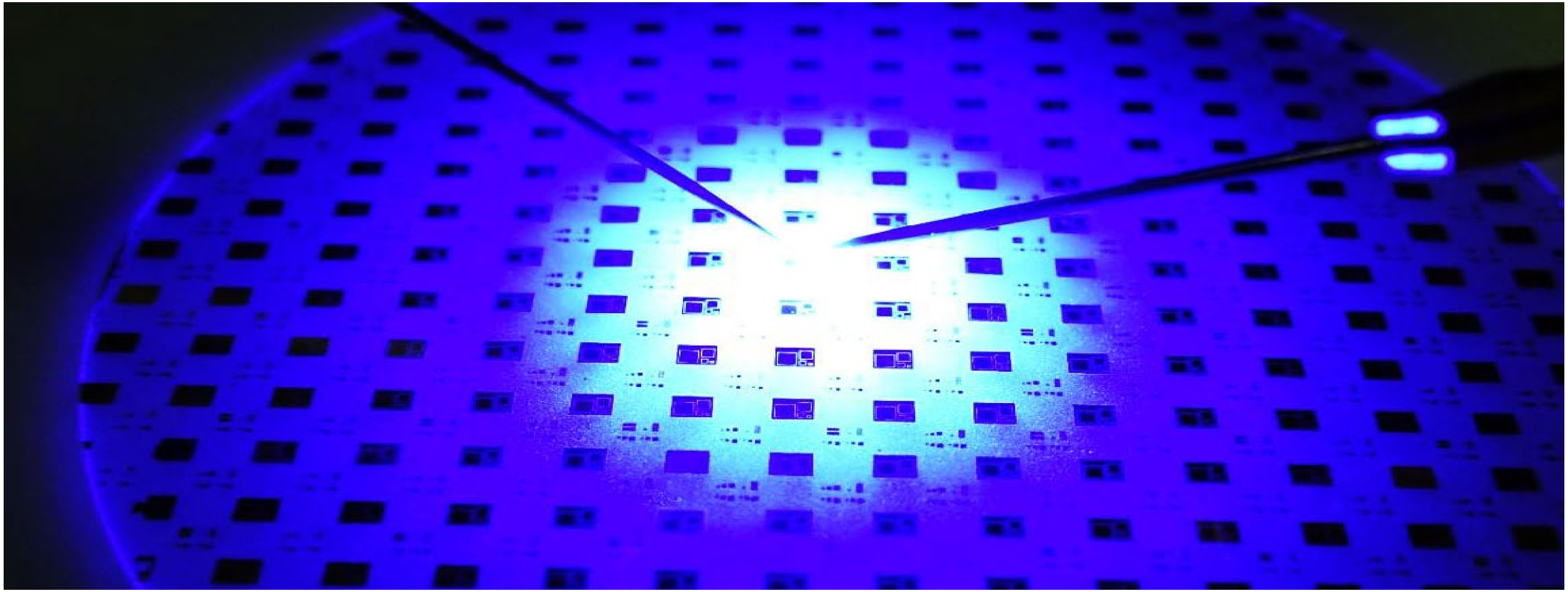
III-nitride semiconductors



Nicolas Grandjean
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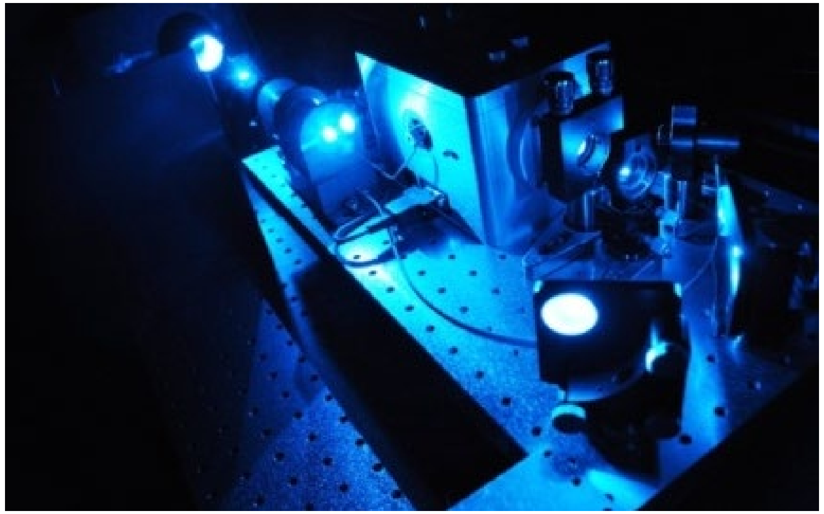
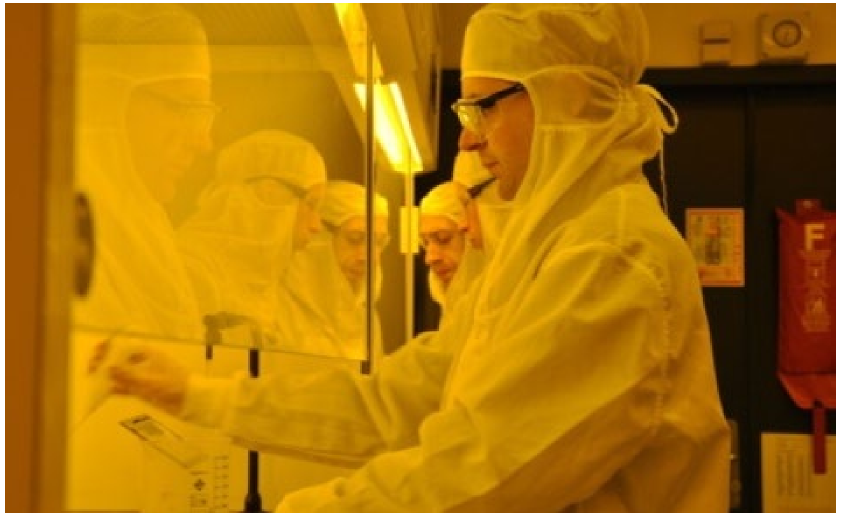
LASPE - IPHYS

III-nitride semiconductors (AlGaInN): Physics and Devices





Growth facilities for III-nitrides

2 MOCVD reactors and 1 MBE system

Characterization

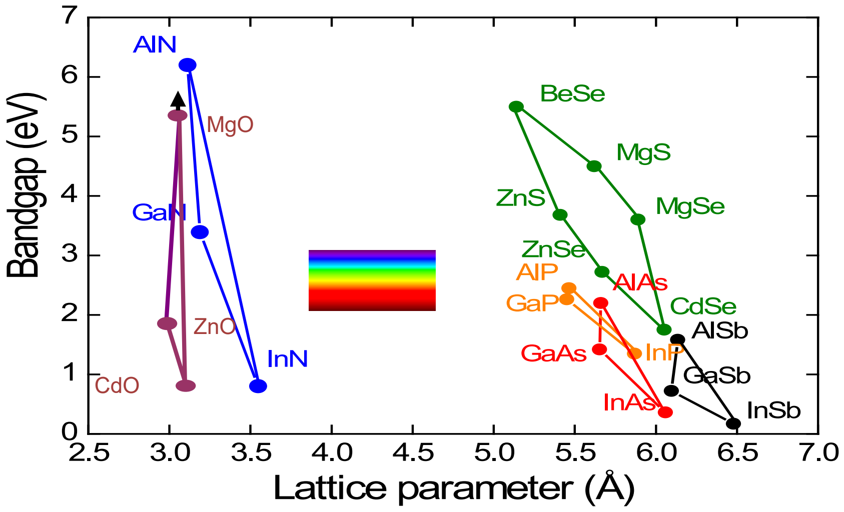
Optical spectroscopy, XRD, AFM, ...

Processing

Clean-room facilities (IPHYS)

GaN ?

Which semiconductors for blue emission?

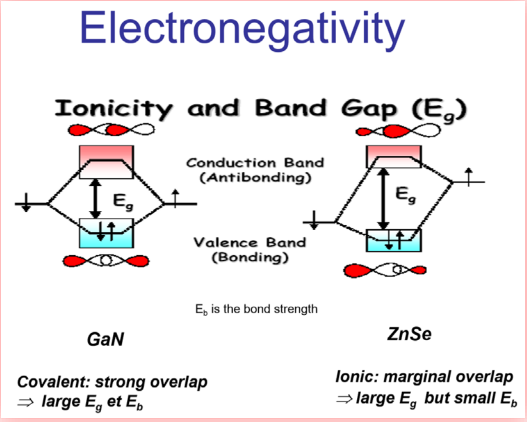


Wide bandgap semiconductors:

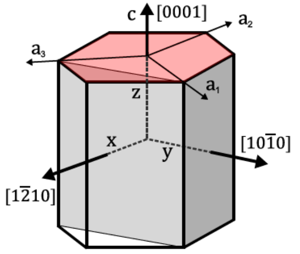
II-VI selenides (Zn,Mg,Cd)Se

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

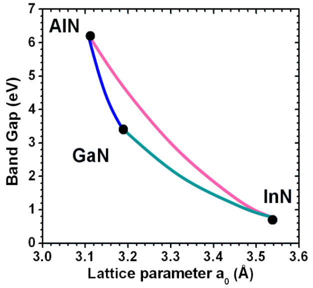
II-VI oxides (Zn,Cd,Mg)O no p-type conductivity



III-V nitride semiconductors



Wurtzite structure



A long list of drawbacks:

