

Growth IV: III-nitrides

## Growth

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EPFL - Switzerland*

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### Growth IV: III-V nitrides

- **GaN homoepitaxy:** kinetic roughening
- **GaN heteroepitaxy:** substrates, dislocations, and polarity
- **InGaN alloys**

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### Growth IV: III-V nitrides

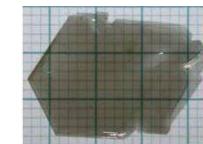
- **GaN homoepitaxy:** kinetic roughening
- **GaN heteroepitaxy:** substrates, dislocations, and polarity
- **InGaN alloys**

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### GaN homoepitaxy

#### ■ GaN substrate

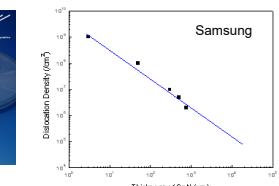
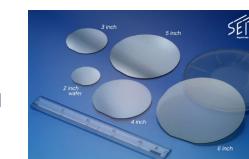
Lack of GaN bulk native substrates  
*produced at Unipress (PL) by high pressure growth - 1 cm<sup>2</sup>*



#### Free-standing (FS) GaN substrates:

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

- Dislocation density:  $\leq 10^6 \text{ cm}^{-2}$
- Size: currently 4 in., 6 in. demonstrated

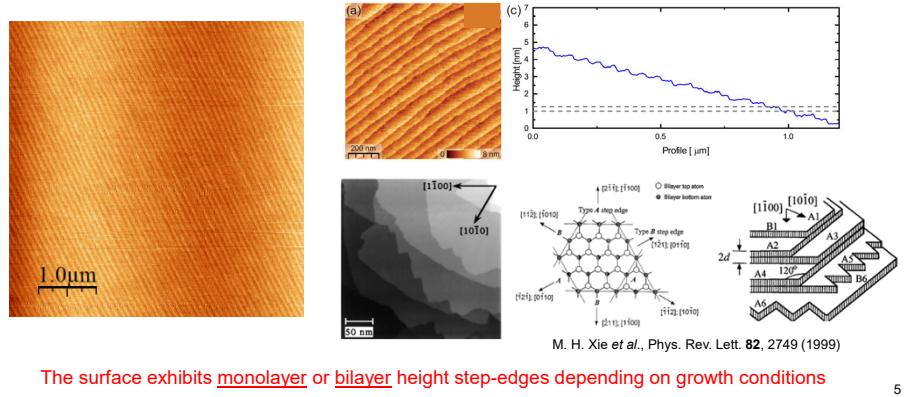


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## GaN homoepitaxy

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GaN on (0001) FS GaN substrate

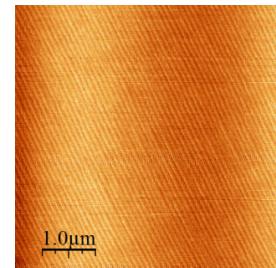


## GaN homoepitaxy

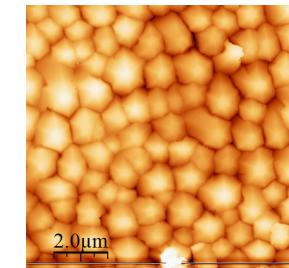
EPFL

Growth of GaN on FS GaN substrate

MOVPE



NH<sub>3</sub>-MBE



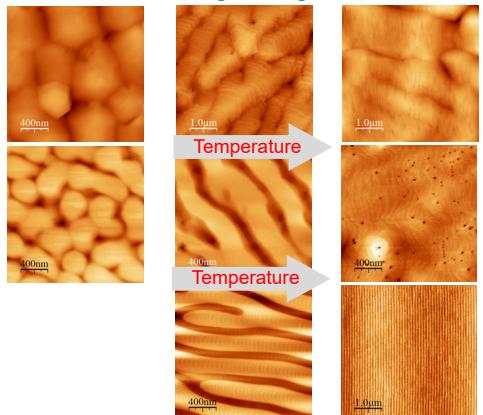
Kinetic roughening

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## GaN homoepitaxy

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ESB-induced surface roughening: hillocks and meandering



NH<sub>3</sub>-MBE

Plasma-MBE

MOVPE

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## Content

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### Growth IV: III-V nitrides

