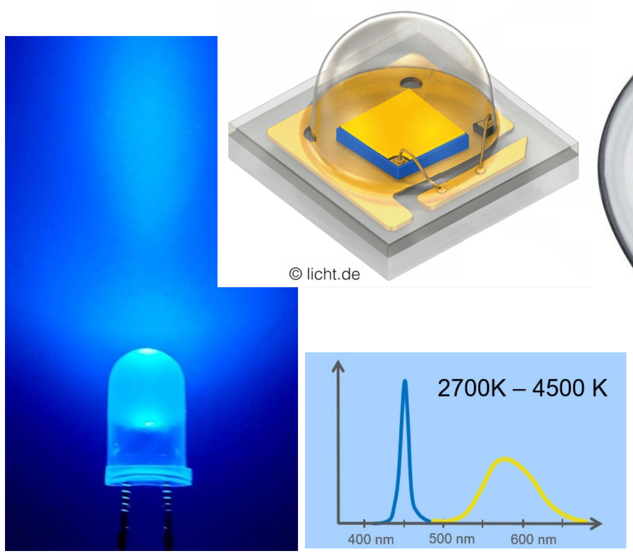
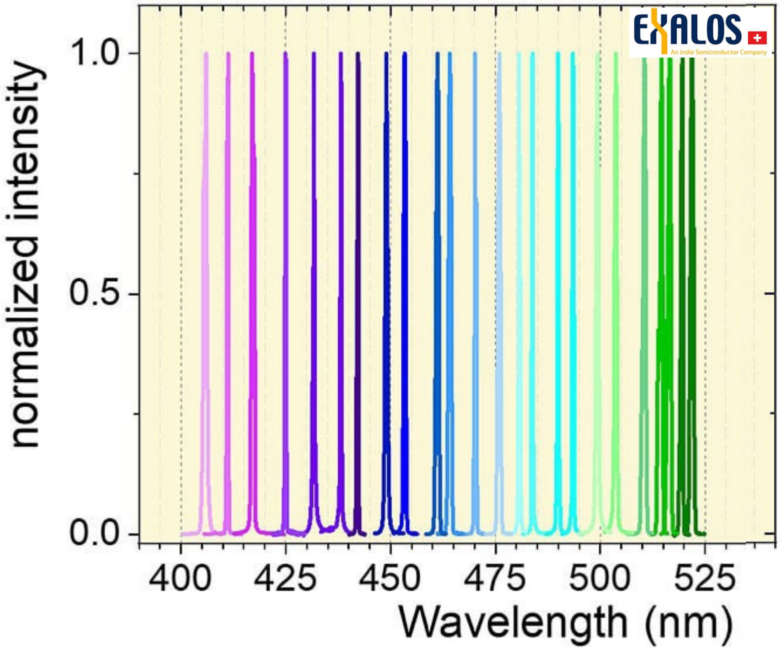
Introduction

▪ Optoelectronics devices

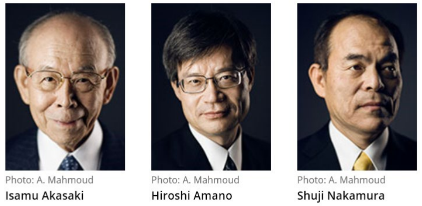






- High-efficiency blue LEDs (IQE>90%, WPE >80%)
- Outstanding luminous efficacy (>150 lm/W)
- Solid-state lighting : 70 billions of € in 2027

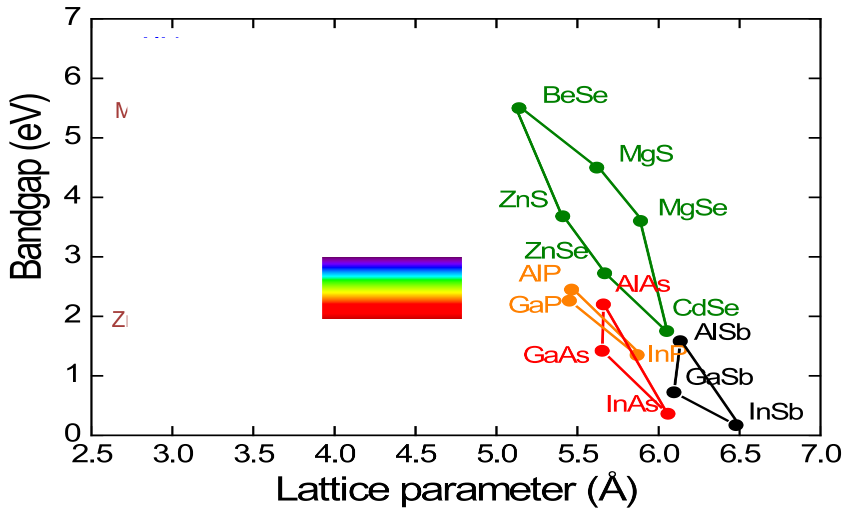
The Nobel Prize in Physics 2014



$$\text{WPE} = P_{out}/P_{in} = \text{EQE} \times \frac{h\nu}{eV}$$

EPFL

Which semiconductors for blue emission?

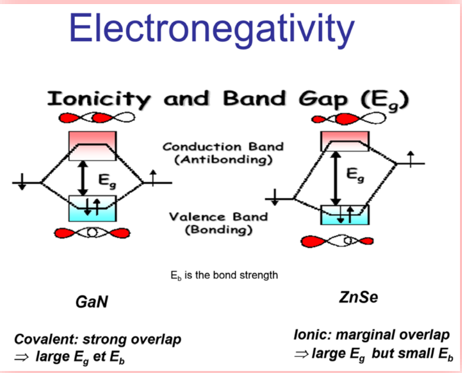


Wide bandgap semiconductors:

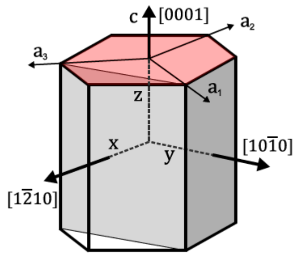
II-VI selenides (Zn,Mg,Cd)Se suffer from fast aging

III-V nitrides (Al,Ga,In)N

II-VI oxides (Zn,Cd,Mg)O no p-type conductivity



III-V nitride semiconductors



Wurtzite structure

A long list of drawbacks:

- Lack of GaN substrate
- Lattice mismatch between binaries
- Deep Mg acceptor (160 meV)

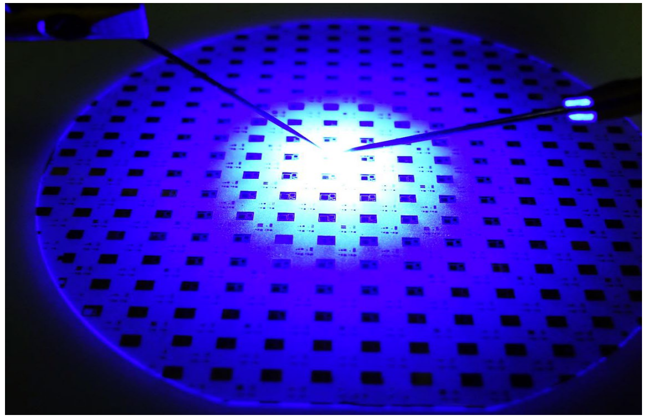
- The first studies date back to the 60s
- Revival in Japan in the 80s
- 1993: first high-brighneess blue LED

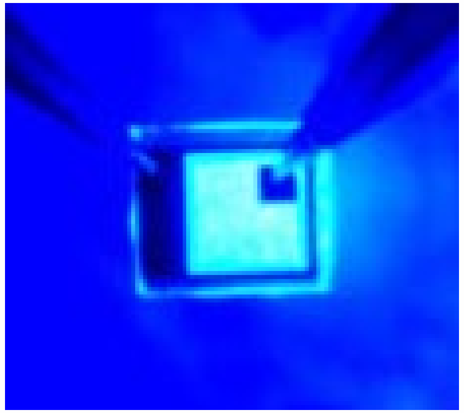
Nakamura *et al.*, Appl. Phys. Lett. 64, 1687 (1994)

GaN heteroepitaxy

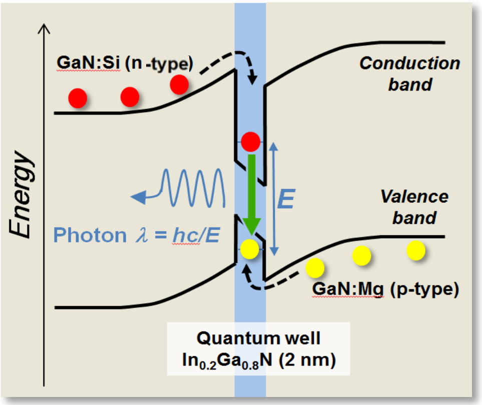
■ Main growth issues

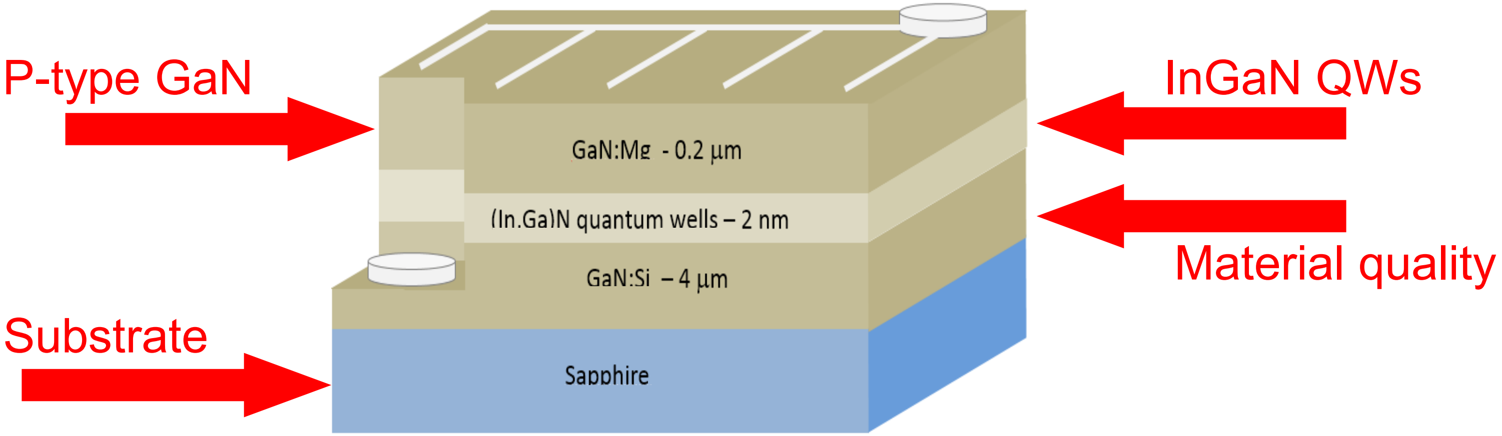
Wafer size:
50-150mm in diameter





Die size:
400x400 μm^2 to 2x2 mm^2





Epitaxial Growth:
How are these structures grown in practice ?

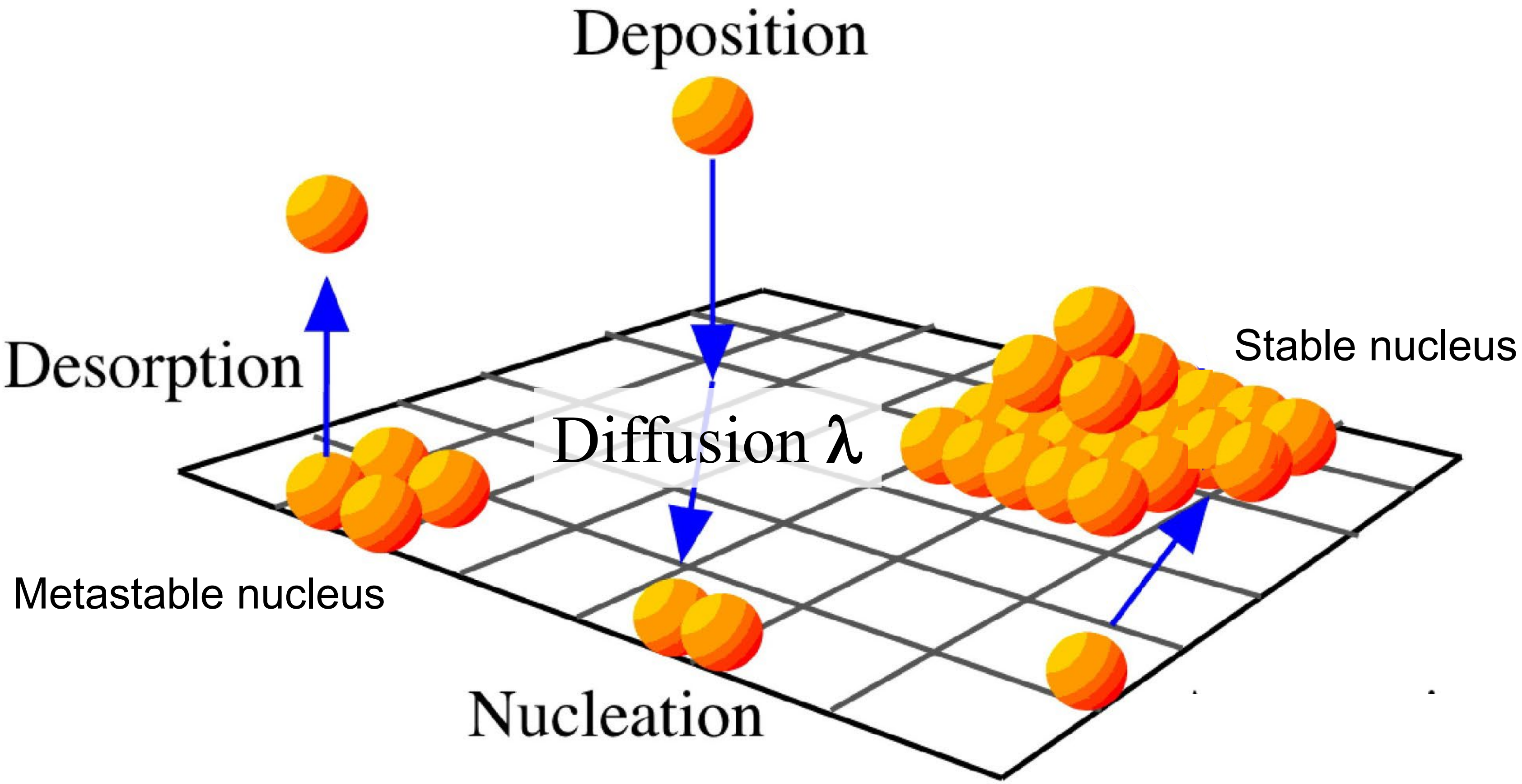
- Growth considerations and device performance

- Main growth techniques for III-nitrides (MOVPE, MBE)

- Growth of III-nitride structures

- Advanced topics relevant to epitaxy

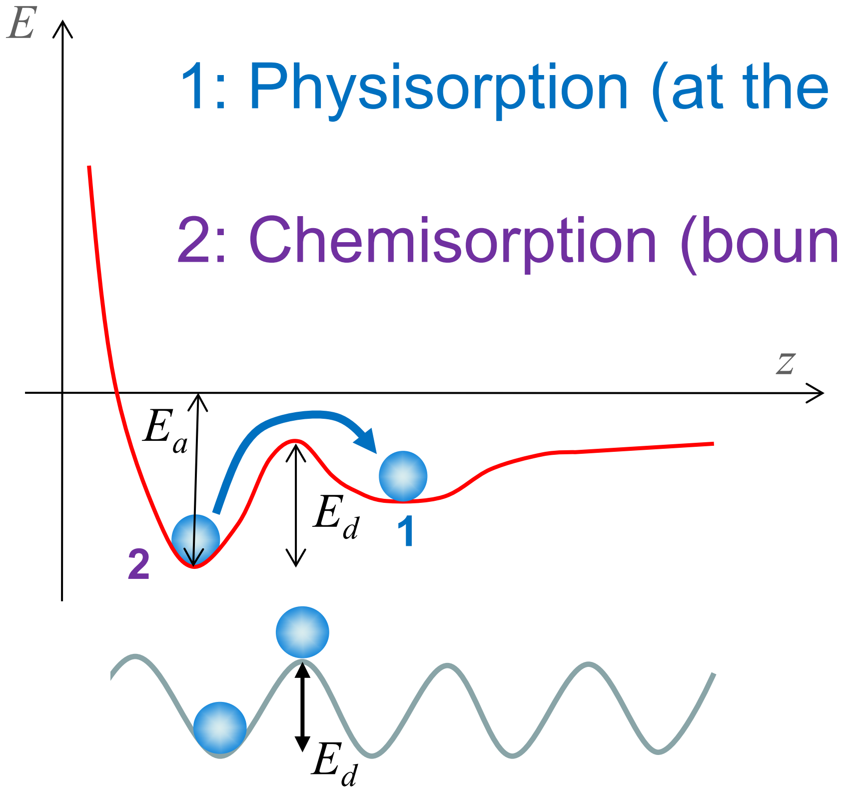
Growth starts with nucleation



λ is the diffusion length

EPFL

Surface diffusion length



1: Physisorption (at the surface)

2: Chemisorption (bound to the crystal)

Residence time

$$\tau = \nu_0^{-1} \exp(E_a/kT)$$

ν_0 : *frequency hopping*

Diffusion coefficient

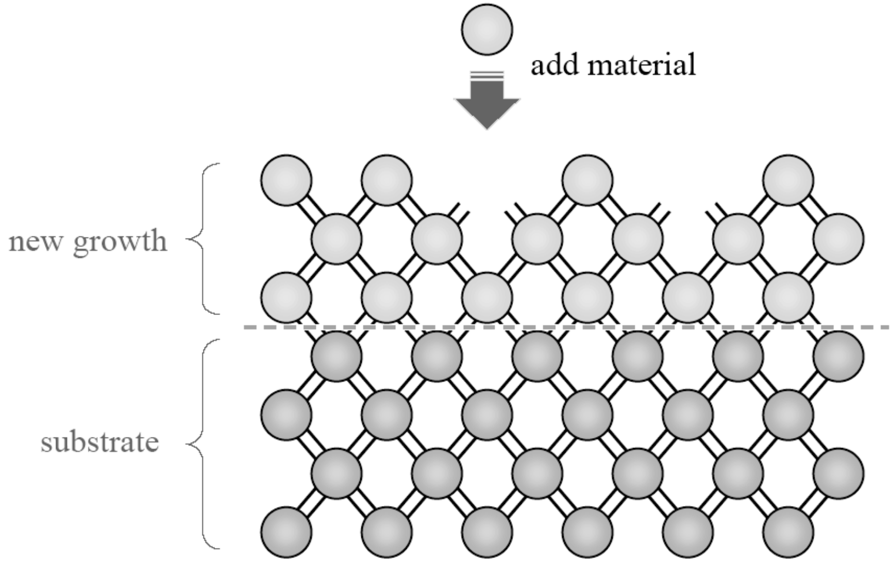
$$D = D_0 \exp(-E_d/kT)$$

$$\lambda = 2\sqrt{\tau D}$$ *diffusion length*

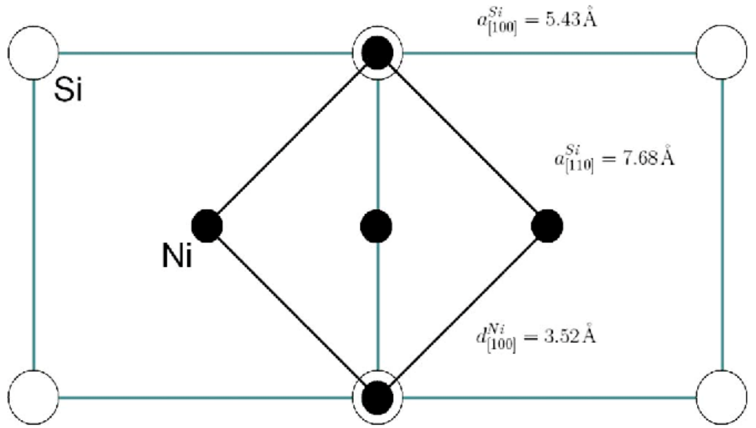
$\lambda = \sqrt{2n\tau D}$ (n: dimensionality)

λ can be controlled by the temperature and the surface chemistry (V/III ratio, surfactant)

What is Epitaxial Growth?



Nickel on silicon (001) substrate



The crystal structure of the growing layer is imposed by the substrate

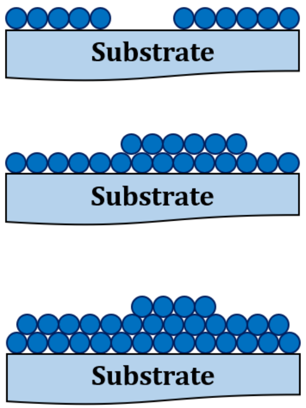
⇨ Epitaxial relationship

Growth modes

❑ Frank – Van der Merwe (2D)

→ $\gamma_{substrate} \geq \gamma_{layer} + \gamma_{interface}$

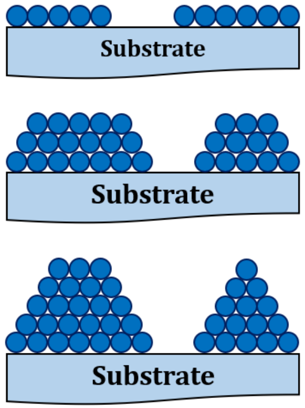
→ Complete wetting of the surface
→ Formation of **2D islands: layer-by-layer**



❑ Volmer-Weber (3D)

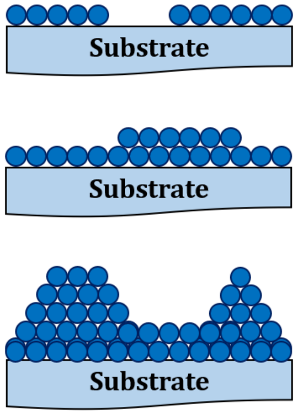
→ $\gamma_{substrate} < \gamma_{layer} + \gamma_{interface}$

→ Formation of **3D islands**



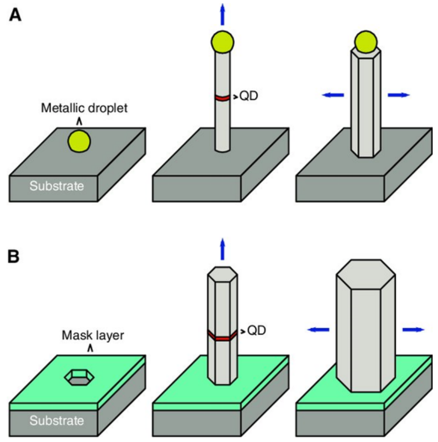
❑ Stranski-Krastanov (2D-3D)

→ Complete wetting of the surface, followed by a 2D-3D growth mode transition at a given thickness



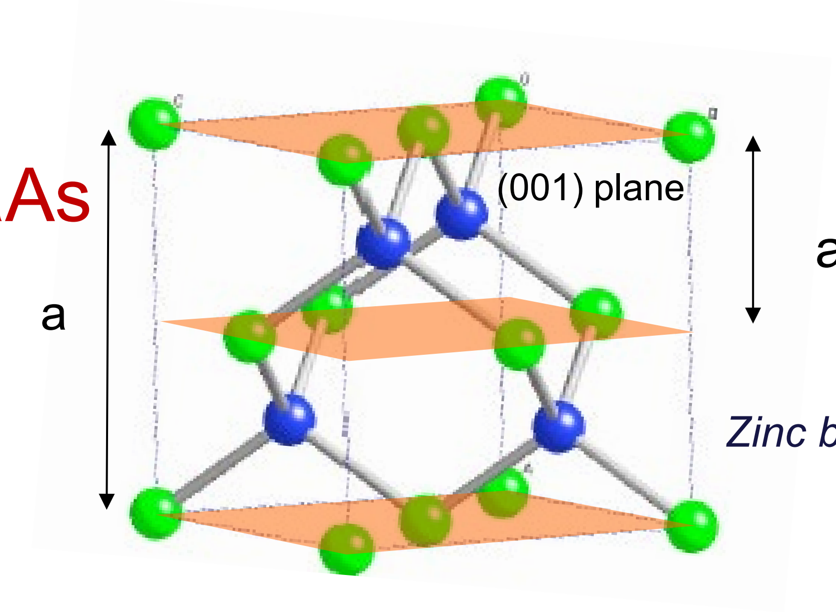
❑ 3D growth - Wires

→ Micro- or nano-wires
A) Vapor-Liquid-Solid with a catalyst (Au)
B) Catalyst-free



What is a monolayer for a compound semiconductor (GaAs, GaN)?