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

Introduction

GaN – a historical overview

1971: Optical properties of GaN (Ilegems-Bell Labs)
- Rather good material quality BUT p-type conductivity lacking

1988: A Breakthrough (Akasaki-Japan)
- Demonstration of p-type doping using Mg

1993: High-brightness blue LEDs (Nakamura at Nichia)
- *GaN research start*

Candela-class high-brightness InGaN/AlGaN double-heterostructure blue-light-emitting diodes

Shuji Nakamura, Takashi Mukai, and Masayuki Senoh
Department of Research and Development, Nichia Chemical Industries, Ltd., 491 Oka, Kaminaka, Anan, Tokushima 774, Japan

(Received 2 December 1993; accepted for publication 5 January 1994)

1993: GaN transistor

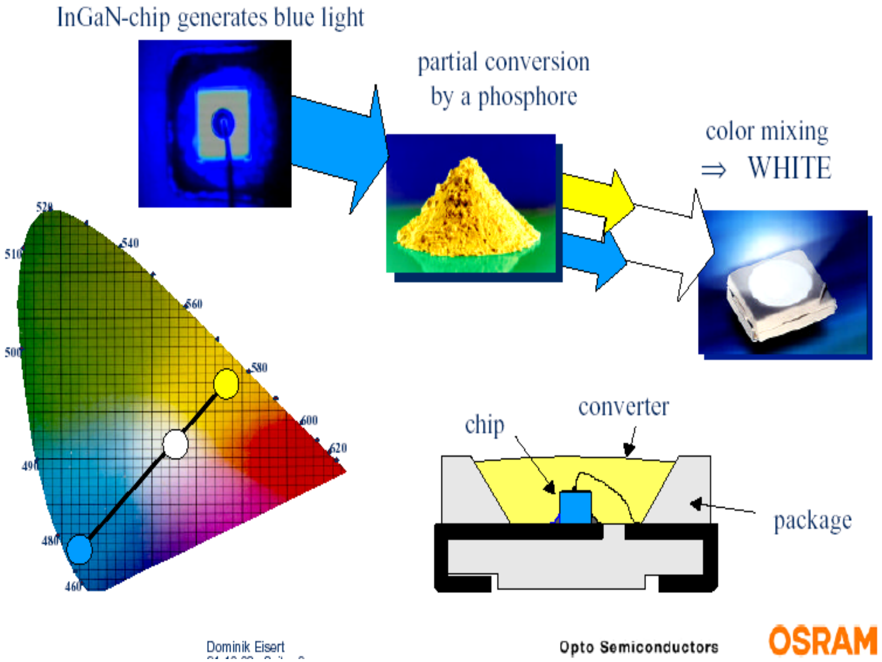
1995: Blue laser diode (Nakamura at Nichia)

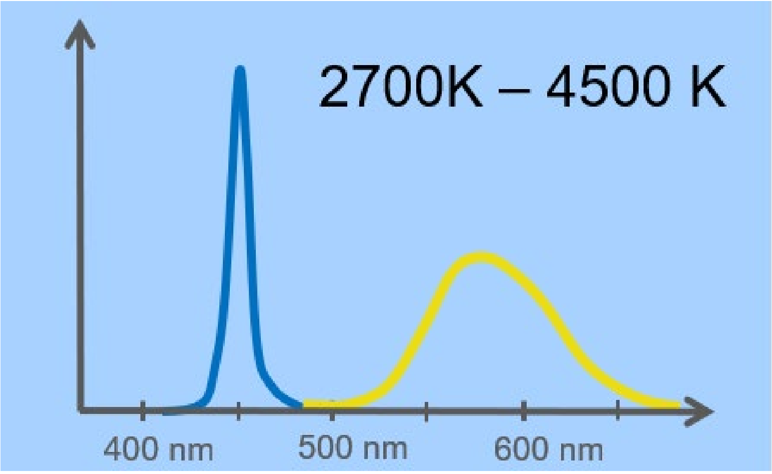
1997: white LEDs for lighting application (Nakamura at Nichia)

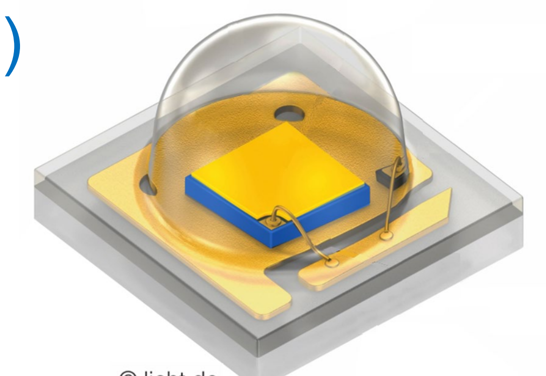
2000-: Green lasers and GaN HEMTs (High-frequency)

2020-: VCSELs, GaN power transistor, microLEDs

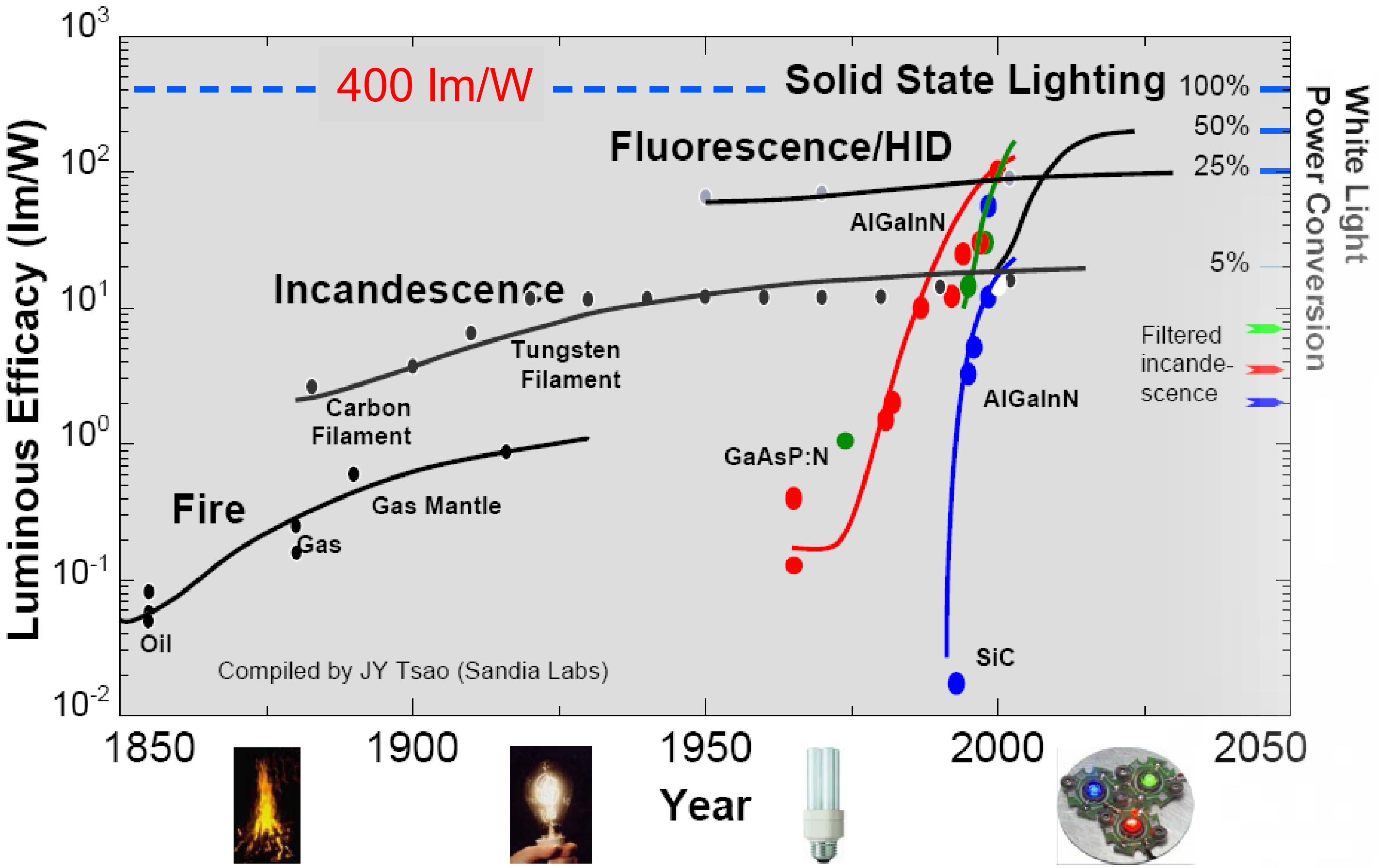
- Blue LEDs are extremely efficient
- Wall plug efficiency > 80% (Internal quantum efficiency > 90%)






© licht.de

Luminous efficacy of light sources



Incandescent lamp: 15 lm/W
Fluorescent lamp: 50-100 lm/W

LED lamp: 100-150 lm/W

Introduction

The Nobel Prize in Physics 2014

Photo: A. Mahmoud
Isamu Akasaki

Photo: A. Mahmoud
Hiroshi Amano

Photo: A. Mahmoud
Shuji Nakamura

The Nobel Prize in Physics 2014 was awarded jointly to Isamu Akasaki, Hiroshi Amano and Shuji Nakamura *"for the invention of efficient blue light-emitting diodes which has enabled bright and energy-saving white light sources"*.