- **GaN homoepitaxy:** kinetic roughening
- **GaN heteroepitaxy:** substrates, dislocations, and polarity
- **InGaN alloys**

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## GaN heteroepitaxy

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### The substrate: sapphire

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

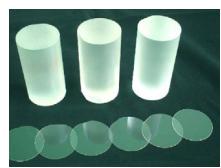
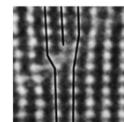
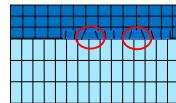
Lattice mismatch to GaN

$\text{Al}_2\text{O}_3$  (0001): +16 %

6H-SiC (0001): -3.5 %

Si (111): -17 %

Dislocations



Sapphire (0001) is the most commonly used substrate (up to 8 in.)

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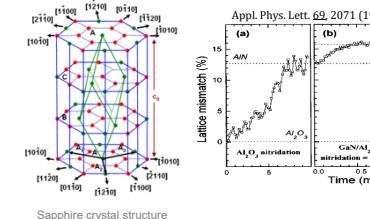
9

## GaN heteroepitaxy

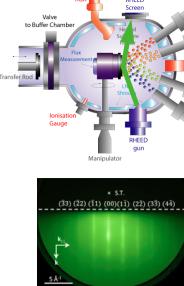
EPFL

### The substrate: sapphire

Sapphire nitridation (exposure to  $\text{NH}_3$ )  $\Rightarrow$  formation of AlN



Aluminum hexagonal sublattice lying in the c-plane of  $\text{Al}_2\text{O}_3$  crystal  
 $\Rightarrow$  AlN layer at the surface upon  $\text{NH}_3$  exposure at high temperature



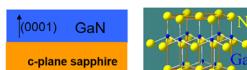
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## GaN heteroepitaxy

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### GaN polarity

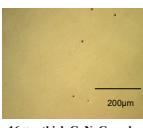
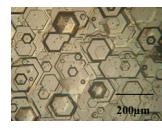


PHYSICAL REVIEW APPLIED 5, 054004 (2016)

Polarity Control in Group-III Nitrides beyond Pragmatism  
 Stefan Mohn,<sup>1,\*</sup> Natalia Solyachuk,<sup>1,2</sup> Tomasz Matuk,<sup>3</sup> Ronny Kirsch,<sup>3</sup> Marc P. Hoffman,<sup>3</sup> Ramon Collao,<sup>3</sup> Ameris Courville,<sup>3</sup> Rosa Di Felice,<sup>3</sup> Zlatko Stipe,<sup>3</sup> Philippe Vennigues,<sup>3</sup> and Martin Albrecht<sup>3</sup>

JOURNAL OF APPLIED PHYSICS 82, 053501 (1997)  
 Impact of sapphire nitridation on formation of Al-polar inversion domains  
 in N-polar AlN epitaxial layers  
 N. Solyachuk,<sup>1,2</sup> T. Matuk,<sup>3</sup> A. Courville,<sup>3</sup> K. March,<sup>3</sup> D. Tottereau,<sup>3</sup> P. Vennigues,<sup>3</sup>  
 and M. Albrecht<sup>3</sup>

Aluminum oxynitride layer controls the polarity of GaN epilayer  
 $\Rightarrow$  Ga polarity allows growing high purity GaN layers



surface chemistry  
 controls the polarity

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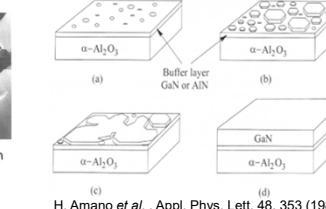
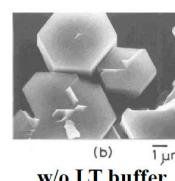
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## GaN heteroepitaxy

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### GaN on sapphire substrate

The low-temperature buffer layer



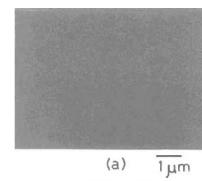
H. Amano *et al.*, Appl. Phys. Lett. 48, 353 (1986)

#### Two-step growth procedure:

- 1) Buffer layer (25 nm) at low-temperature (500°C)
- 2) Growth at high-temperature (1050-1100°C)



