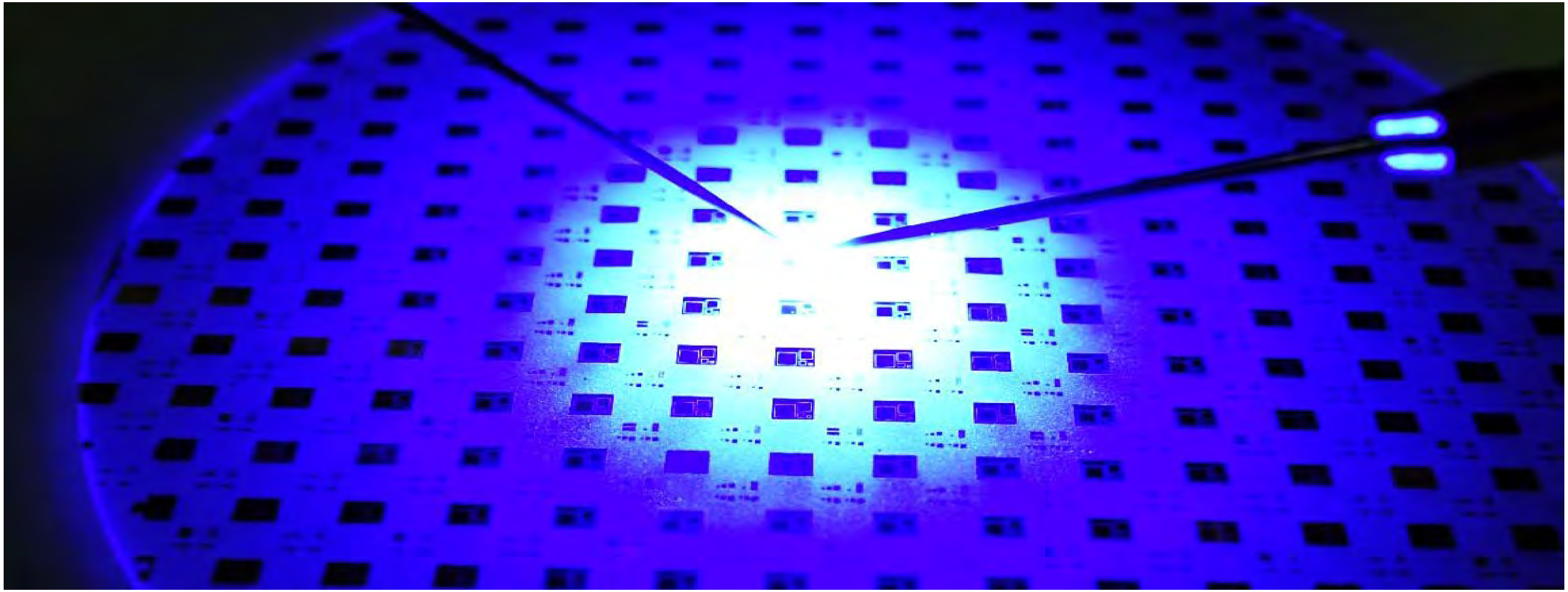
III-nitride semiconductors



Nicolas Grandjean
Institute of Physics
EPFL - Switzerland

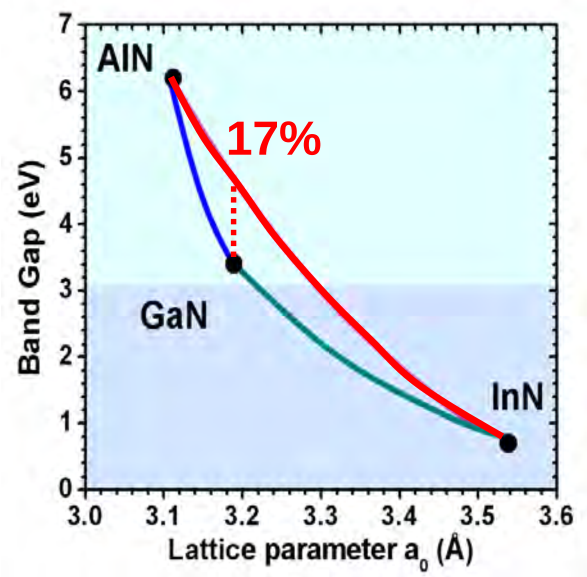
nicolas.grandjean@epfl.ch

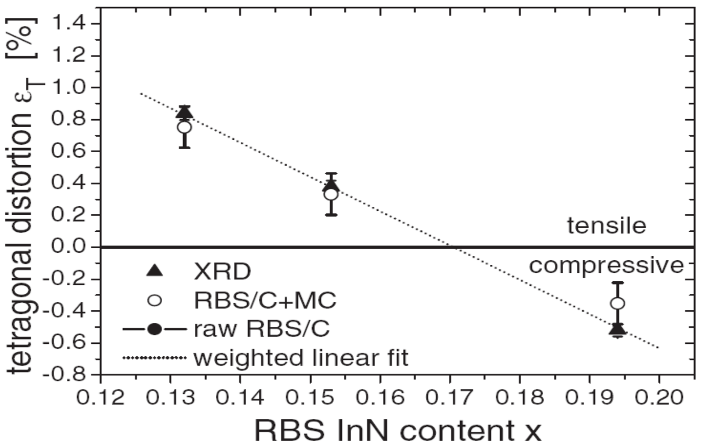
Content

Part I: growth of III-V nitrides

- **GaN heteroepitaxy:** substrates, dislocations, and polarity
- **InGaN quantum wells:** indium composition fluctuations
- **InAlN alloys:** lattice-matched but a price to pay
- **p-type doping:** works for GaN but still quite challenging for Al(Ga)N

InAlN alloys





K. Lorentz *et al.*, PRL **97**, 085501 (2006)

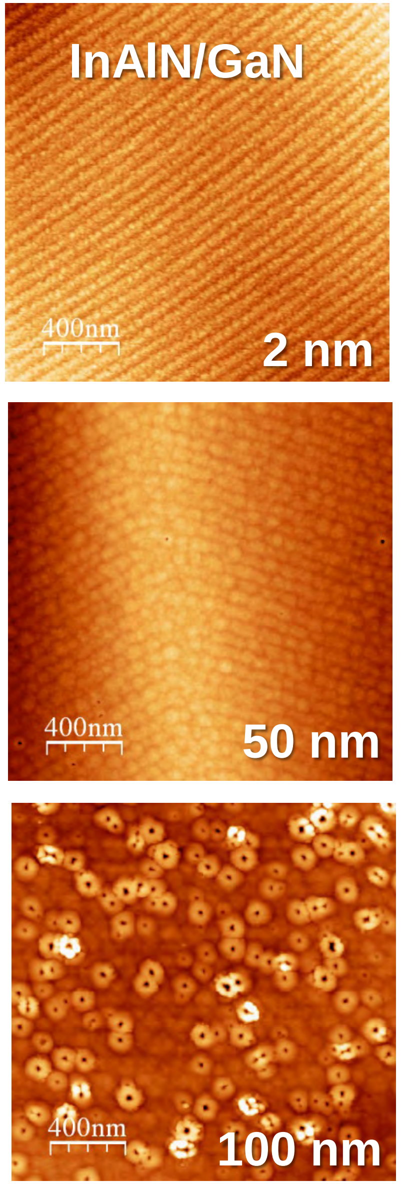
Properties of interest

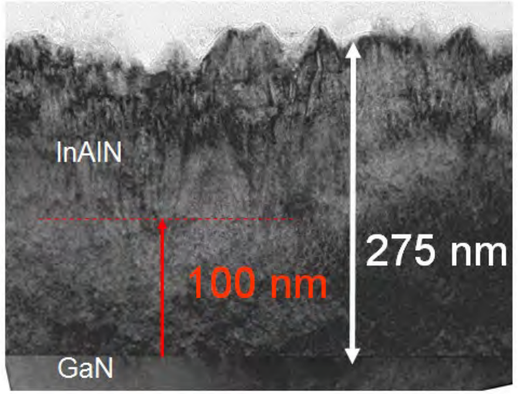
- Large direct bandgap
- Large band offset
- Large refractive index contrast
- High thermal stability

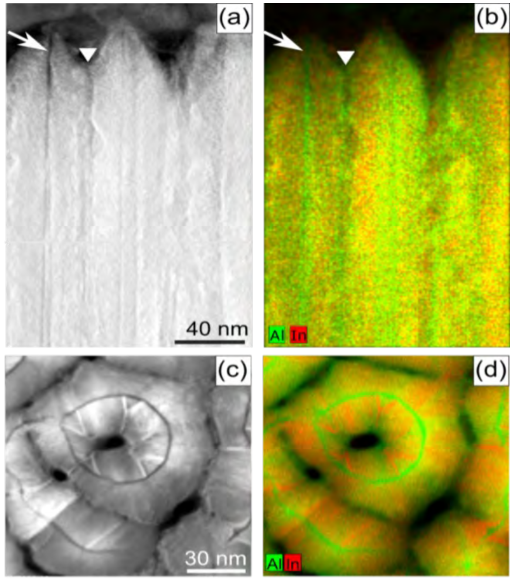
AlInN lattice-matched to GaN for an indium content of **~17%**

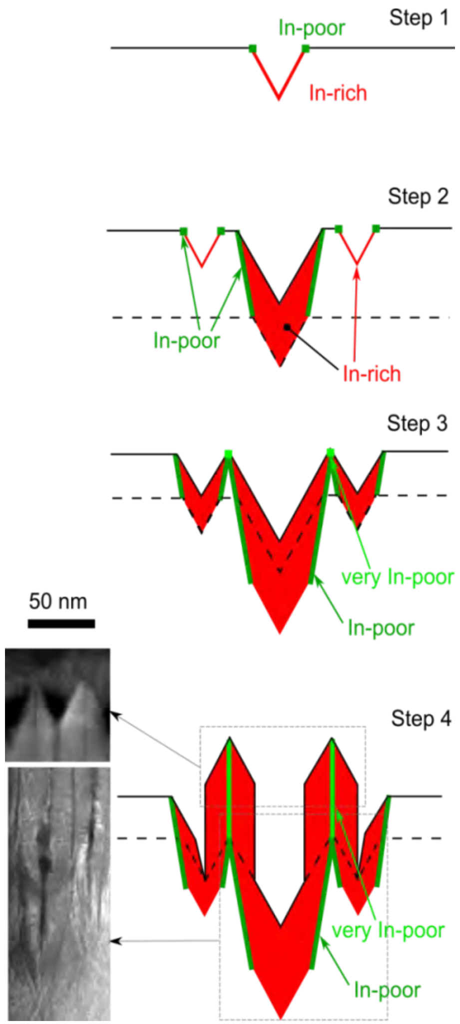
InAlN alloys

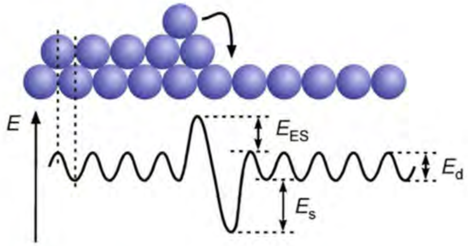
Intrinsic degradation: kinetic roughening leads to V-pits ⇨ phase separation (MOVPE)





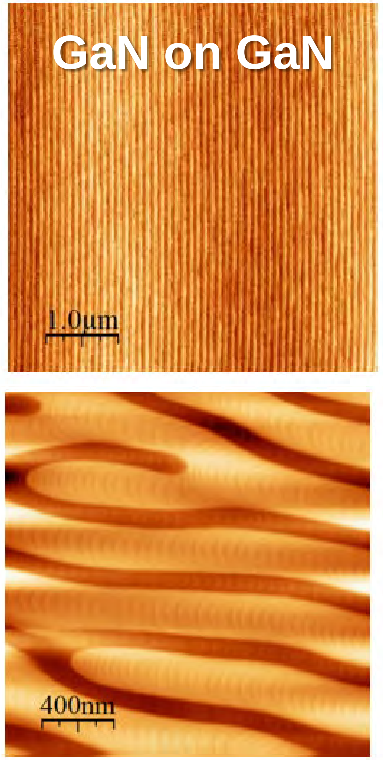






Ehrlich-Schwoebel barrier (ESB):

Asymmetry of the surface potential at a step



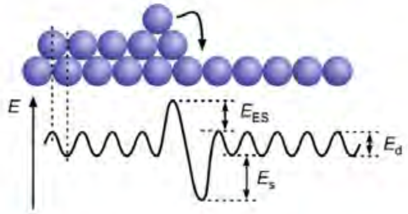
1000°C

850°C

J. Appl. Phys. **113**, 063506 (2013)

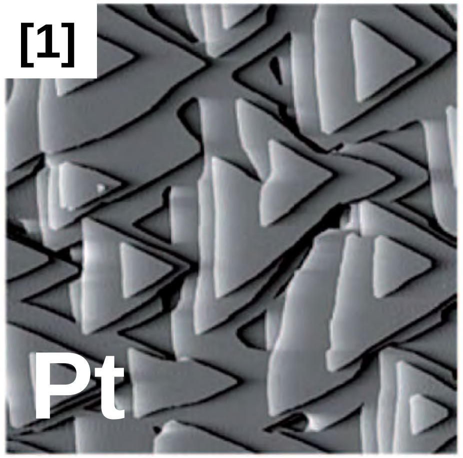
Growth instabilities

ESB-induced surface features

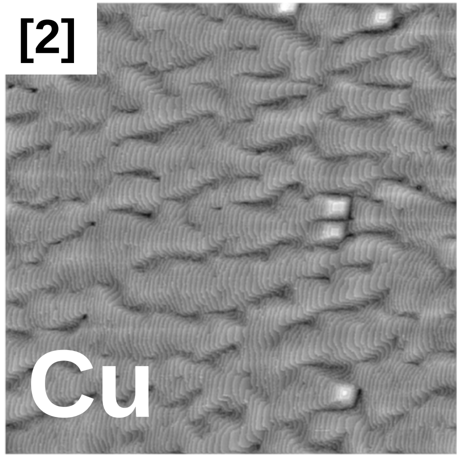


Ehrlich-Schwoebel barrier (ESB):

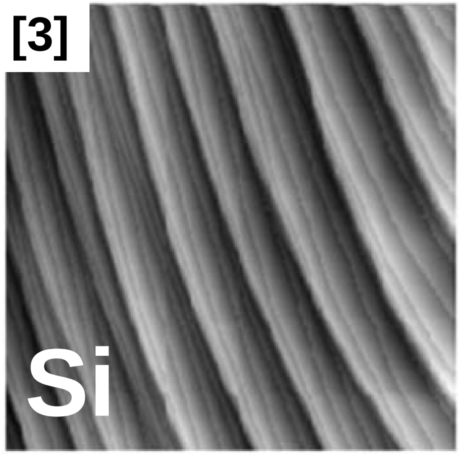
Asymmetry of the surface potential at a step
→ Difference in nearest neighbors to attach to



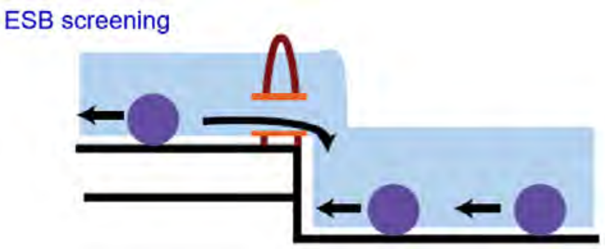
Hillocks



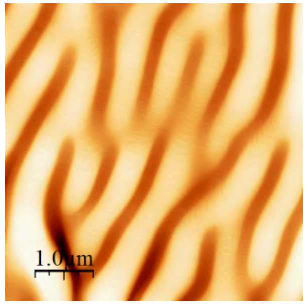
Step-meandering



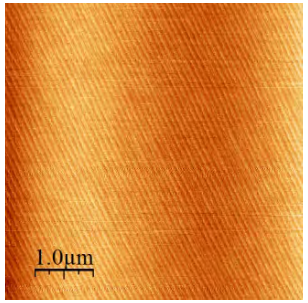
Step-bunching



GaN at low temperature (850°C)