Lighting: 11% of total electricity consumption in the US (US - Energy information administration)

Savings potential of 15 billion kWh per year in the EU-25 (EU - Institute for Energy and Transport)

Outline

Part I: growth of III-V nitrides

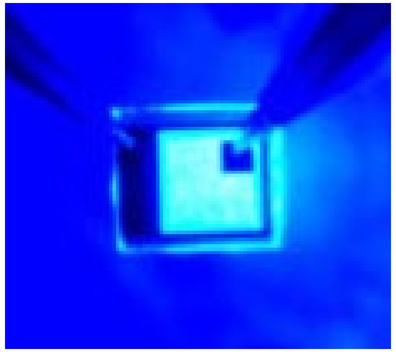
- **GaN heteroepitaxy:** substrates, dislocations, and polarity
- **InGaN quantum wells:** indium composition fluctuations
- **InAlN alloys:** lattice-matched but a price to pay
- **p-type doping:** works for GaN but still quite challenging for Al(Ga)N

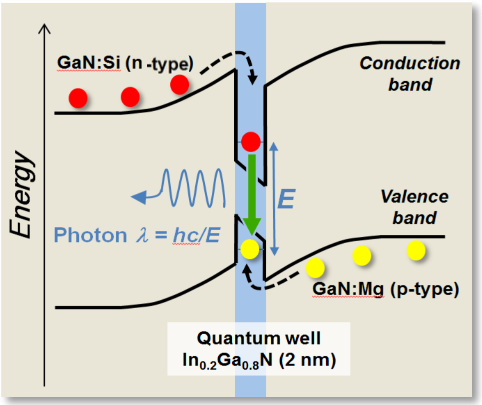
Part II: Can we make red LEDs from III-nitrides?

GaN heteroepitaxy

- Main growth issues

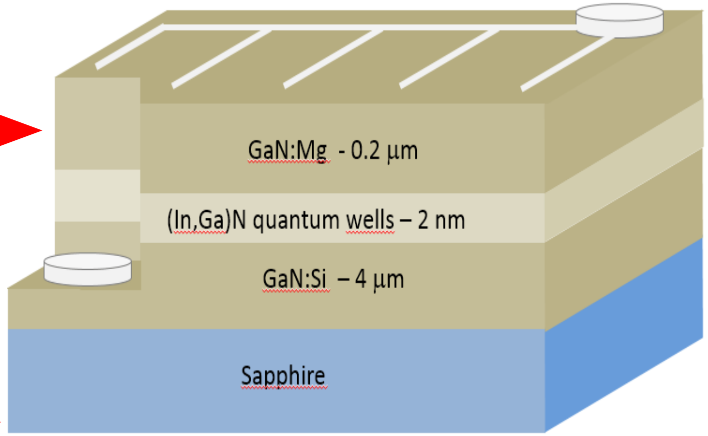
Typical size: 400x400 μm^2 to 2x2 mm^2





P-type GaN

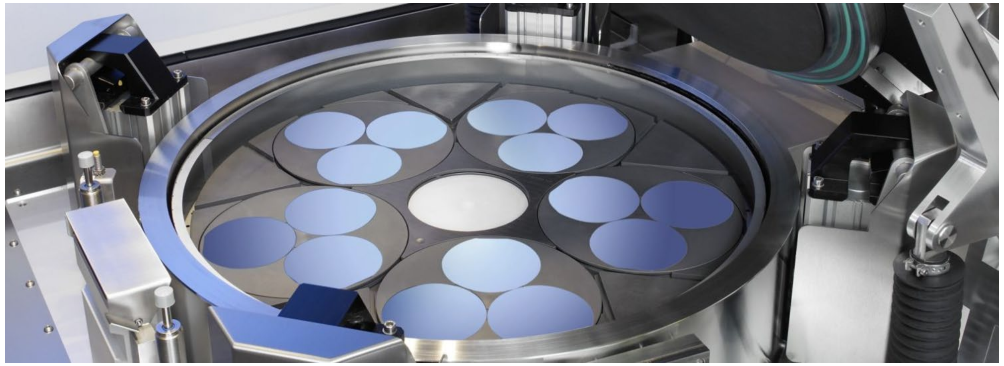
Substrate



InGaN QWs

Growth technique: MOVPE only so far

15 × 4 in.

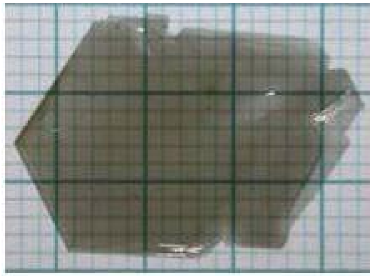


GaN heteroepitaxy

- The substrate: GaN

Lack of GaN bulk native substrates

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

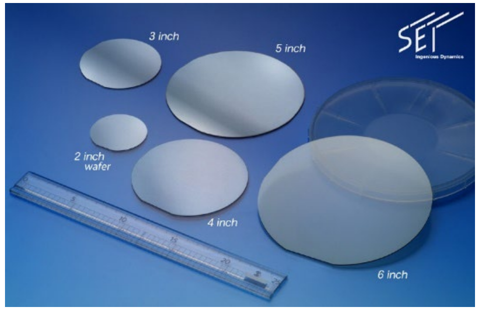


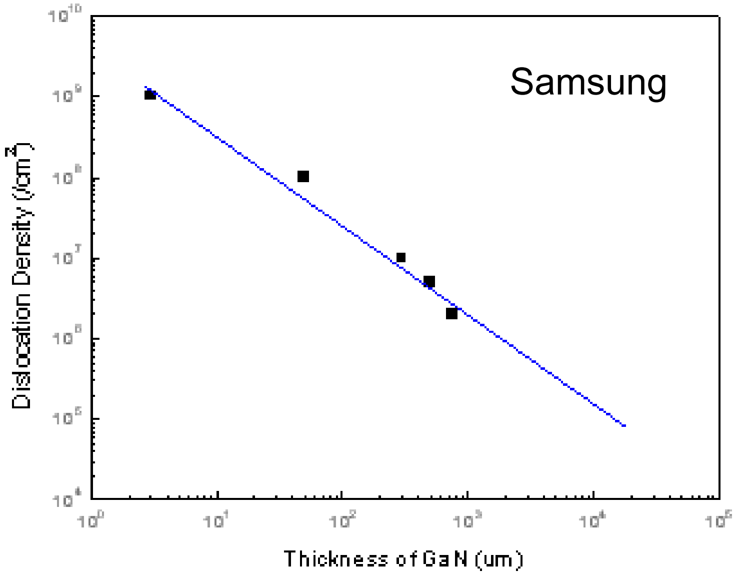
Free-standing GaN substrates:

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





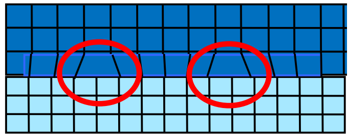
The substrate: sapphire

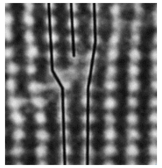
GaN technology has been developed on sapphire from the 80's

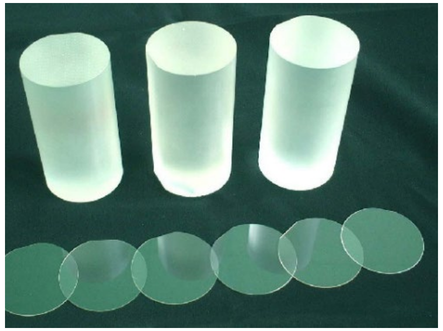
Lattice mismatch to GaN

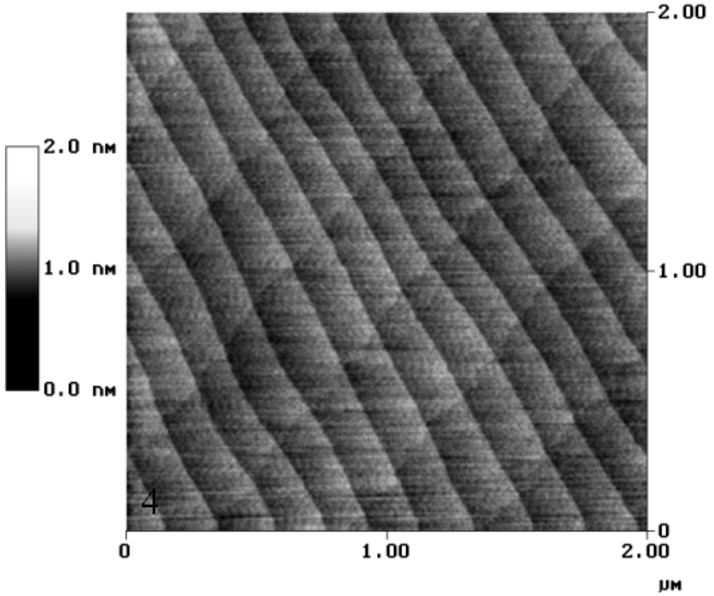
Al_2O_3 (0001):	+16 %
6H-SiC (0001):	-3.5 %
Si (111):	-17 %

Dislocations







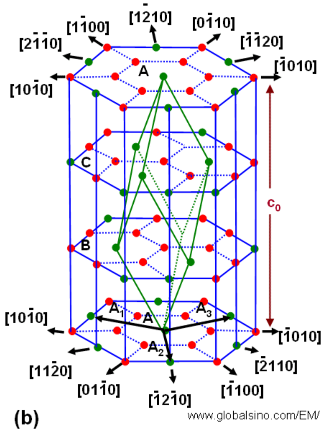


Sapphire (0001) is the most commonly used substrate

size : 6 in.