GaAs

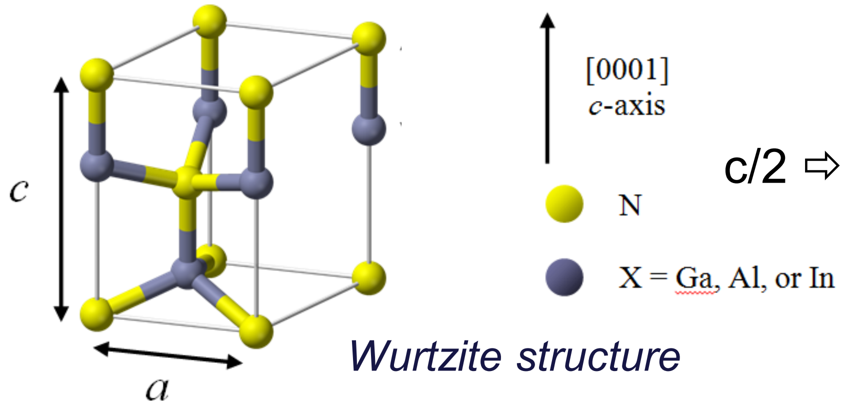


a/2 ⇨ 1 GaAs molecular monolayer (ML)
= 1 Ga plane and 1 As plane (2.83 Å)

Zinc blende structure

GaN

(0001) plane



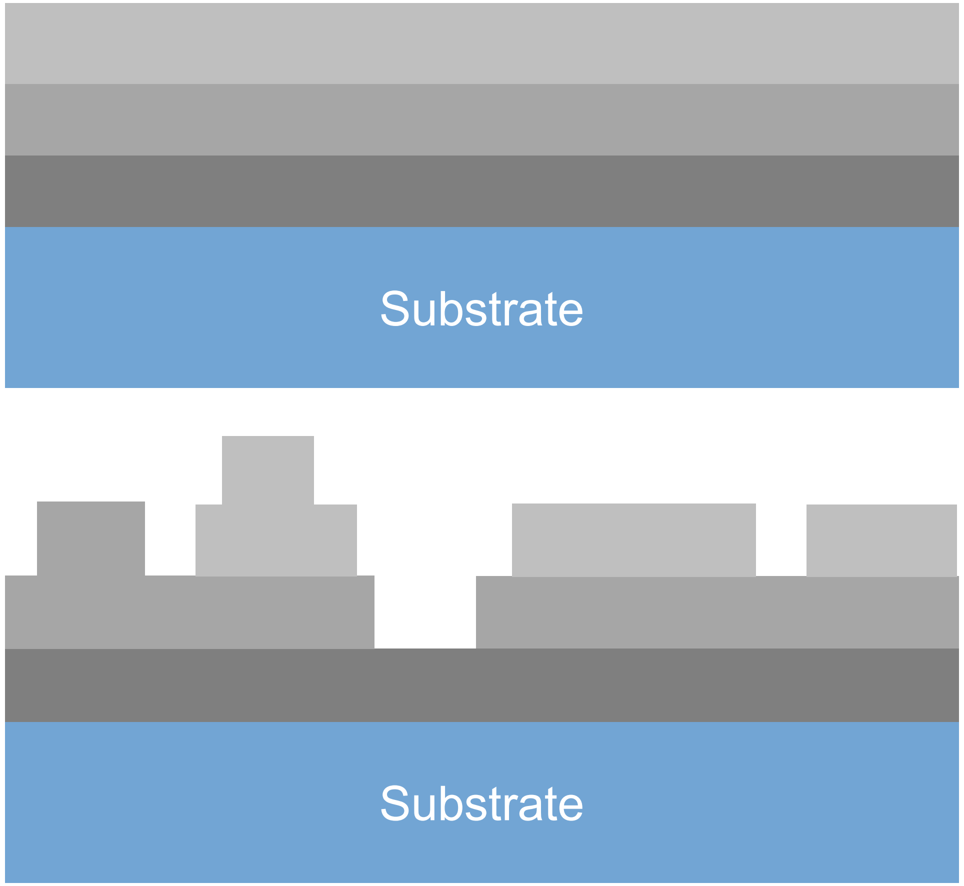
c/2 ⇨ GaN ML = 1 Ga plane and 1 N plane (2.59 Å)

Wurtzite structure

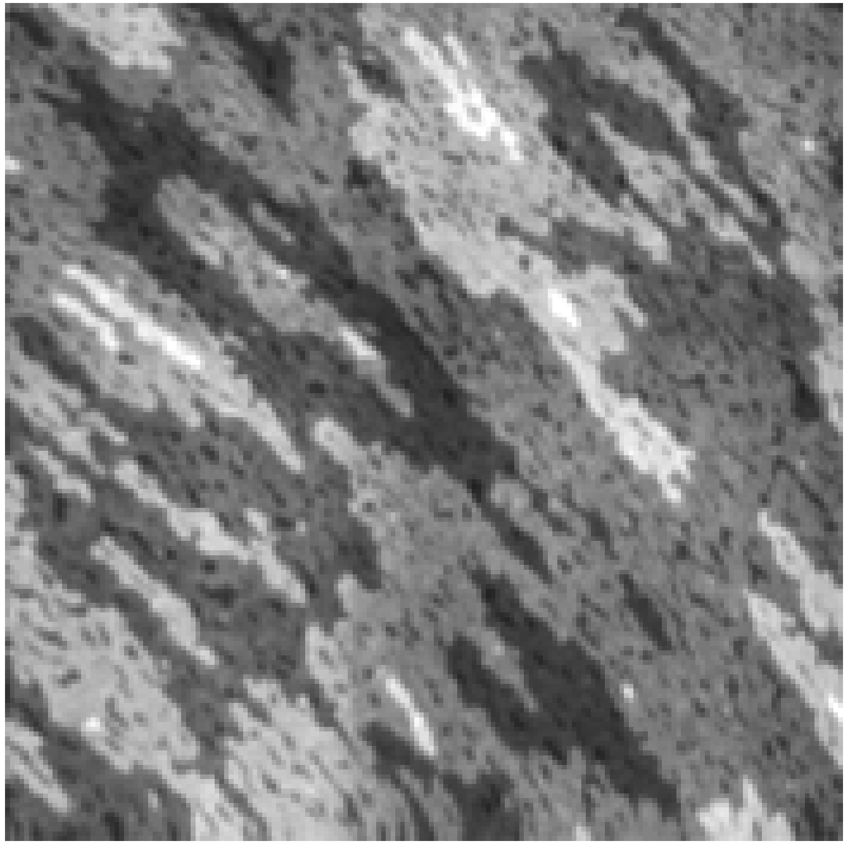
2D layer-by-layer growth mode

ideal case

real case



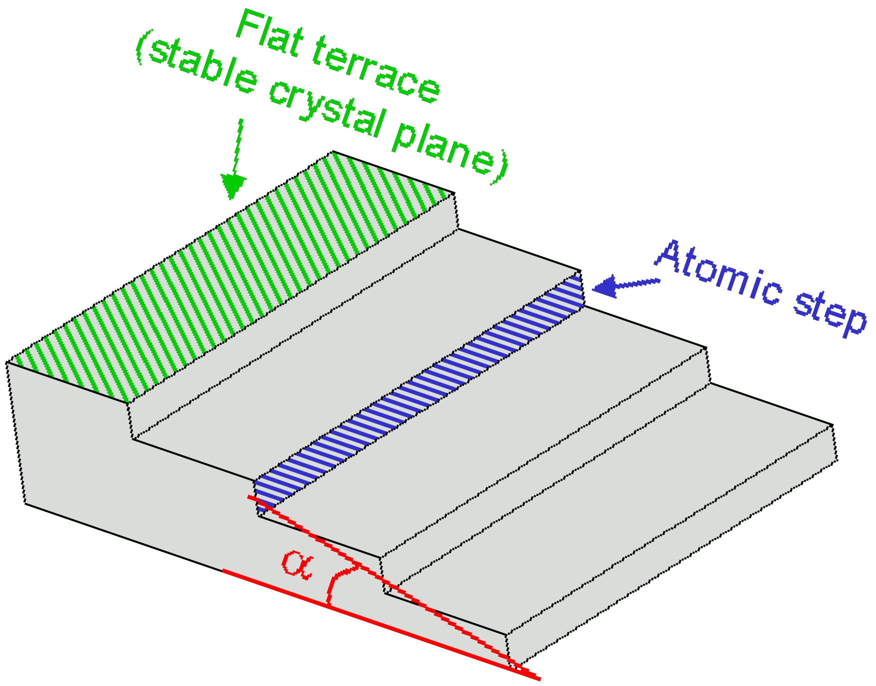
GaAs(001) surface by STM



400 x 400 nm²

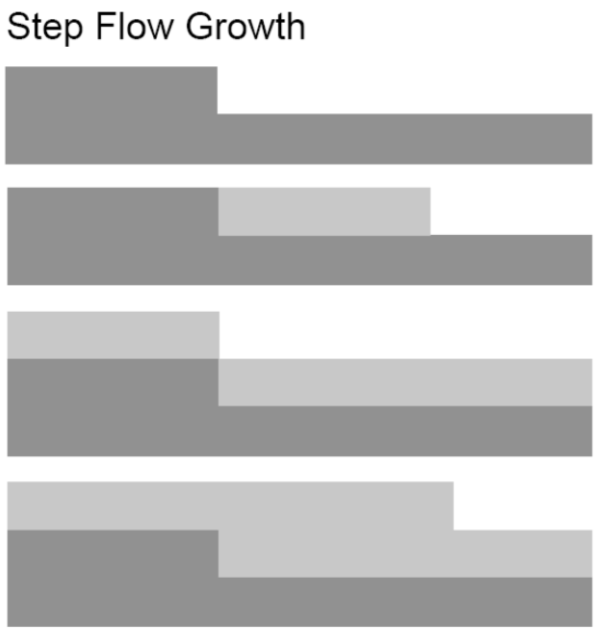
Phys. Rev. *B* 55, R4879(R) (*1997*)

Step-flow growth mode



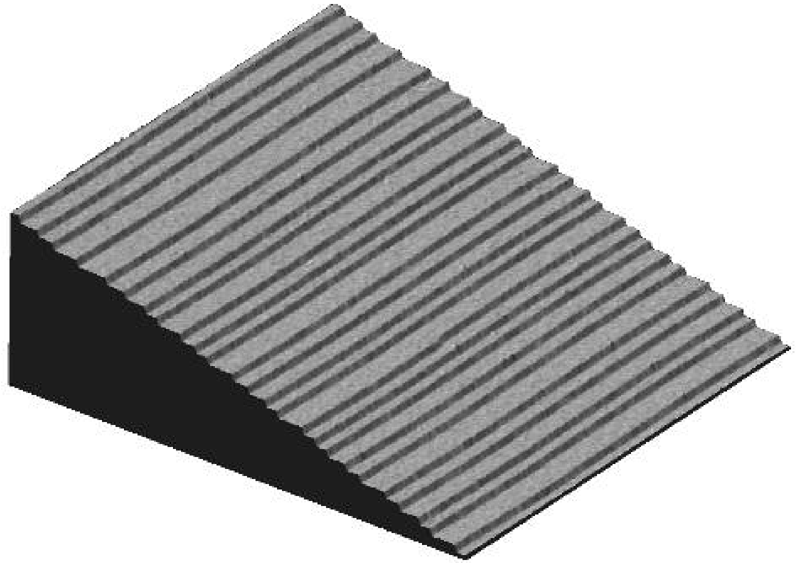
« vicinal » (misoriented) surface

Terrace length (GaN):
miscut: $\alpha = 0.2° \Rightarrow 75$ nm



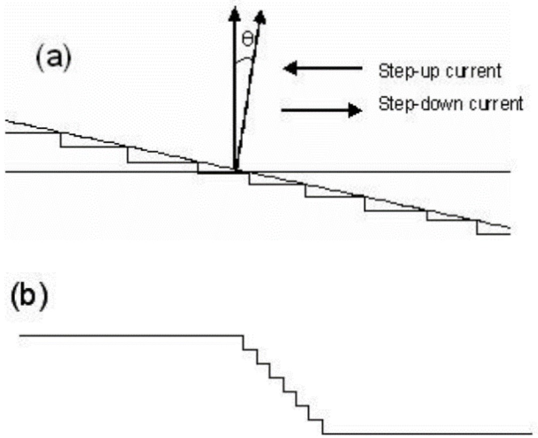
Surface morphology does not change

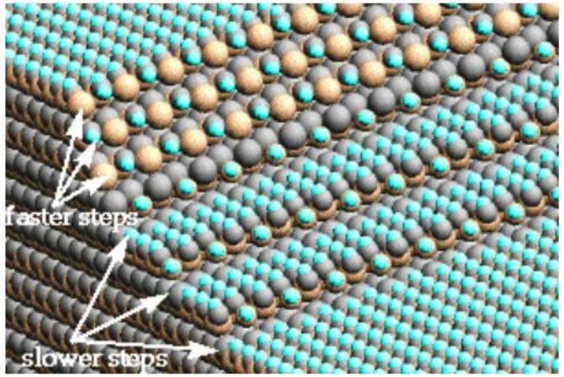
AFM image - Silicon



2D step-flow growth mode

Step bunching

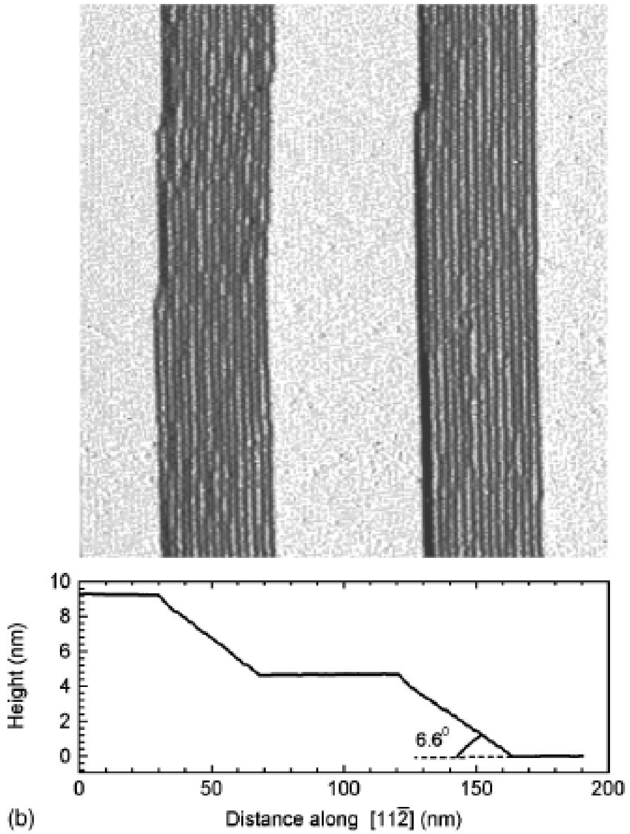




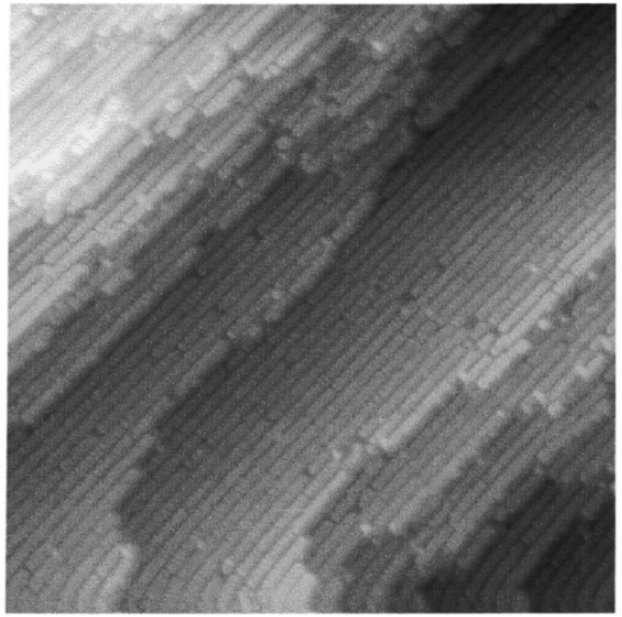
JOURNAL OF APPLIED PHYSICS VOLUME 84, NUMBER 1 1 JULY 1998

Formation of regular step arrays on Si(111)7×7

J.-L. Lin, D. Y. Petrovykh, J. Viernow,[a] F. K. Men,[b] D. J. Seo,[c] and F. J. Himpsel
Department of Physics, University of Wisconsin Madison, 1150 University Avenue, Madison, Wisconsin 53706-1390



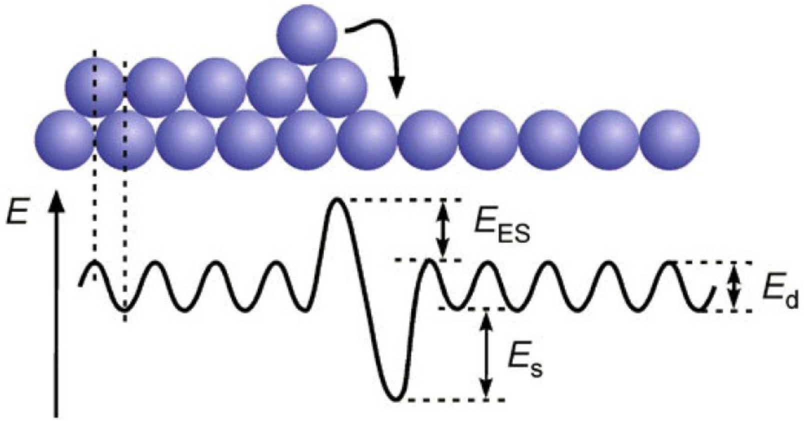
GaAs (STM image) 75 x 75 nm²



Disorder: step bunching

Growth instabilities - origin

Ehrlich and Hudda, J. Chem. Phys. **44**, 1039 (1966)
Schwoebel and Shipsey, JAP **37**, 3682 (1966)



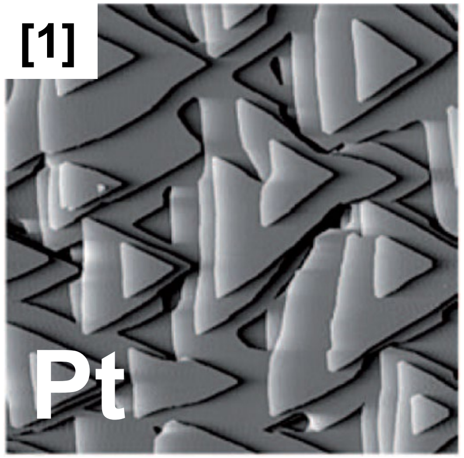
Ehrlich-Schwoebel barrier (ESB):

Asymmetry of the surface potential at a step
→ Difference in nearest neighbors to attach to

Growth instabilities

ESB-induced surface features

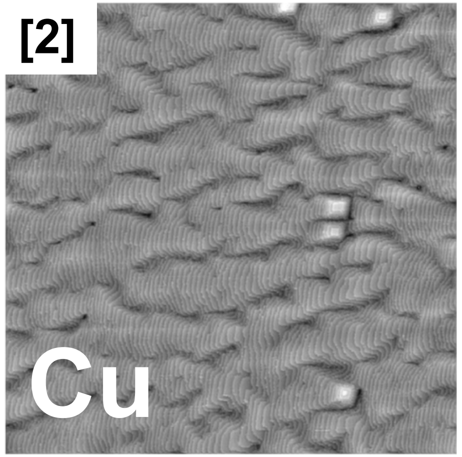
[1]



Hillocks

J Krug, *Kinetic pattern formation at solid surfaces,* in: *Collective dynamics of nonlinear and disordered systems*

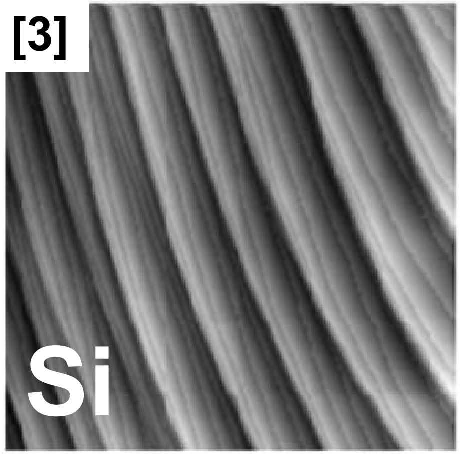
[2]



Step-meandering

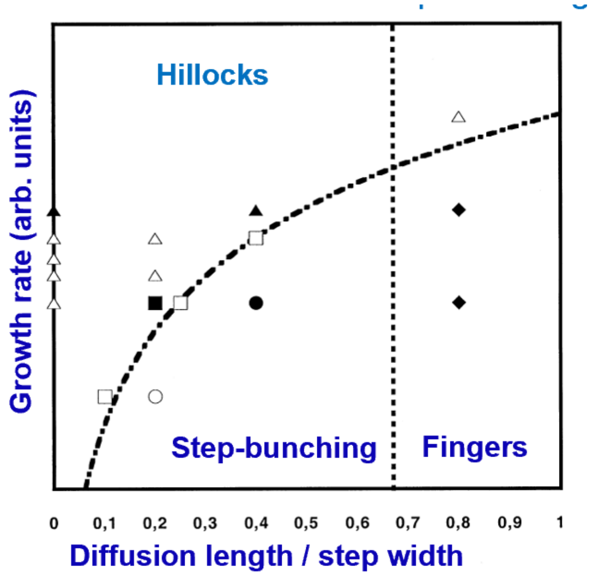
T Maroutian *et al.*, Phys. Rev. B **64,** 165401 (2001)

[3]



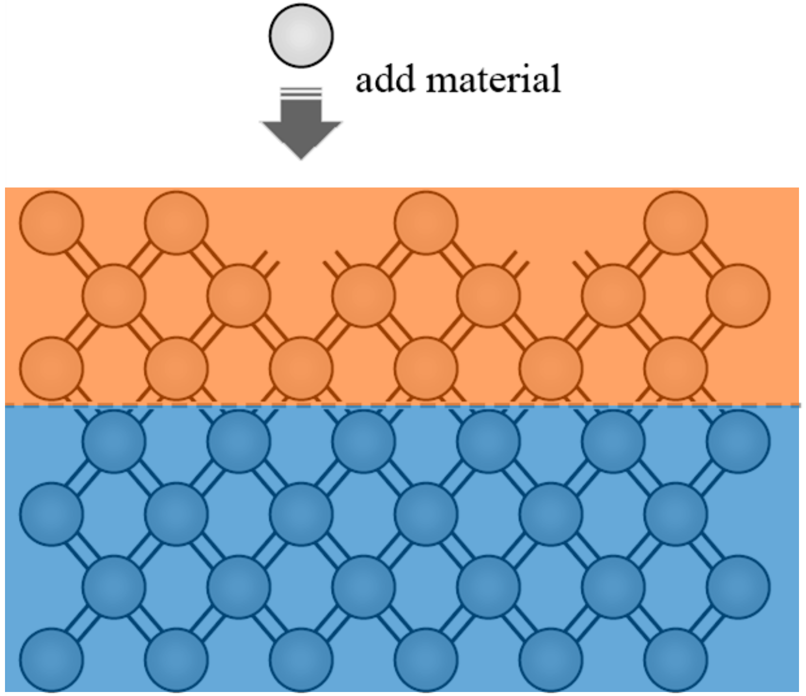
Step-bunching

Y N Yang *et al.*, Surf. Sci. **356,** 101 (1996)



Vladimirova *et al.*,
JCG 220, 631-636 (2000)

Heteroepitaxial growth

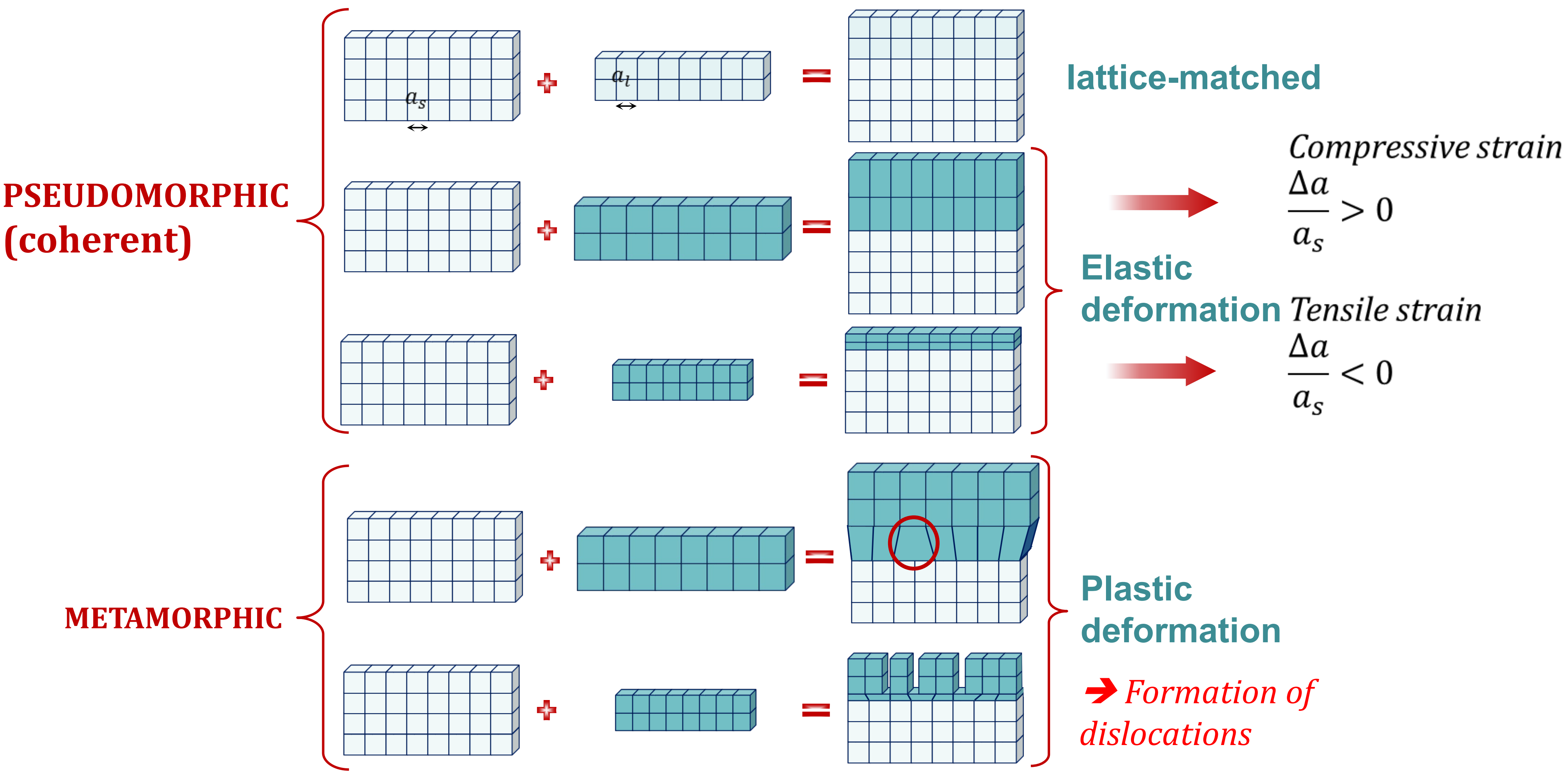


- When does heteroepitaxy matter?