N_2 as carrier gas



H_2 as carrier gas

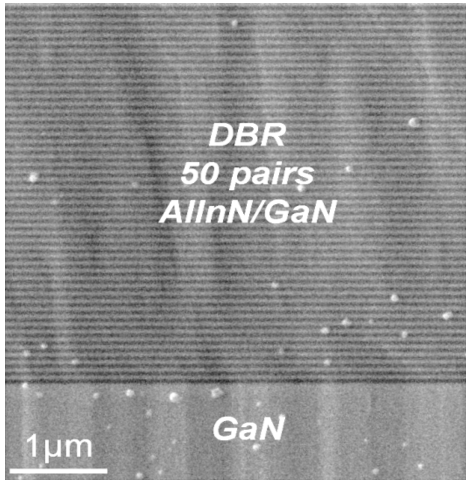
[1] J Krug, *Kinetic pattern formation at solid surfaces,* in: *Collective dynamics of nonlinear and disordered systems*

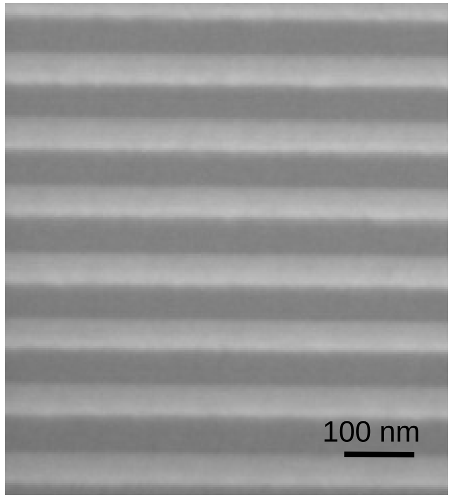
[2] T Maroutian *et al.*, Phys. Rev. B **64,** 165401 (2001)

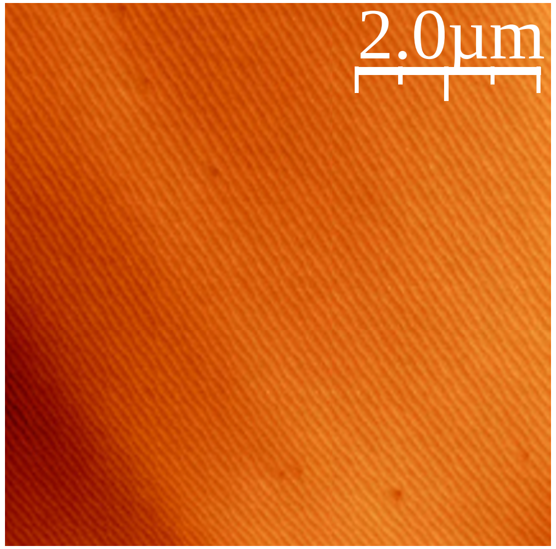
[3] Y N Yang *et al.*, Surf. Sci. **356,** 101 (1996)

InAlN alloys

InAlN/GaN distributed Bragg reflectors

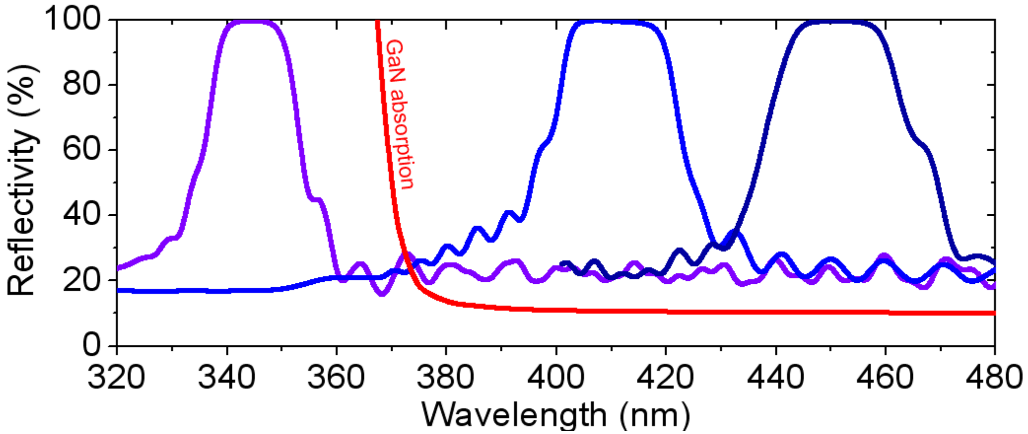






Free-standing GaN

Carlin & Ilegems, Appl. Phys. Lett. **83**, 668 (2003)



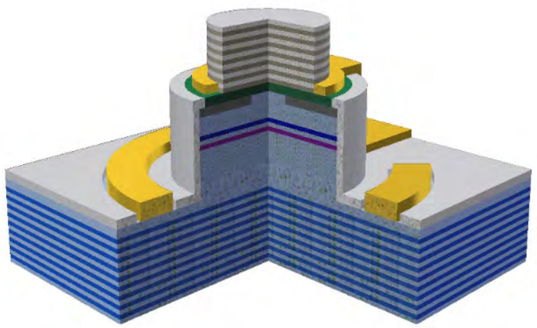
Reflectivity > 99.5%

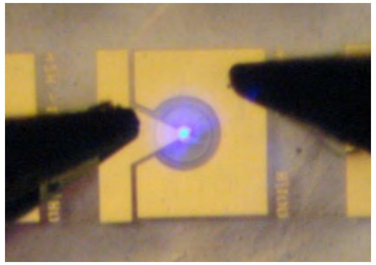
J. Phys. D: Appl. Phys **40**, 6328 (2007)

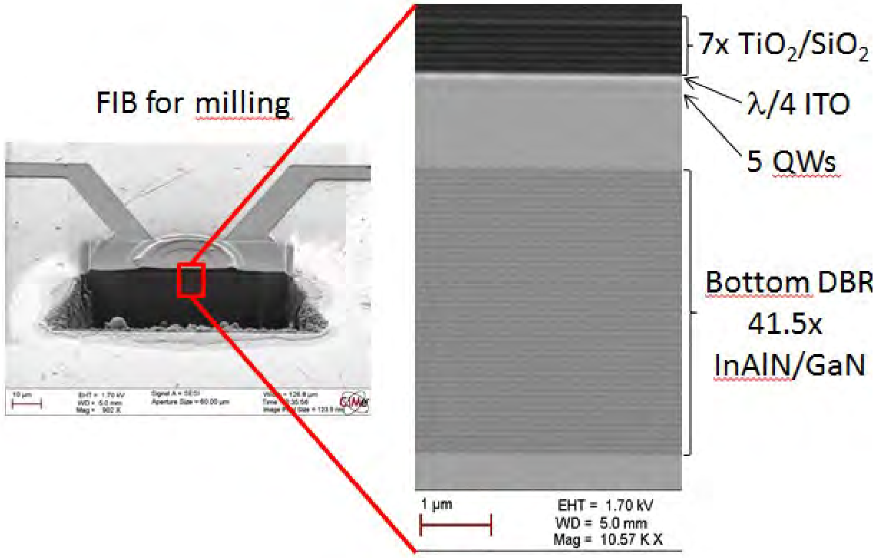
J. Appl. Phys. **97**, 084505 (2005)

InAlN alloys

Vertical cavity surface emitting laser (VCSEL)







5 March 2021

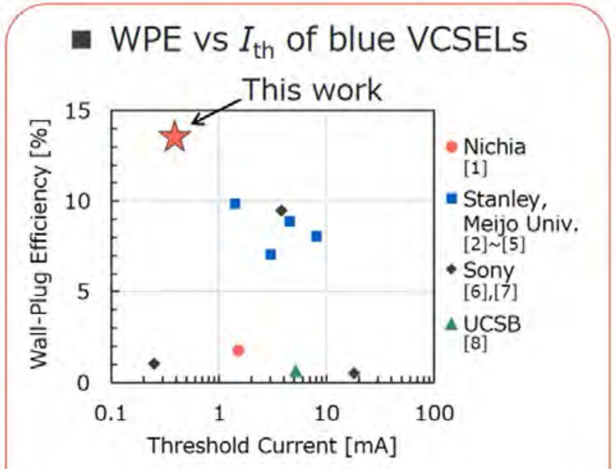
Blue and green GaN-based vertical-cavity surface-emitting lasers with AlInN/GaN DBR

Kenichi Terao, Hitoshi Nagai, Daisuke Morita, Shingo Masui, Tomoya Yanamoto, Shin-ichi Nagahama

Author Affiliations -

Kenichi Terao,[1] Hitoshi Nagai,[1] Daisuke Morita,[1] Shingo Masui,[1] Tomoya Yanamoto,[1] Shin-ichi Nagahama[1]

[1]Nichia Corp. (Japan)



[1] D. Kasahara *et al.*, Appl. Phys. Express **4** (2011) 072103.
[2] M. Kuramoto *et al.*, Appl. Phys. Lett. **112** (2018) 111104
[3] M. Kuramoto *et al.*, Appl. Phys. Express **11** (2018) 112101
[4] M. Kuramoto *et al.*, Appl. Phys. Lett. **115** (2019) 041101
[5] M. Kuramoto *et al.*, Appl. Phys. Express **13** (2020) 082005
[6] T. Hamaguchi *et al.*, Phys. Status Solidi A **213** (2016) 1170
[7] T. Hamaguchi *et al.*, Jpn. J. Appl. Phys. **58** (2019) SC0806
[8] J. A. Kearns *et al.*, Optics express **27** (2019) 23707

NICHIA

Appl. Phys. Lett. 101, 151113 (2012)

Content

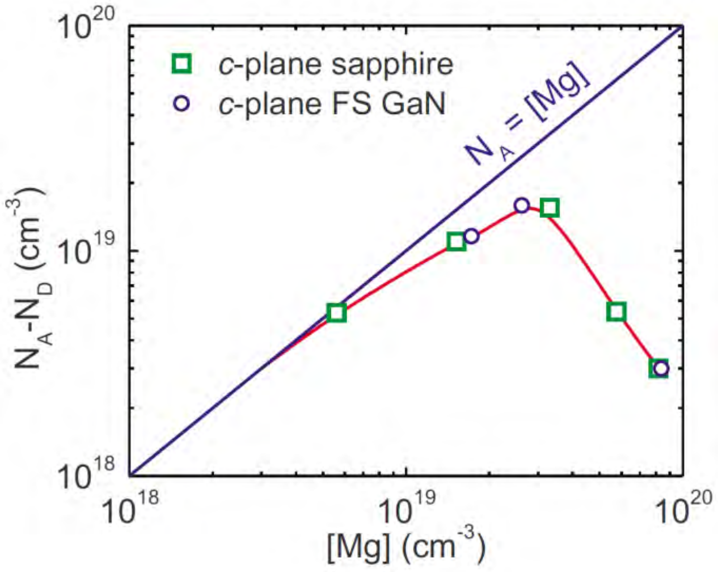
Part I: growth of III-V nitrides

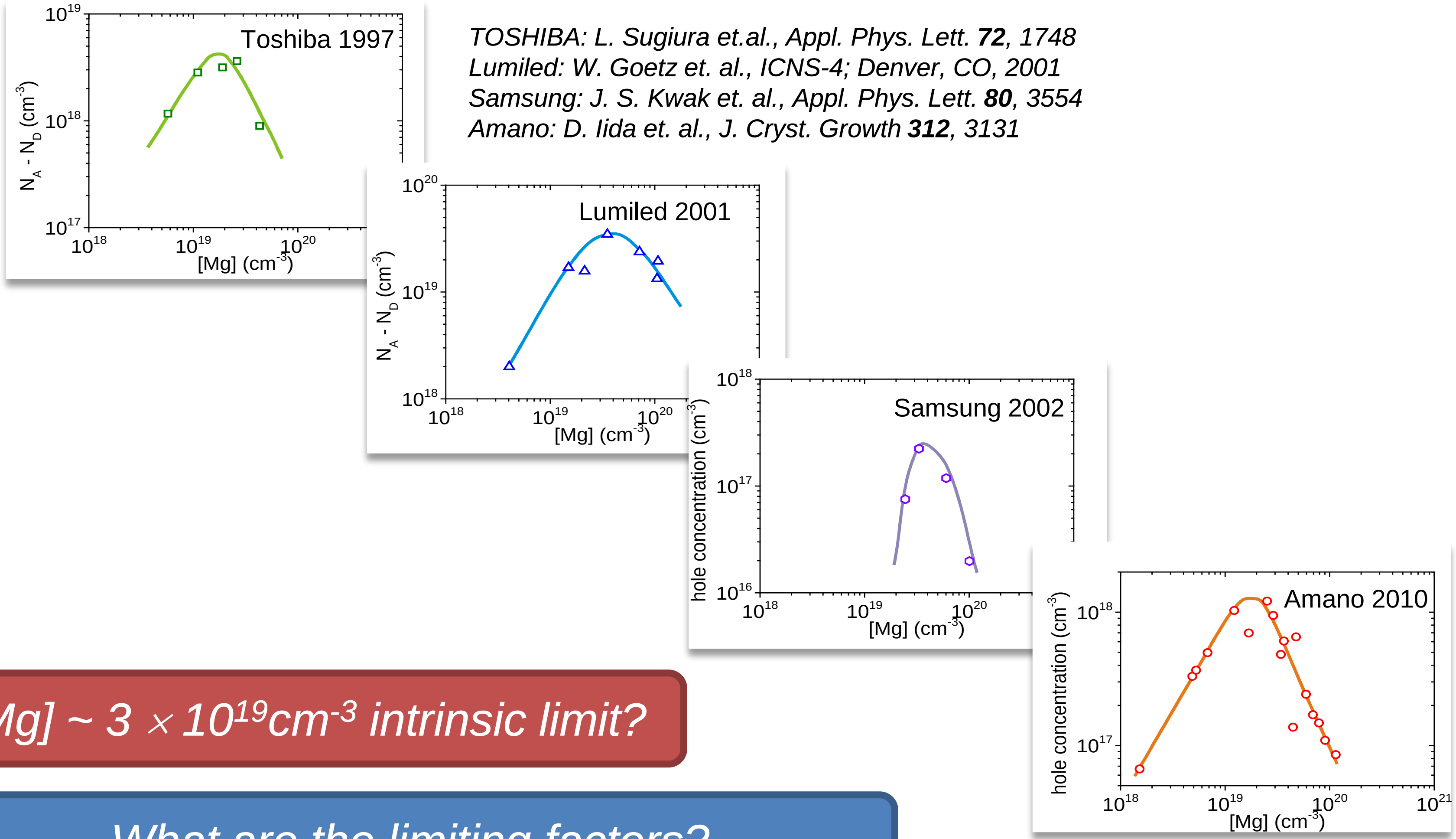
- **GaN heteroepitaxy:** substrates, dislocations, and polarity
- **InGaN quantum wells:** indium composition fluctuations
- **InAlN alloys:** lattice-matched but a price to pay
- **p-type doping:** works for GaN but still quite challenging for Al(Ga)N

P-type doping

p-type GaN layers grown by MOCVD

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



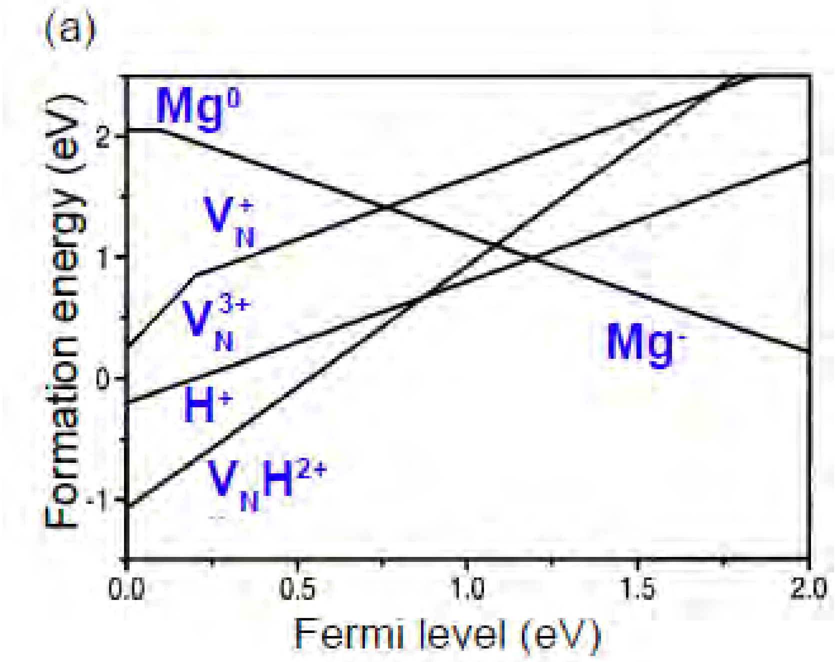


TOSHIBA: L. Sugiura et.al., Appl. Phys. Lett. ***72****, 1748*
Lumiled: W. Goetz et. al., ICNS-4; Denver, CO, 2001
Samsung: J. S. Kwak et. al., Appl. Phys. Lett. ***80****, 3554*
Amano: D. Iida et. al., J. Cryst. Growth ***312****, 3131*

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

What are the limiting factors?