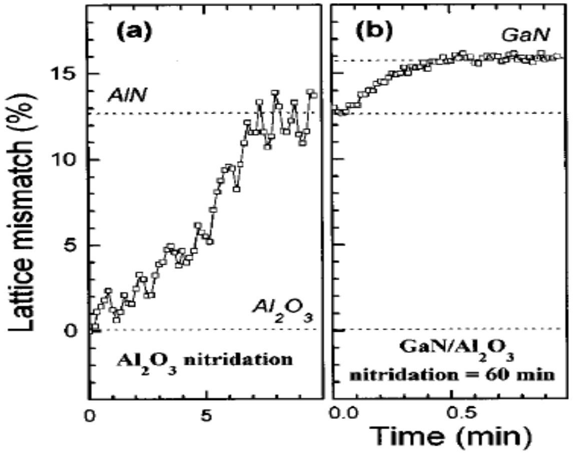
The substrate: sapphire

Sapphire nitridation ⇨ formation of an AlN layer

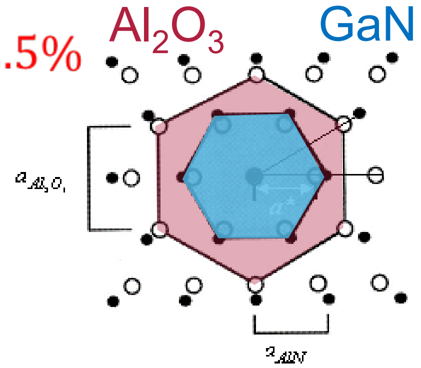


Sapphire crystal structure

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



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



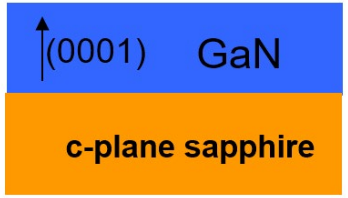
GaN/sapphire epitaxial relationship

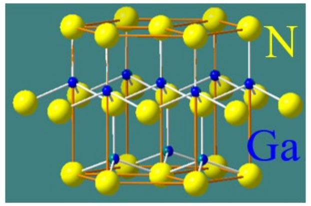
Aluminum hexagonal sublattice lying in the c-plane of Al_2O_3 crystal

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

EPFL

GaN polarity





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

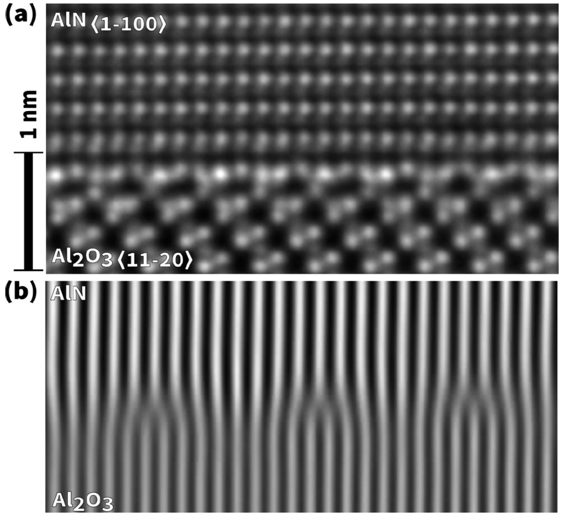
Polarity Control in Group-III Nitrides beyond Pragmatism

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)

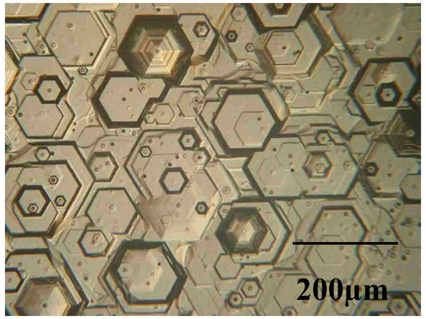
Impact of sapphire nitridation on formation of Al-polar inversion domains in N-polar AlN epitaxial layers

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

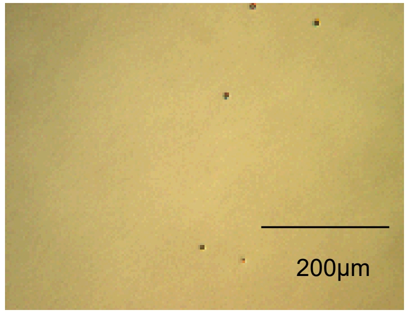


Aluminum oxynitride layer controls the polarity of GaN epilayer

⇒ Ga polarity allows growing high purity GaN layers



16 µm thick GaN, N polar



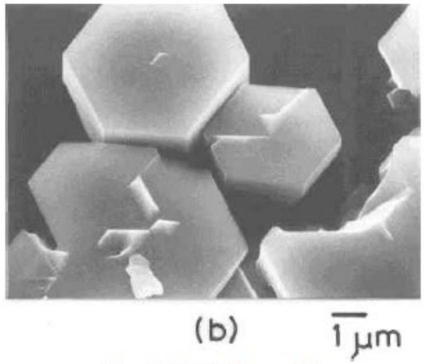
16 µm thick GaN, Ga polar

Take-home message: surface chemistry controls the polarity

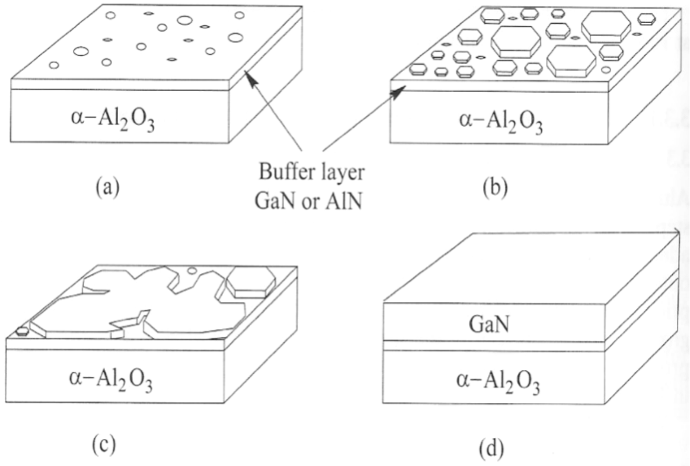
GaN heteroepitaxy

■ GaN on sapphire

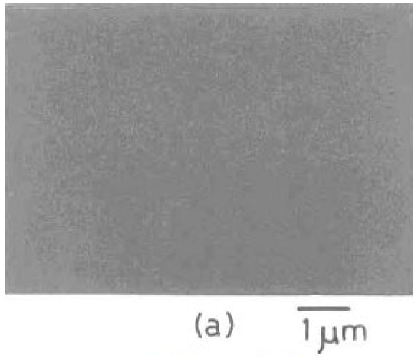
The low temperature buffer layer



w/o LT buffer



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



w LT buffer

Two-step growth procedure:

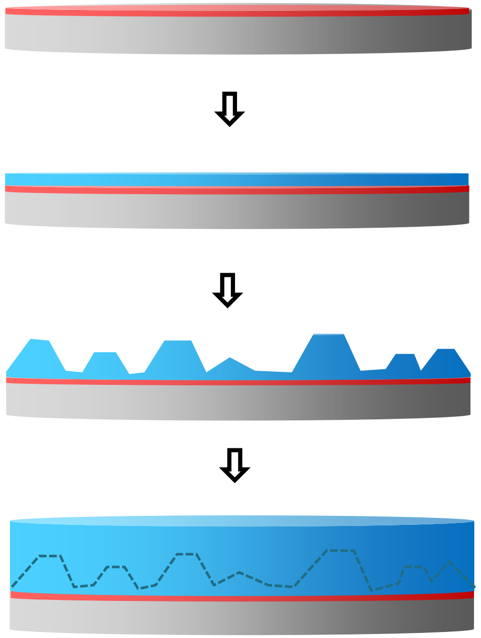
1) a thin AlN buffer layer (25 nm) deposited at low-temperature (500°C)

2) growth at high-temperature (1050-1100°C)

GaN heteroepitaxy

■ GaN on sapphire

3D islands to reduce the dislocation density



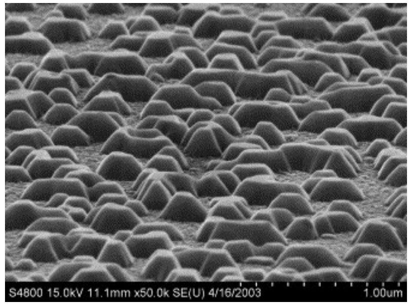
Nitridation
AlN formation

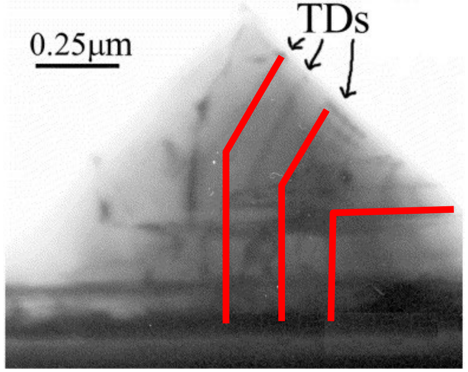
GaN LT buffer layer
(500°C)