GaN buffer layer to  
 improve the crystal quality



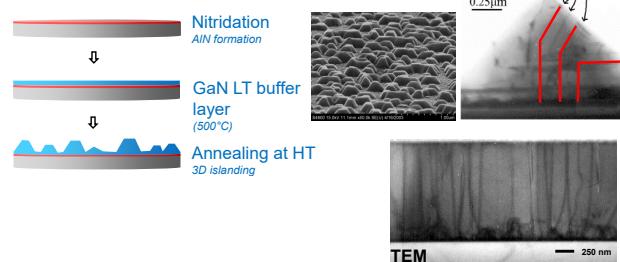
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## GaN heteroepitaxy

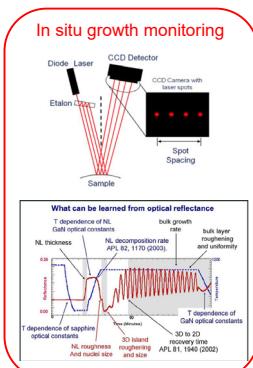
**EPFL**

### ■ GaN on sapphire

3D islands to reduce the dislocation density



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

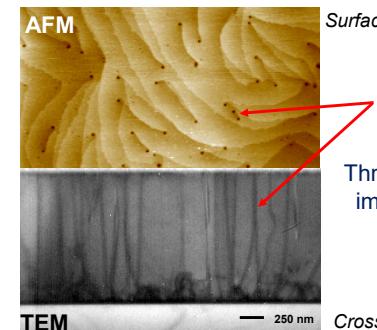


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## GaN heteroepitaxy

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



Dislocations

Threading dislocations are supposed to impact the active region of LEDs/LDs  
⇒ low impact in blue LEDs

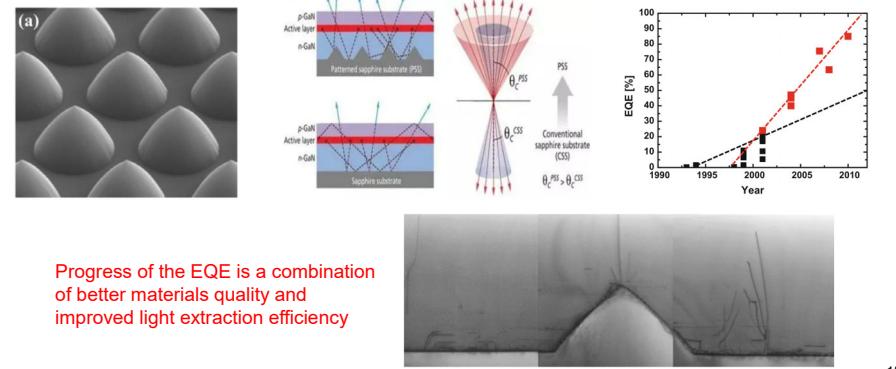
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## GaN heteroepitaxy

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### ■ GaN on patterned sapphire substrate (PSS)



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## GaN heteroepitaxy

**EPFL**

### ■ GaN on Silicon substrate

#### Lattice mismatch

Al<sub>2</sub>O<sub>3</sub> (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

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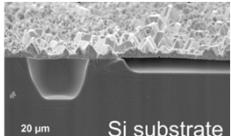
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## GaN heteroepitaxy

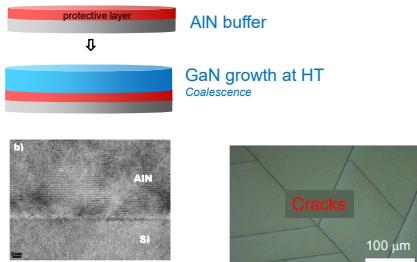
EPFL

### ■ GaN on Silicon substrate

Silicon surface is decomposed when exposed to Ga and NH<sub>3</sub> 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<sup>10</sup> cm<sup>-2</sup>

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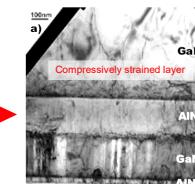
## GaN heteroepitaxy