- Growth on foreign substrates
- Heterostructures: quantum wells, quantum dots, Bragg mirrors

Elastic *versus* plastic deformation

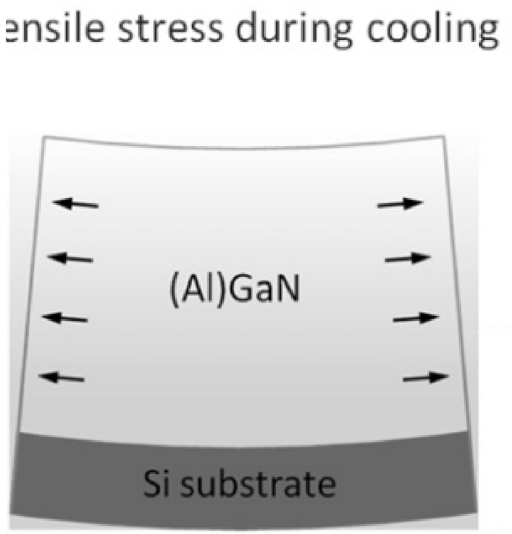
$$\frac{\Delta a}{a_s} = \frac{a_l - a_s}{a_s} = 0$$

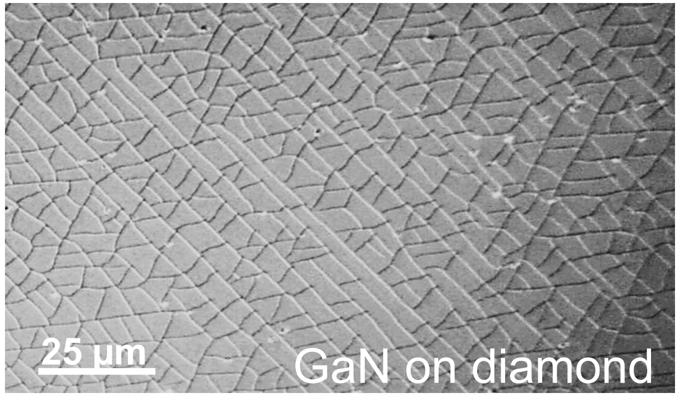


Strain ε

induced by:

- **Lattice-mismach**
- **Different thermal expansion coefficients between the substrate and the epilayers**





Materials	AlN	Sapphire	Si (111)	Diamond
$\frac{\alpha_{GaN}-\alpha}{\alpha}$ (%)	34.7	-16.1	115	373.5

Strain

Lattice mismatch: $\Delta a/a = (a_l - a_s)/a_s$

Strain: $\varepsilon_{//} = (a_s - a_l)/a_l$

Ex: AlN/GaN

$a_{GaN} = 3.189$ Å and $a_{AlN} = 3.112$ Å

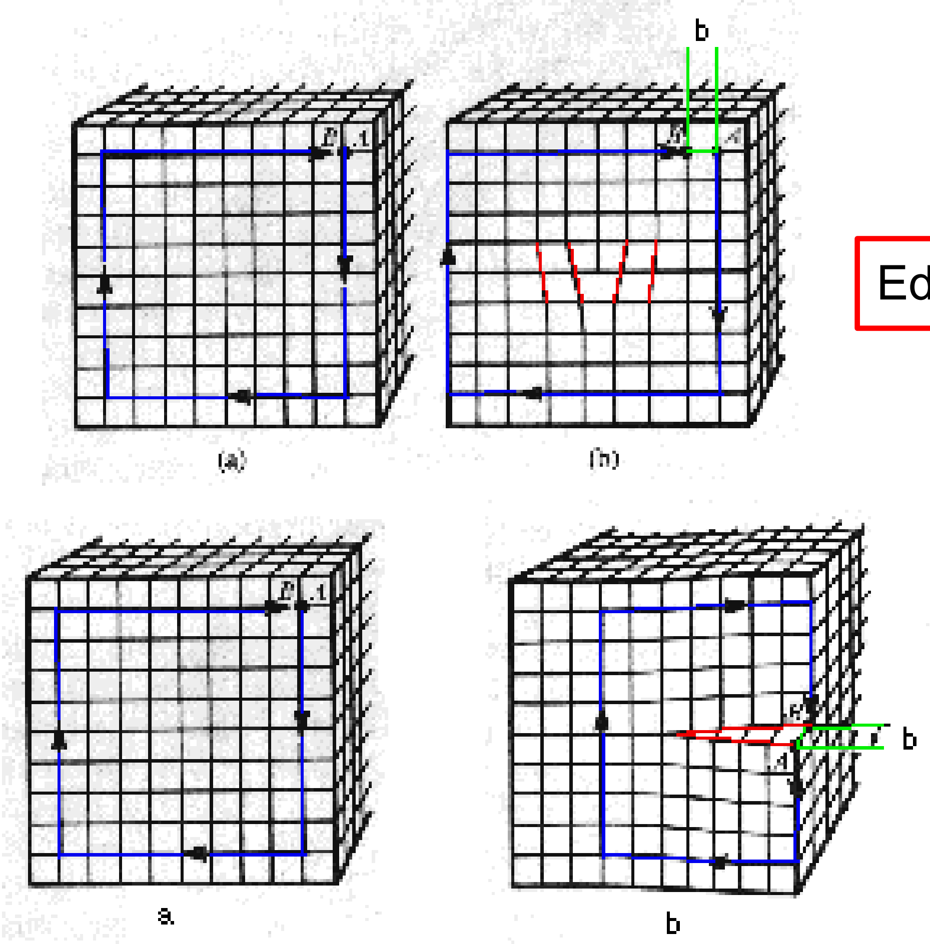
GaN on AlN: $\Delta a/a = 2.47$ % and $\varepsilon = -2.42$ %

$\varepsilon < 0$ compressive strain

$\varepsilon > 0$ tensile strain

Dislocations

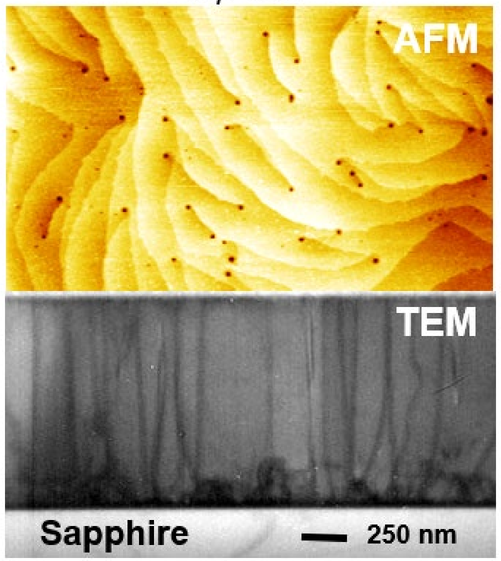
Burgers vector b



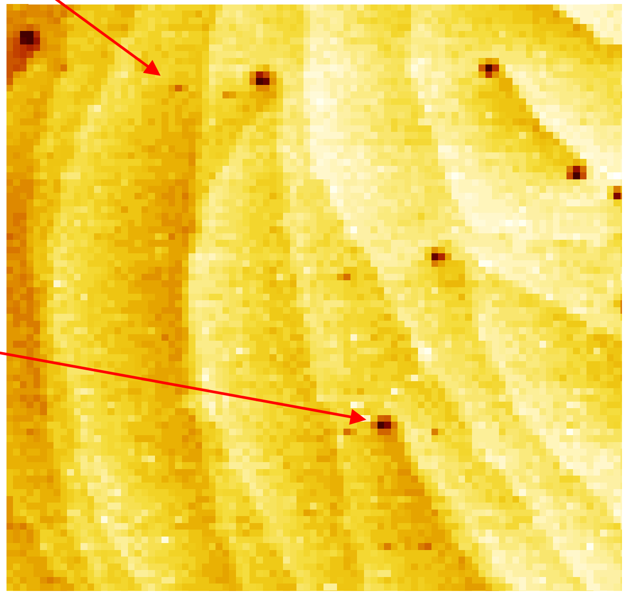
Edge type dislocation

Screw type dislocation

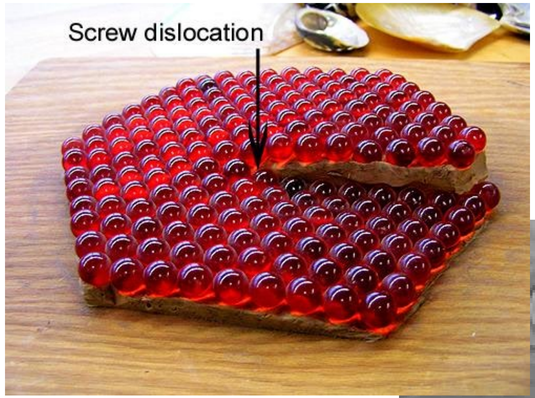
Top view

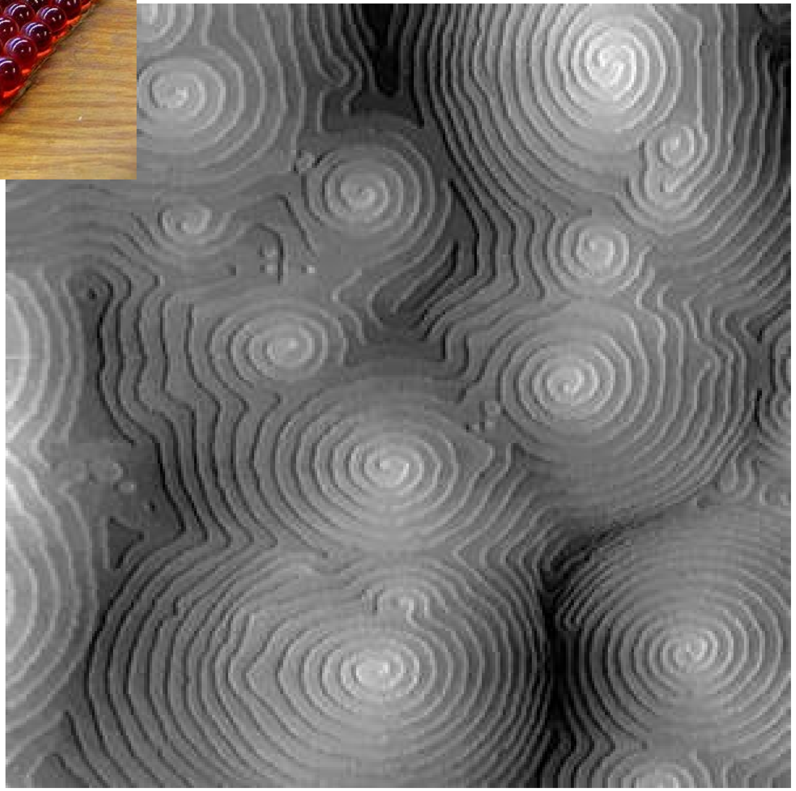


Cross-section

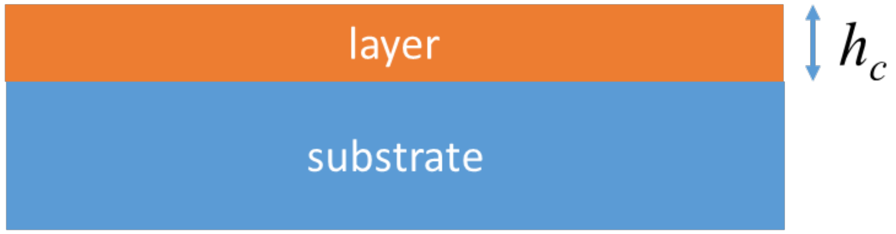


Spiral growth induced by screw-type dislocations





Critical thickness for a 2D layer



Critical thickness h_c: maximum thickness until plstic relaxation occurs (introduction of dislocations)

h_c depends on the lattice mismatch, and can be less than 1 nm

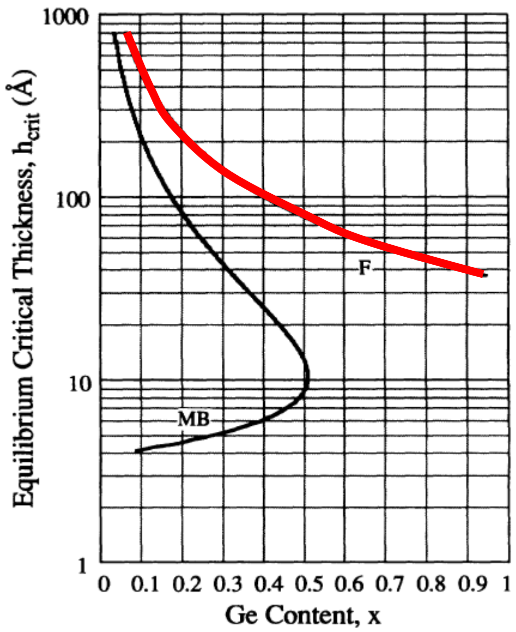


FIG. 3. Comparison of predicted equilibrium critical thickness h_{crit} for relaxation models based on elastically noninteracting (MB: Matthews-Blakeslee) and interacting (F: this study) misfit dislocations as a function of Ge content x.

VOLUME 73, NUMBER 20 PHYSICAL REVIEW LETTERS 14 NOVEMBER 1994

New Approach in Equilibrium Theory for Strained Layer Relaxation

A. Fischer, H. Kühne, and H. Richter

$$x = [b \cos\lambda / (0.0836 h_{crit})] \times (1 + \{[1 - (\nu/4)]/[4\pi \cos^2\lambda(1+\nu)]\} \ln(h_{crit}/b))$$

λ: angle between the Burgers vector and the interface

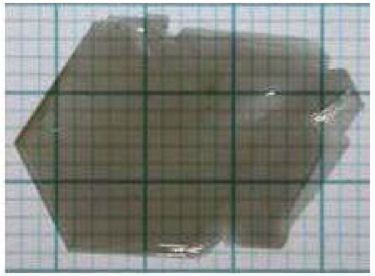
GaN growth

GaN heteroepitaxy

The substrate: GaN

Lack of GaN bulk native substrates

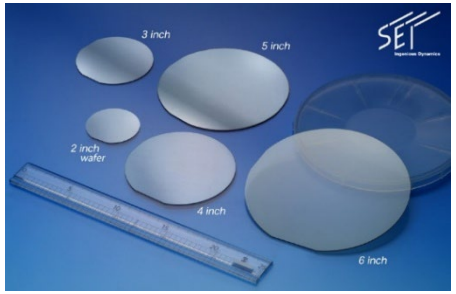
produced at Unipress (PL) by high pressure growth - 1 cm²



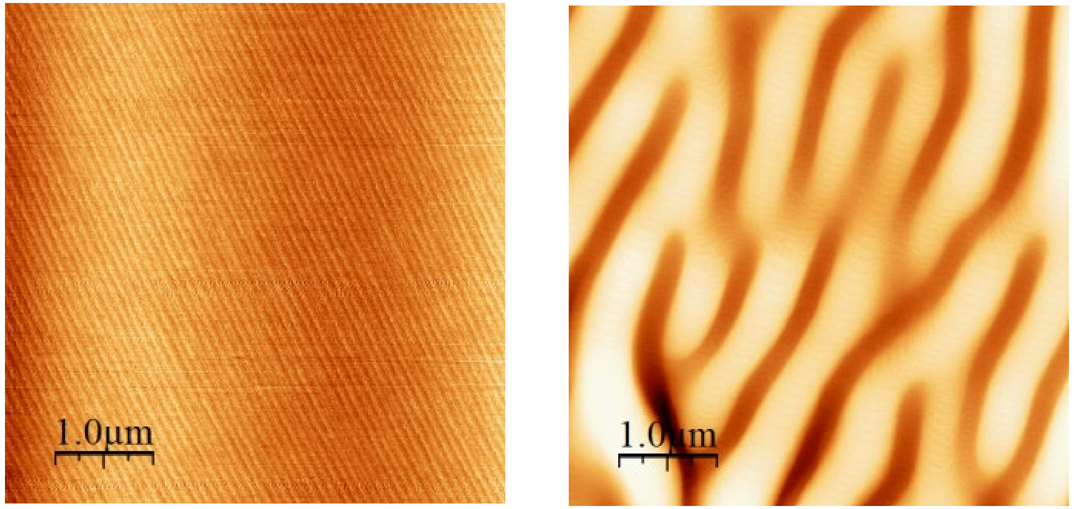
Free-standing GaN substrates:

HVPE growth on GaAs or sapphire, followed by substrate removal or by amonothermal growth

- Dislocation density: <10^6 cm^{-2}
- Size: currently 4 in., 6 in. demonstrated



1000°C 850°C



J. Cryst. Growth 433, 36 (2016)

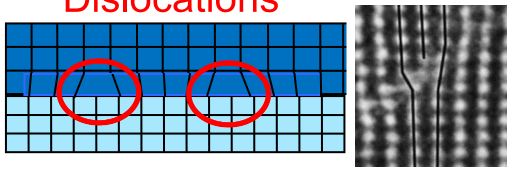
GaN heteroepitaxy

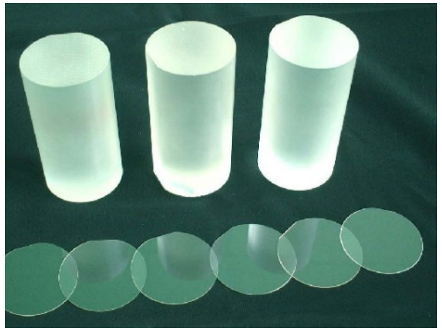
- The substrate: sapphire

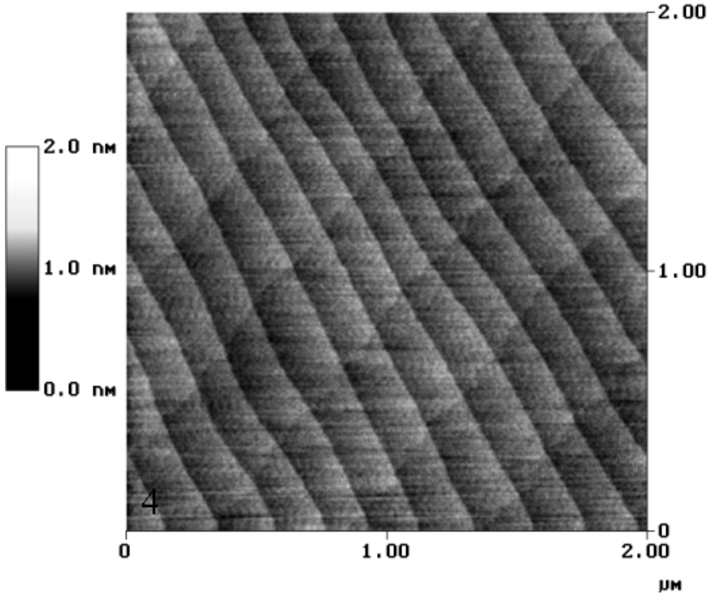
GaN technology has been developed on sapphire from the 80's

Lattice mismatch to GaN

Al_2O_3 (0001):	+16 %
6H-SiC (0001):	-3.5 %
Si (111):	-17 %





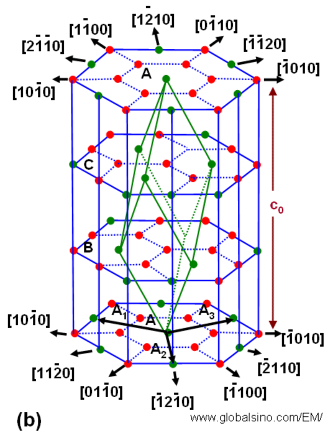


Sapphire (0001) is the most commonly used substrate

size : 6 in.