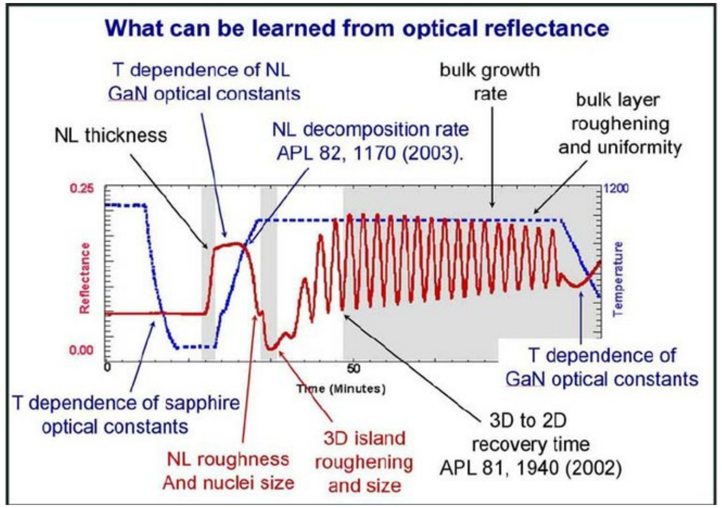
Annealing at HT with H_2
3D islanding

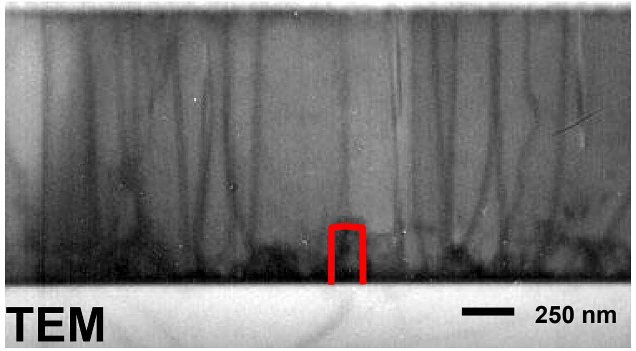
Growth at HT (>1000°C)
Coalescence

Nakamura 1992





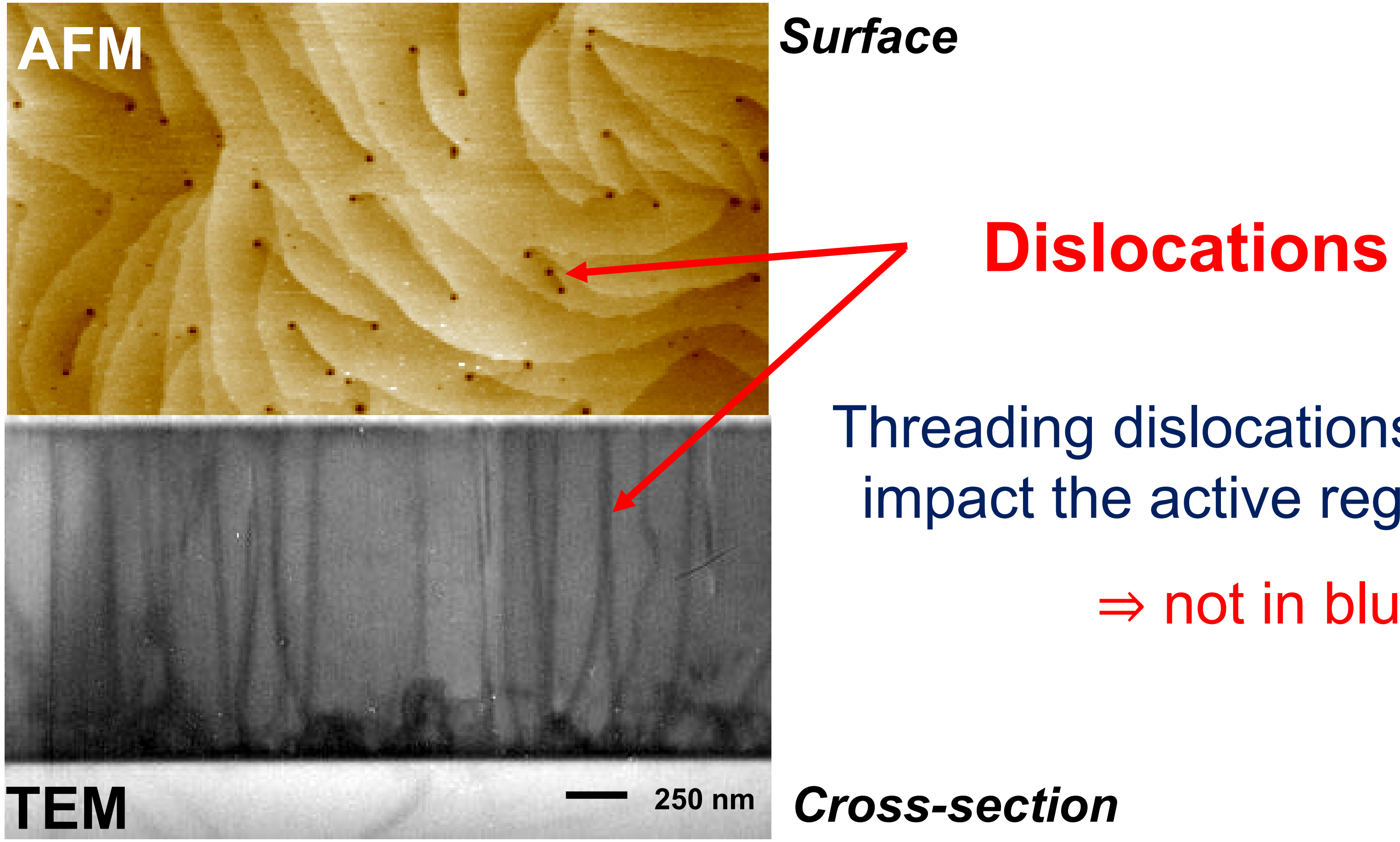




Dislocation density reduced from 10^{10} to $5x10^{7}$ cm^{-2}

GaN heteroepitaxy

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



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

⇒ not in blue LEDs

GaN heteroepitaxy

GaN on Silicon substrate

Lattice mismatch

Al_2O_3 (0001): +16 %

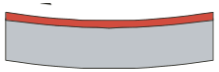
6H-SiC (0001): -3.5 %

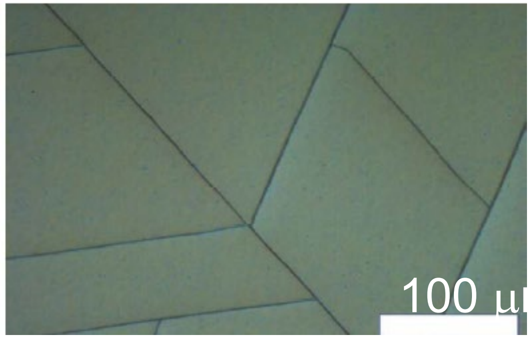
Si (111): -17 %

(GaAs/Si: +4 %)

Thermal expansion coefficient mismatch

Si (111): 115 % ⇨ tensile strain

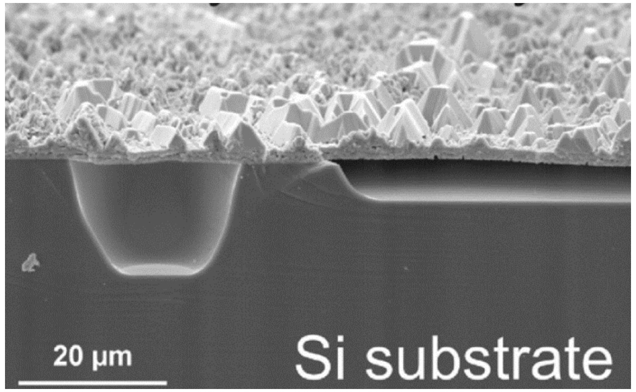




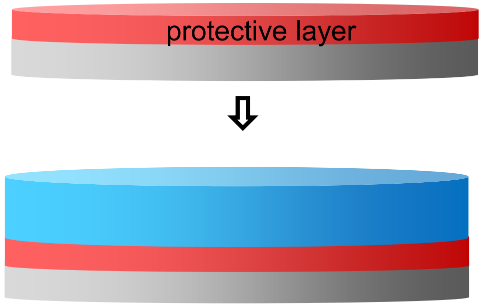
Epilayer cracking when cooling down the wafer from 1000°C to room-temperature

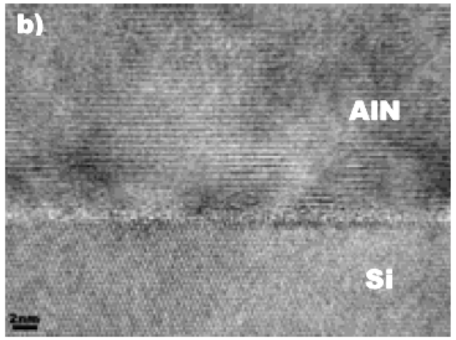
GaN on Silicon substrate

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)