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.

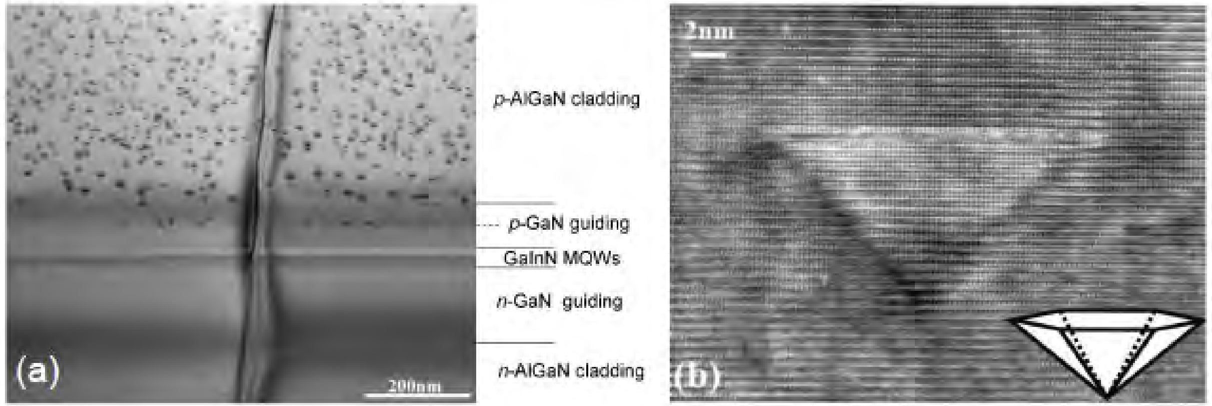


Figure 2.4: (a) Cross-sectional TEM image of an LD showing the presence of pyramidal inversion domains [89]. (b) High resolution TEM image along the [11$\bar{2}$0] zone axis of a pyramidal inversion domain [91].

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.

Content

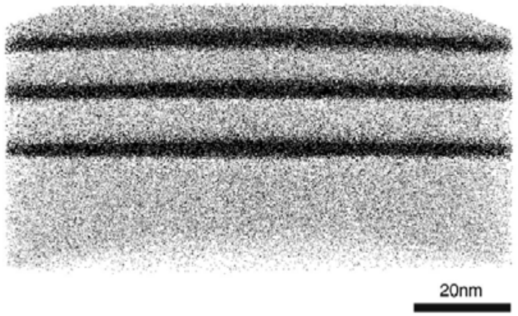
Part II: The efficiency of blue LEDs

- **Dislocations are eventually not detrimental**
- **The InGaN underlayer**
- **Surface defects**

Dislocations are eventually not detrimental

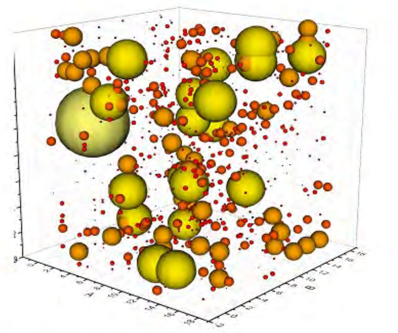
Impact of dislocations

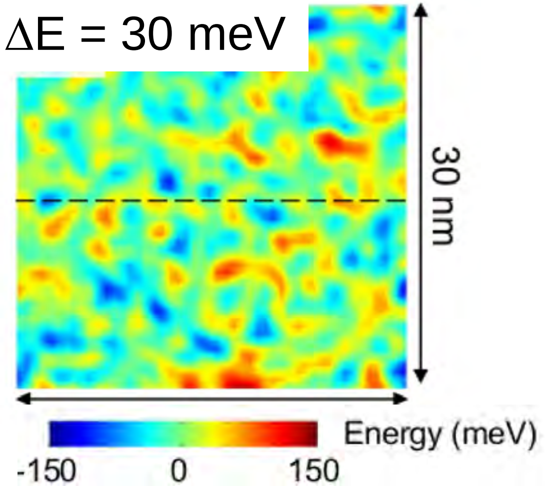
Atom probe tomography - InGaN/GaN QWs



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)

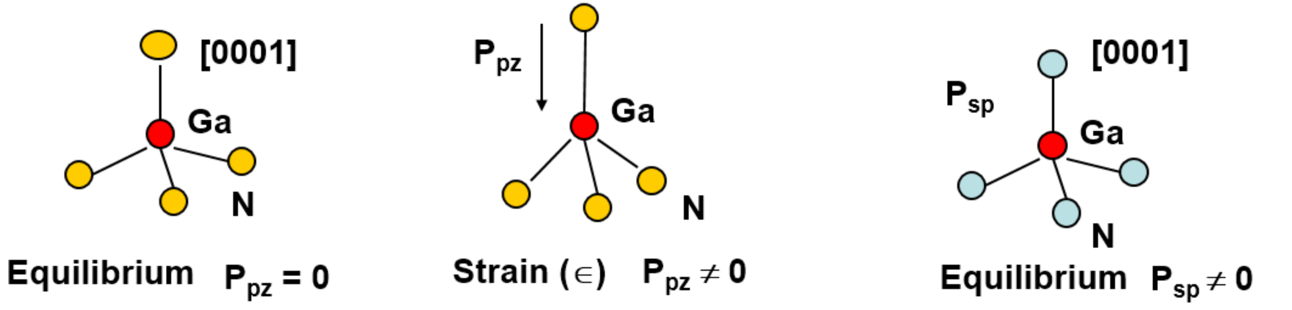
- **Random alloy fluctuations strongly reduce the diffusion coefficient**

⇒ low carrier diffusion

Dislocations are eventually not detrimental

Piezoelectric and spontaneous polarizations in non-centrosymetric crystals

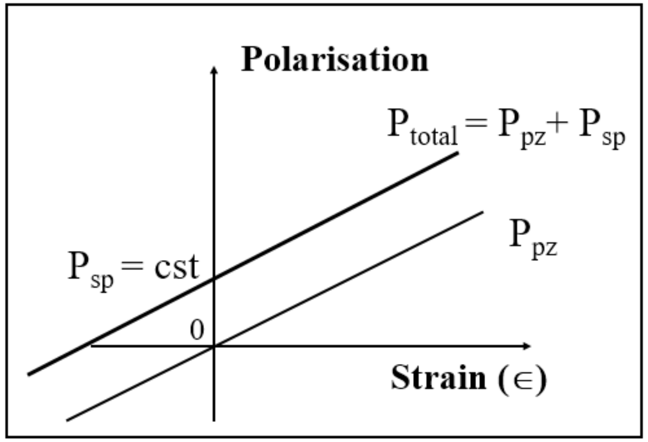
Piezoelectric (cubic & wurtzite) — Spontaneous (wurtzite)



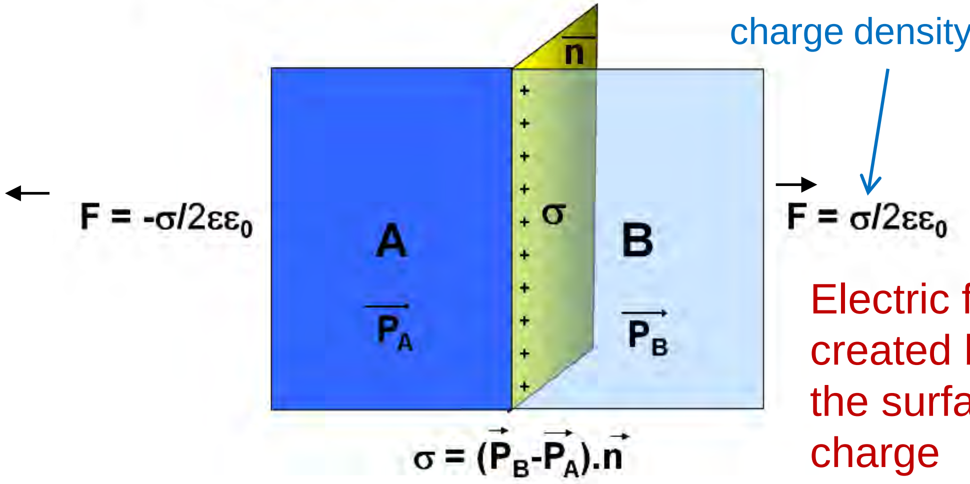
Macroscopic polarization:

Difference between the barycenters of positive and negative charges

$$P_{total} = P_{pz} + P_{sp}$$



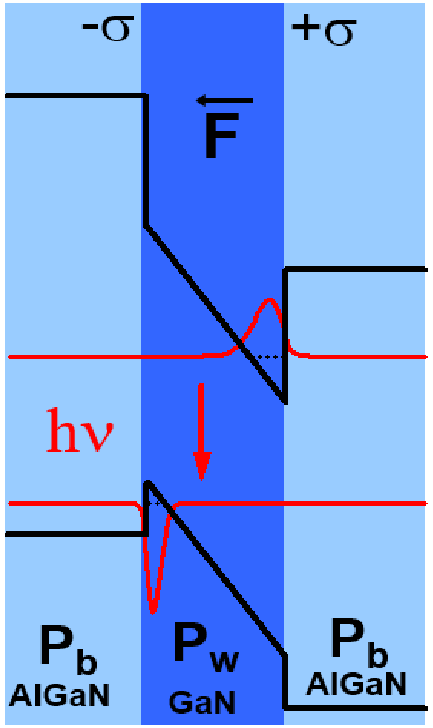
Polarization sheet charge density



Electric field created by the surface charge

Dislocations are eventually not detrimental

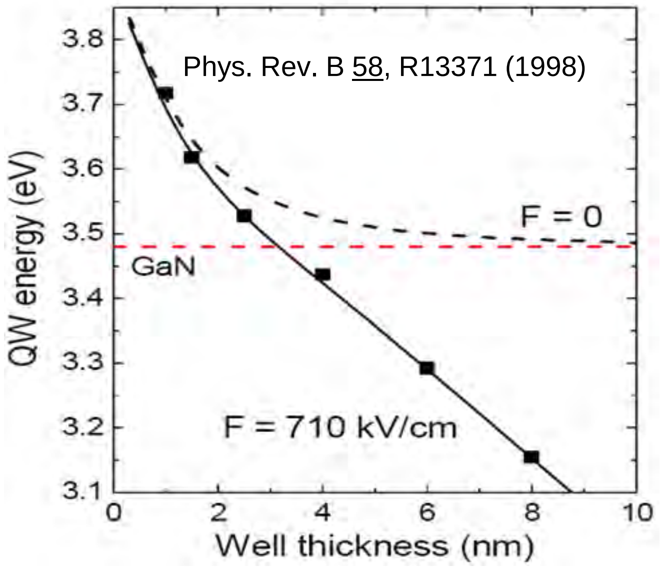
Quantum confined Stark effect



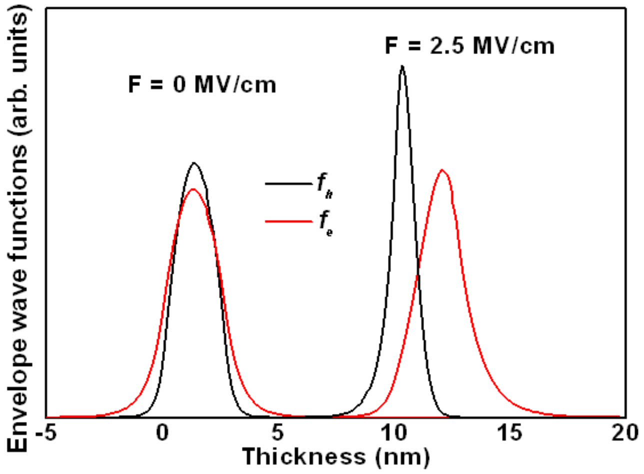
$$F = \frac{\sigma}{\varepsilon\varepsilon_0}$$

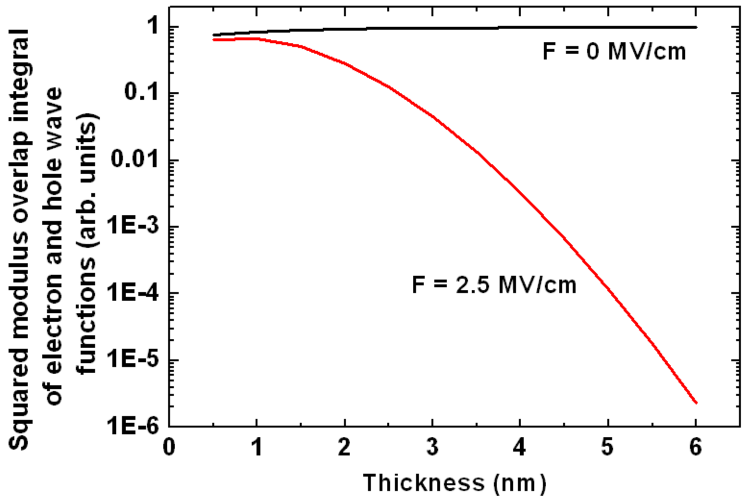
- red-shift of the QW transition energy

$$E = E_g + E_e + E_h - e\,L\,F$$



- Decrease of the oscillator strength

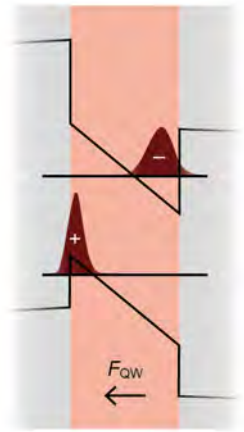




Dislocations are eventually not detrimental

Impact of the large internal electric field

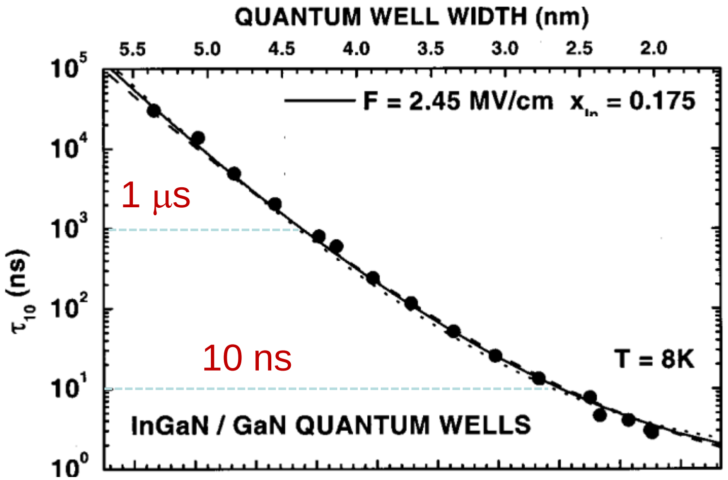
F_{QW} = 2-3 MV/cm



Quantum Confined Stark Effect (QCSE)

Radiative lifetime: $\tau_R \propto \frac{1}{\langle \varphi_e | \varphi_h \rangle^2}$

Few 10s of nanoseconds for blue LEDs



P. Lefebvre,..., NG, J.Massies *et al.*, APL 78, 1252 (2001)

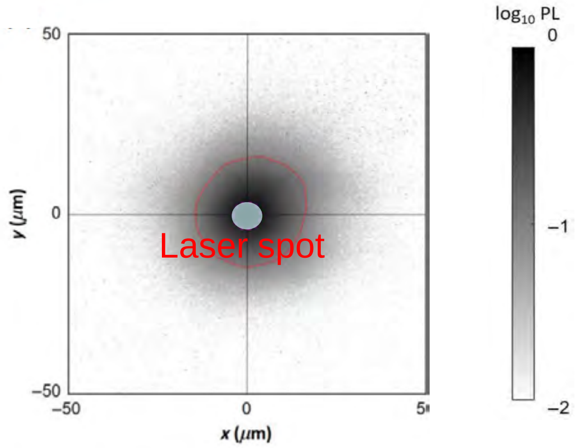
$$IQE = \frac{\tau_{NR}}{\tau_{NR} + \tau_R}$$

Not too critical as τ_{NR} is inversely proportional to the e-h wavefunction overlap