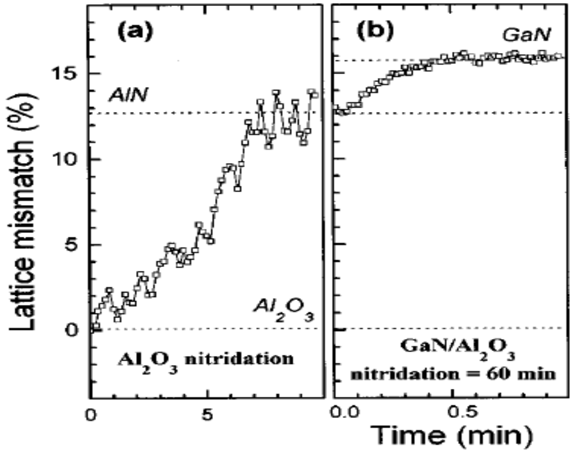
The substrate: sapphire

Sapphire nitridation (exposure to NH_3) ⇨ formation of AlN

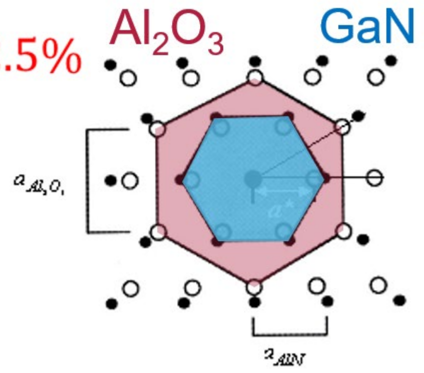


Sapphire crystal structure

Appl. Phys. Lett. 69, 2071 (1996)



$$\frac{\Delta a}{a} = 2.5\%$$



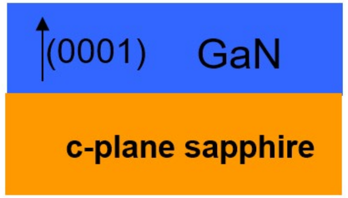
GaN/sapphire epitaxial relationship

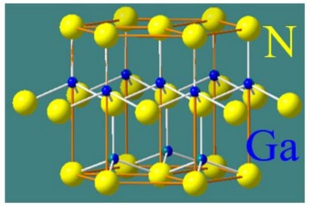
Aluminum hexagonal sublattice lying in the c-plane of Al_2O_3 crystal

⇨ AlN layer at the surface upon NH_3 exposure at high temperature

GaN heteroepitaxy

GaN polarity





PHYSICAL REVIEW APPLIED **5**, 054004 (2016)

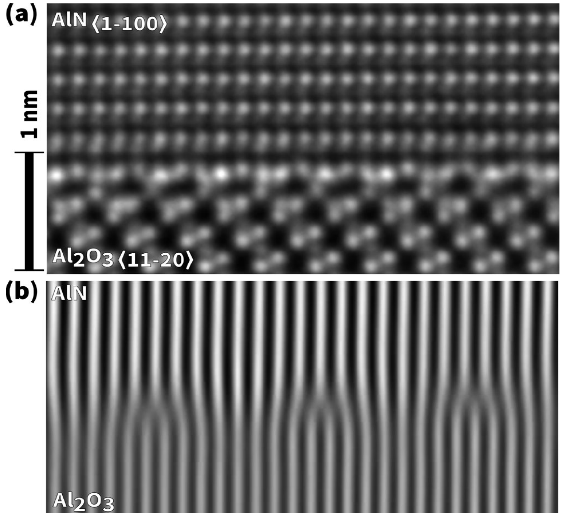
Polarity Control in Group-III Nitrides beyond Pragmatism

Stefan Mohn,[1,*] Natalia Stolyarchuk,[1,2] Toni Markurt,[1] Ronny Kirste,[3] Marc P. Hoffmann,[3] Ramón Collazo,[3] Aimeric Courville,[2] Rosa Di Felice,[4,5] Zlatko Sitar,[3] Philippe Vennéguès,[2] and Martin Albrecht[1]

JOURNAL OF APPLIED PHYSICS **122**, 155303 (2017)

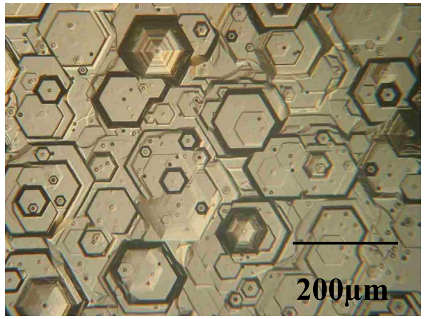
Impact of sapphire nitridation on formation of Al-polar inversion domains in N-polar AlN epitaxial layers

N. Stolyarchuk,[1,2] T. Markurt,[1] A. Courville,[2] K. March,[3] O. Tottereau,[2] P. Vennéguès,[2] and M. Albrecht[1]

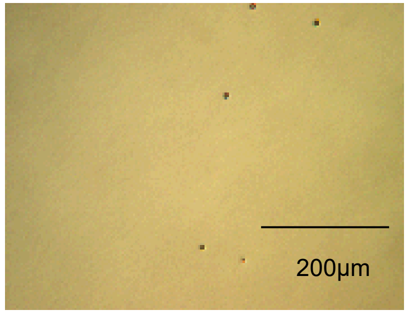


Aluminum oxynitride layer controls the polarity of GaN epilayer

$\Rightarrow$ Ga polarity allows growing high purity GaN layers



16 µm thick GaN, N polar

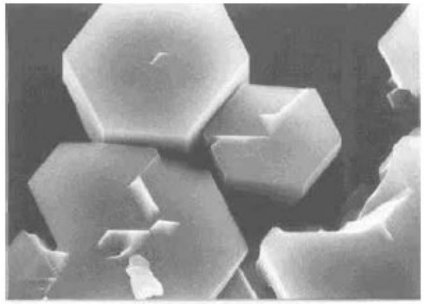


16 µm thick GaN, Ga polar

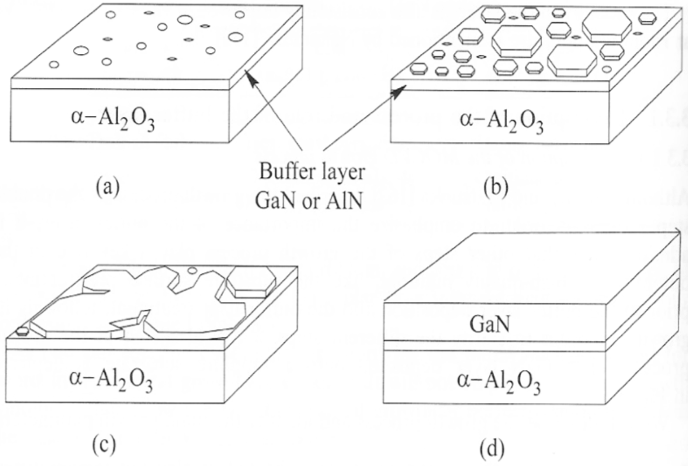
surface chemistry controls the polarity

■ GaN on sapphire

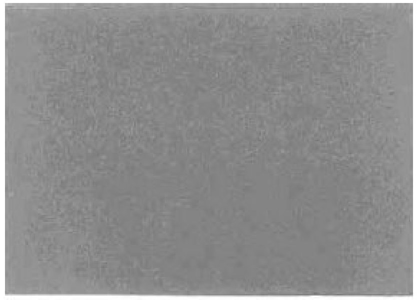
The low temperature buffer layer



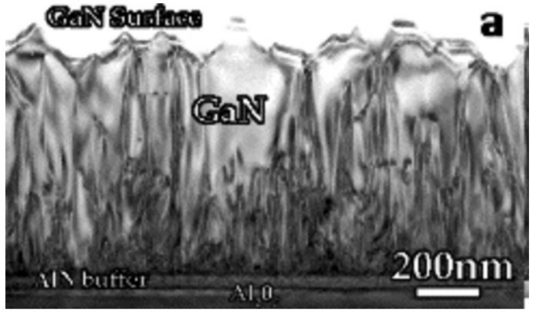
w/o LT buffer



H. Amano *et al.* , Appl. Phys. Lett. 48, 353 (1986)



w LT buffer



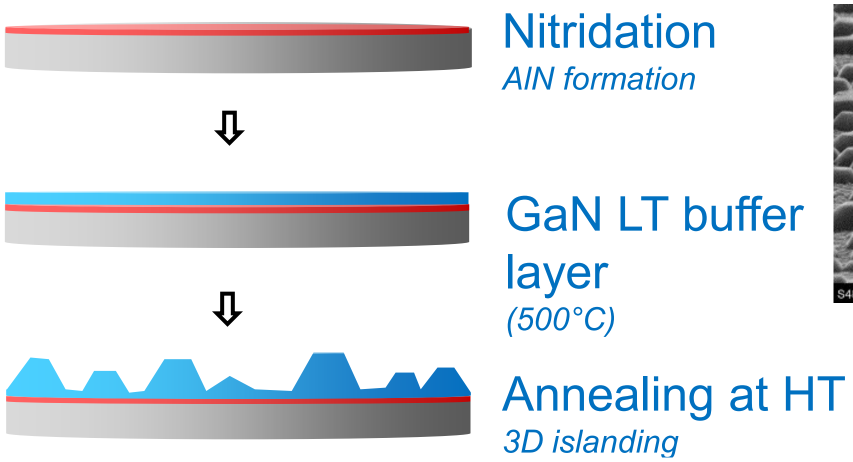
Dislocation density > 10^{10} cm^{-2}

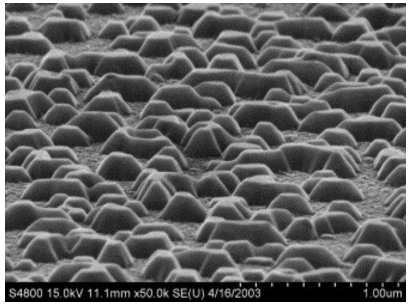
Two-step growth procedure:

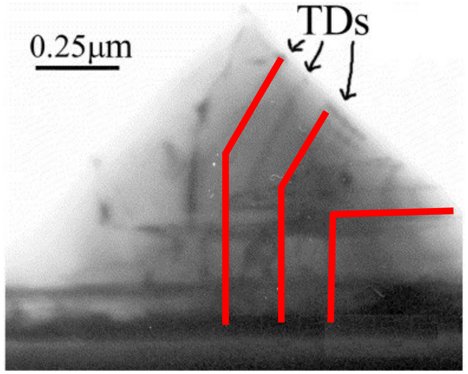
1) a thin AlN buffer layer (25 nm) at low-temperature (500°C)
2) growth at high-temperature (1000°C-1100°C)

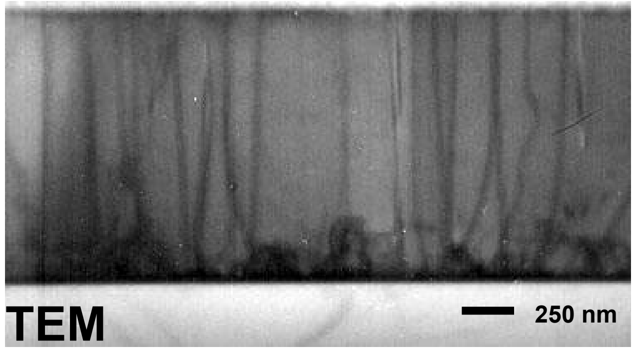
GaN on sapphire

3D islands to reduce the dislocation density

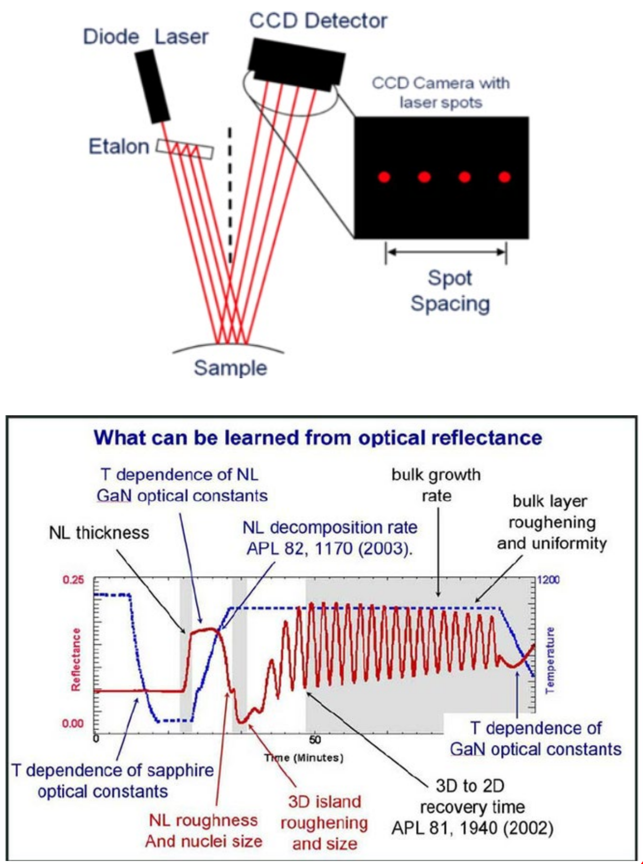








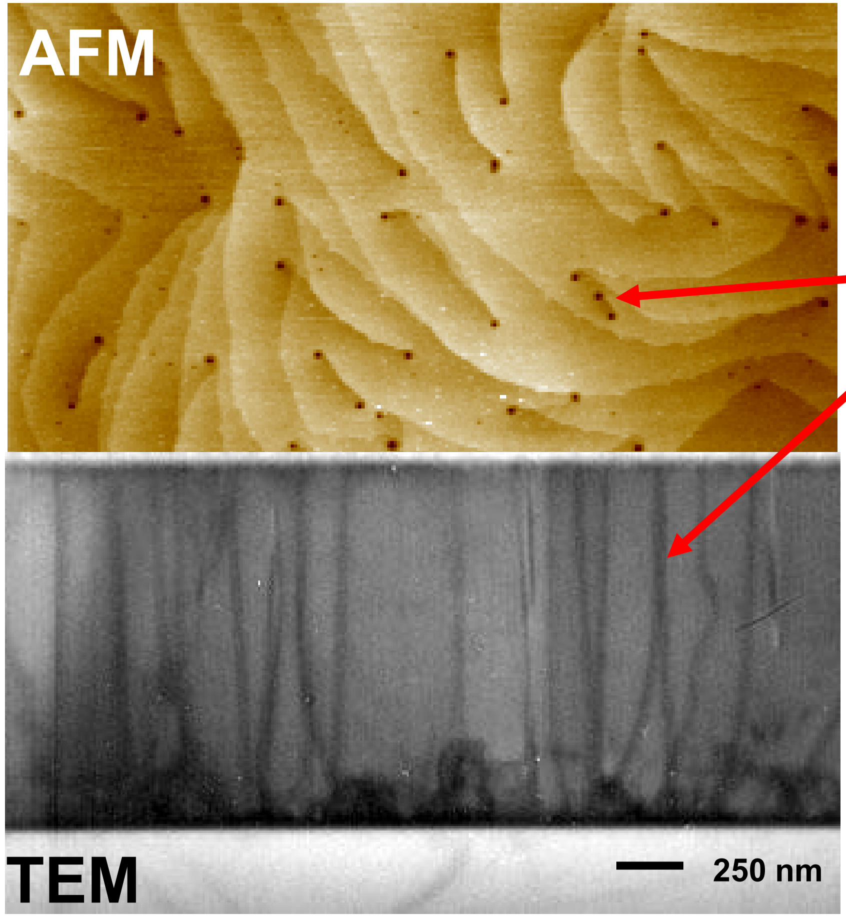
In situ growth monitoring



Dislocation density reduced from 10^{10} to below 10^{8} cm^{-2}

GaN heteroepitaxy

Dislocation density = $5x10^7$-10^8 cm^{-2} in commercial blue LEDs



Surface

Dislocations

Threading dislocations are supposed to impact the active region of LEDs/LDs

⇒ low impact in blue LEDs

Cross-section

GaN heteroepitaxy

- GaN on Silicon substrate

Lattice mismatch

Al_2O_3 (0001): +16 %

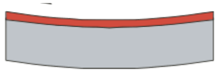
6H-SiC (0001): -3.5 %

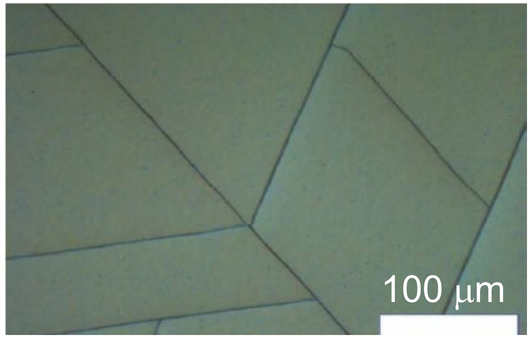
Si (111): -17 %

(GaAs/Si: +4 %)

Thermal expansion coefficient mismatch

Si (111): 115 % ⇨ tensile strain



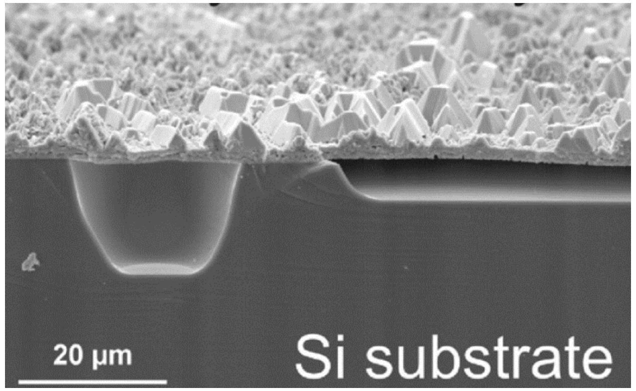


Epilayer cracking when cooling down the wafer from 1000°C to room-temperature

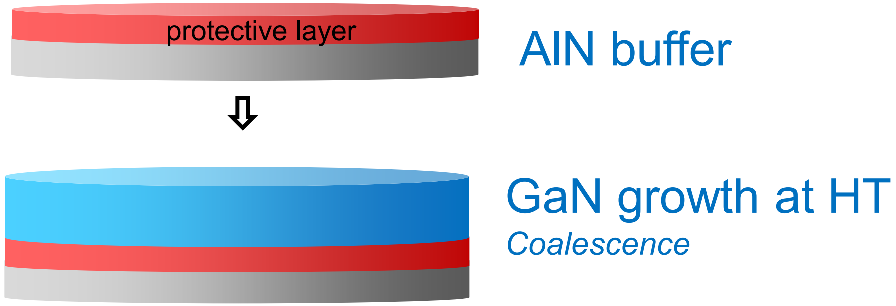
GaN heteroepitaxy

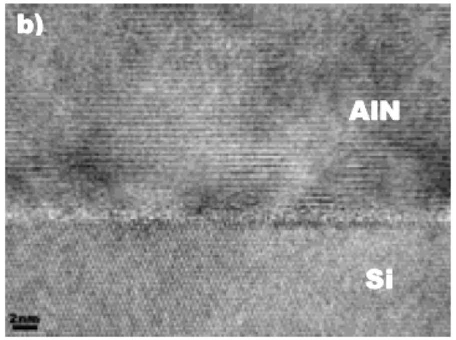
■ GaN on Silicon substrate

Silicon surface is decomposed when exposed to Ga and NH_3 at high temperature

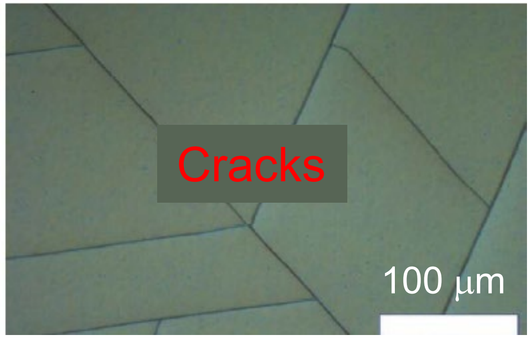


A. Dadgar et al. Journal of Crystal Growth 248, 556 (2003)





phys. stat. sol. (a) 188, No. 2, 501 (2001)

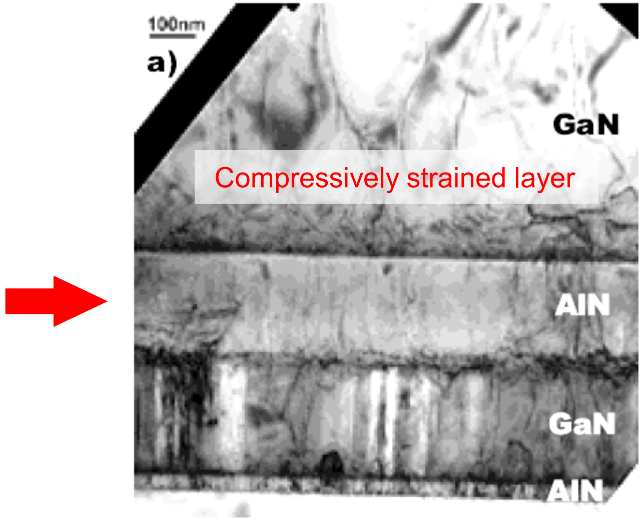


Dislocation density >10^{10} cm^{-2}

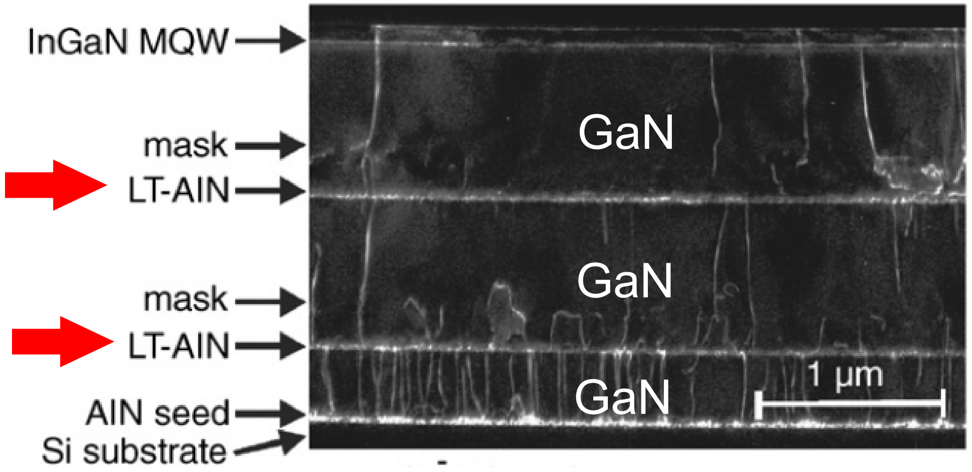
GaN on Silicon substrate

Strain engineering to avoid layer cracking

→ compressive strain is introduced during growth



D. Ducateau et al., IEEE Electron Device Letter 27, 1 (2006)

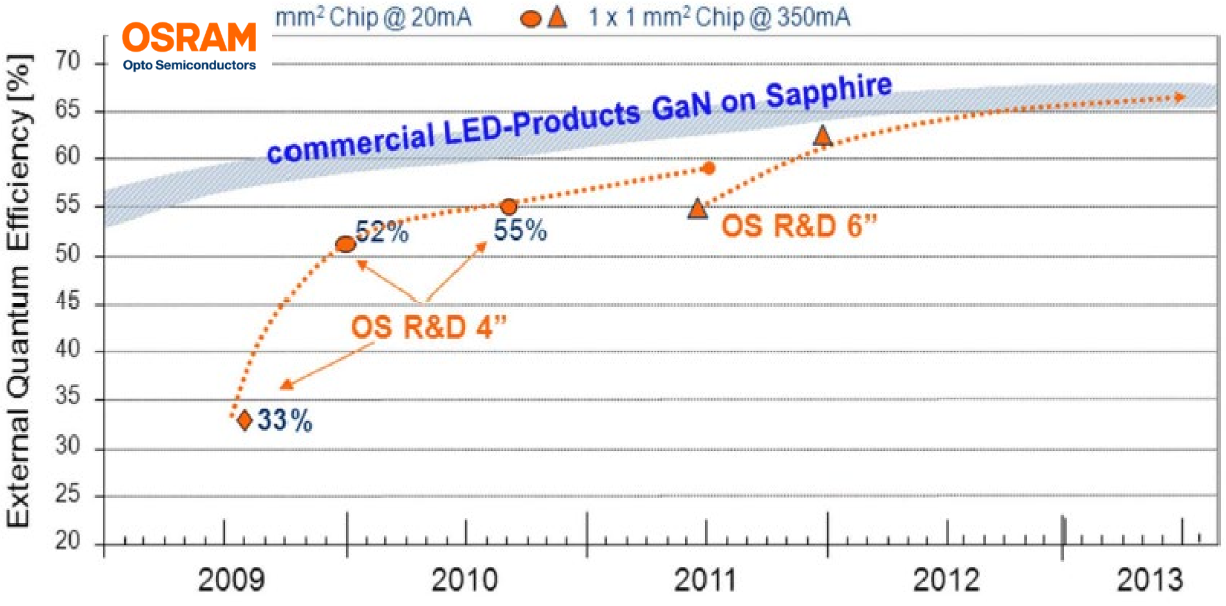


A. Dadgar et al., Journal of Crystal Growth 248, 556 (2003)

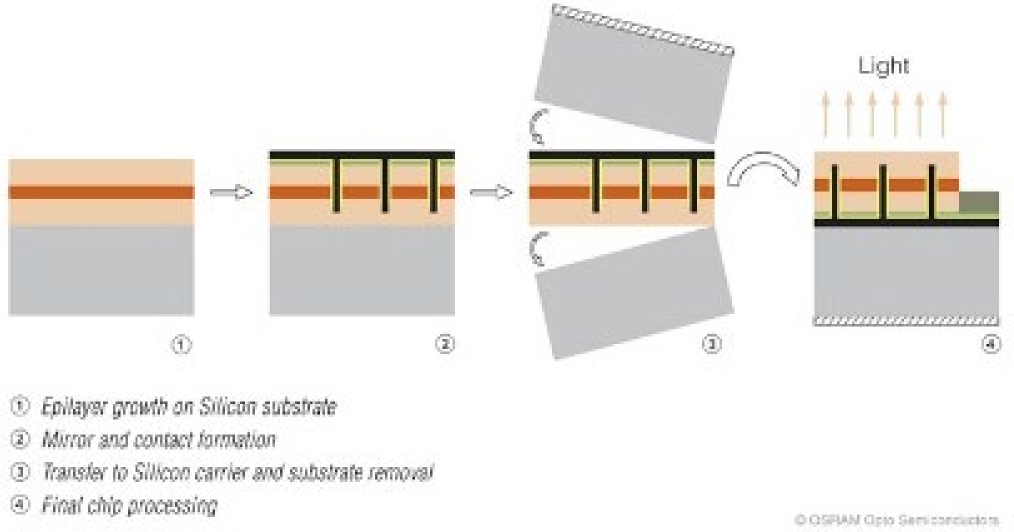
EPFL

GaN on Silicon substrate

Blue LEDs on Si



Courtesy of Dr. U. Steegmüller, Osram-OS



GaN on Silicon: typ. ~110 lm/W	2015
GaN on Sapphire: typ. ~118 lm/W	

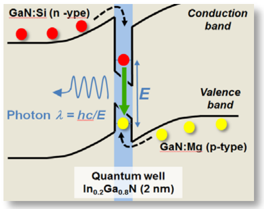
Internal quantum efficiency: 90 % on silicon (95% on sapphire)