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

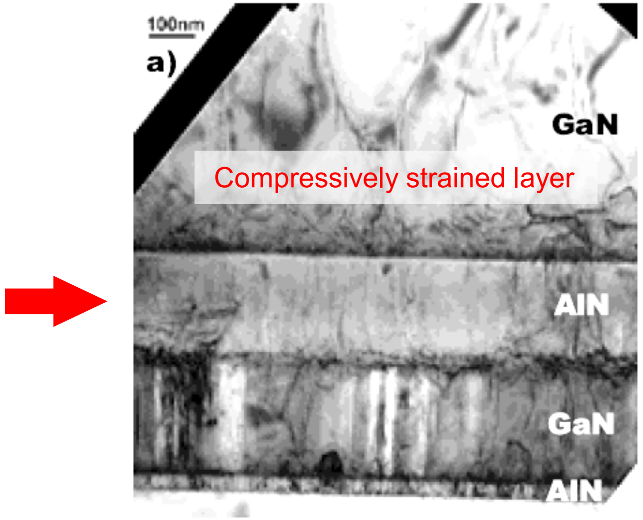
phys. stat. sol. (a) 188, No. 2, 501 (2001)

GaN heteroepitaxy

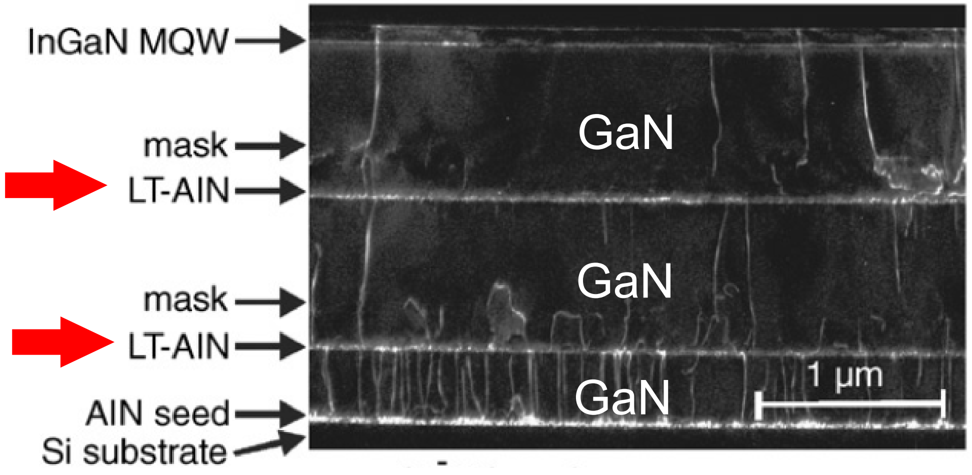
GaN on Silicon substrate

Strain engineering to avoid layer cracking

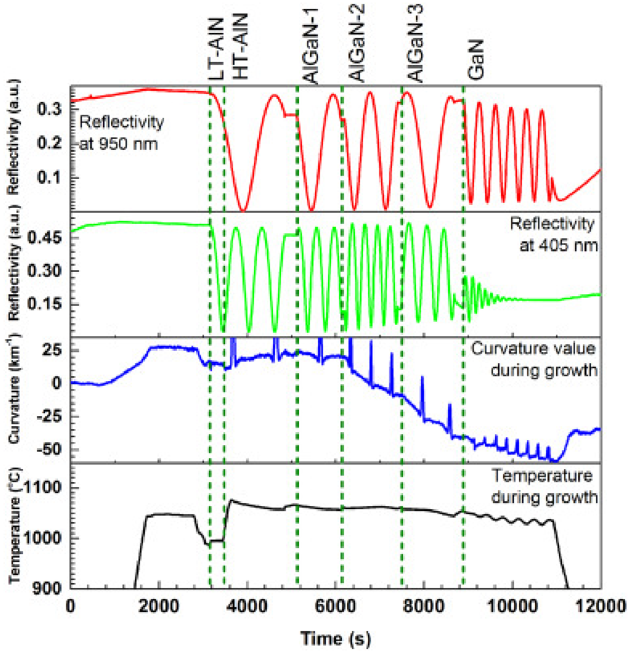
→ compressive strain is introduced during growth



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



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



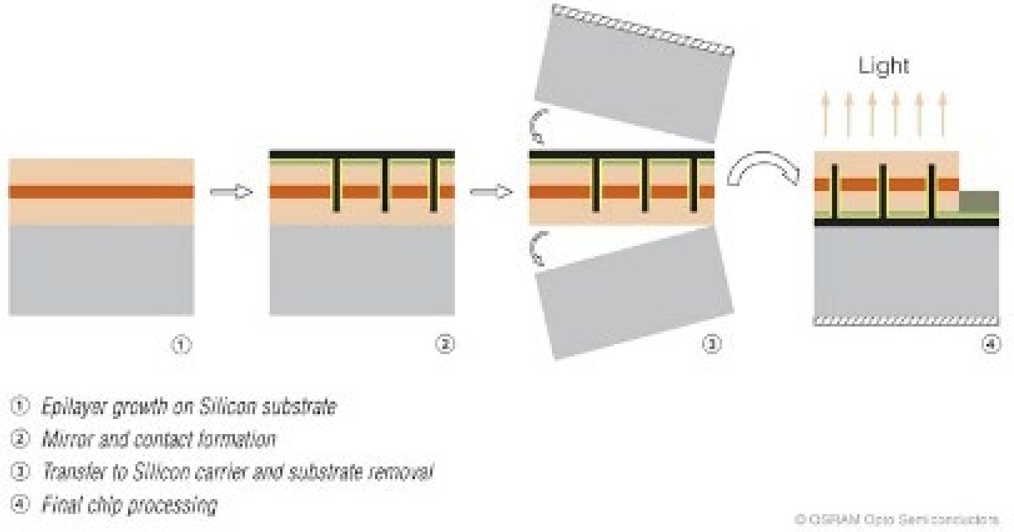
A. Kadir et al., Thin Solid Films 663, 73 (2018)

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)

Content

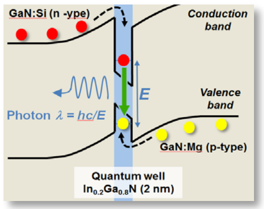
Part I: growth of III-V nitrides

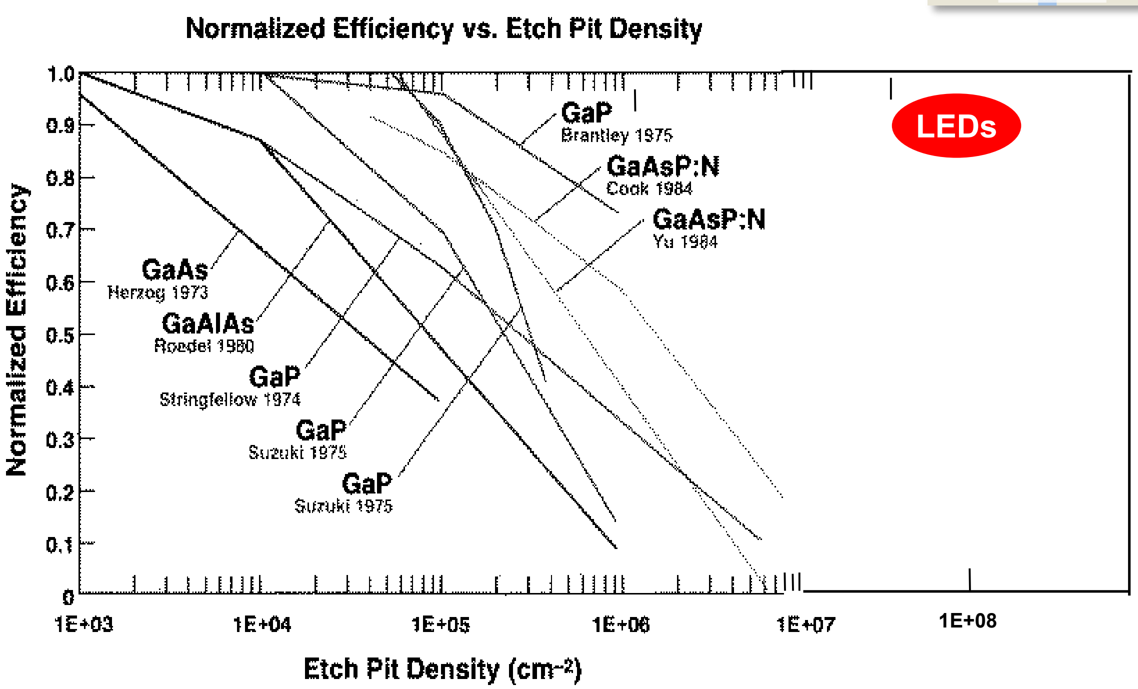
- **GaN heteroepitaxy:** substrates, dislocations, and polarity
- **InGaN quantum wells:** indium composition fluctuations
- **InAlN alloys:** lattice-matched but a price to pay
- **p-type doping:** works for GaN but still quite challenging for Al(Ga)N