EPFL

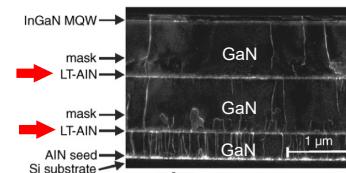
### ■ GaN on Silicon substrate

Strain engineering to avoid layer cracking

→ compressive strain is introduced during growth



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



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

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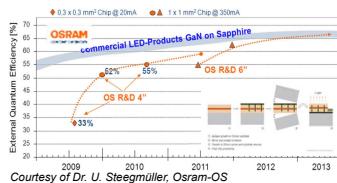
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## GaN heteroepitaxy

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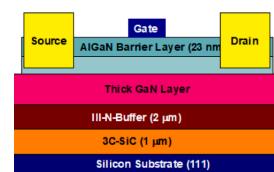
### ■ GaN on silicon substrate

#### Blue LEDs on Si



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

#### GaN-on-Si for electronics



J. Ajayan et al., Mat. Sc. Semicond. Processing 151, 106982 (2022)

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## Content

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### Growth IV: III-V nitrides

- GaN homoepitaxy: kinetic roughening

- GaN heteroepitaxy: substrates, dislocations, and polarity

- InGaN alloys

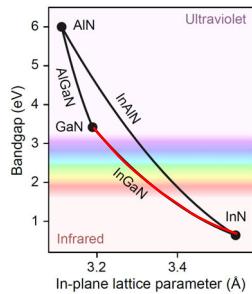
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## InGaN alloys

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### ■ Materials issues



- InN bandgap of 0.65 eV  
⇒ InGaN alloy covers the whole visible spectrum
- Severe drawbacks:
  - Very large lattice mismatch with GaN (11%)
  - Poor quality for high In content
  - Huge piezoelectric polarization field in InGaN/GaN QWs (16 MV/cm for InN/GaN QWs)
  - Poor thermal stability for  $x > 0.2$

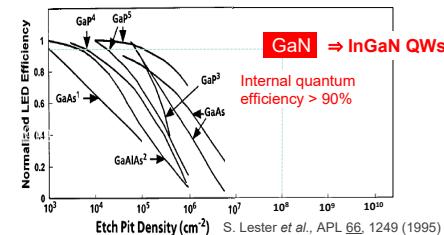
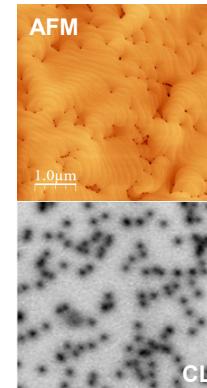
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## InGaN alloys

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### Efficiency of blue LEDs: impact of dislocations



Is InGaN a magic alloy ?

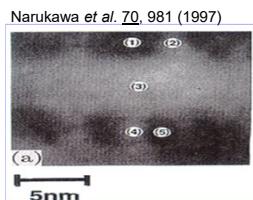
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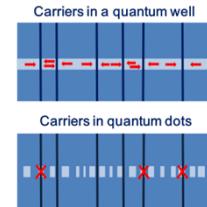
## InGaN alloys

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### ■ Indium clustering



TEM image of InGaN/GaN QWs



Gérard and Weisbuch (patent 1990)

Indium-rich clusters in InGaN QWs act as quantum dots

Efficiency of LEDs : carrier localization prevents their diffusion towards dislocations

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## InGaN alloys

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### ■ Indium clustering

TEM image of InGaN/GaN QWs grown by MOCVD

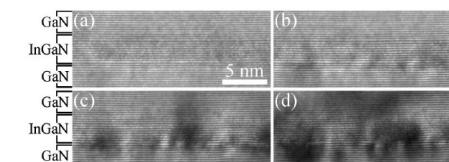


FIG. 3. (0002) lattice fringe images showing strain contrast evolution in an  $\text{In}_{0.22}\text{Ga}_{0.78}\text{N}/\text{GaN}$  MQW during exposure to a 200 kV electron beam flux of  $\sim 35 \text{ A cm}^{-2}$  after: (a) 20, (b) 220, (c) 420, and (d) 620 s.