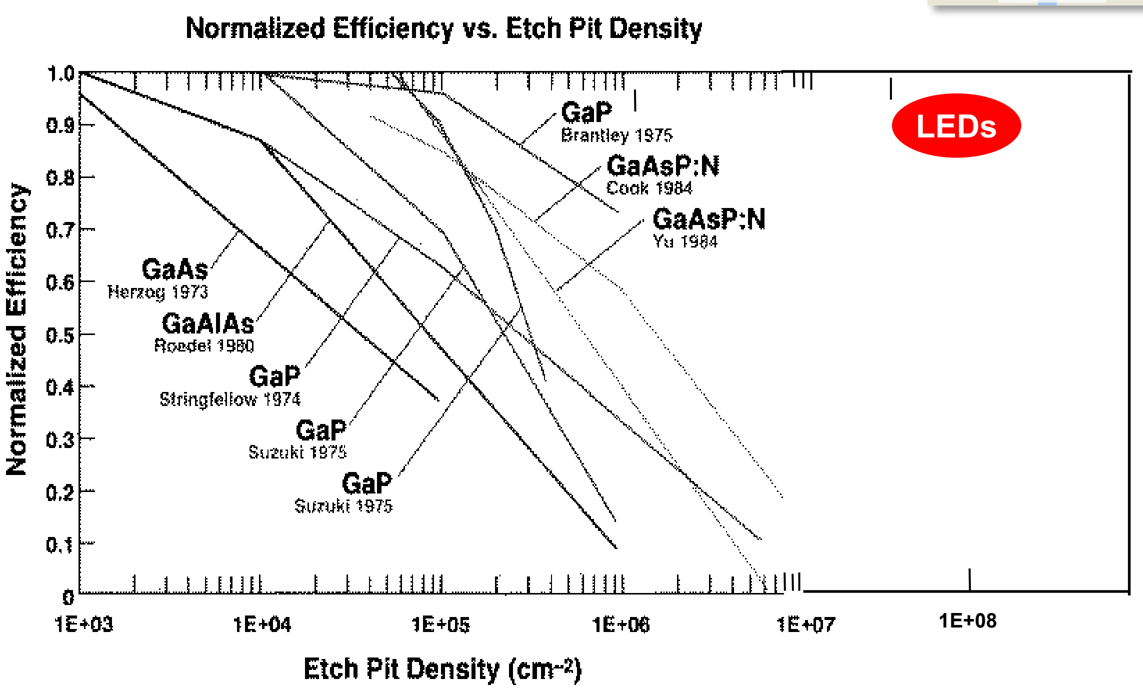
Growth and LED efficiency

InGaN quantum wells

Internal quantum efficiency of blue LEDs

Internal quantum efficiency (IQE): $\frac{\#Photons}{\#Electrons}$





LEDs: high efficiency (IQE>90%) despite high density of dislocations

InGaN quantum wells

Internal quantum efficiency of blue LEDs

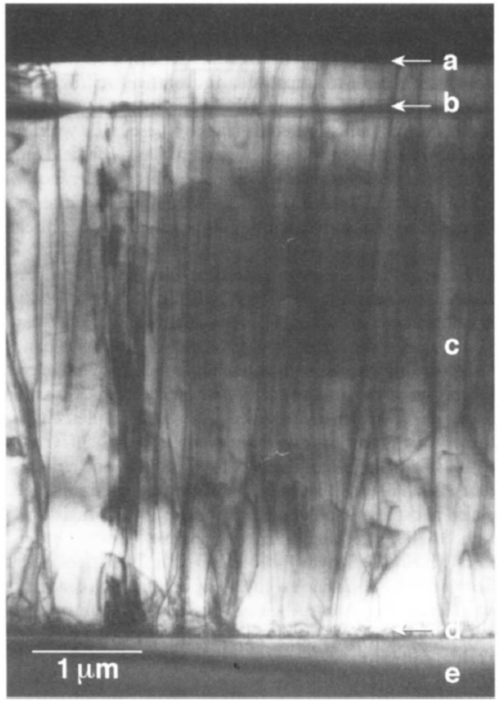


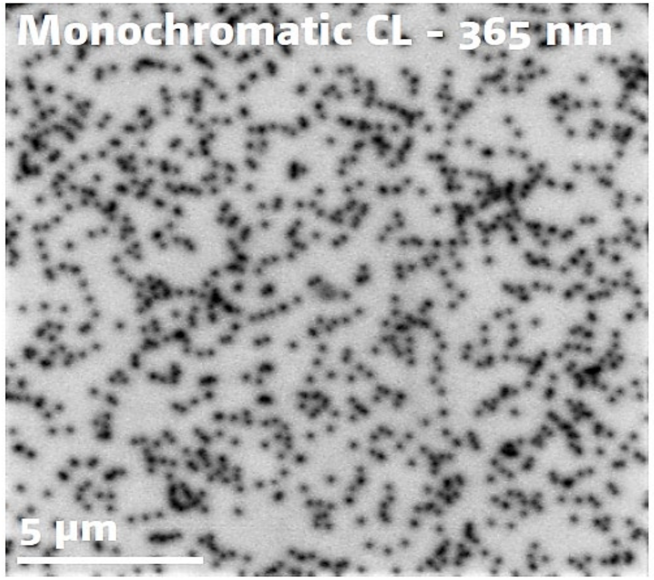
Figure 4 Cross-section transmission electron microscopy view of a high-efficiency Nichia blue LED. The dislocation density of 10^{10} cm^{-2} is remarkably high for such an efficient and durable device. Indicated in the figure are the top surface of the film (a), the active region (b), the main GaN film (c), the buffer layer (d), and the sapphire substrate (e).

NATURE | VOL 386 | 27 MARCH 1997 review article

Nitride-based semiconductors for blue and green light-emitting devices

F. A. Ponce & D. P. Bour

Most surprising was that, compared with LEDs fabricated using other semiconductors, the light-emitting efficiencies of these GaN-based LEDs were remarkably insensitive to extended lattice defects such as dislocations in the films. Transmission electron microscopy (TEM) studies[32] indicated that the material contained 10^{10} dislocations per square centimetre, more than six orders of magnitude above any other material used for LED fabrication.



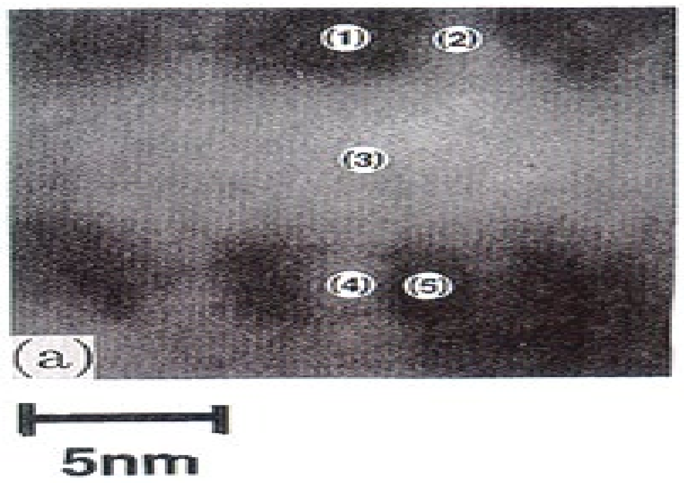
Number of dislocations - 882
Threading dislocation density - 3.1E8 cm^{-2}

Dislocations are non-radiative recombination centers in GaN

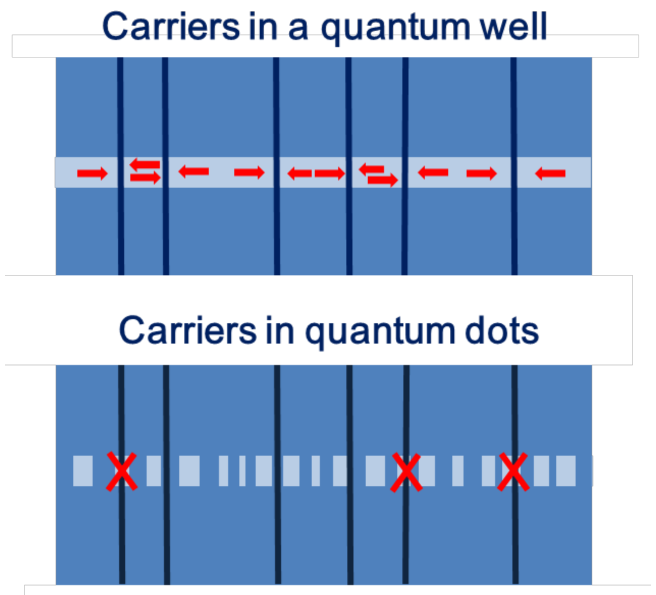
InGaN quantum wells

■ Quantum wells or quantum dots?

Narukawa *et al*. 70, 981 (1997)



TEM image of InGaN/GaN QWs



Gérard and Weisbuch (patent 1990)

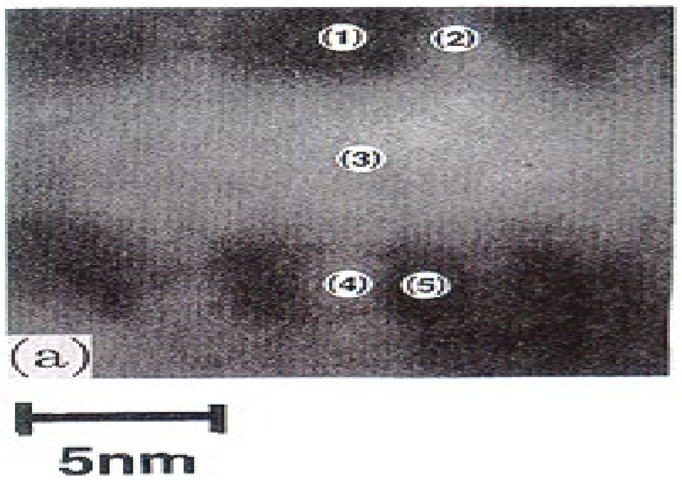
Indium-rich clusters in InGaN QWs act as quantum dots

Common understanding (end of the 90s): the localization of carriers in self-formed QDs prevents their non-radiative recombination on dislocations

InGaN quantum wells

■ Quantum wells or quantum dots?

TEM image of InGaN/GaN QWs grown by MOCVD



Narukawa et al. APL (1997)

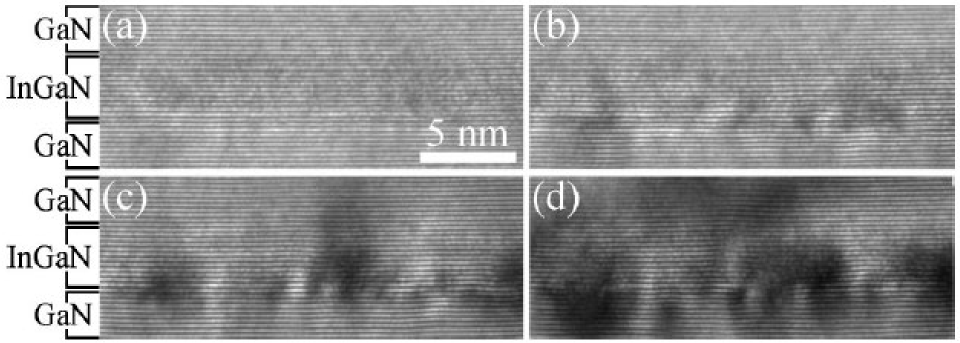


FIG. 3. (0002) lattice fringe images showing strain contrast evolution in an $In_{0.22}Ga_{0.78}N$/GaN MQW during exposure to a 200 kV electron beam flux of ~35 A cm^{-2} after: (a) 20, (b) 220, (c) 420, and (d) 620 s.

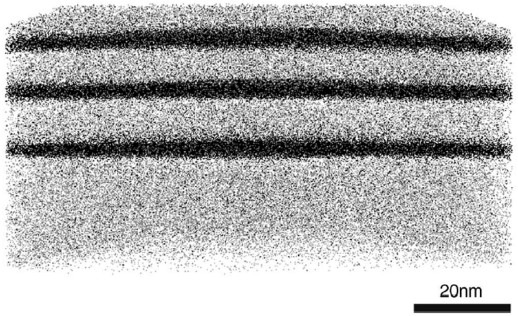
T. Smeeton *et al*, APL 83, 5419 (2003)

⇨ Indium clustering induced by e-beam irradiation during TEM observation

InGaN quantum wells

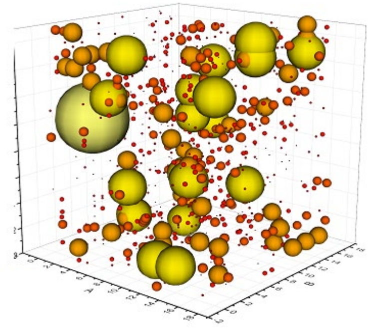
Impact of dislocations

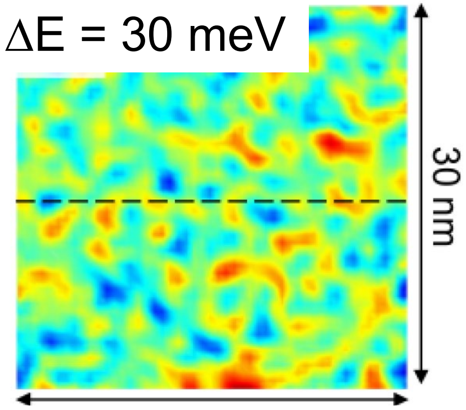
Atom probe tomography - InGaN/GaN QWs



M.J. Galtrey *et al.,* JAP 104, 013524 (2008)

- No evidence of In-rich clusters
- InGaN is a pure random alloy
- Local In atom distribution variations





M. Piccardo *et al*, PRB 95, 144205 (2017)

Sample	Diffusion constant (cm^2/s)
Bulk GaAs[a]	20
GaAs/AlGaAs quantum well	56
Bulk GaN[c]	From 1.6 to 2.0
50 nm InGaN layer[d]	2.1
InGaN/GaN quantum wells[e]	From 0.51 to 0.62

J. Danhof *et al.,* PRB 84, 035324 (2011)

- **Random alloy fluctuations strongly reduce the diffusion coefficient**

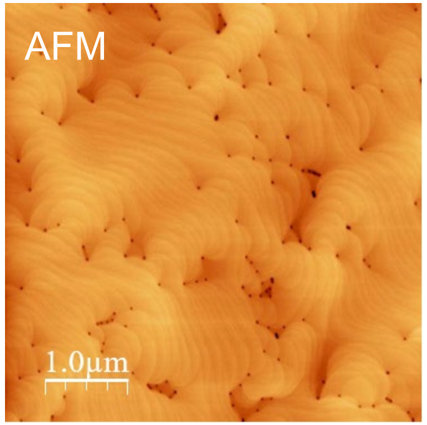
⇒ low carrier diffusion

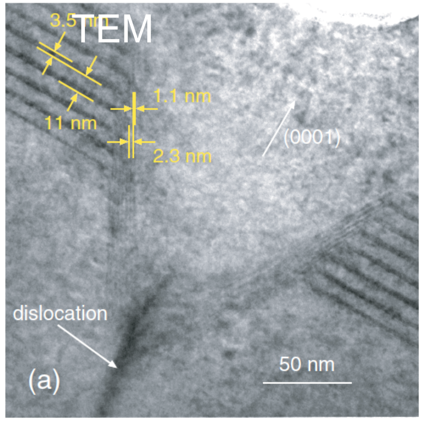
⇒ "carrier localization"

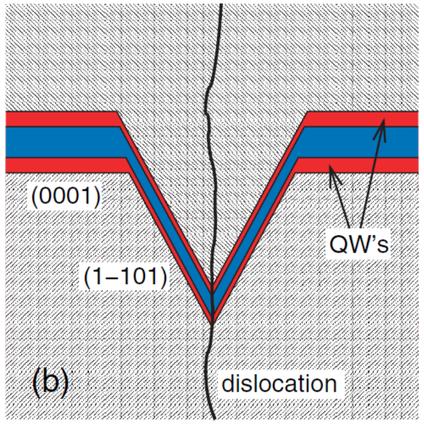
When the surface morphology comes to play

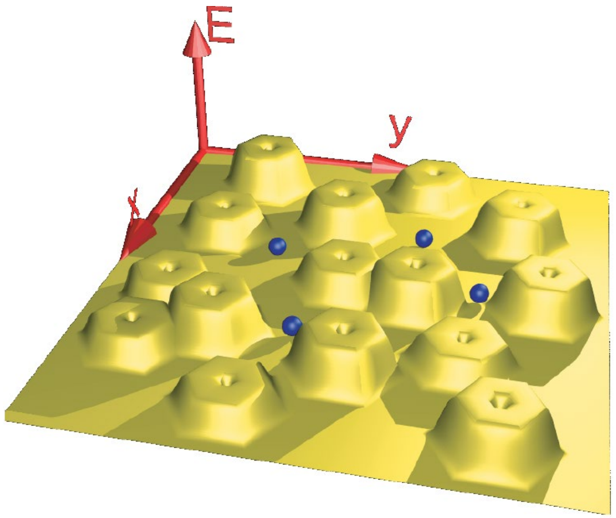
- The dislocation density is about 10^8 cm^{-2} (5×10^7 cm^{-2} in the best case)
- The diffusion length is larger than 1 μm

⇒ IQE higher than 90% ?









A. Hangleiter *et al.*, PRL 95, 127402 (2005)

Dislocation termination create V-pits that form an energy barrier around dislocations: dislocations are inactive in InGaN QWs.

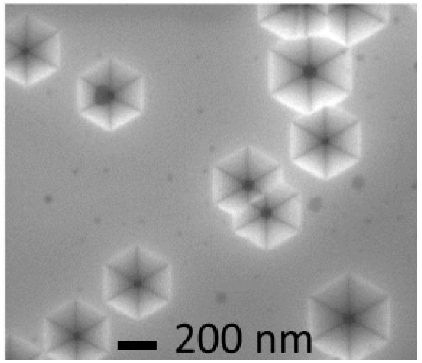
Growth engineering for efficient dislocation screening

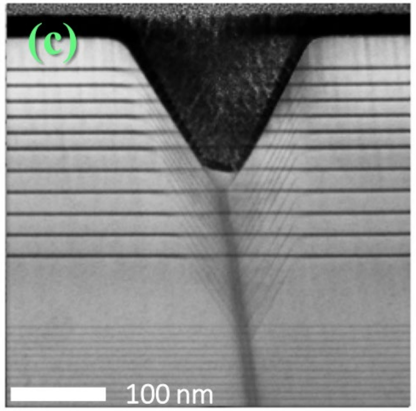
RESEARCH ARTICLE | MARCH 04 2015

Manipulation of nanoscale V-pits to optimize internal quantum efficiency of InGaN multiple quantum wells

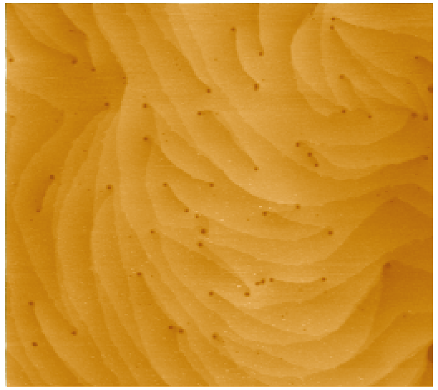
Chiao-Yun Chang ; Heng Li; Yang-Ta Shih; Tien-Chang Lu

Appl. Phys. Lett. 106, 091104 (2015)

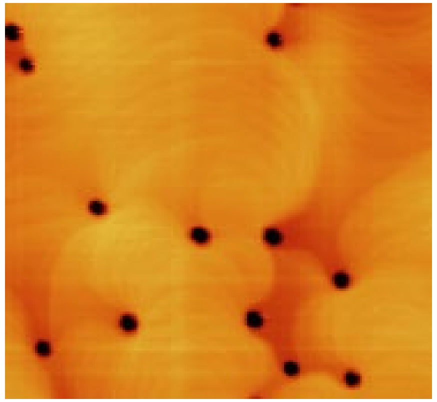




High-temperature growth of GaN (1000°C)

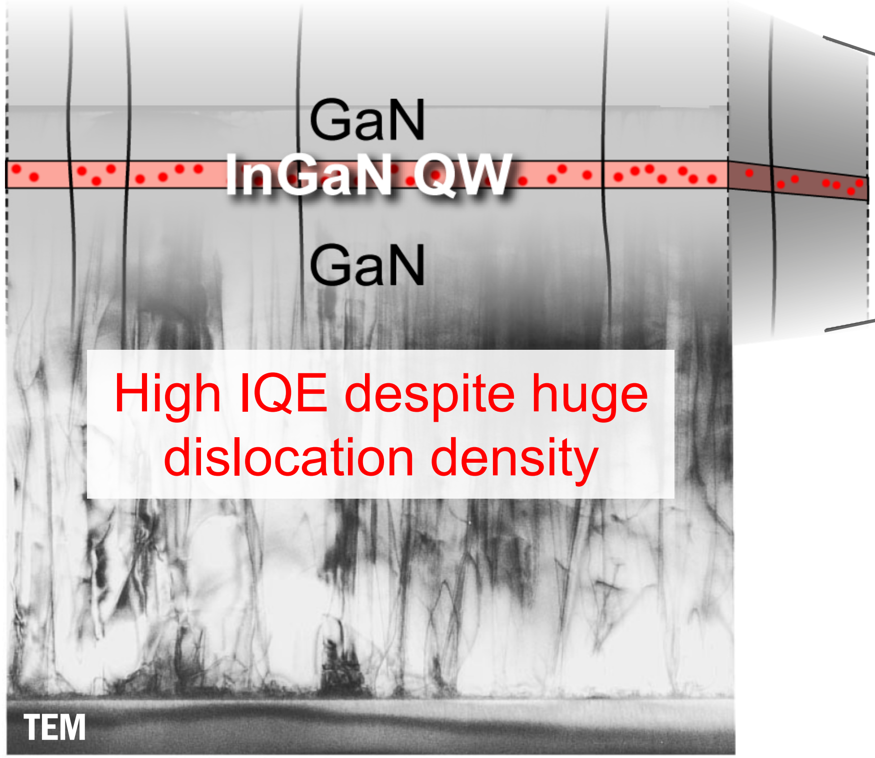


Low-temperature growth of Ga(In)N (<800°C)

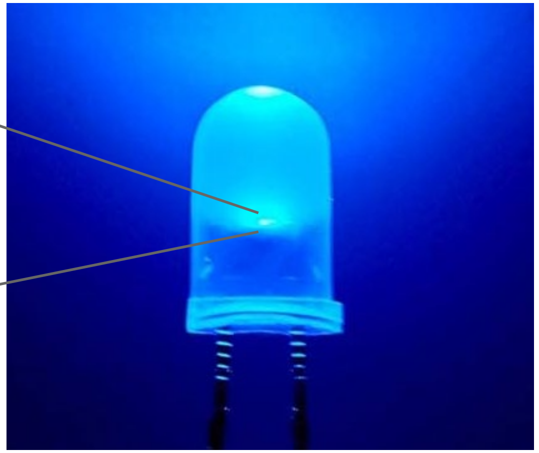


- Dislocations and point defects

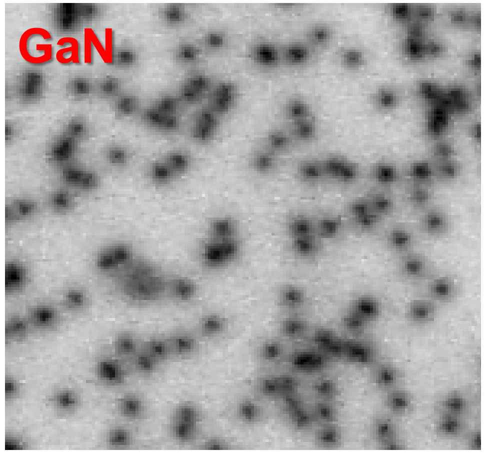
Blue LED cross section TEM

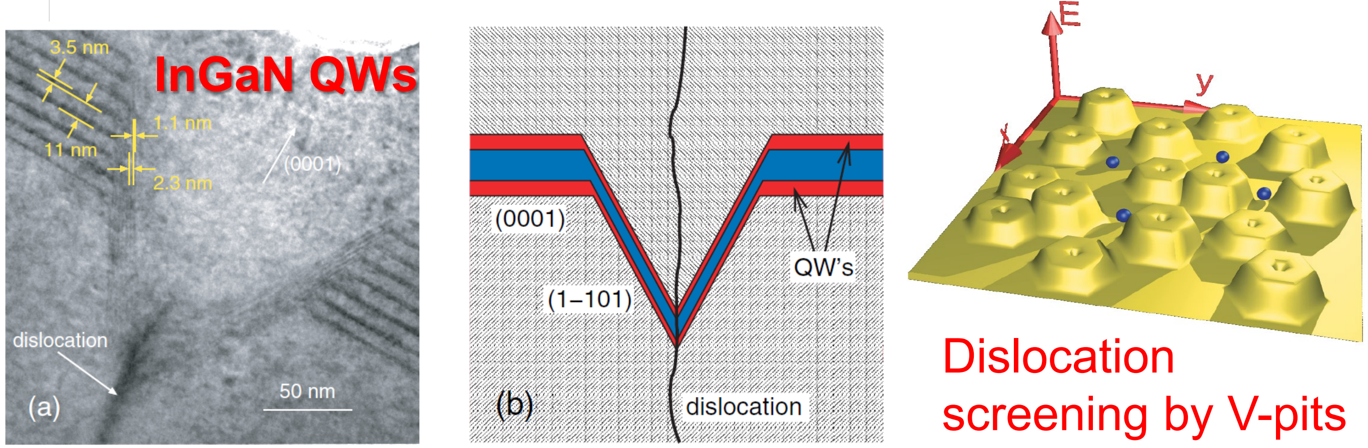


F.A. Ponce and D.P. Bour, Nature 386, 351 (1997)



Cathodoluminescence (CL)





Dislocation screening by V-pits

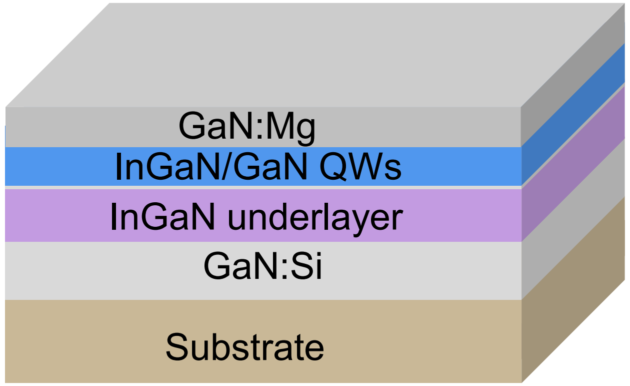
A. Hangleiter *et al.*, PRL 95, 127402 (2005)

In blue LEDs, IQE is slightly impacted by dislocations

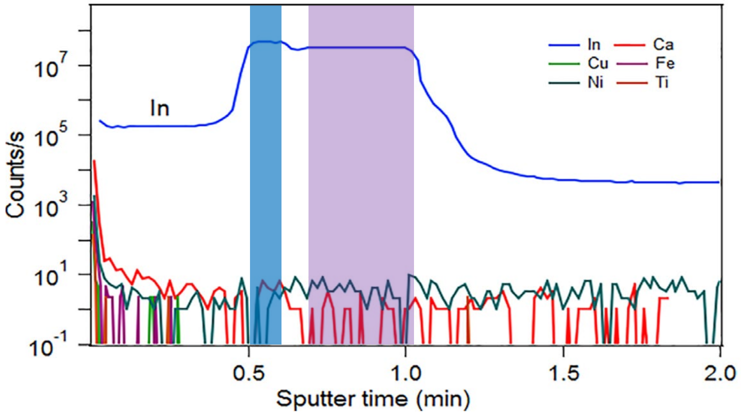
⇒ What about native point defects and/or impurities?