A. David *et al*., Phys. Rev. Appl. 11, 031001 (2019)

300K photoluminescence imaging of an InGaN/GaN QW on bulk GaN

A. David, Phys. Rev. Appl. 15, 054015 (2021)



- Long radiative lifetime results in rather large diffusion length

$$\lambda = 2\sqrt{\tau D}$$

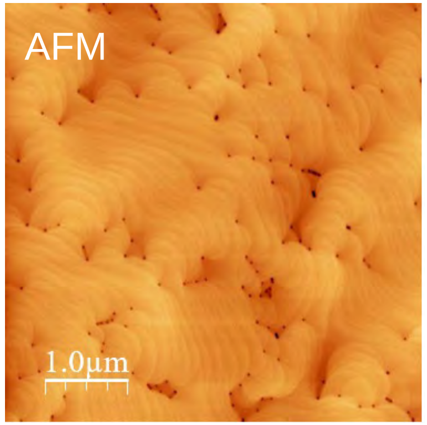
⇒ Diffusion length > 1μm

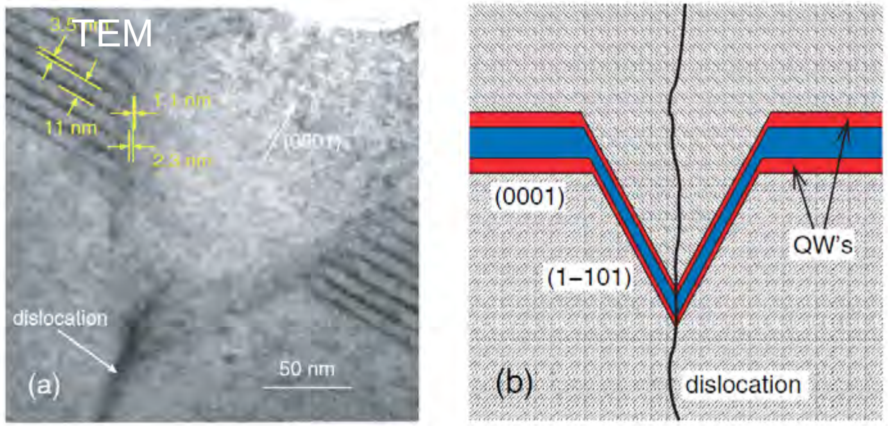
Dislocations are eventually not detrimental

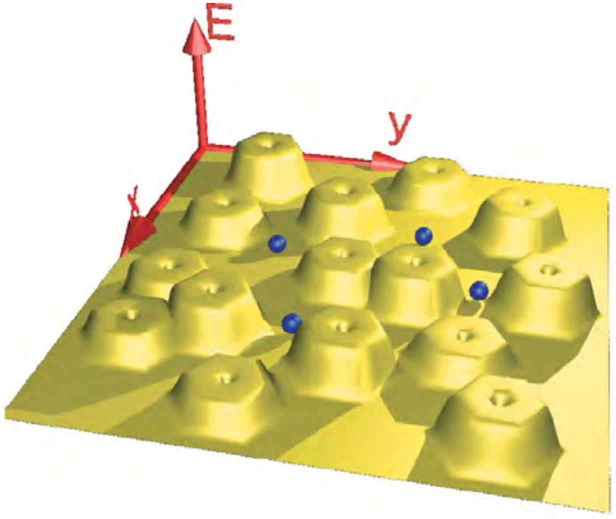
When the surface morphology comes to play

- 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

Content

Part II: The efficiency of blue LEDs

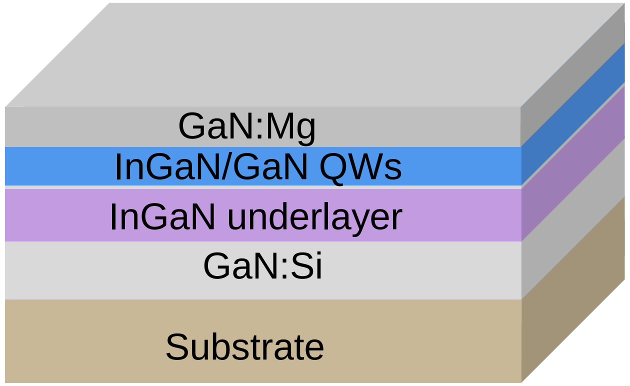
- Dislocations are eventually not detrimental
- **The InGaN underlayer**
- Surface defects

In blue LEDs, IQE is slightly impacted by dislocations

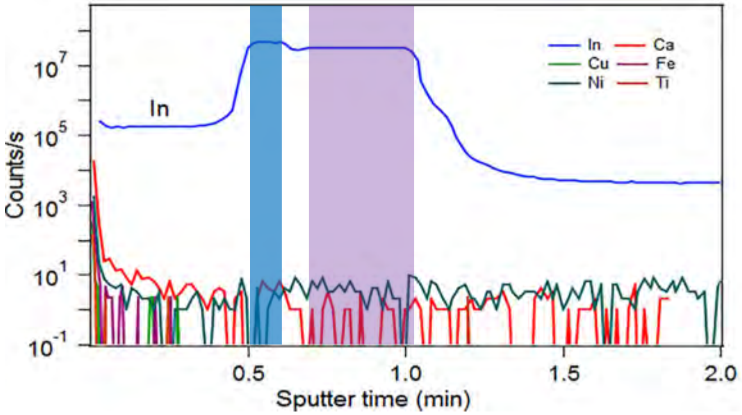
⇒ What about native point defects and/or impurities?

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 to limit internal losses
- Either a superlattice or a bulk layer

What is the purpose of this InGaN underlayer?

EPFL

Proposed mechanisms

Promote V-pit formation

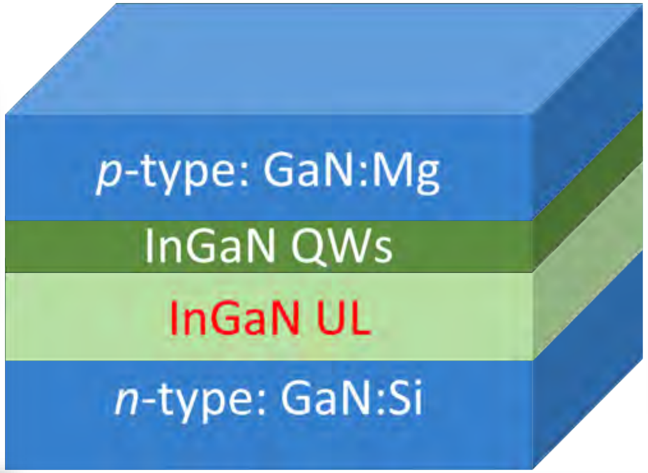
Zhao *et al.*, Solid State Elec. 54, 1119 (2010)

Reduction of threading dislocation density

Li *et al.*, Appl. Phys. Lett. 102, 04115 (2013)

Less non-radiative centers

Akasaka *et al.*, Appl. Phys. Lett. 85, 3089 (2004)
Armstrong *et al.*, Appl. Phys. Lett. 117, 134501 (2015)



Strain mitigation

Nanhui *et al.*, Solid State Elec. 51, 860 (2007)
Li *et al.*, App. Phys. Lett. 102, 04115 (2013)
Okada *et al.*, J. Appl. Phys. 117, 025708 (2015)

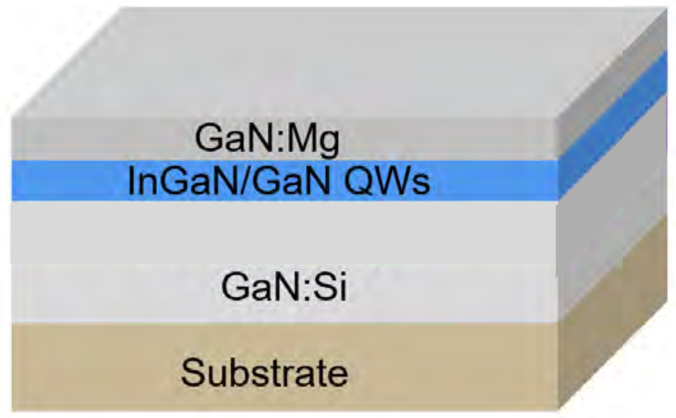
Higher injection efficiency

Takahashi *et al.*, Physica E 21, 876 (2004)
Otsuji *et al.*, J. Appl. Phys. 100, 113105 (2006)
Ju *et al.*, J. Appl. Phys. 102, 053519 (2007)
Xia *et al.*, IEEE 57, 2639 (2010)

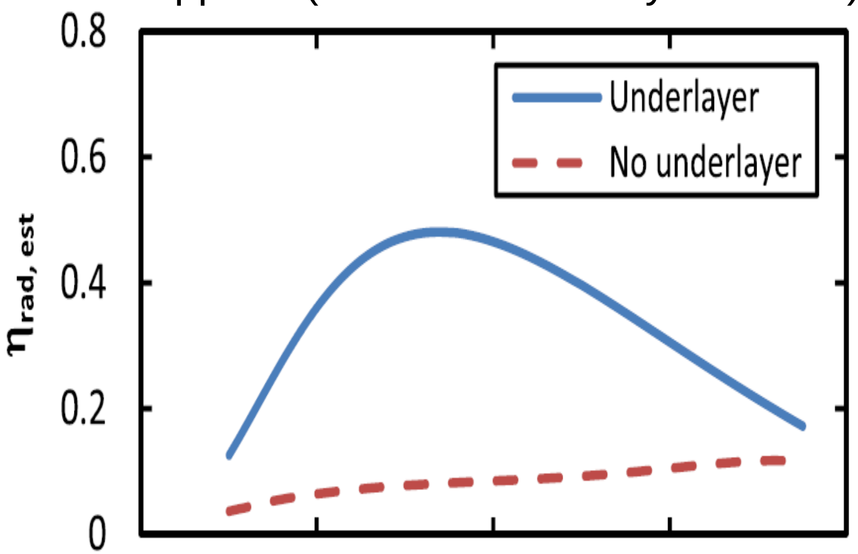
Electric field reduction

Davies *et al.*, pss (b) 252, 866 (2015)
J.-Y. Park *et al.*, pss (a) 213, 1610 (2016)

Point defects in InGaN/GaN QWs

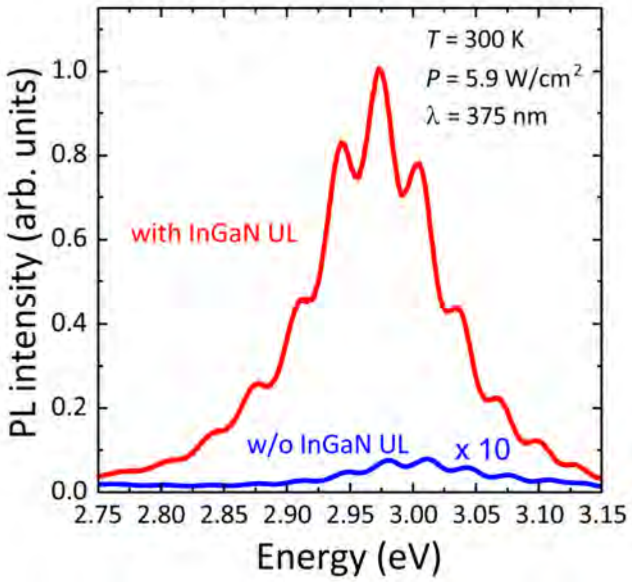


Sapphire (dislocation density~10^8 cm^{-2})



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

GaN (dislocation density ~10^6 cm^{-2})

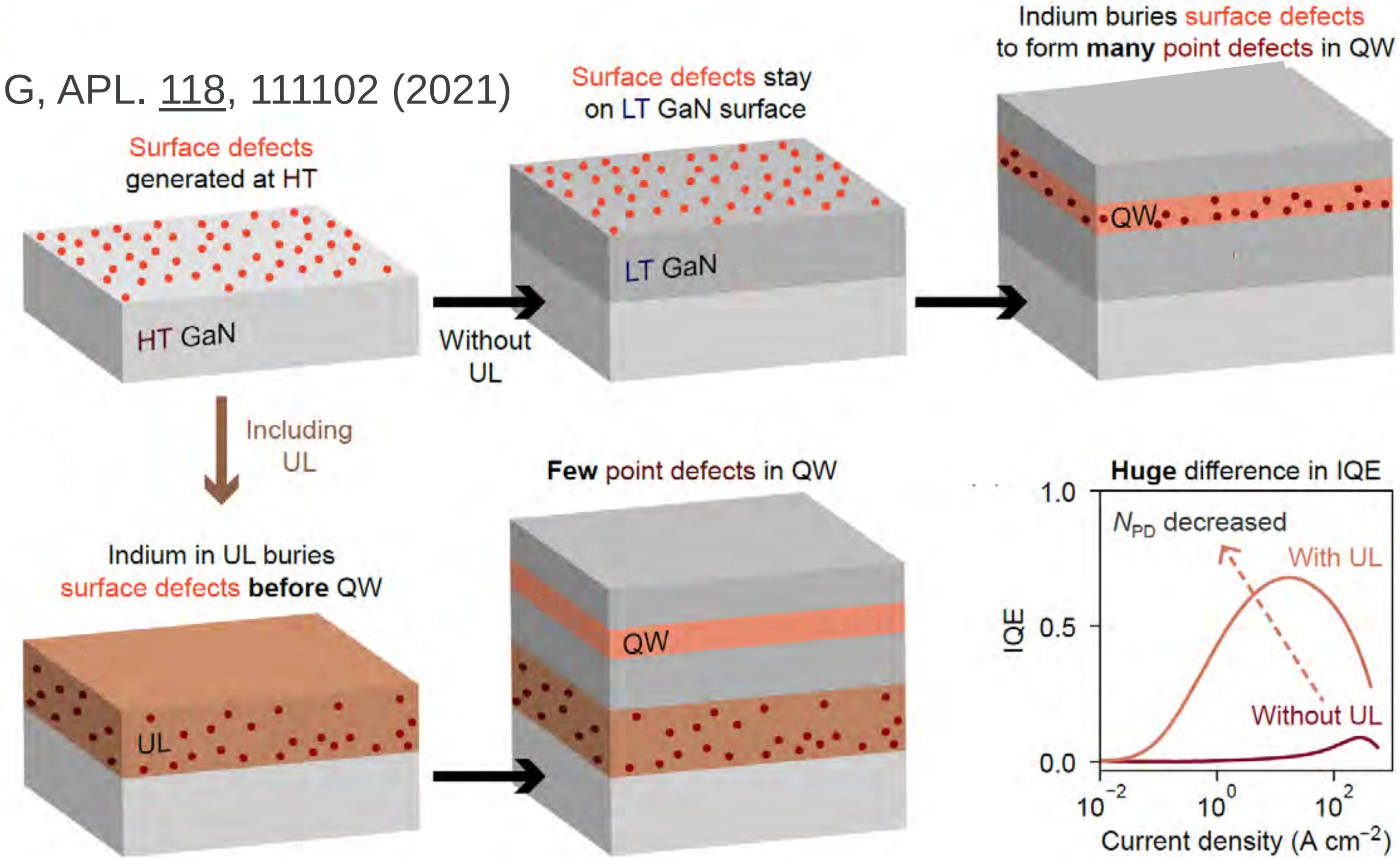


C. Haller,..NG, APL 111, 262101 (2017)

➲ 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}

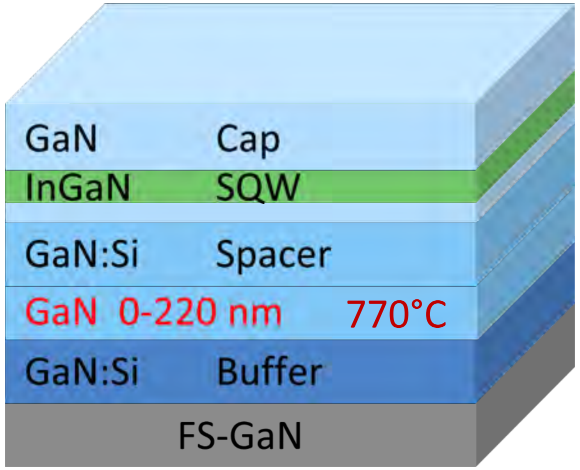
T. Weatherley,... NG, NanoLett. 21, 5217 (2021)