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

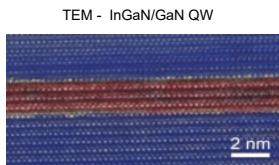
⇒ Indium clustering induced by e-beam irradiation during TEM observation

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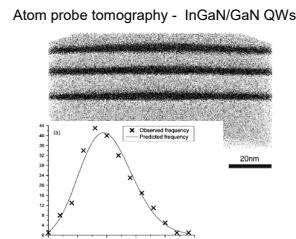
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## InGaN alloys

### ■ InGaN is a perfectly disordered alloy



No evidence In-rich clusters



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

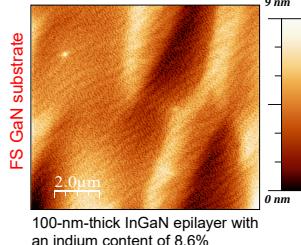
The indium distribution correspond to that of a random alloy: no clustering

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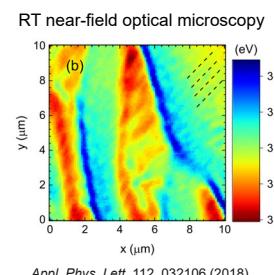
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## InGaN alloys

### ■ InGaN thick layers on FS GaN



100-nm-thick InGaN epilayer with an indium content of 8.6%



Appl. Phys. Lett. 112, 032106 (2018)

- Indium content depends on surface misorientation
- the higher the misorientation the lower the In content

G. Franssen et al., phys. stat. sol. (c) 5, 1485 (2008)

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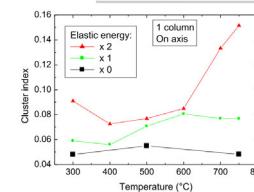
## InGaN alloys

### ■ Indium clustering



Why and how In composition fluctuations appear in InGaN?

Jean-Yves Duboz<sup>1</sup>, Wanda Isnard, Jesus Zuniga-Perez, Jean Massies



Monte Carlo simulations:

In clusters may form for high indium content alloys

⇒ Enhanced by strain

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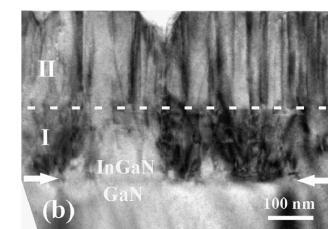
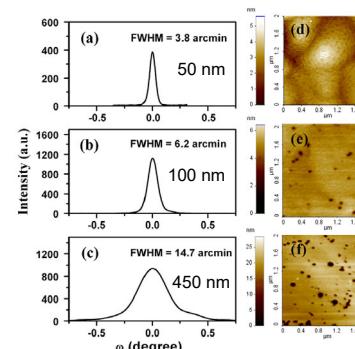
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## InGaN alloys

### ■ InGaN thick layers on sapphire

## InGaN alloys

### ■ InGaN thick layers on sapphire



$x=0.19$

$x=0.10$

H. Wang et al., Physica B 405 4668 (2010)

- Formation of V-pits when growing thick InGaN layers on GaN/sapphire template.
- Increase of In content when the layer is relaxed.

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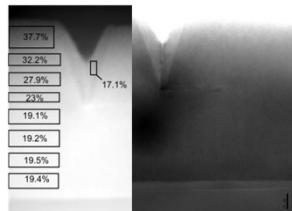
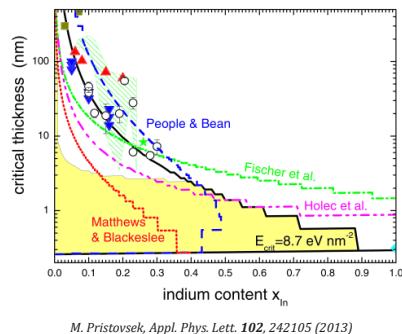
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## InGaN alloys

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### ■ Critical thickness of InGaN layers on GaN



- V-shape defects
- Dislocation and stacking faults
- Pulling effect (due to strain relaxation)

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## InGaN alloys

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### ■ Maximum indium content for coherent InGaN on GaN

PHYSICAL REVIEW MATERIALS 2, 011601(R) (2018)

Rapid Communications Editor's Suggestion

#### Elastically frustrated rehybridization: Origin of chemical order and compositional limits in InGaN quantum wells

L. Lymperakis,<sup>1,\*</sup> T. Schulz,<sup>2,3</sup> C. Freyoldt,<sup>1</sup> M. Antekere,<sup>2</sup> Z. Chen,<sup>1</sup> X. Zheng,<sup>1</sup> B. Shen,<sup>1</sup> C. Chizra,<sup>4</sup> M. Siekacz,<sup>5</sup> X. Q. Wang,<sup>3,6,7</sup> M. Albrecht,<sup>1</sup> and J. Neugebauer<sup>1</sup>