The InGaN underlayer

High efficiency LED



SIMS profile recorded on a commercial LED epiwafer grown by MOVPE

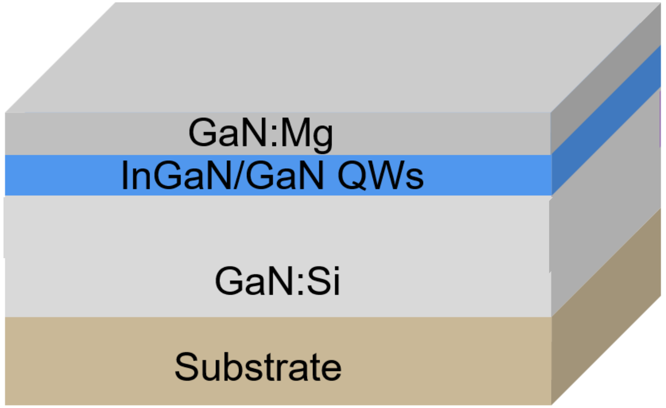


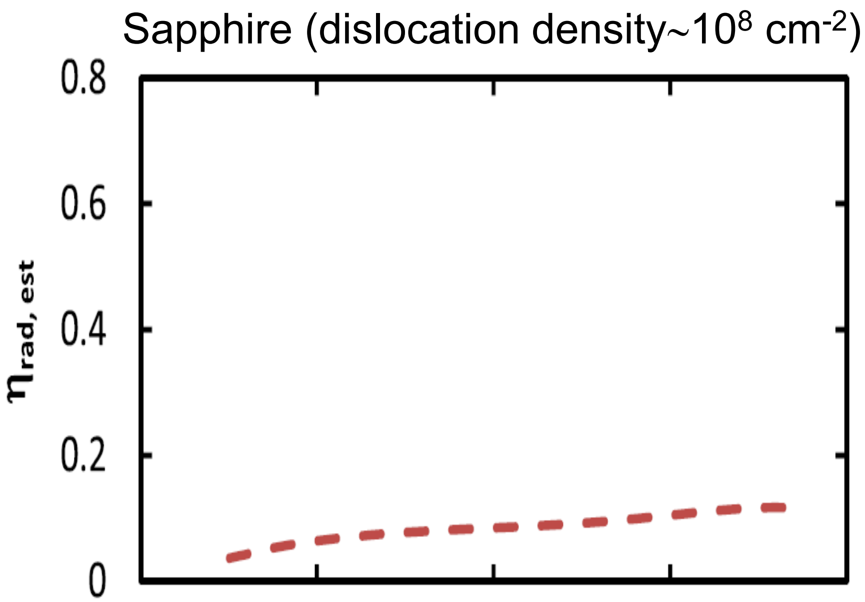
Young *et al.*, APL 109, 212103 (2016)

- Present in all blue LEDs
- Low indium content (typically 3%)
- Either a superlattice or a bulk layer

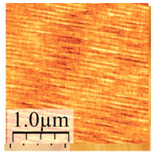
What is the purpose of this InGaN underlayer?

Point defects in InGaN/GaN QWs





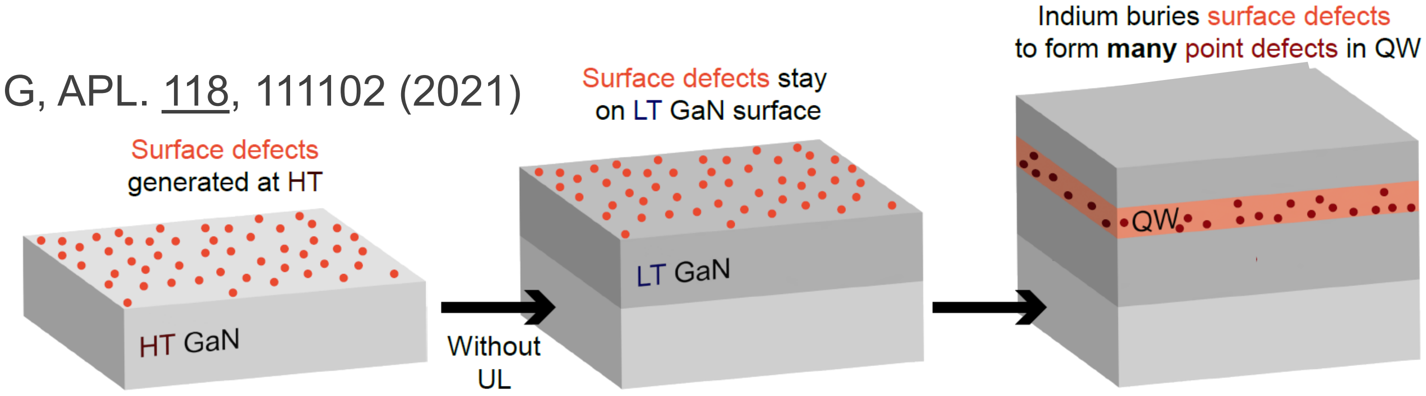
Armstrong *et al.*, JAP 117, 134501 (2015)



➲ The InGaN underlayer (UL) increases the efficiency independently of the presence of dislocations

Role of the InGaN UL

Y. Chen,... NG, APL. 118, 111102 (2021)



[SRH] ~10^{16} cm^{-3}

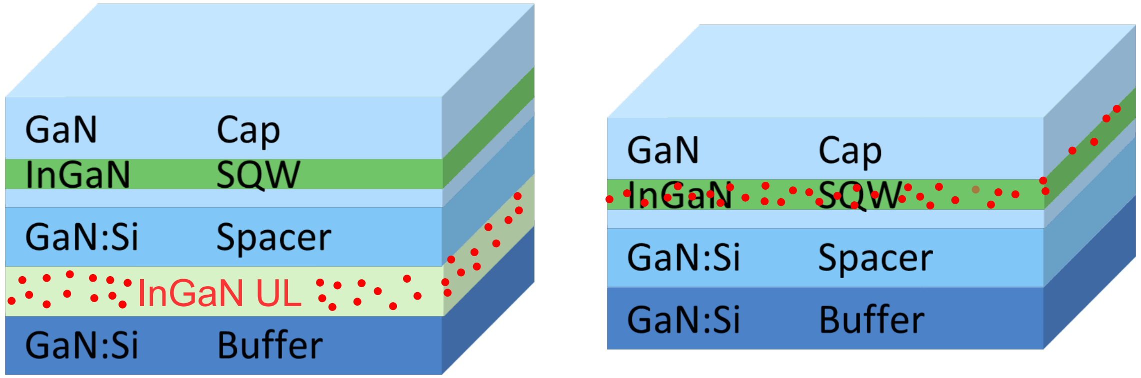
T. Weatherley,... NG, NanoLett. 21, 5217 (2021)

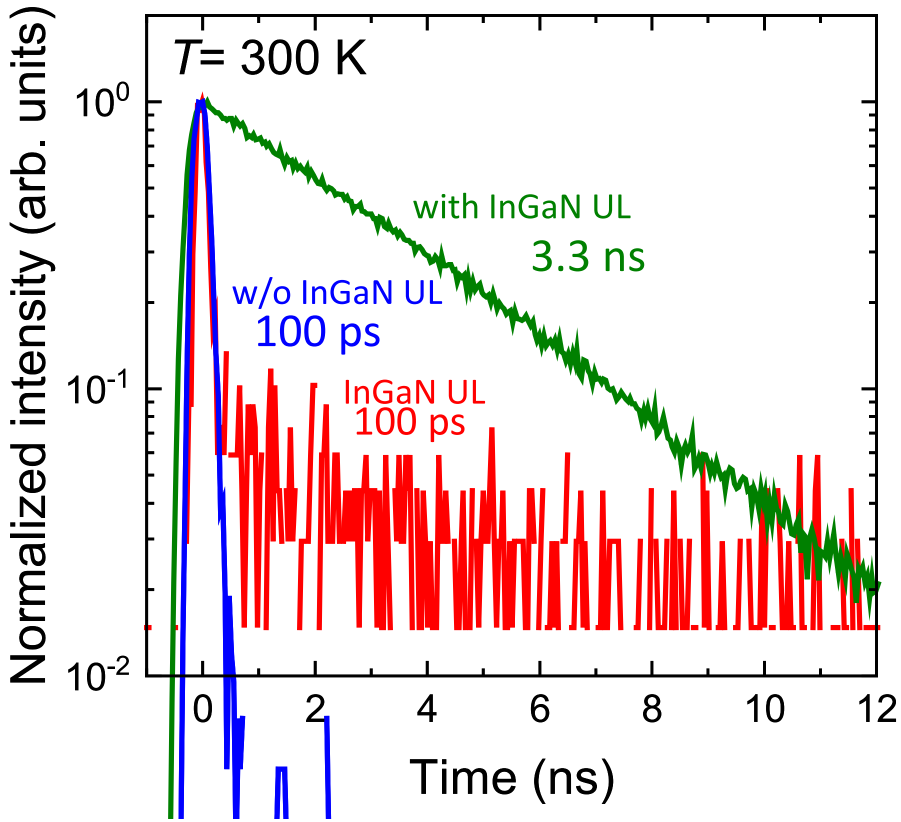
Surface defects (SDs) react with In atoms that create deep traps in the QWs

Burying impurities/defects at the surface

Point defects and/or impurities ➡ SRH recombination ➡ $\tau_{eff} = \frac{\tau_{nr}\,\tau_r}{\tau_{nr} + \tau_r}$ *Time-resolved photoluminescence*

2.7 nm thick $In_{0.12}Ga_{0.88}N$ Single QW





➲ with InGaN UL: longer effective lifetime

⇒ much less SRH recombination

Experimental approach

- Probe: a single InGaN/GaN QW (*2.7 nm, $x \approx 0.12$*)
- MOCVD growth

  Reactor 1: Aixtron 3x2” CCS - stainless steel showerhead

  Reactor 2: Aixtron 200/4 RF-S - quartz liner

  TEGa for InGaN UL and QW (but similar results with TMGa)

- Optical characterization

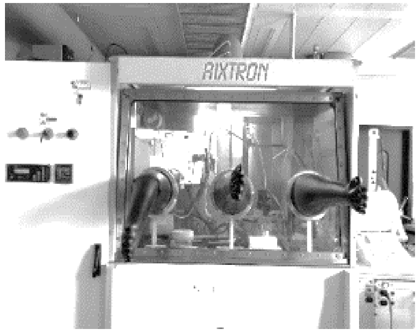
  300 K PL with resonant excitation (375 nm cw laser, ~0.3 W/cm^2)

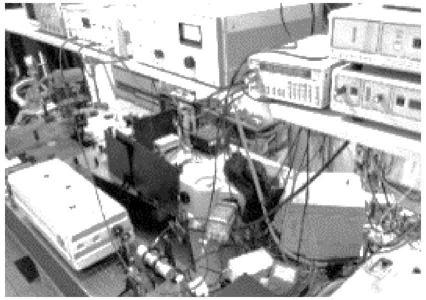
  300 K time-resolved PL ⇒ *effective lifetime*

Effective lifetime: $$\frac{1}{\tau_{eff}} = \frac{1}{\tau_R} + \frac{1}{\tau_{NR}}$$

$$IQE \propto \frac{\tau_{eff}}{\tau_R}$$

τ_R *is constant for a given QW*





Surface defects and indium interaction

Modeling of the effective lifetime

Hypothesis: the incorporation of a SD in InGaN alloy generates a NRC

$$\frac{1}{\tau_{eff}} = \frac{1}{\tau_0} + \frac{1}{\tau_{NR,SD}}$$

- τ_0: lifetime of the QW free of NRCs induced by the SDs
- $\tau_{NR,SD}$: non−radiative lifetime depending on SD incorporation

$$\tau_{NR,SD} \propto \frac{1}{[SD]_{QW}}$$ with $[SD]_{QW}$ the concentration of SDs incorporated in the QW

- θ_0 : initial density of SDs after the GaN buffer grown at high-temperature
- SDs segregate at the growth front: $[SD]_{QW} \propto \theta_0 R^N$ K. Muraki *et al.*, APL 61, 557 (1992)

  with *N* the number of deposited monolayers

  R the segregation coefficient (probability to pass from the n^{th} layer to the $n+1^{th}$ layer)
- SDs are buried when they interact with indium atoms: $R = R_{GaN} - xp$

  with R_{GaN} the segregation coefficient of SDs in GaN

  x the indium composition of the InGaN underlayer

  p the interaction efficiency between indium atoms and SDs

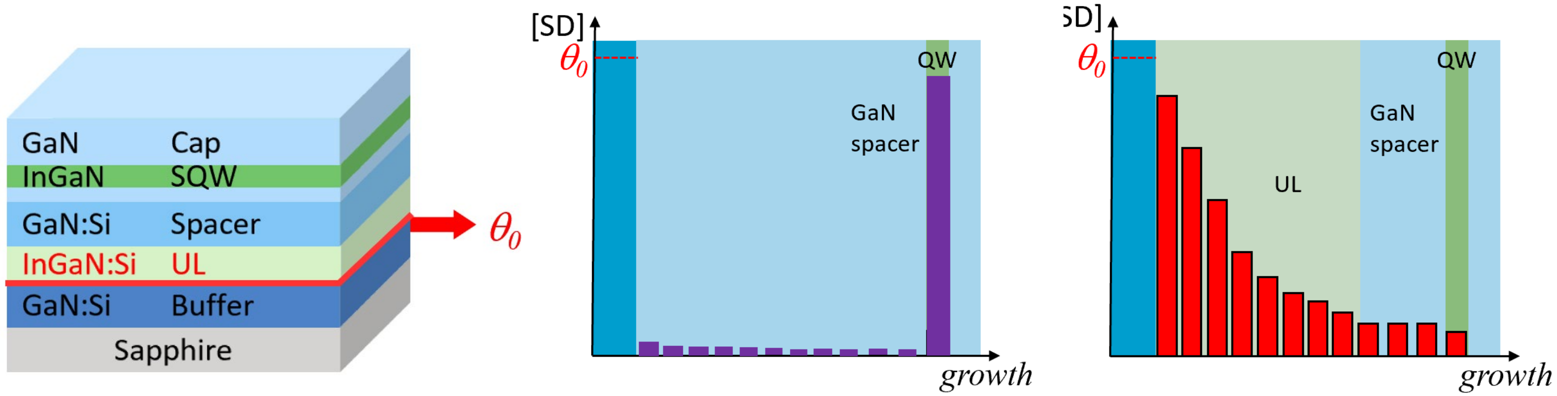
Modeling of the effective lifetime

$$\tau_{eff} = \tau_0 \cdot \frac{1}{1 + \left(\tau_0 \cdot C_{n,p} \cdot C_{QW} \cdot \theta_0 \left(R_{GaN} - x \cdot p\right)^N\right)}$$

SDs after the growth of N monolayers of $In_xGa_{1-x}N$ UL

Capture coefficient of SRH centers induced by SD incorporation

Number of SD trapped in the QW: $C_{QW} = \left(1 - \left(R_{GaN} - x_{QW}p\right)^{N_{QW}}\right)/L_{QW}$

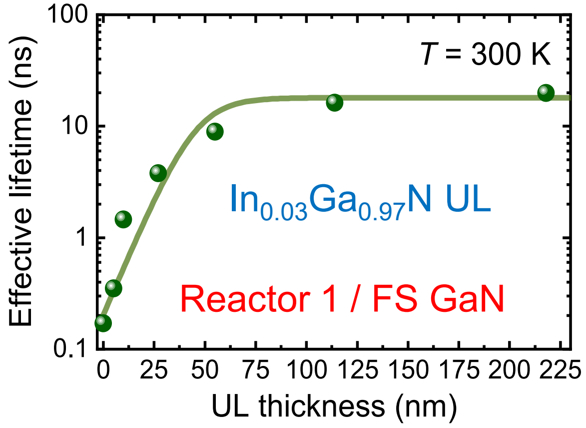


APL 113, 111106 (2018)

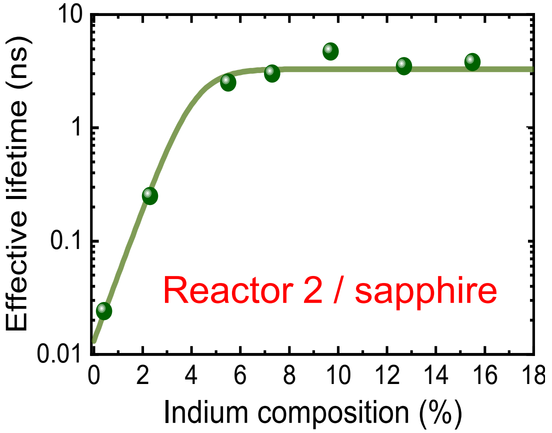
Modeling of the effective lifetime

InGaN UL

Thickness dependence

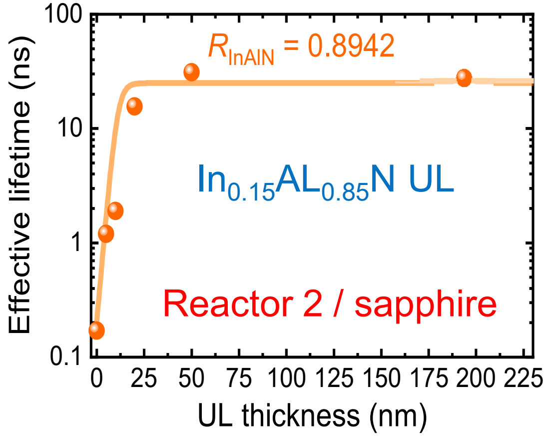


Composition dependence

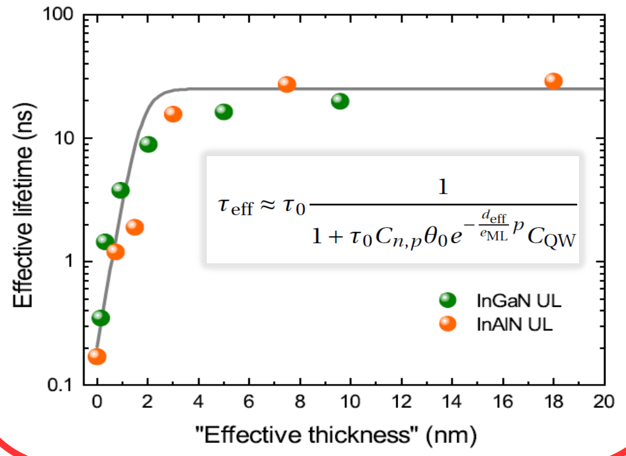


InAlN UL

Thickness dependence



Effective thickness: $d_{eff} = x\, d_{UL}$



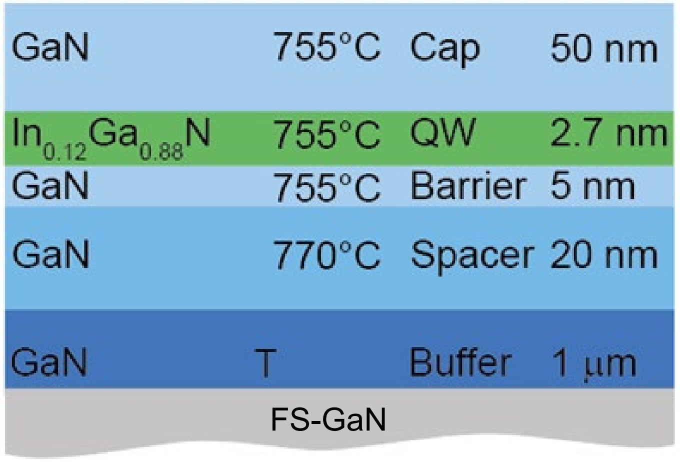
$$\tau_{\mathrm{eff}} \approx \tau_0 \frac{1}{1 + \tau_0 C_{n,p} \theta_0 e^{-\frac{d_{\mathrm{eff}}}{e_{\mathrm{ML}}} p} C_{\mathrm{QW}}}$$

- ➲ SD interaction with indium is independent of the material
- ➲ Same behavior whatever the MOCVD reactor/substrate
- ➲ **Strong interaction between indium atoms and SDs**

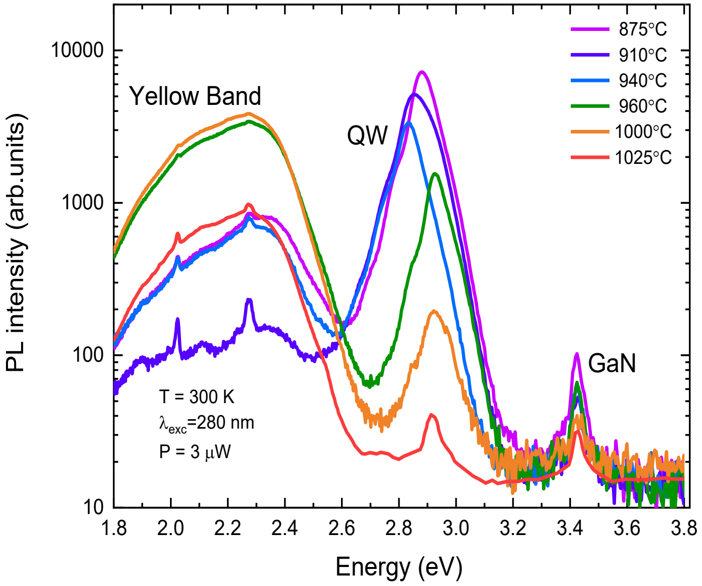
APL 113, 111106 (2018)

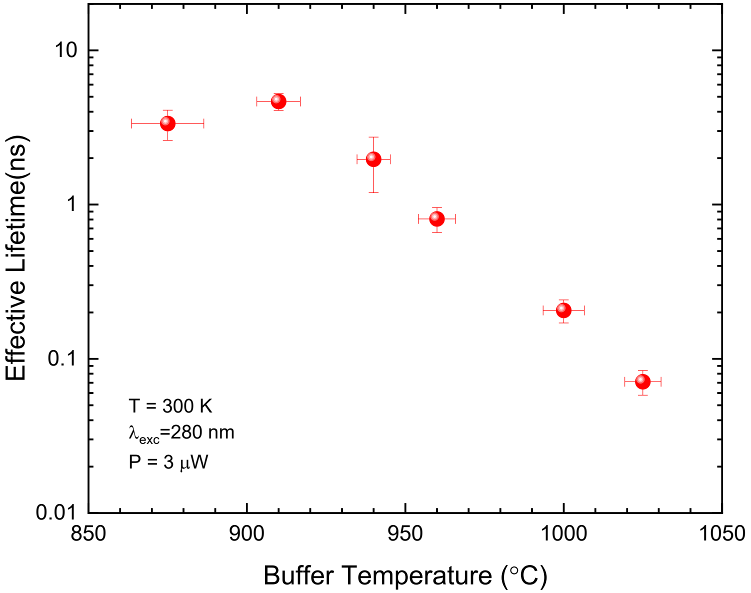
Impact of the growth temperature

InGaN SQW grown on 1 μm thick GaN buffer on FS-GaN substrate



$T_{buffer}(°C)$ = 875, 910, 935, 995, 1050





➲ The HT growth of GaN buffer generates surface defects

Appl. Phys. Lett. 118, 111102 (2021)

- What could be these surface defects?