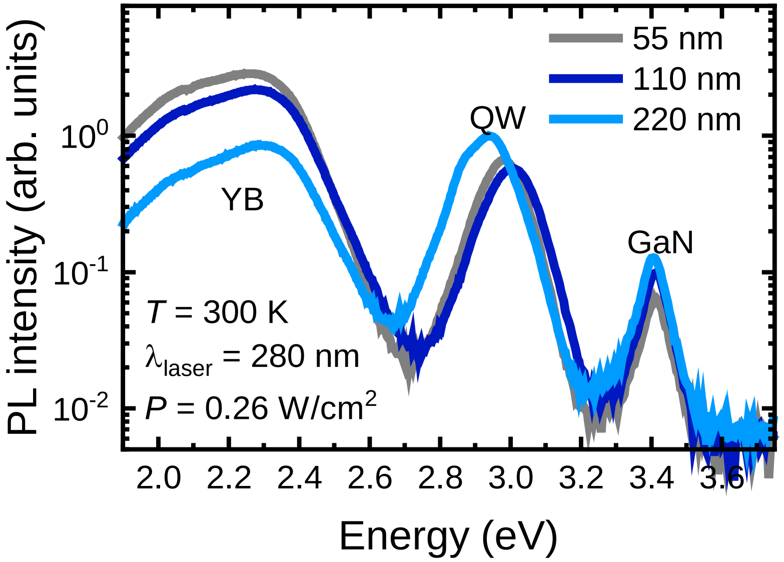
C. Haller, ... NG, APL 113, 111106 (2018)

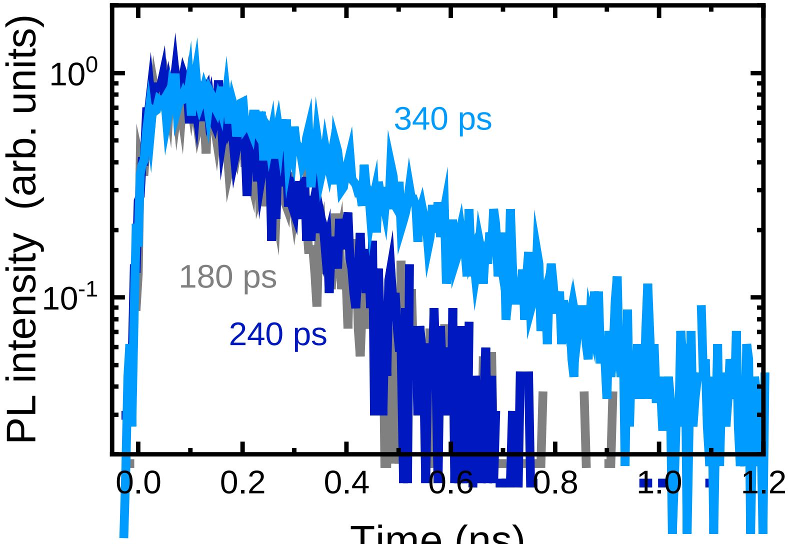
Surface defects (SDs) react with In atoms that create deep traps in the QWs

Burying impurities/defects with low-temperature GaN underlayer

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







➲ Slight increase of the efficiency with low-temperature GaN underlayer

APPLIED PHYSICS LETTERS VOLUME 85, NUMBER 15 11 OCTOBER 2004

High luminescent efficiency of InGaN multiple quantum wells grown on InGaN underlying layers

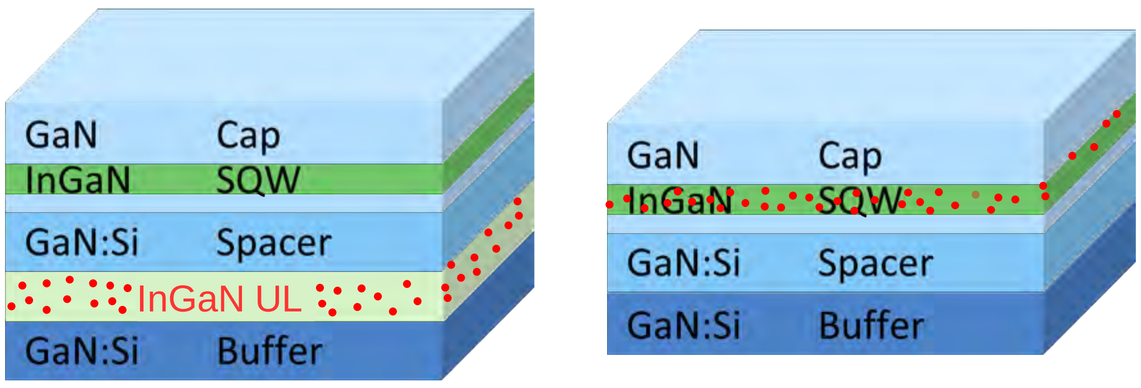
Tetsuya Akasaka,[a)] Hideki Gotoh, Tadashi Saito, and Toshiki Makimoto
NTT Basic Research Laboratories, NTT Corporation, 3-1 Morinosato-Wakamiya, Atsugi-shi, Kanagawa, 243-0198 Japan

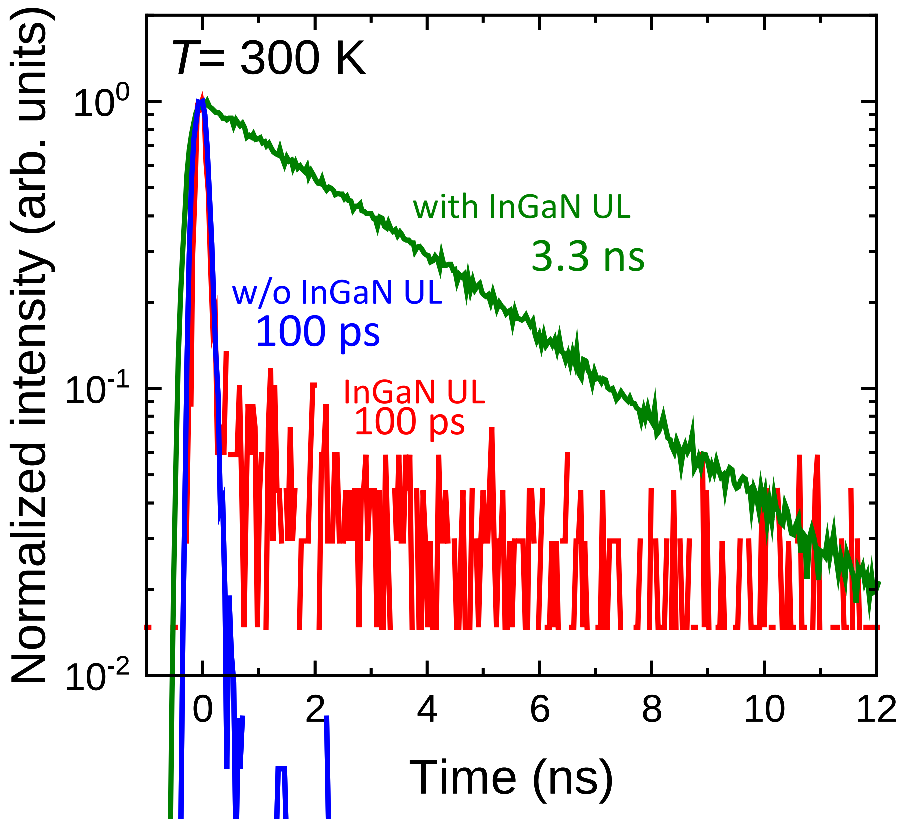
Indium is the “key” ingredient

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

Modeling of the effective lifetime

Hypothesis: the incorporation of SDs in InGaN alloy generates NRCs

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

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

$[SD]_{QW}$ the concentration of SDs inducing NRCs

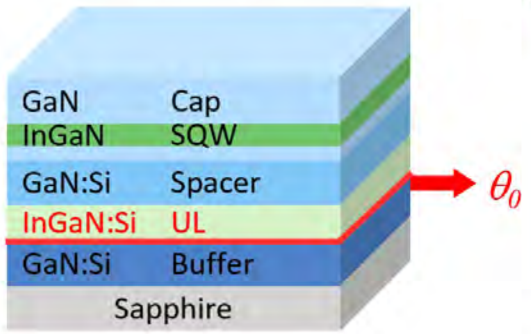
$$\tau_{NR,SD} \propto \frac{1}{[SD]_{QW}}$$

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

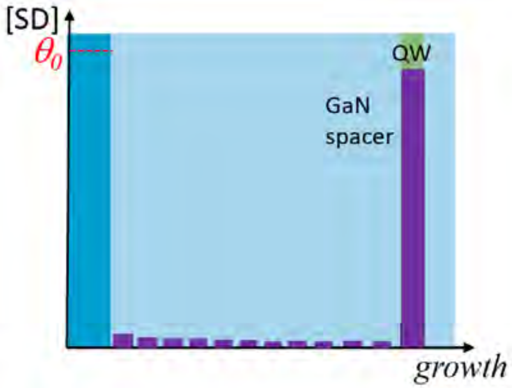
$C_{n,p}$: Capture coefficient of SRH centers induced by SD incorporation

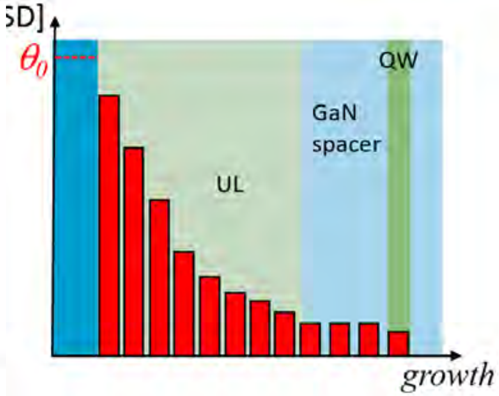
C_{QW}: Number of SD trapped in the QW: $C_{QW} = \left(1 - \left(R_{GaN} - x_{QW} p\right)^{N_{QW}}\right) / L_{QW}$

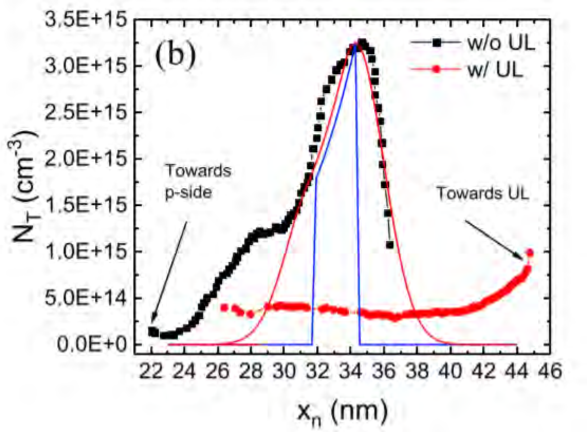
$\theta_0 \left(R_{GaN} - x \cdot p\right)^N$: SDs after the growth of N monolayers of $In_xGa_{1-x}N$ UL



APL 113, 111106 (2018)





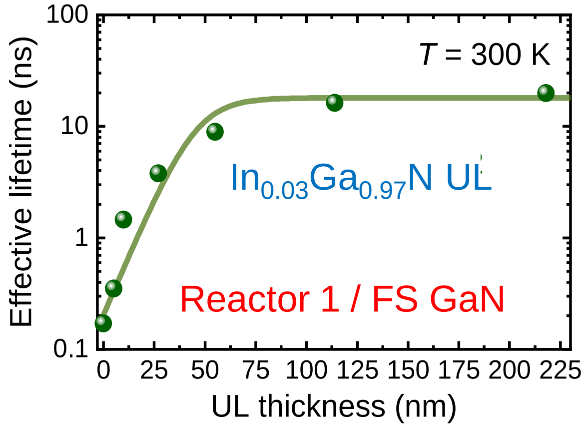


J. Appl. Phys. 126, 125708 (2019)

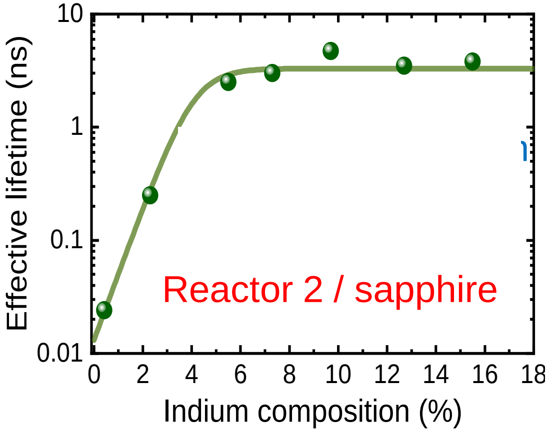
Modeling of the effective lifetime

InGaN UL

Thickness dependence

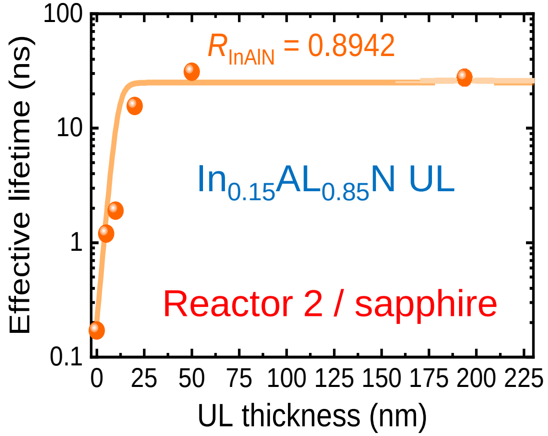


Composition dependence

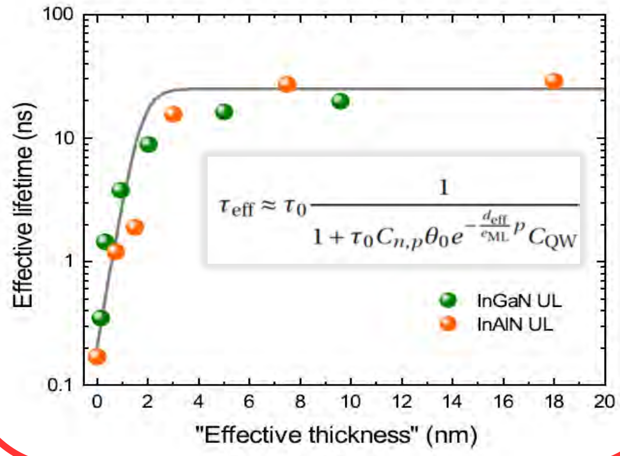


InAlN UL

Thickness dependence



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



- ➲ 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)

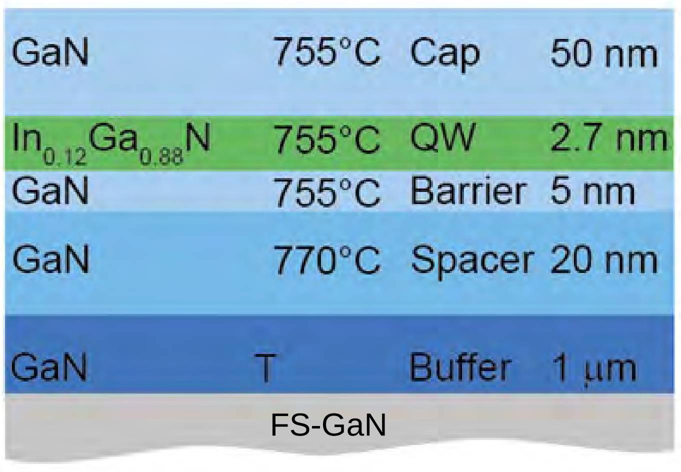
Content

Part II: The efficiency of blue LEDs

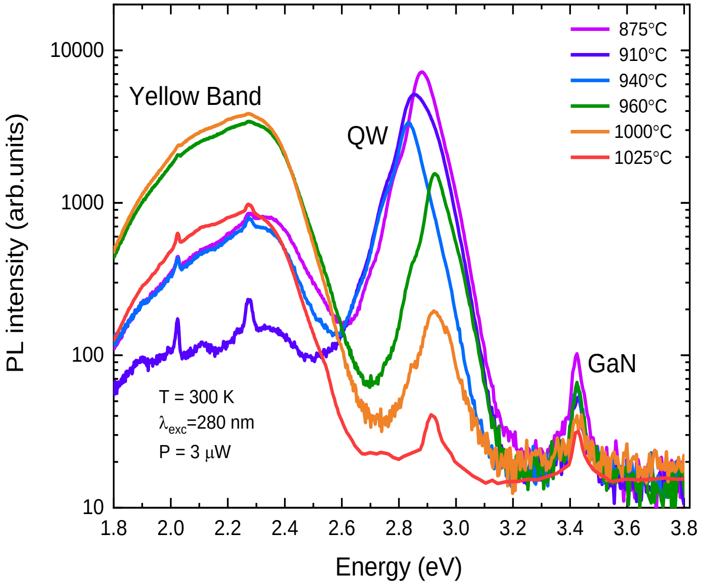
- Dislocations are eventually not detrimental
- The InGaN underlayer
- **Surface defects**