GaN heteroepitaxy

■ Internal quantum efficiency of blue LEDs

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





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

Internal quantum efficiency of blue LEDs

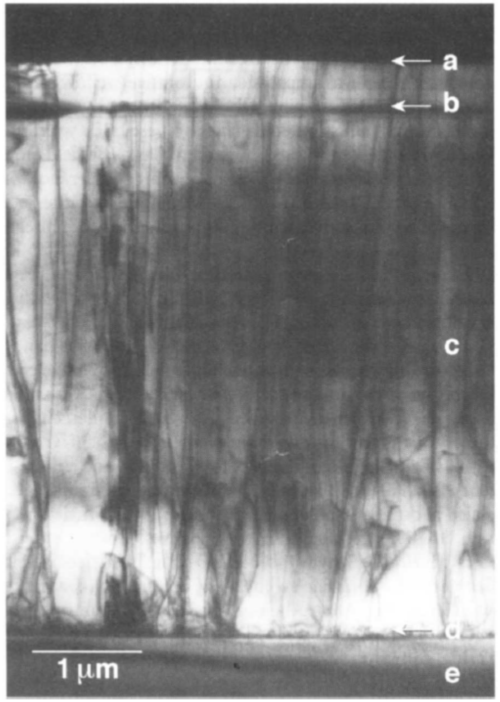


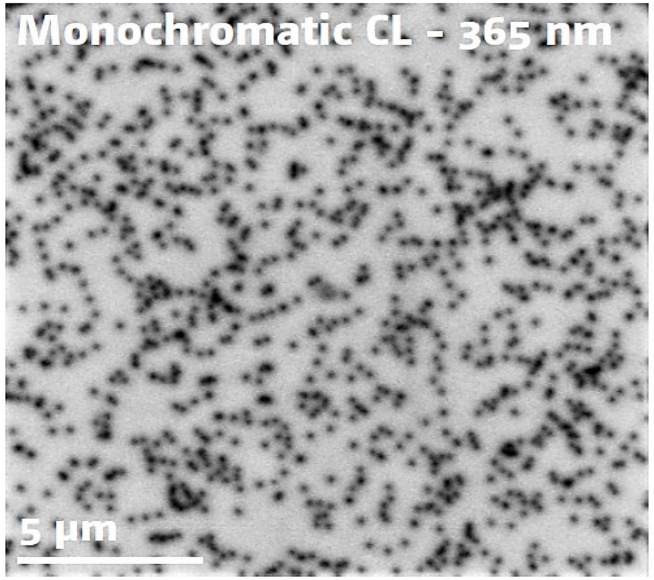
Figure 4 Cross-section transmission electron microscopy view of a high-efficiency Nichia blue LED. The dislocation density of 10^{10} cm^{-2} is remarkably high for such an efficient and durable device. Indicated in the figure are the top surface of the film (a), the active region (b), the main GaN film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

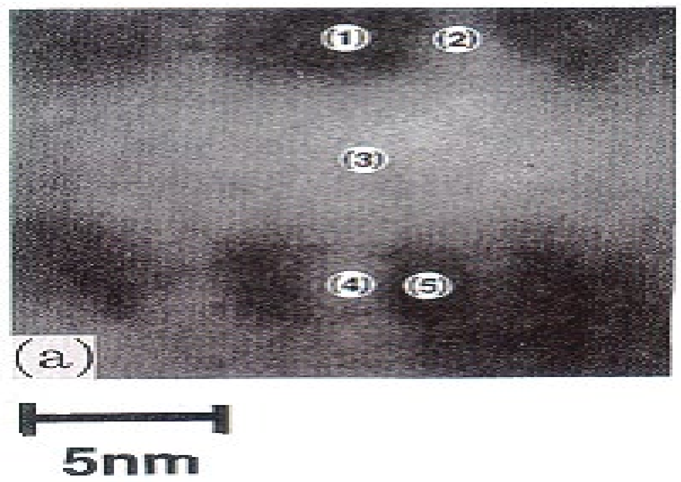


Number of dislocations - 882
Threading dislocation density - 3.1E8 cm^{-2}

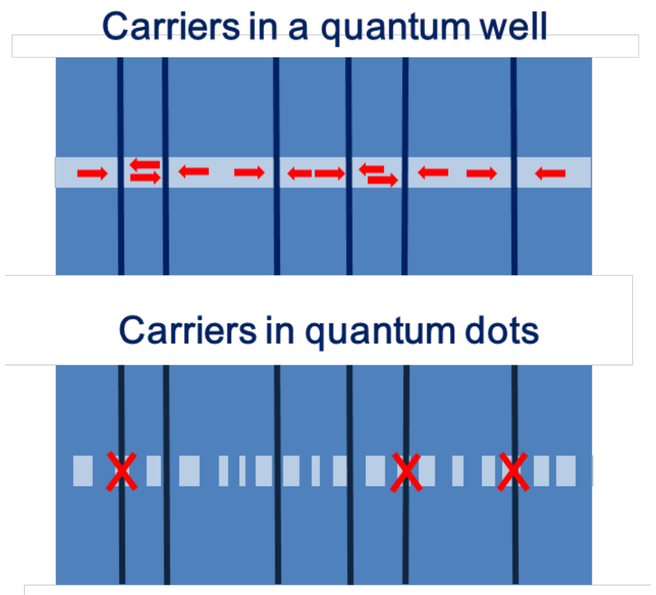
InGaN quantum wells

- Quantum wells or quantum dots?

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



TEM image of InGaN/GaN QWs



Gérard and Weisbuch (patent 1990)

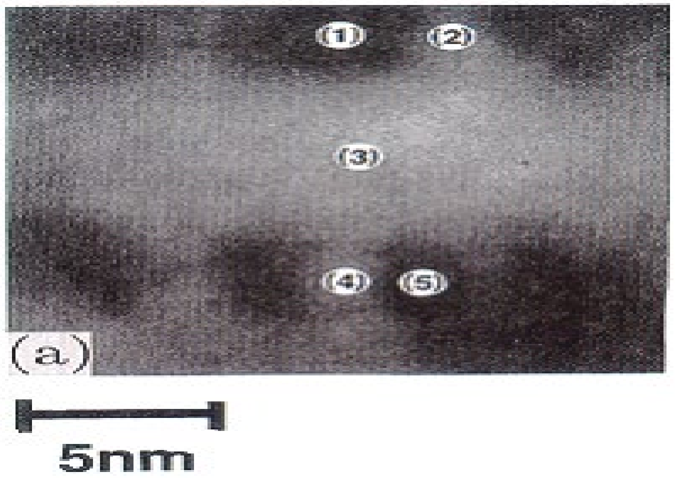
Indium-rich clusters in InGaN QWs act as quantum dots

Carrier localization prevents radiative efficiency collapse

InGaN quantum wells

■ Quantum wells or quantum dots?

TEM image of InGaN/GaN QWs grown by MOCVD



Narukawa et al. APL (1997)

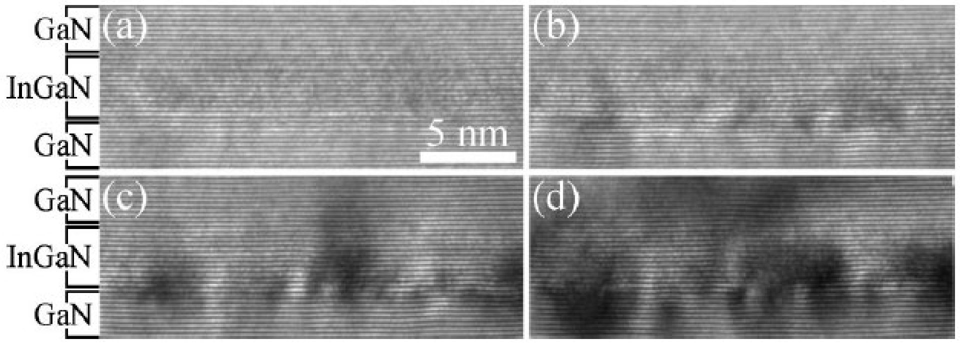


FIG. 3. (0002) lattice fringe images showing strain contrast evolution in an $In_{0.22}Ga_{0.78}N$/GaN MQW during exposure to a 200 kV electron beam flux of ~35 A cm^{-2} after: (a) 20, (b) 220, (c) 420, and (d) 620 s.

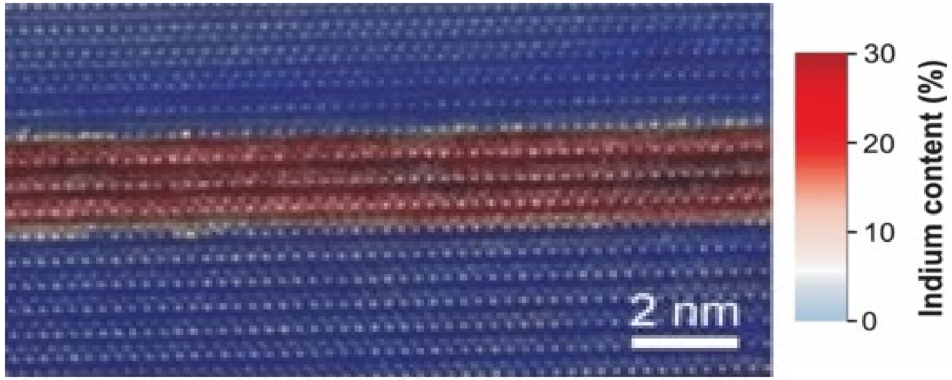
T. Smeeton *et al*, APL 83, 5419 (2003)