Li, C, O, Na, Mg, P, K, Ca, Fe, Ti, Cr, Ni, Cu, Zn, Mo (SIMS at EAG Laboratories)

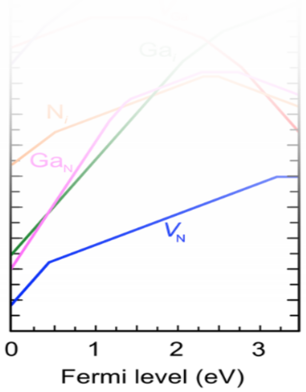
Impurities

Measured concentration:	[C] = 2×10^{16} cm^{-3}	[O] = 7×10^{16} cm^{-3}	[Fe] = 4×10^{14} cm^{-3}	[Ca] < 2×10^{14} cm^{-3}
Critical concentration:	[C] > 4×10^{17} cm^{-3}	[O] > 2×10^{17} cm^{-3}	[Fe] > 1×10^{15} cm^{-3}	[Ca] > 1×10^{14} cm^{-3}

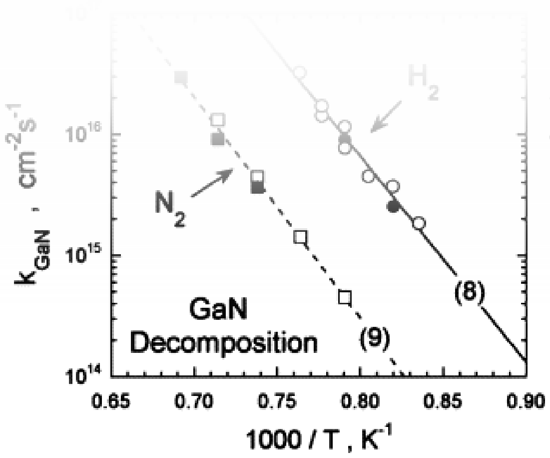
⇒ no correlation between impurities and QW efficiency (detection limit?)

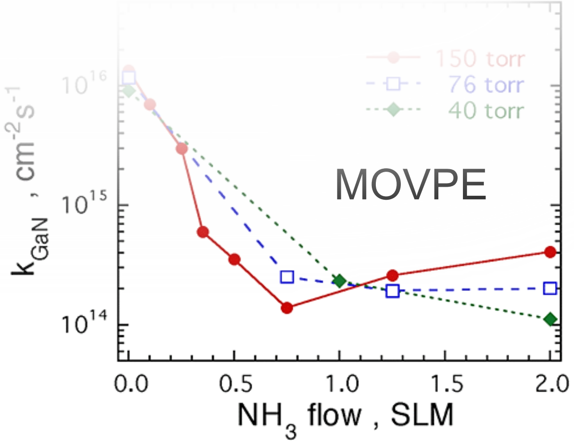
Could the **low stability** of GaN surface (Ga-polar) at **high temperature** impact the InGaN quantum well efficiency?

Point defects



J.L. Lyons, G.G. van de Walle
npj Comput Mater 3, 12 (2017)

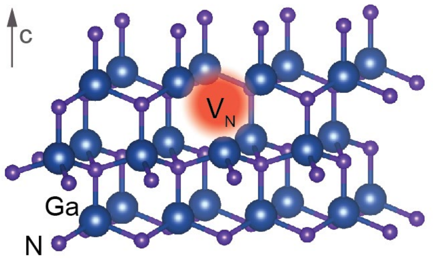




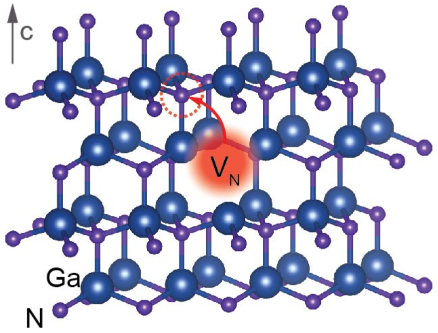
GaN (0001) surface is unstable

EPFL

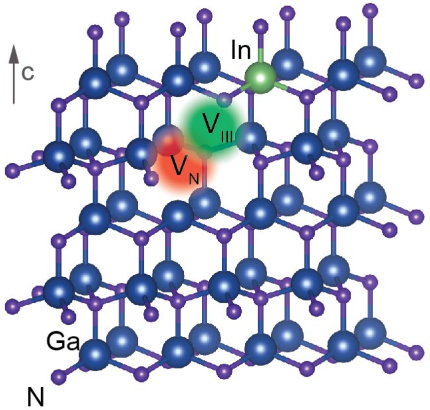
Tentative mechanism



HT GaN growth (>900°C): V_N at the surface with high concentration due to a lower formation energy but they do not incorporate (high formation energy in the bulk)



LT GaN growth (<800°C): V_N are no longer generated at the surface but they segregate due to the high formation energy in the bulk

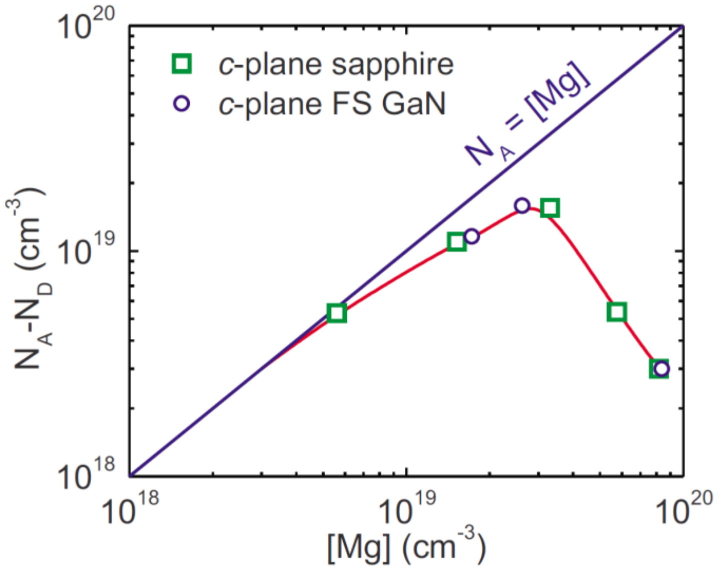


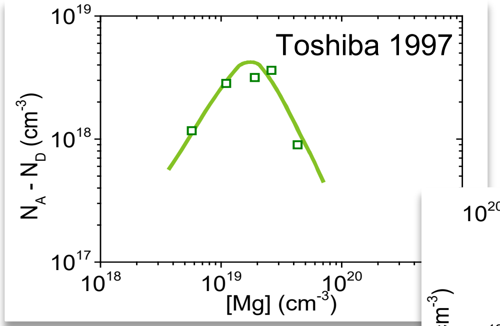
InGaN growth: incorporation of V_N *via* the creation of V_N-V_{In} divacancies acting as NRCs

Doping

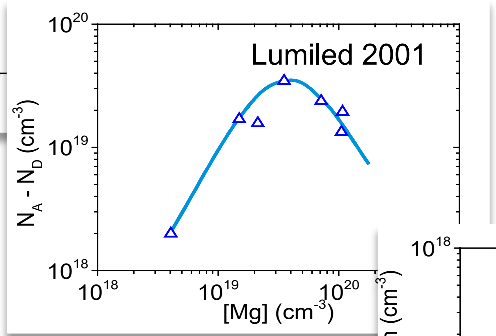
p-type GaN layers grown by MOCVD

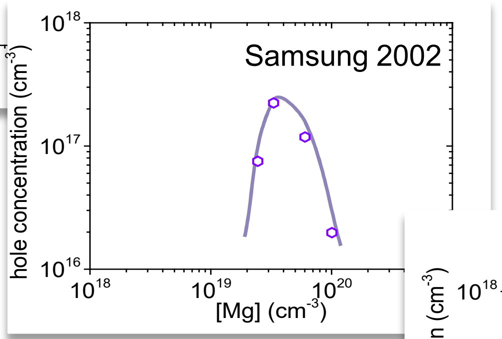
E_A ~ 160 meV → high [Mg] needed as only few % are ionized at room-temperature

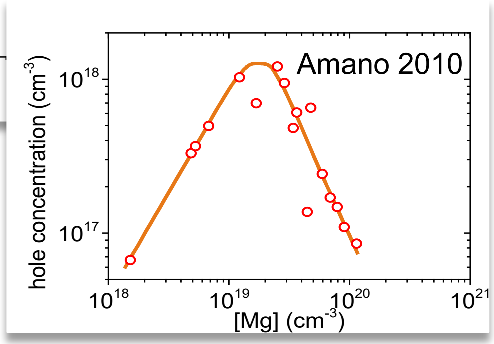




TOSHIBA: L. Sugiura et.al., Appl. Phys. Lett. **72**, 1748
Lumiled: W. Goetz et. al., ICNS-4; Denver, CO, 2001
Samsung: J. S. Kwak et. al., Appl. Phys. Lett. **80**, 3554
Amano: D. Iida et. al., J. Cryst. Growth **312**, 3131



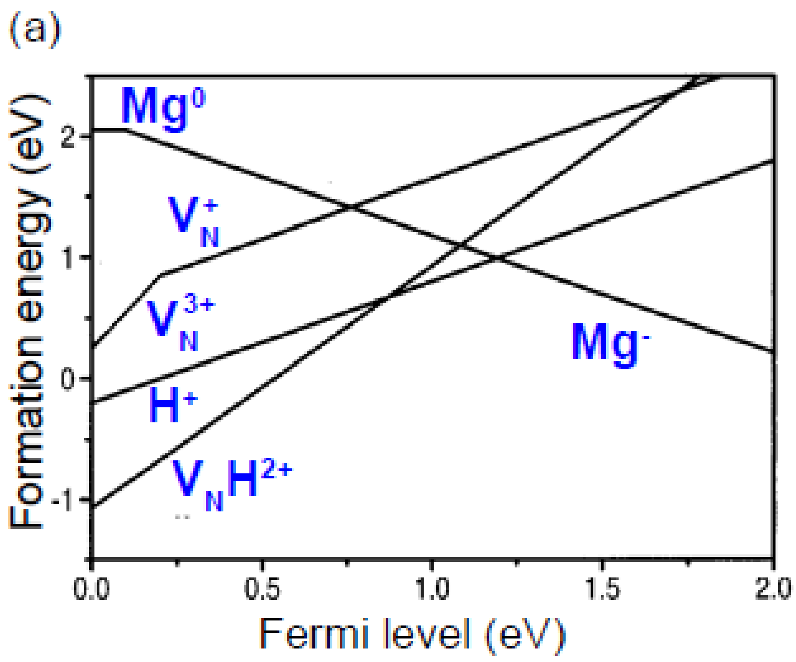




[Mg] ~ 3 × 10^{19} cm^{-3} intrinsic limit?

EPFL

Compensation: nitrogen vacancies



Formation energy of nitrogen vacancies decreases when the Fermi level closes the valence band

C. G. Van de Walle, “Interactions of hydrogen with native defects in GaN,” *Phys. Rev. B*, vol. 56, no. 16, p. R10020, 1997.

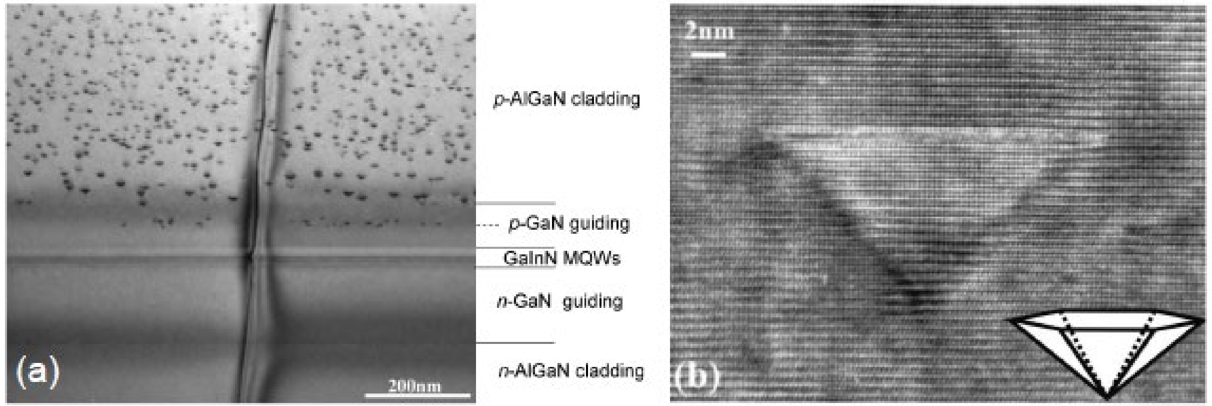
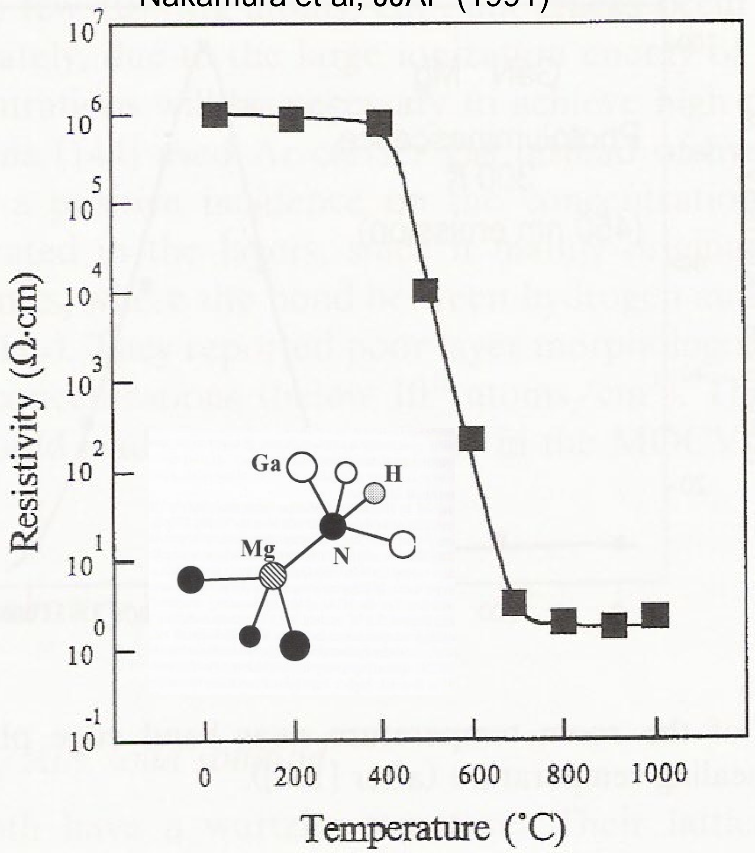


Figure 2.4: (a) Cross-sectional TEM image of an LD showing the presence of pyramidal inversion domains [89]. (b) High resolution TEM image along the [11$\bar{2}$0] zone axis of a pyramidal inversion domain [91].

P. Vennegues, M. Benaissa, B. Beaumont, E. Feltin, P. De Mierry, S. Dalmasso, M. Leroux, and P. Gibart, “Pyramidal defects in metalorganic vapor phase epitaxial Mg doped GaN,” *Appl. Phys. Lett.*, vol. 77, no. 6, p. 880, 2000.

Passivation by hydrogen

Nakamura et al, JJAP (1991)



P-type conductivity is achieved using Mg. However, Mg is passivated by hydrogen due to complex formation.

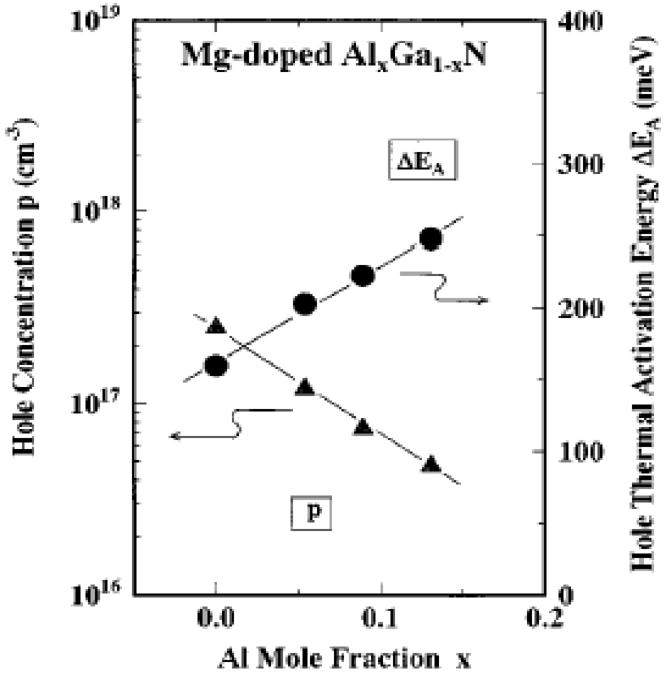
Activation of Mg atoms either by thermal annealing or electron beam irradiation.

■ p-type of AlGaN and deep UV LEDs

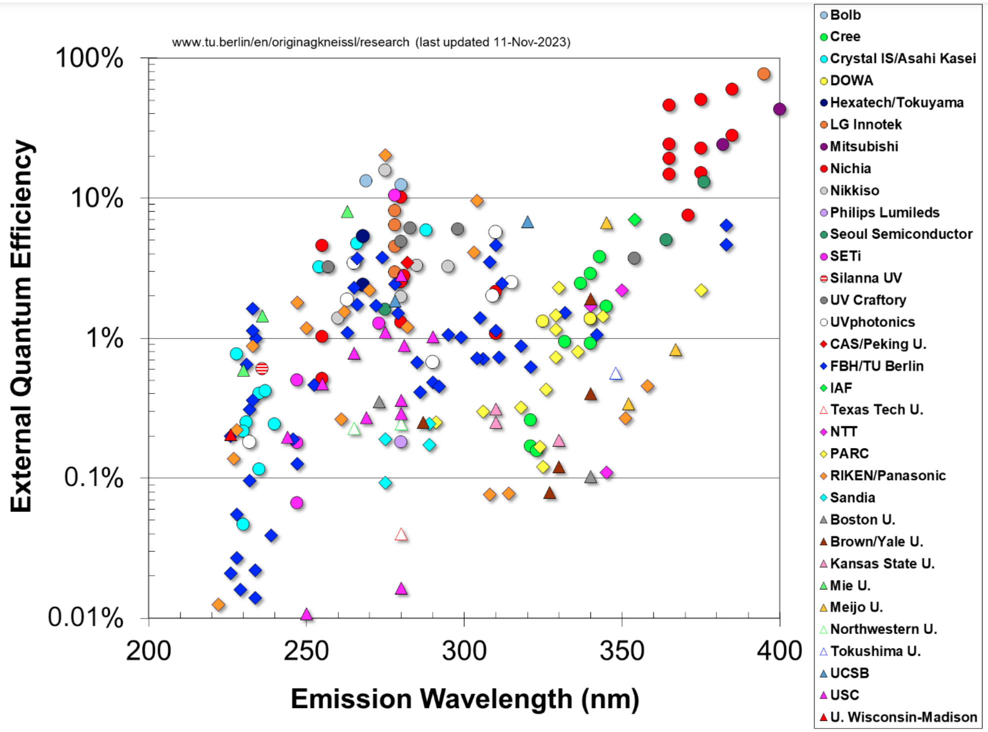
P-type doping of AlGaN alloys is much more difficult than for GaN layers.

The hole concentration rapidly decreases with increasing Al composition. This is the consequence of a larger activation energy.

Suzuki et al, JCG (1998)



Deep UV LEDs



Kneissl, M., Seong, TY., Han, J. *et al.* The emergence and prospects of deep-ultraviolet light-emitting diode technologies. *Nat. Photonics* **13**, 233–244 (2019).

Growth techniques

Main growth techniques:

Chemical

Hydride vapor phase epitaxy (HVPE)

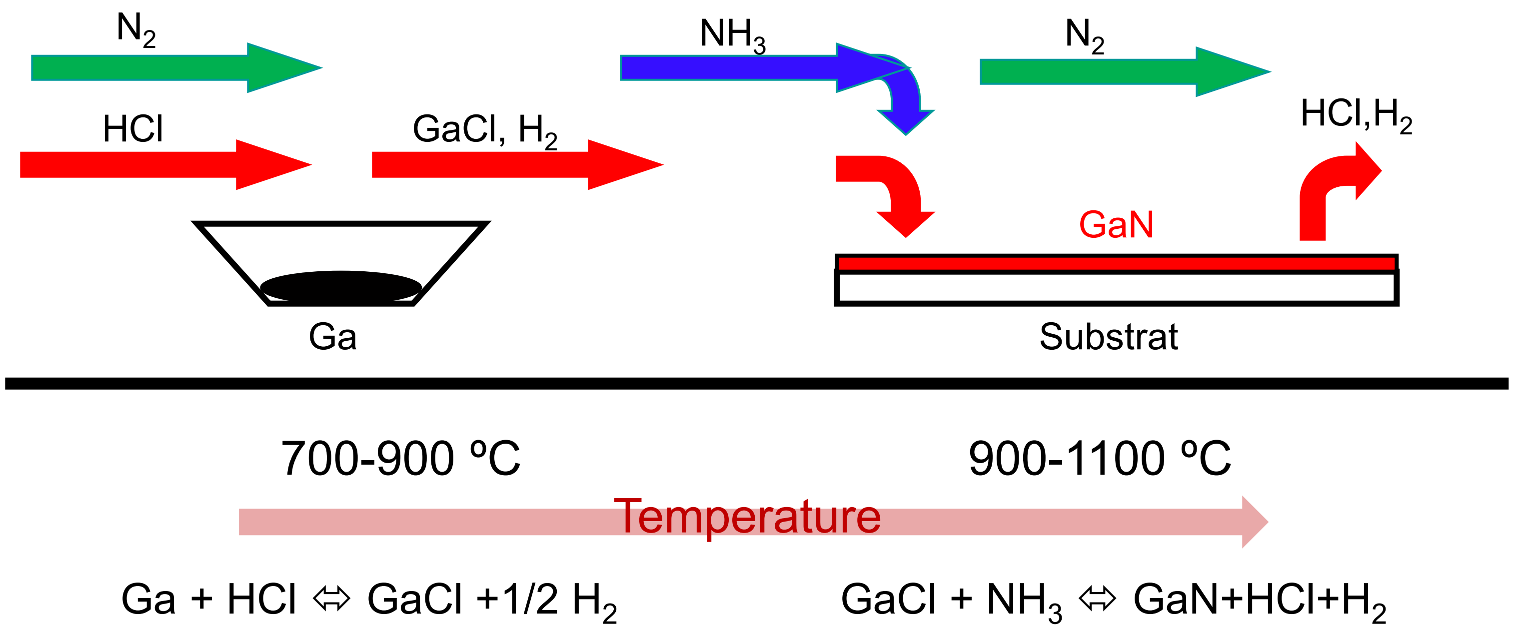
Metal-organics vapor phase epitaxy (MOVPE)

Metal-organics chemical vapor deposition (MOCVD)

Physical

Molecular beam epitaxy (MBE)

Hydride vapor phase epitaxy (HVPE)



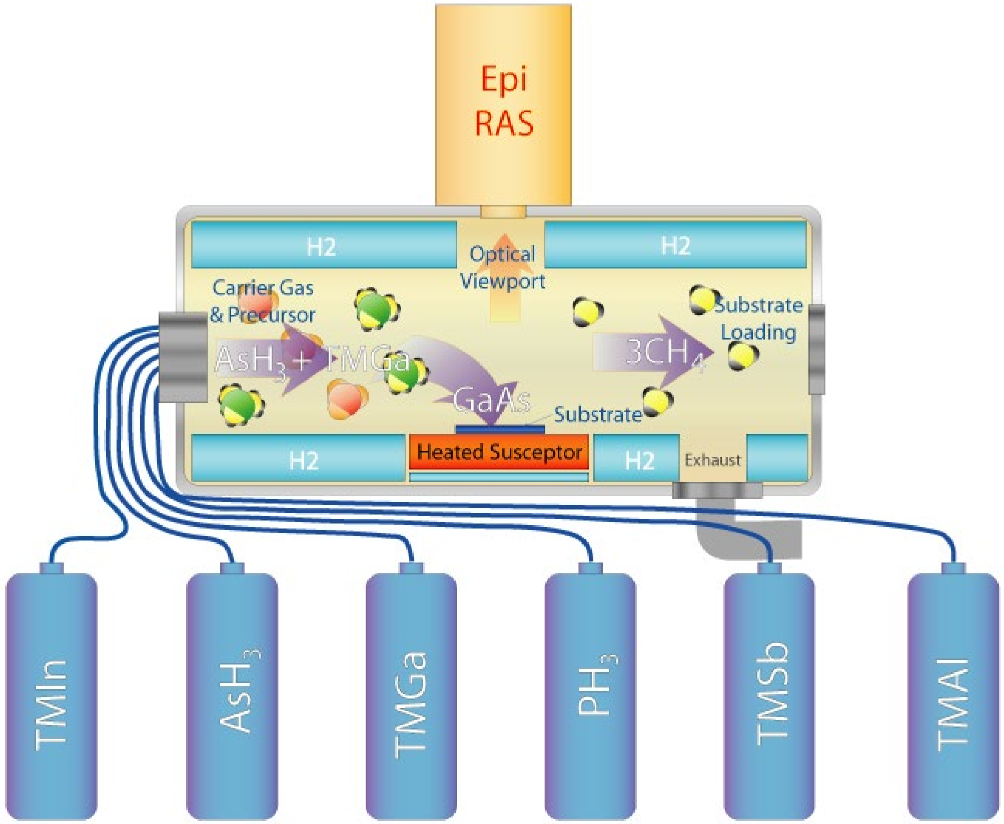
Operates near equilibrium:

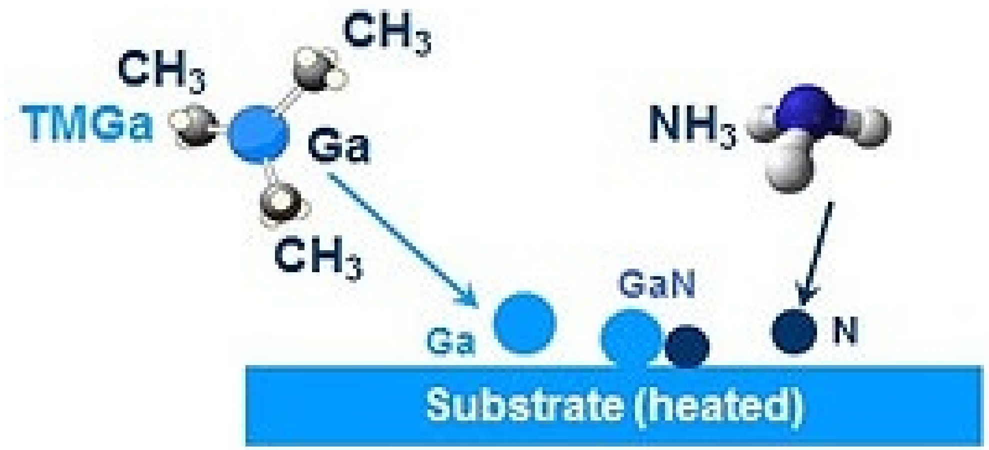
Growth rate > 100µm/h

Use for making free-standing GaN substrates

EPFL

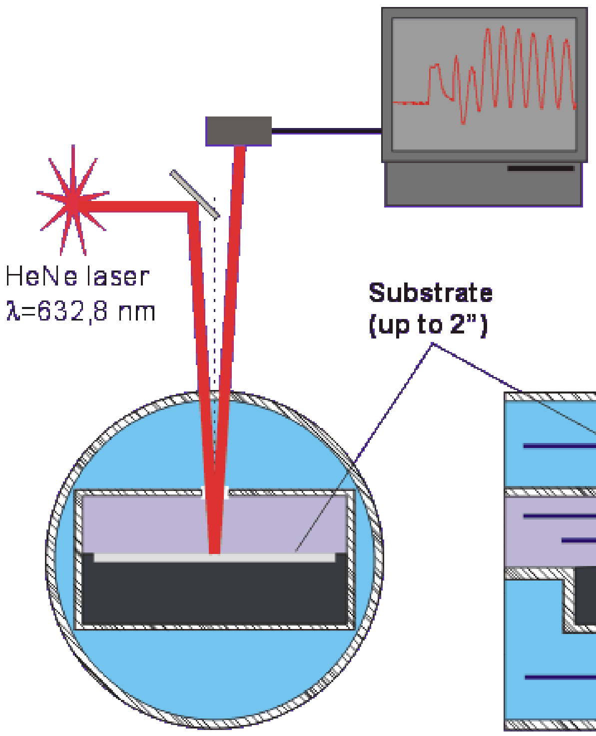
Metal-organic vapor phase epitaxy (MOVPE)

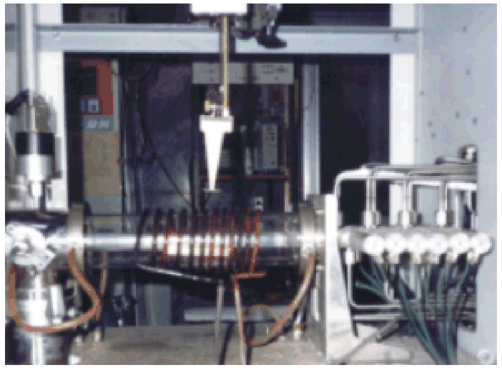


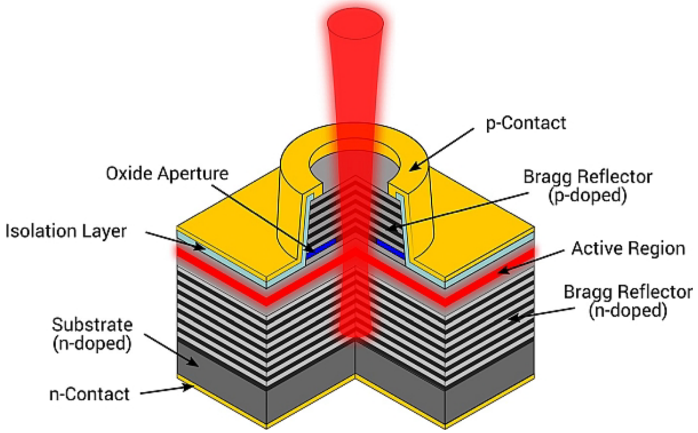


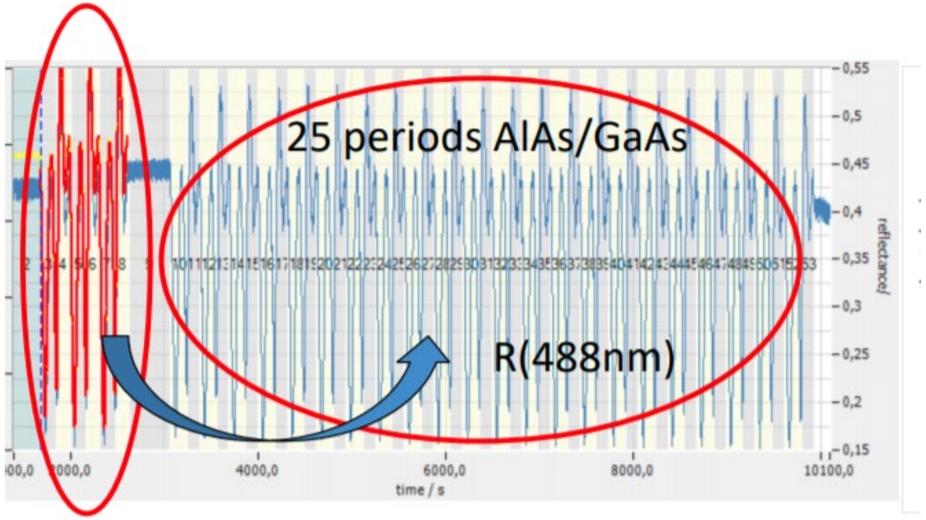
Metal-organic vapor phase epitaxy (MOVPE)

In situ reflectivity







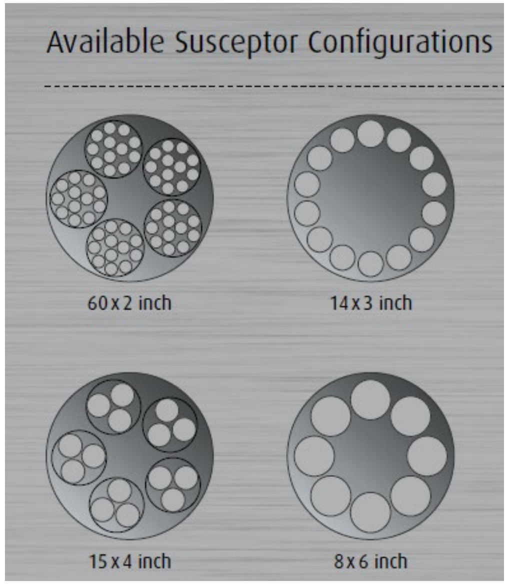


Metal-organic vapor phase epitaxy (MOVPE)

Production systems

 # wafers per run: 124x4” and 48x6”

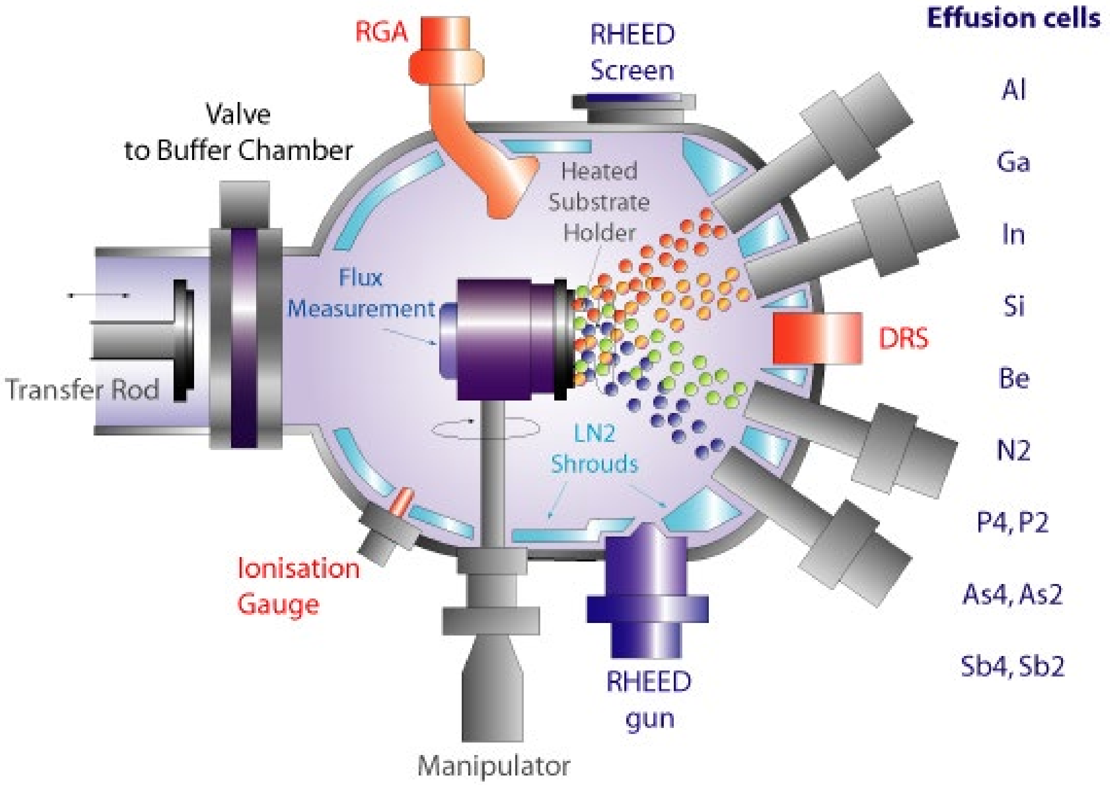
Production systems



GaAs/InP based Optoelectronics and Electronic Devices

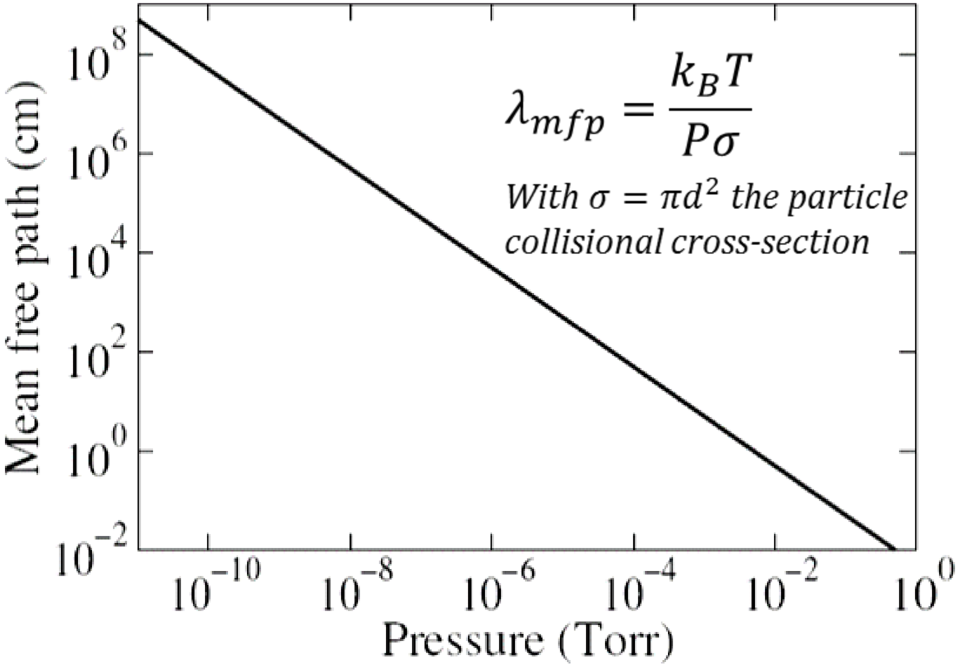
GaN blue LEDs (solid state lighting)

Molecular Beam Epitaxy (MBE)



Ultra-high vacuum

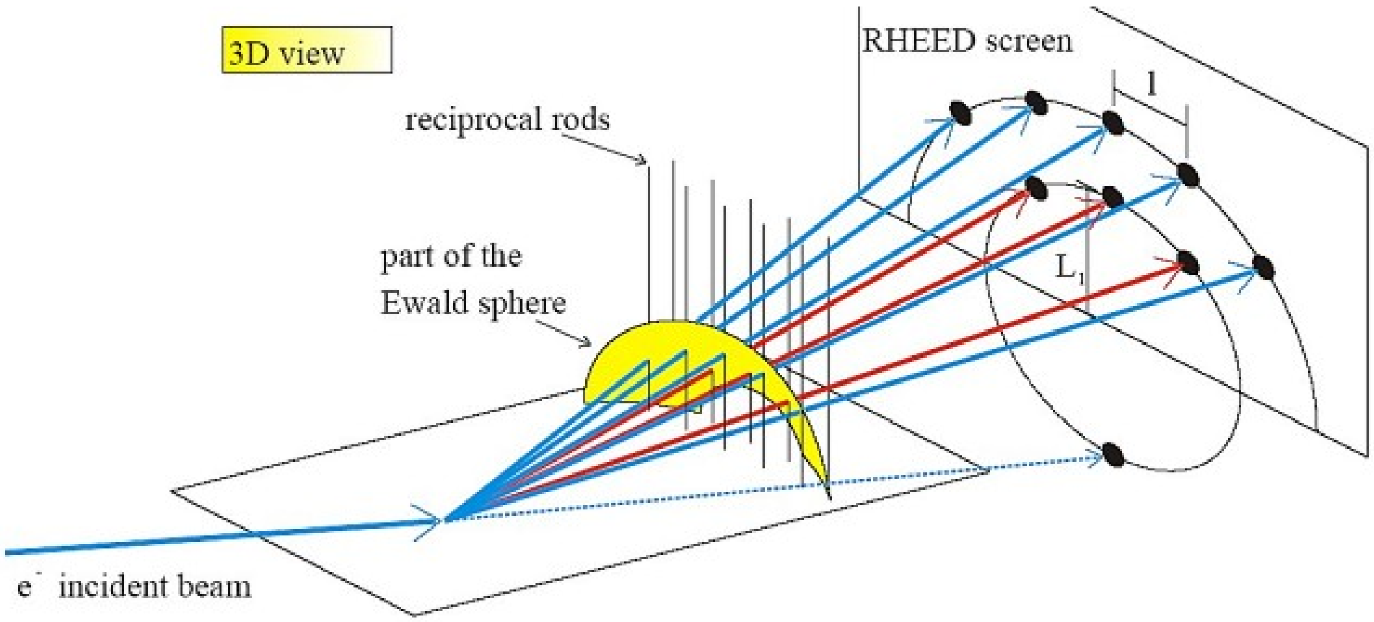
✓ No interaction between atomic fluxes



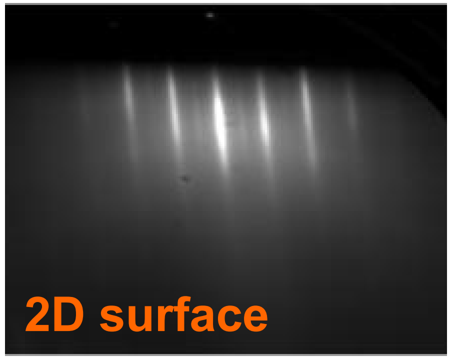
✓ Use of *in situ* electron-beam monitoring (RHEED)

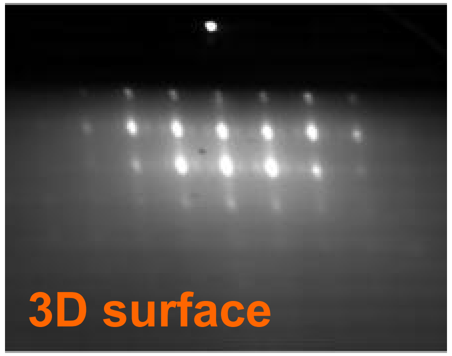
Molecular Beam Epitaxy (MBE)

In situ Reflection High-Energy Electron Diffraction



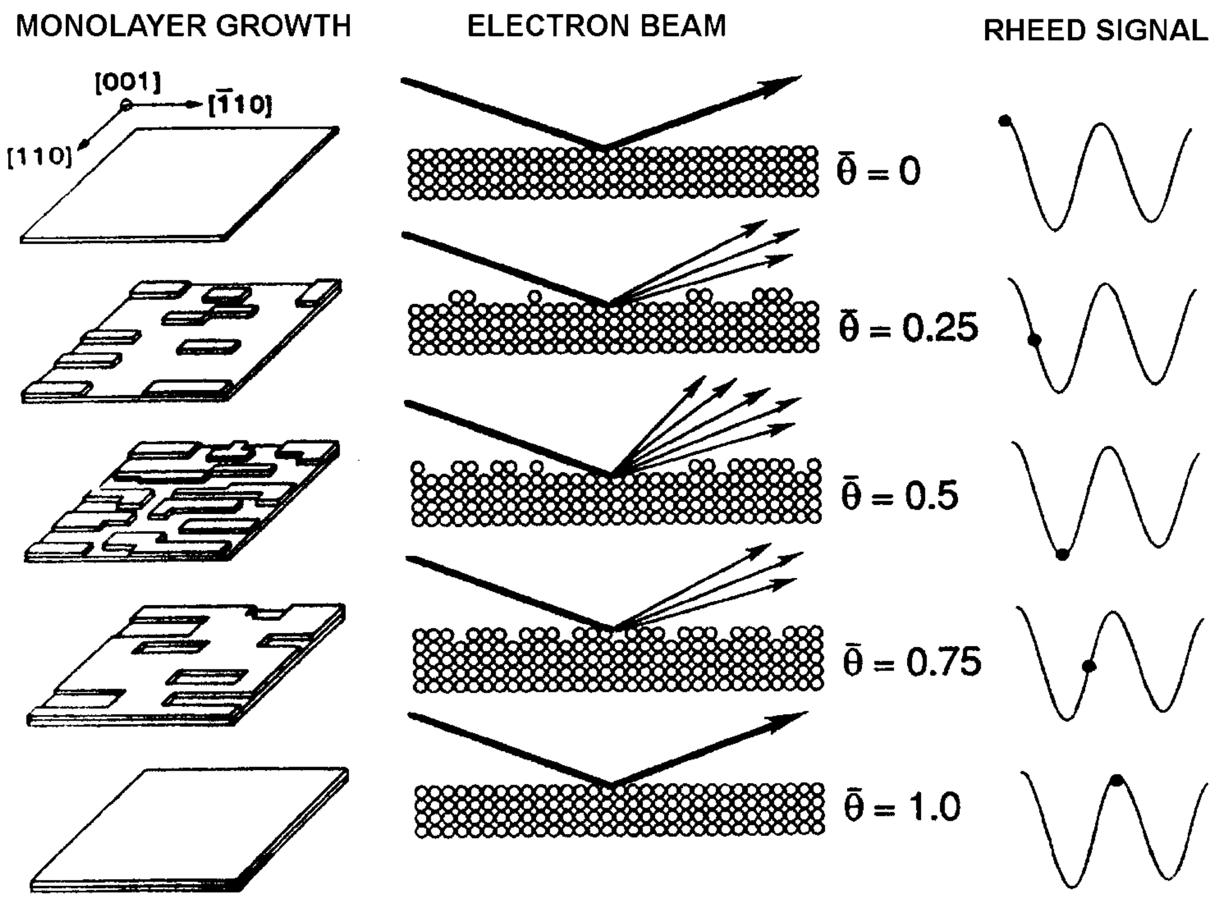
http://www.wmi.badw.de/methods/leed_rheed.htm



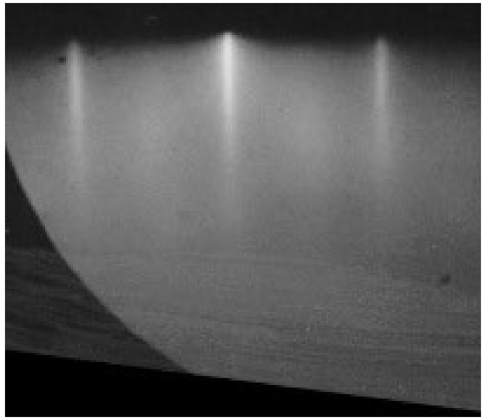


➢ **Surface roughness**

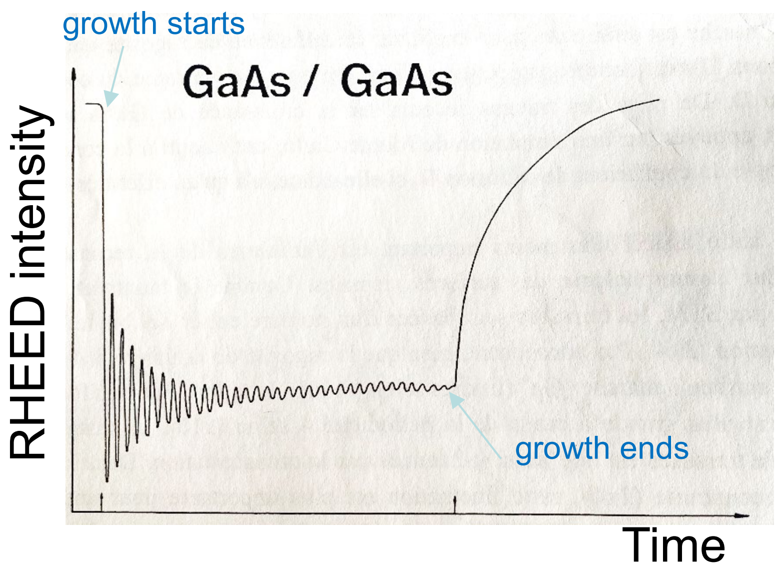
MBE growth: *in situ* monitoring with RHEED



J.H. *Neave*, B.A. *Joyce*, P.J. Dobson, N. Norton. Appl. Phys. A, 31 (1983)



Usually, new 2D-islands tend to appear on large growing 2D-islands → **damped oscillations**

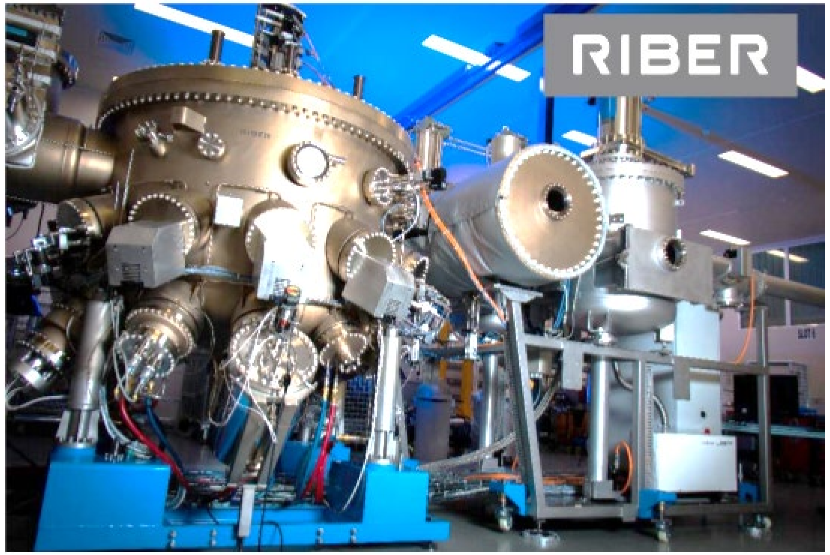


Molecular Beam Epitaxy (MBE)

Research

- Up to 4'' wafers
- II-VI, III-V (As, P, Sb, N), Oxides, SiGe, etc…

Production



- Up to 5 × 8'' or 8 × 6'' wafers
- Mainly for GaAs-based HEMTs & HBTs
- Opportunities for VCSELs