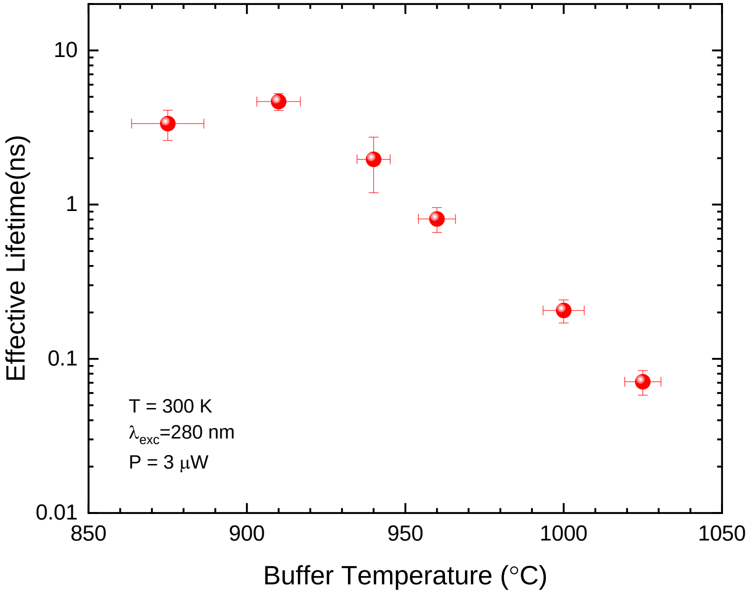
Impact of the growth temperature

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



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

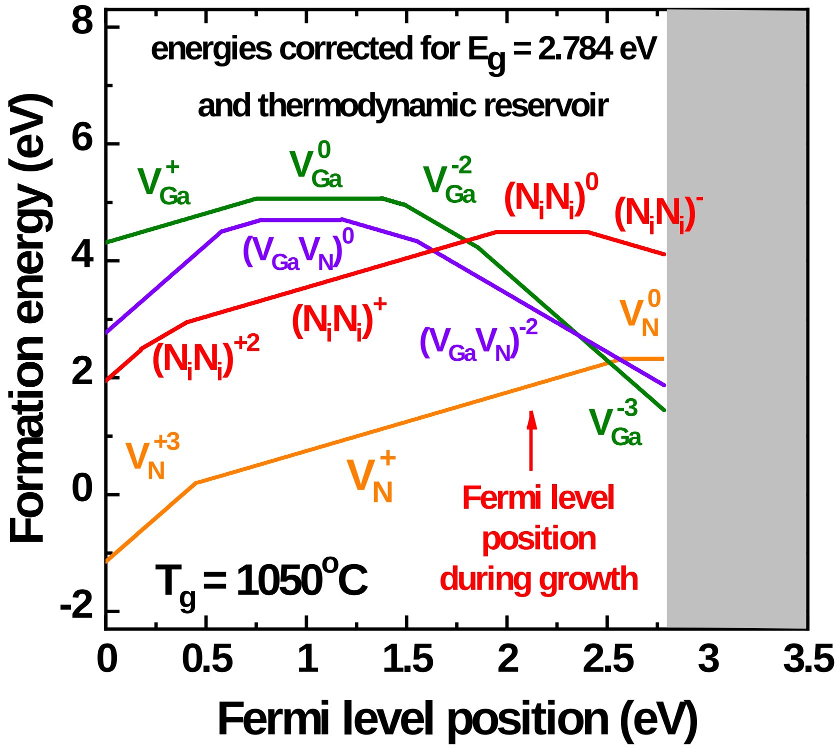




➲ The HT growth of GaN buffer generates surface defects

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

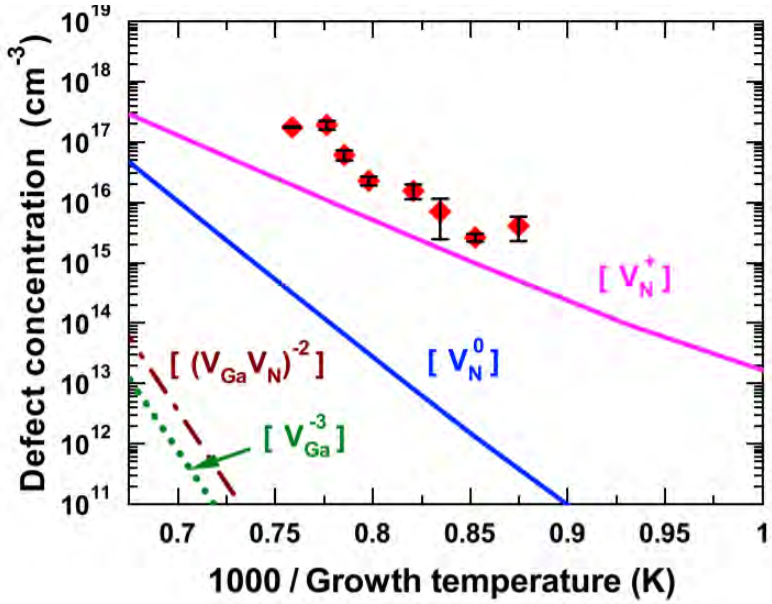
Native defects in GaN



Q. Yan et al., Appl. Phys. Lett. 100, 142110 (2012)
I. C. Diallo et al., Phys. Rev. Appl. 6, 064002 (2016)
J. L. Lyons et al., npj Comput. Mater. 3, 12 (2017)

- Bandgap shrinks with increasing temperature
  - Rescaling the formation energy

V_N has the lowest formation energy (1.7 eV)



PHYSICAL REVIEW B VOLUME 20, NUMBER 12 15 DECEMBER 1979

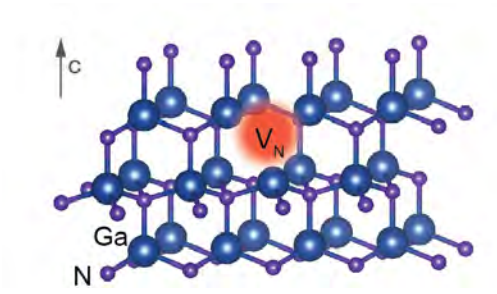
Vacancies near semiconductor surfaces

Murray S. Daw and D. L. Smith
California Institute of Technology, Pasadena, California 91125

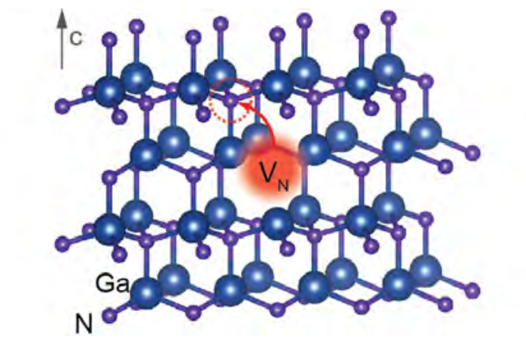
Appl. Phys. Lett. 118, 111102 (2021)

Surface defects

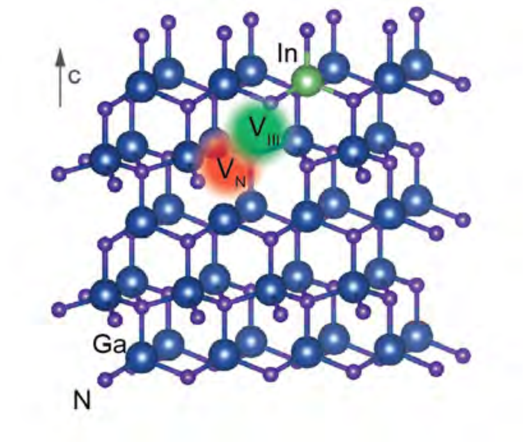
Tentative mechanism



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)



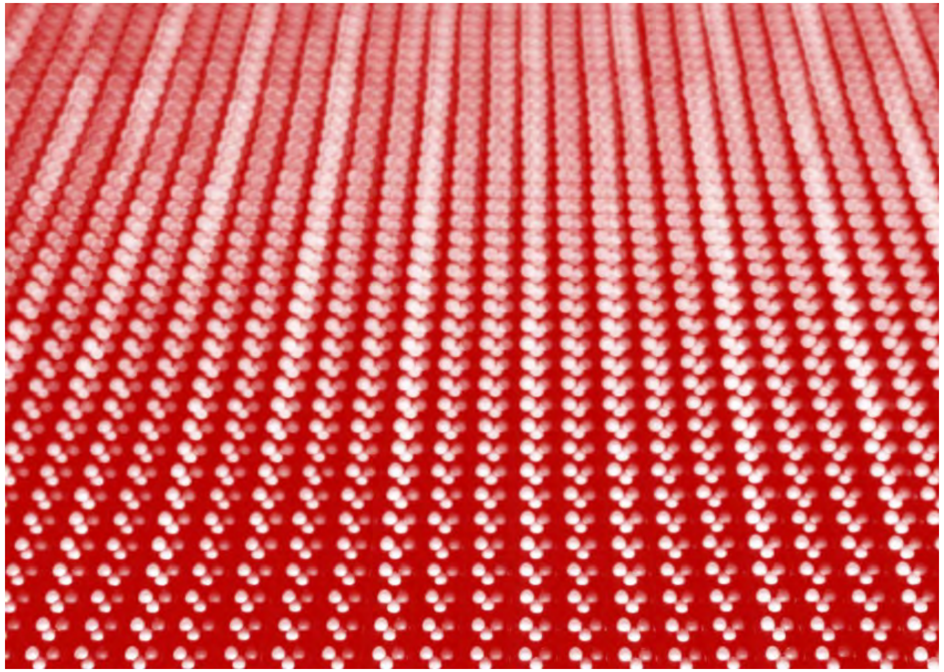
LT GaN growth (<800°C): V_N are no longer generated at the surface but they segregate due to the high formation energy in the bulk



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

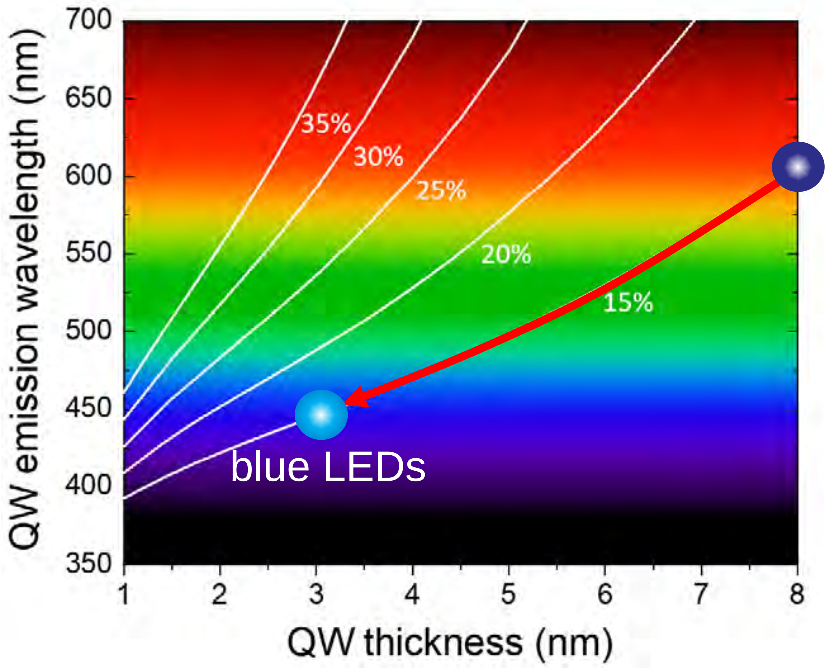
Part III: Are III-nitrides suitable for red LEDs?

- **How to push the wavelength to the red?**
- **Less strain for more indium**



EPFL

- InGaN/GaN QW emission wavelength

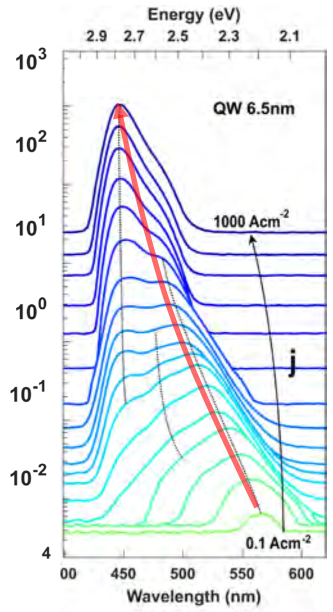


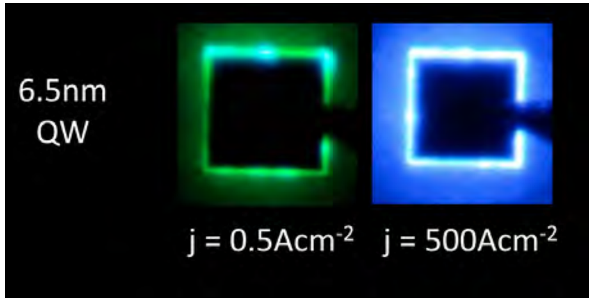
$$E_{QW} = E_g^{InGaN} + E_{conf}^{e,h} - qL_wF$$ Stark shift

$$x = 15\% \Rightarrow F \approx 1.5\ MV/cm$$

Red emission (~610 nm) with 15% In and $L_w = 8$ nm

The indium content must be larger than 30%





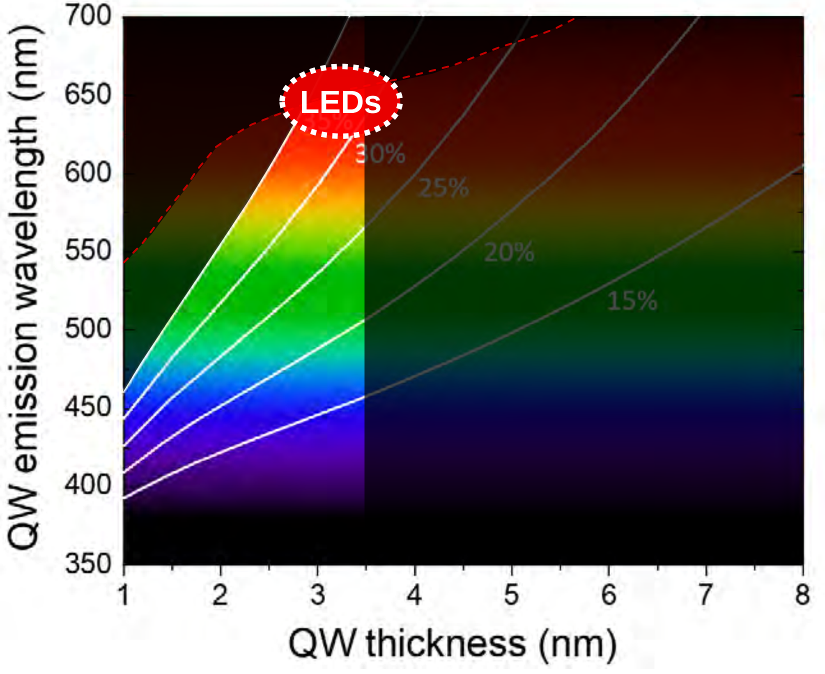
- Screening of the electric field induces a strong blue-shift

$\Rightarrow L_w$ lower than 4 nm

M. Hajdel *et al.*, Materials 15, 237 (2022)

How to push the wavelength to the Red ?

- InGaN/GaN QW emission wavelength



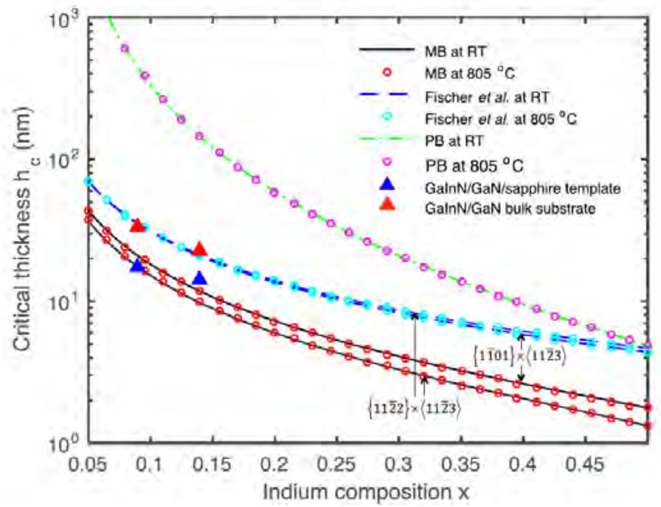
$$E_{QW} = E_g^{InGaN} + E_{conf}^{e,h} - qL_wF$$ Indium content

« ... less than 35% In composition is normally reported.”