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

InGaN quantum wells

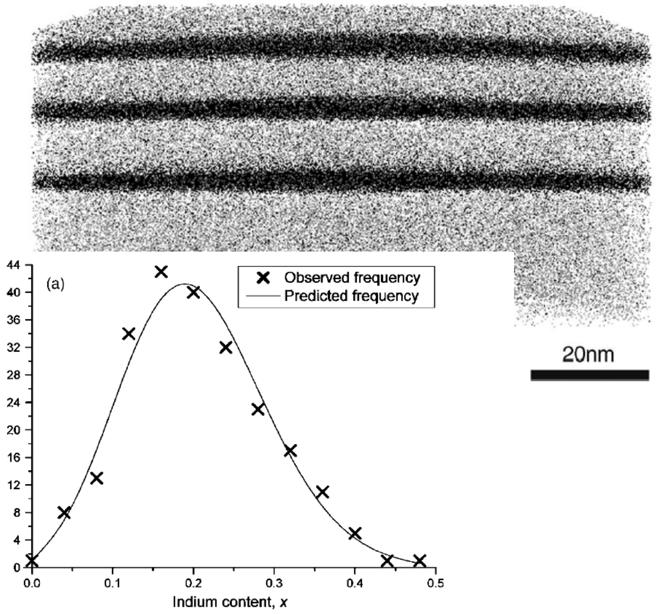
- InGaN is a perfectly disordered alloy

TEM - InGaN/GaN QW



No evidence In-rich clusters

Atom probe tomography - InGaN/GaN QWs



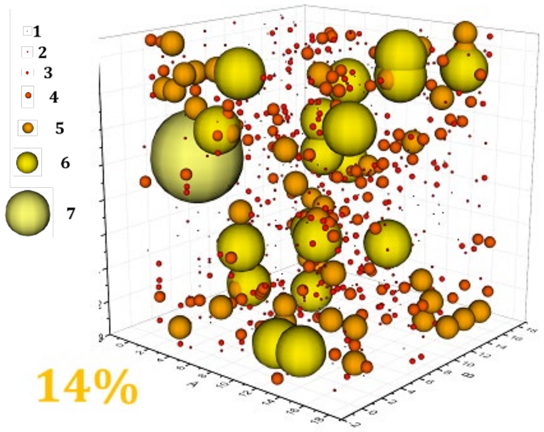
M.J. Galtrey *et al.*, JAP 104, 013524 (2008)

The indium distribution correspond to that of a random alloy

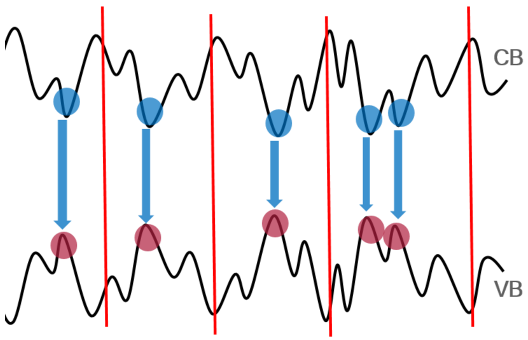
InGaN quantum wells

EPFL

■ InGaN QW potential fluctuations

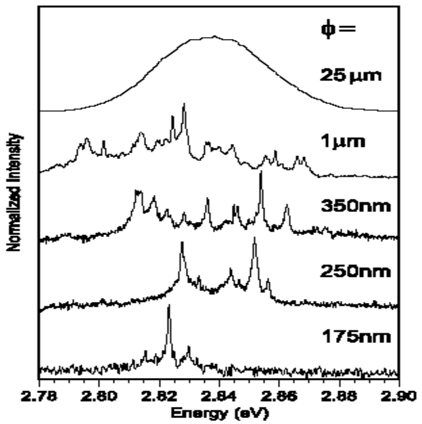


Schematic view of indium second nearest neighbor occupation in InGaN alloy



InN bandgap: 0.6 eV
GaN bandgap 3.4 eV

μ-PL on $In_{0.15}Ga_{0.85}N$/GaN QWs



Single emission line like InAs single quantum dot

Schömig *et al*, PRL 92, 106802 (2004)

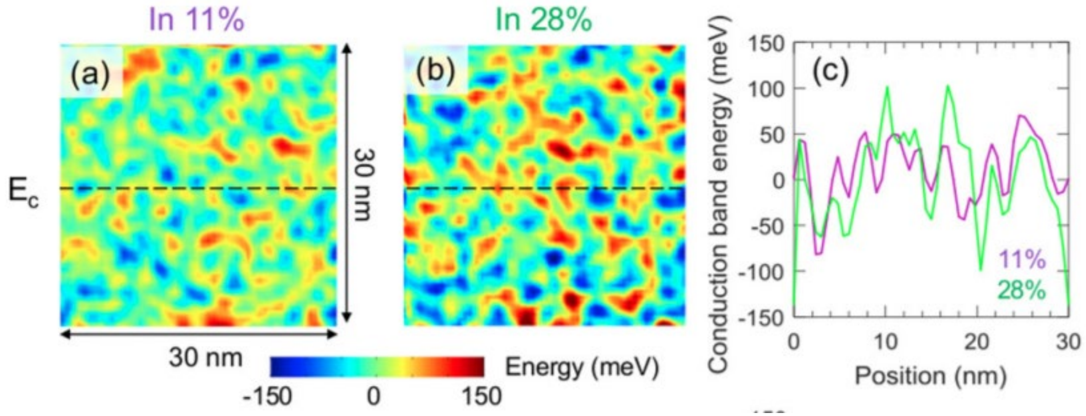
The atomic disorder is exemplified by QD-like emission at low temperature

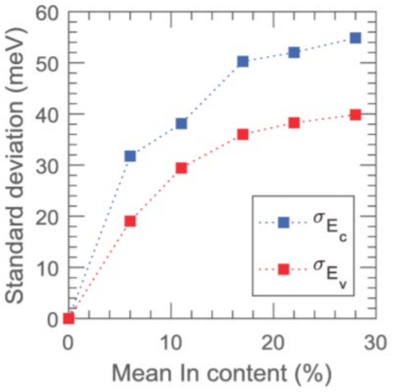
InGaN QW potential fluctuations

PHYSICAL REVIEW B **95**, 144205 (2017)

Localization landscape theory of disorder in semiconductors.
II. Urbach tails of disordered quantum well layers

Marco Piccardo,[1,2,*] Chi-Kang Li,[3] Yuh-Renn Wu,[3] James S. Speck,[2] Bastien Bonef,[2] Robert M. Farrell,[2] Marcel Filoche,[1] Lucio Martinelli,[1] Jacques Peretti,[1] and Claude Weisbuch[1,2]
[1]*Laboratoire de Physique de la Matière Condensée, Ecole polytechnique, CNRS, Université Paris Saclay, 91128 Palaiseau Cedex, France*
[2]*Materials Department, University of California, Santa Barbara, California 93106, USA*
[3]*Graduate Institute of Photonics and Optoelectronics and Department of Electrical Engineering, National Taiwan University, Taipei 10617, Taiwan*





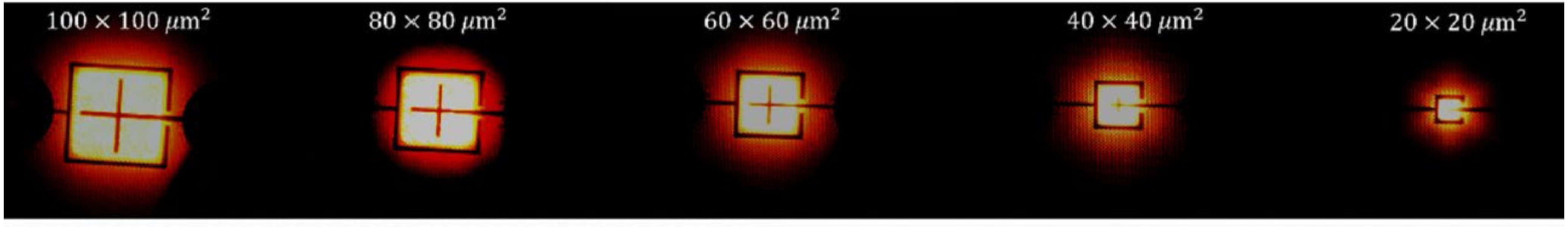
Sample	Diffusion constant (cm^2/s)
Bulk GaAs[a]	20
GaAs/AlGaAs quantum well	56
Bulk GaN[c]	From 1.6 to 2.0
50 nm InGaN layer[d]	2.1
InGaN/GaN quantum wells[e]	From 0.51 to 0.62

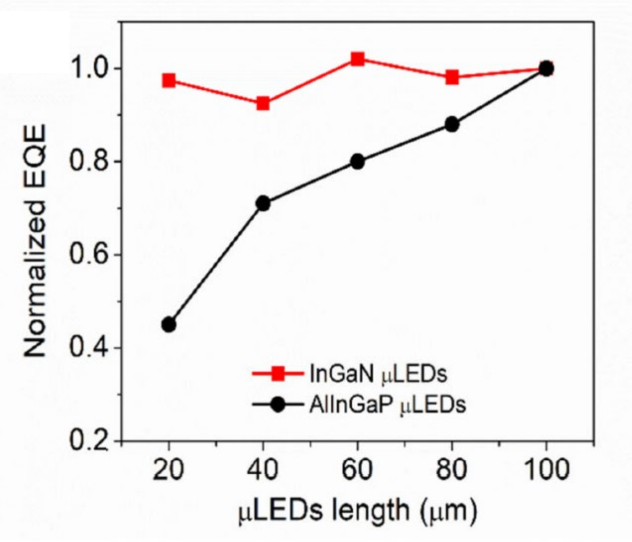
J. Danhof *et al.*, PRB 84, 035324 (2011)

InGaN quantum wells

- InGaN MicroLEDs for RGB displays

Less sensitive to sidewall non-radiative recombination





P. Li *et al*., Crystals 12, 541 (2022)

- Lower diffusion coefficient results in shorter diffusion length

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

⇒ suitable for microLEDs