<sup>1</sup>Max-Planck-Institut für Eisenforschung GmbH, Max-Planck-Strasse 1, 40237 Düsseldorf, Germany

<sup>2</sup>Institute for Crystal Growth, Berlin, Germany

<sup>3</sup>State Key Laboratory of Artificial Microstructure Physics, Institute of Physics, Chinese Academy of Sciences, Beijing 100080, China

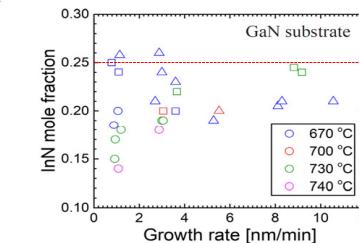
<sup>4</sup>Paul Drude Institute for Solid State Physics, Berlin, Germany

<sup>5</sup>Institute of High Pressure Physics, Polish Academy of Sciences, Sokolowska 20/22, 01-142 Warsaw, Poland

<sup>6</sup>Collaborative Innovation Center of Quantum Matter, Beijing, China

(\*Received 16 May 2017; revised manuscript received 14 July 2017; published 8 January 2018)

Nominal InN monolayers grown by molecular beam epitaxy on GaN(0001) are investigated combining *in situ* reflectivity high-energy-loss fine-structure (RHEED), transmission electron microscopy (TEM), and density functional theory (DFT). TEM reveals a chemical ordering observed before. Employing DFT, we identify a novel surface stabilization mechanism elastically frustrated rehybridization, which is responsible for the local chemical ordering. The mechanism also sets an incorporation barrier for indium concentrations above 25% and thus fundamentally limits the indium content in coherently strained layers.



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

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

Z. Liu et al., JCG 508, 58 (2019) - Amano's group

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## InGaN alloys

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### ■ Indium composition strongly depends on strain

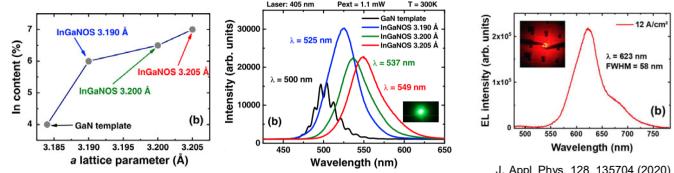
APPLIED PHYSICS LETTERS 110, 262103 (2017)



#### Enhanced In incorporation in full InGaN heterostructure grown on relaxed InGaN pseudo-substrate

A. Even,<sup>1</sup> G. Laval,<sup>1</sup> O. Ledoux,<sup>2</sup> P. Ferret,<sup>1</sup> D. Sotta,<sup>2</sup> E. Guiot,<sup>2</sup> F. Levy,<sup>1</sup> I. C. Robin,<sup>1</sup> and A. Dussaigne<sup>1,8(a)</sup>

<sup>1</sup>University Grenoble Alpes, CEA, LETI, MINATEC Campus, F-38054 Grenoble, France  
<sup>2</sup>Soitec S.A., F-38190 Bérin, France



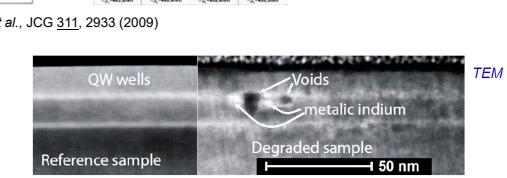
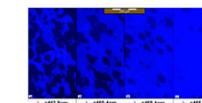
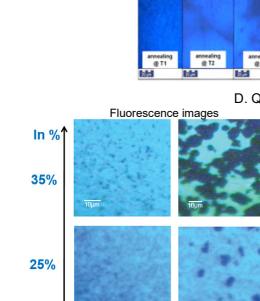
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## InGaN alloys

EPFL

### ■ Thermal stability of high In content InGaN QWs

D. Queren et al., JCG 311, 2933 (2009)



Green laser (LED) QWs require In content >25%

⇒ p-type layer must be grown at LT (<900°C)

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