N. Hu *et al.*, APL 121, 082106 (2022) - Amano’s group

InGaN on GaN critical thickness

G. Ju *et al*., APL 110, 262105 (2017)
Amano’s group



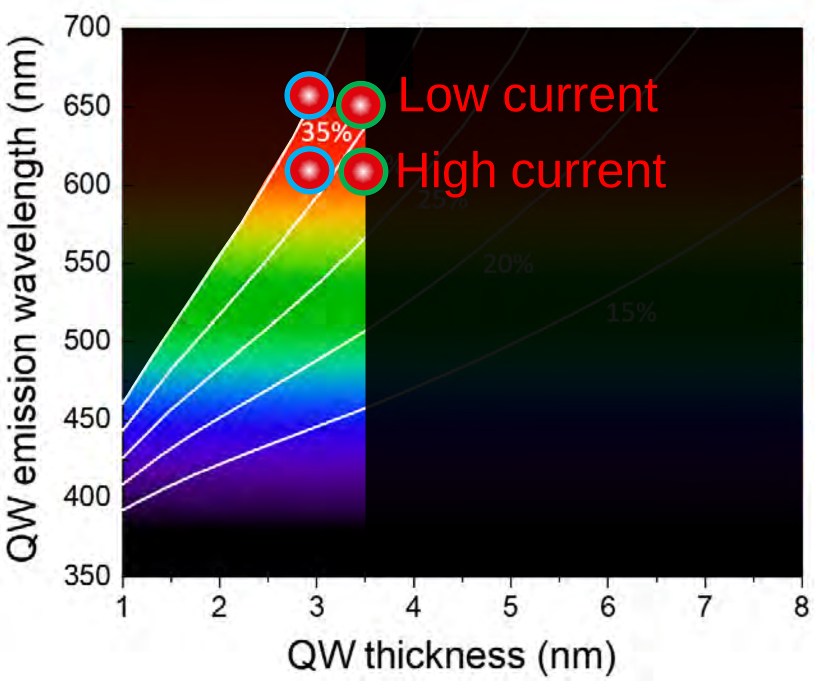
The parameter space for red LEDs is quite limited

In content = 30-35%
L_w = 3-3.5 nm

How to push the wavelength to the Red ?

EPFL

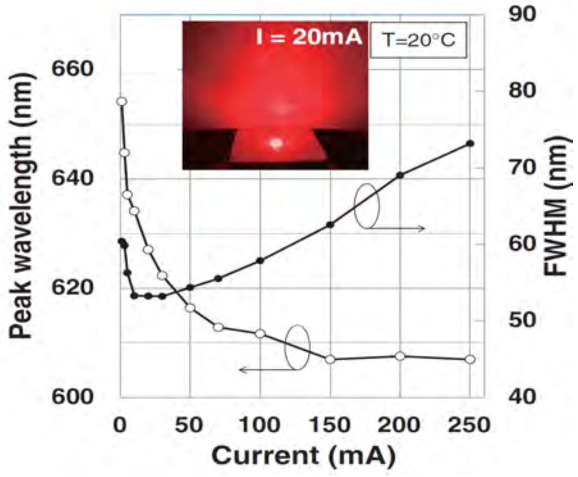
- Red-LEDs on GaN/sapphire template



2014 : Toshiba   J.-I. Hwang *et al.*, APEX 7, 071003 (2014)

x = 0.35, L_w= 3 nm, λ_{max}= 655 nm

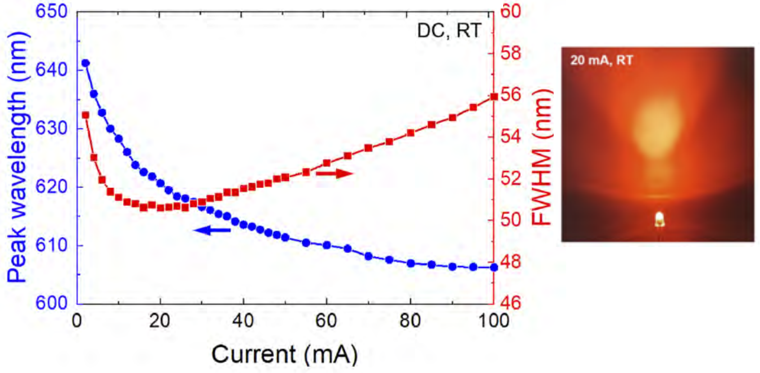
At 20 mA and 629 nm:
- Power = 1.1 mW
- EQE = 2.9%
- WPE = 1.3%



2022 : KAUST   D. Iida *et al.*, AIP Advances 12, 065125 (2022)

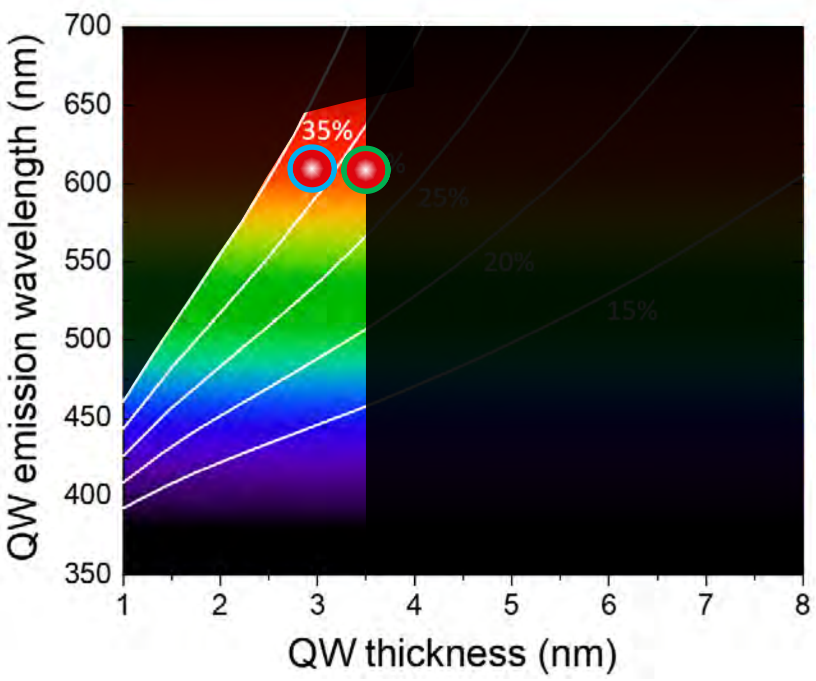
x = 0.32, L_w= 3.5 nm, λ_{max}= 641 nm

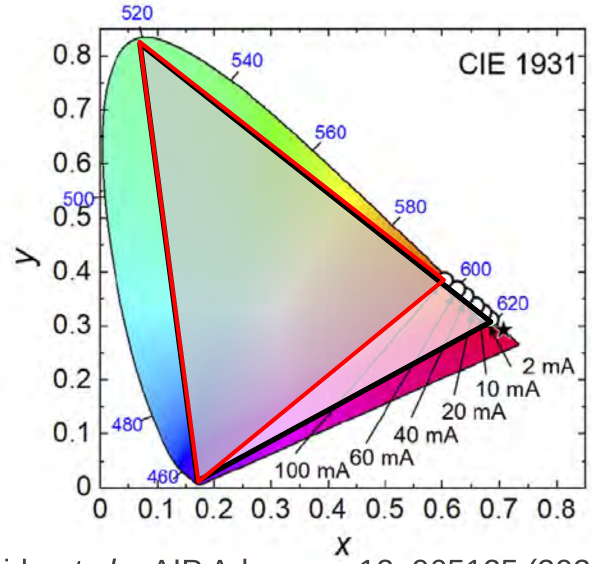
At 20 mA and 621 nm:
- Power = 1.7 mW
- EQE = 4.3%
- WPE = 2.9%



- Red-LEDs on GaN/sapphire template

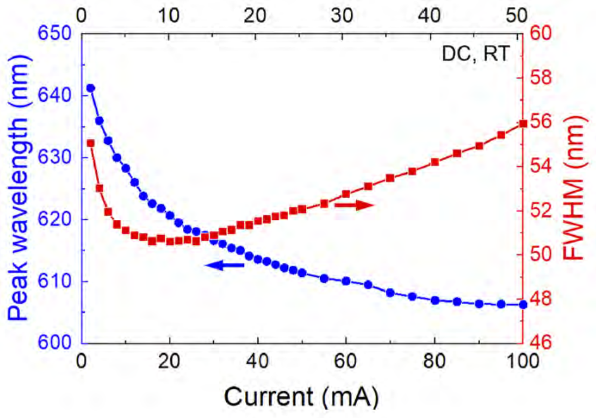
At high current density, due to the field screening and band filling, the emission is barely red (610 nm)





D. Iida *et al.*, AIP Advances 12, 065125 (2022)

The color gamut strongly depends on the “red” wavelength and the FWHM



EL peak ≠ dominant wavelength

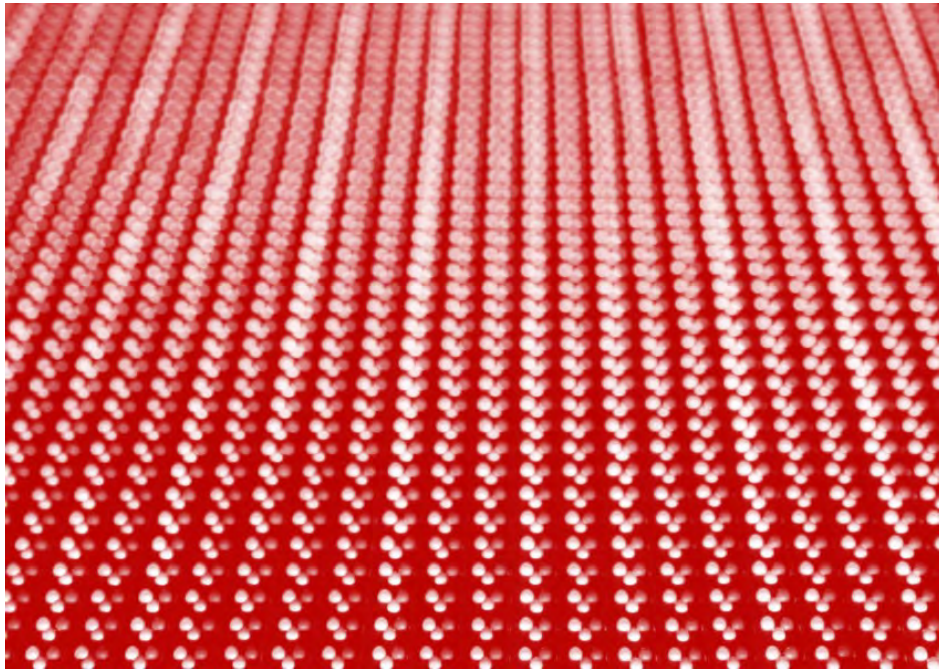
- Extend further the emission wavelength
- Reduce the emission linewidth
- Improve the efficiency

Higher In content ⇒ Decrease the strain

Part III: Are III-nitrides suitable for red LEDs?

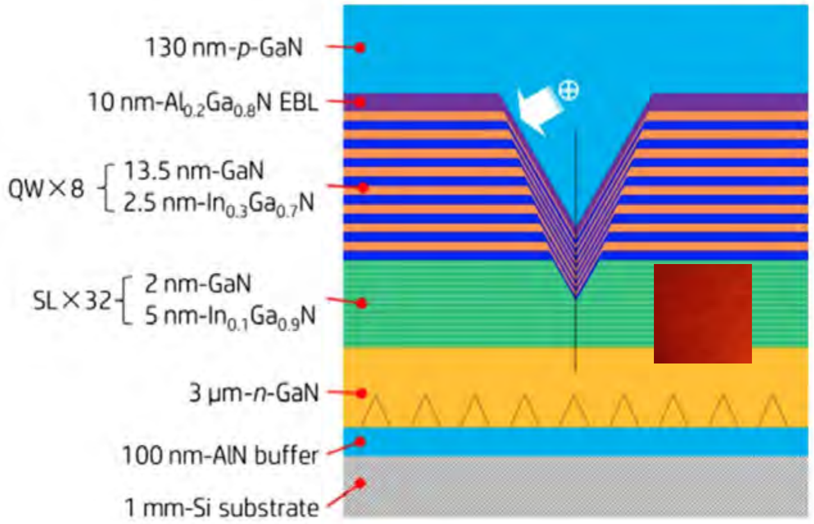
- How to push the wavelength to the red?

- **Less strain for more indium**

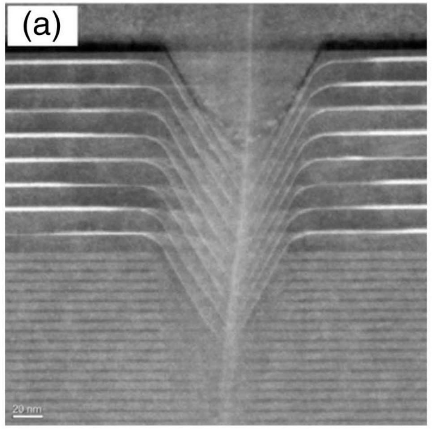


Less strain for more indium

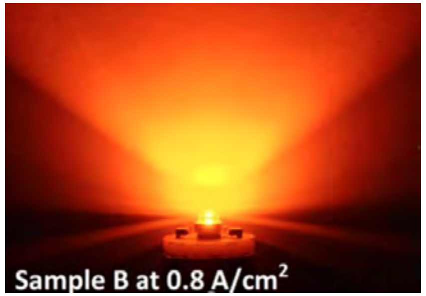
- Strain relaxation from surface morphology and growth on Si(111)

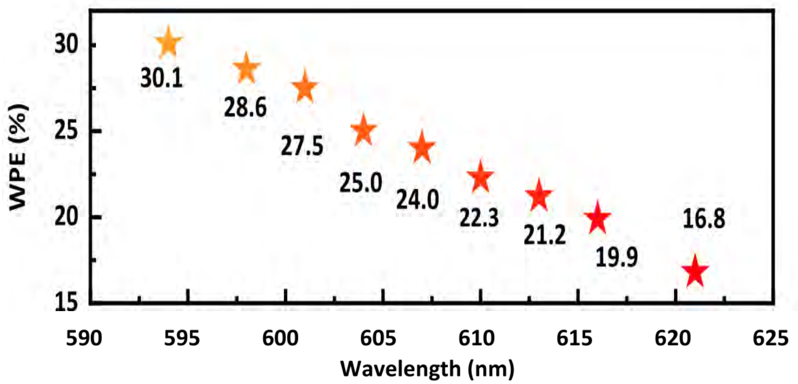


- Growth on silicon
  - ⇒ tensile strain
- Large V-pits
  - ⇒ strain relaxation
  - ⇒ Lateral hole injection



F. Jiang *et al.*, Photonics Research 7, 144 (2019) – Nanchang U.





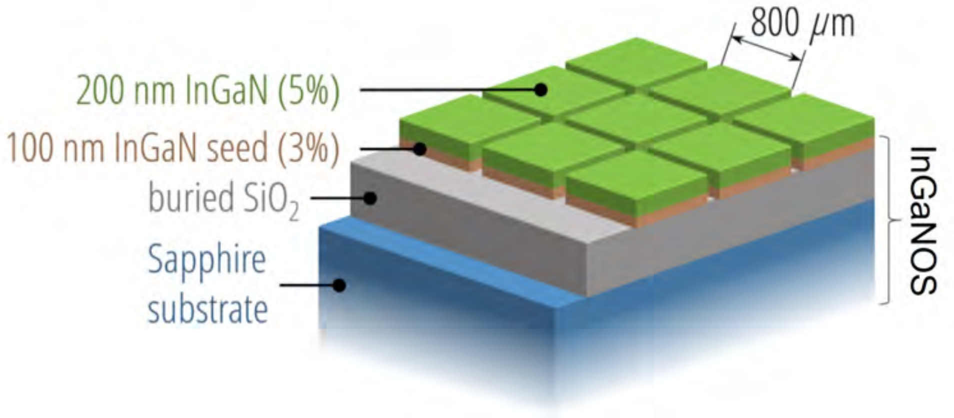
- WPE = 16.8% at 621 nm

Large devices 1x1 mm^2

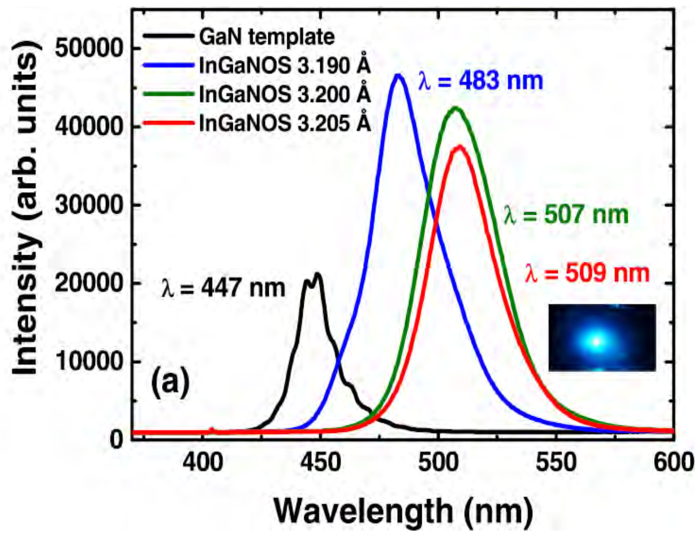
S. Zhang *et al.*, Photonics Research 8, 1671 (2020) Nanchang U.

Less strain for more indium

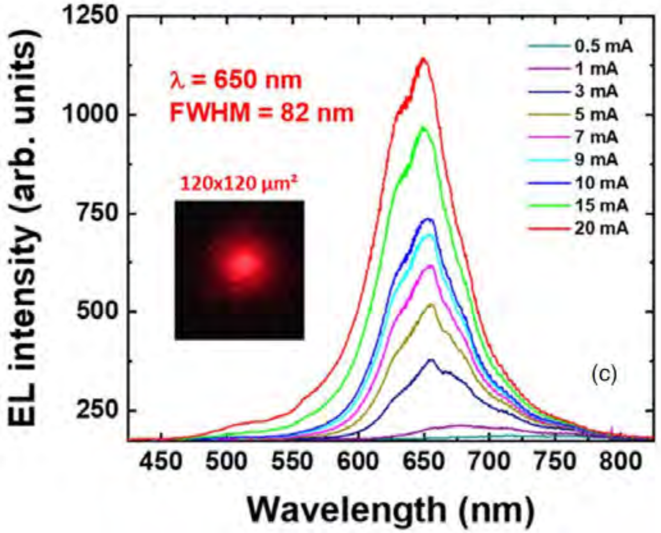
- Pseudo-InGaN substrate (InGaNOS)



- 200nm-thick $In_xGa_{1-x}N$ (x=0.015-0.08) layer on GaN/sapphire
- Transferred using Soitec's Smart Cut™ technology onto a compliant layer
- The InGaN layer is patterned to enable strain relaxation



A. Even *et al.*, APL 110, 262103 (2017)
CEA/LETI and Soitec



A. Dussaigne *et al.*, APEX 14, 092011 (2021)
CEA/LETI and Soitec

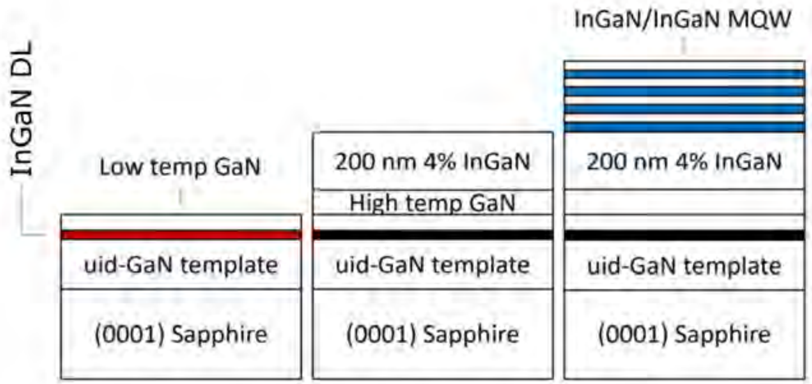
- In content ~40%
- 650 nm with small blueshift

IQE = 10%
EQE = 0.14% (with a LEE<4%)

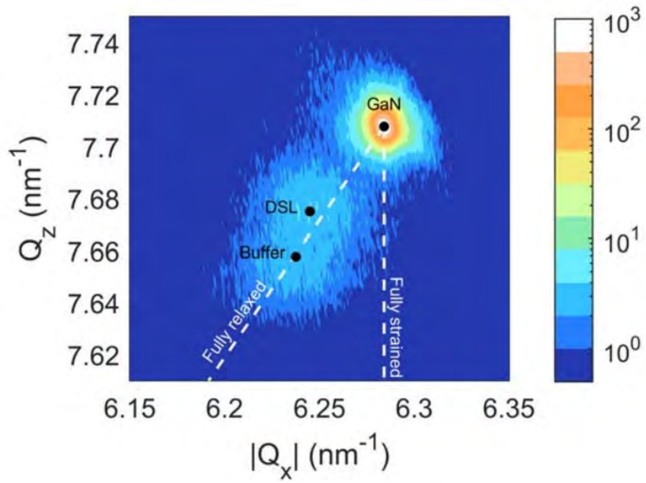
InGaNOS discontinued

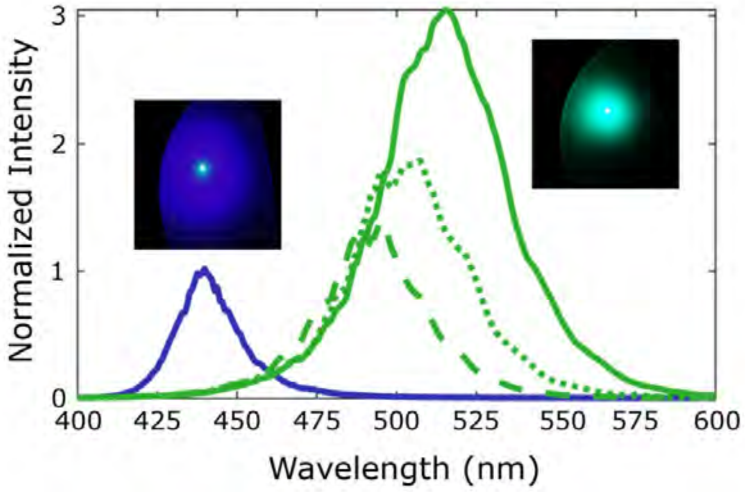
Less strain for more indium

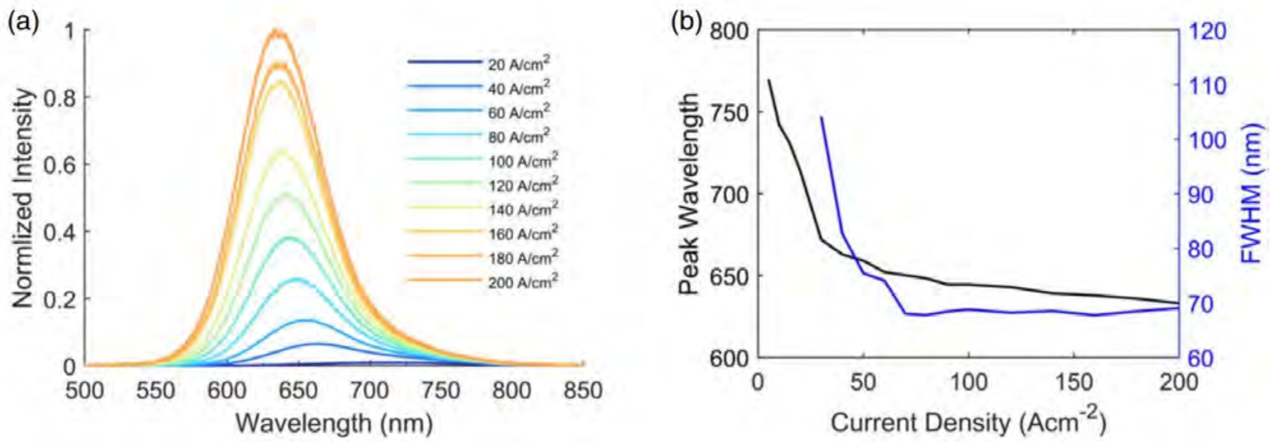
- Pseudo-InGaN substrate *via* decomposition layer



P. Chan *et al.*, APL 119, 131106 (2021) - UCSB







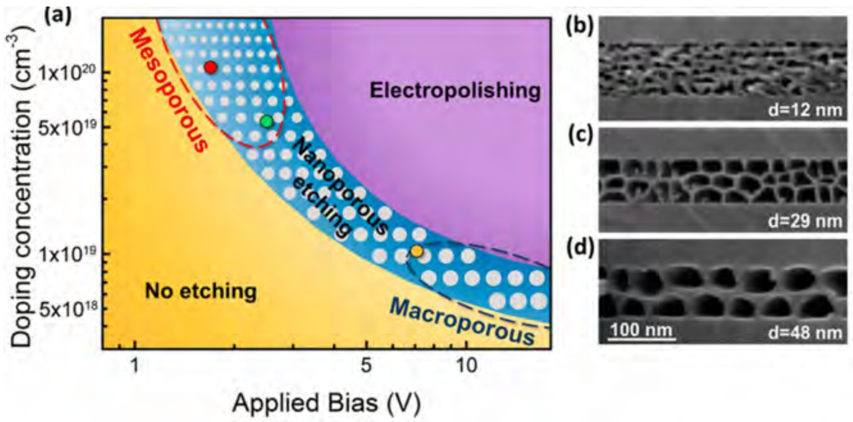
P. Chan *et al.*, APEX 14, 101002 (2021) - UCSB

- 770 nm at low current
- 633 nm at 200 A.cm^{-2}

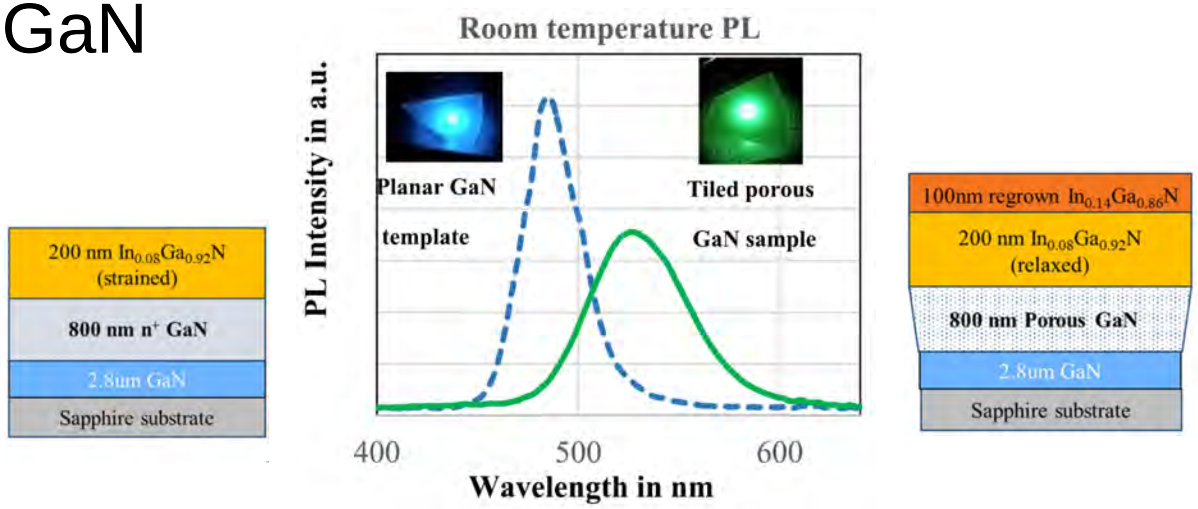
EQE = 0.05% (due to poor surface morphology)

Less strain for more indium

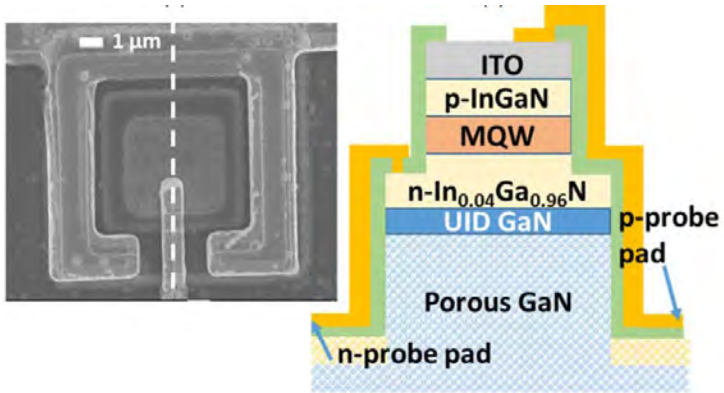
- Strain relaxation from porous GaN

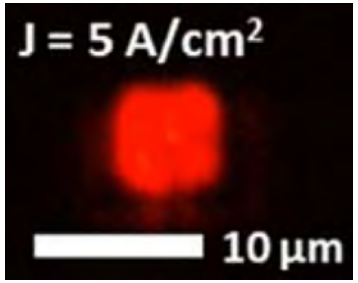


C. Zhang *et al.*, ACS Photonics 2, 980 (2015) – Yale



S.S. Pasayat *et al* ., Semicond. Sci. Technol. 34, 115020 (2019)- UCSB





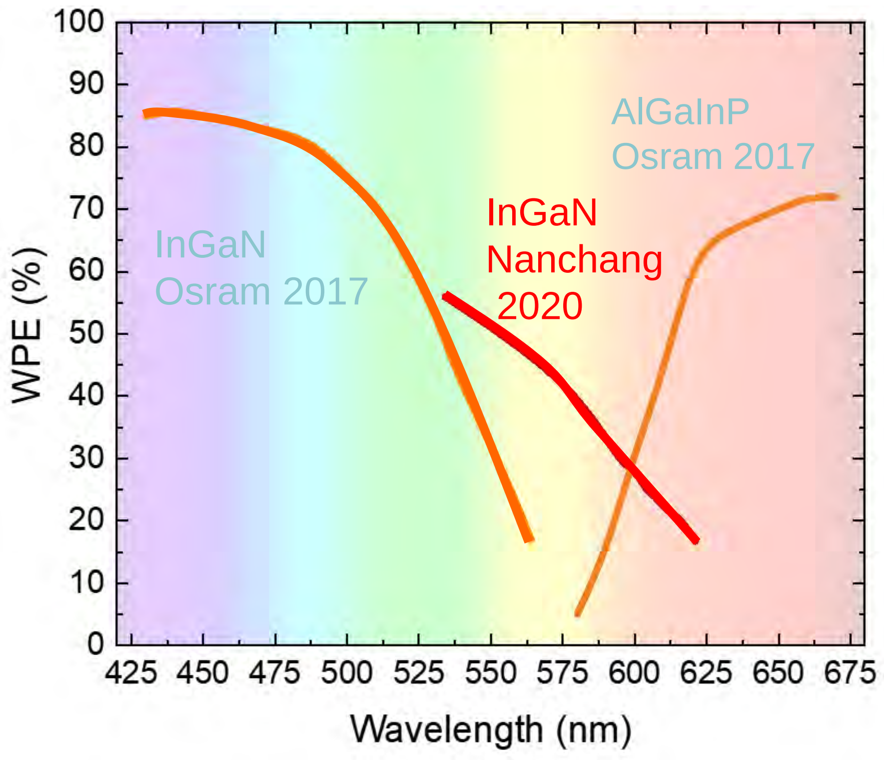
- 632 nm at 10 $A.cm^{-2}$
- 6 µm × 6 µm µLEDs

EQE = 0.2%

S.S. Pasayat *et al*., APEX 14, 011004 (2021) - UCSB

R. Oliver, Cambridge U. and Porotech

WPE of InGaN based LEDs – state of the art



- WPE ≈ 17% at 621 nm
  Large devices 1x1 mm²
  Nanchang U.

- WPE ≈ 2 % at 630 nm
  Small devices 25x25 μm²
  KAUST + National Taiwan U.

➲ The green gap is closing

➲ The III-nitrides may compete for red microLEDs

➲ InGaN pseudo-substrates are needed. Specific MOVPE reactors?