Short-range In-segregation in InGaN and InAlN. Band structure and light emission related effects .

T. Suski
Institute of High Pressure Physics , 'Unipress', Warsaw, Poland

theory: I. Gorczyca ,*'Unipress'* and
N. E. Christensen, A. Svane
Department of Physics and Astronomy, University of Aarhus, Denmark
Experiment: G. Staszczak, G, Franssen, P. Perlin, A. Kaminska, …

Outline

- Info about UNIPRESS (and TopGaN) concerning nitride activity
- Lasers and importance of bulk GaN crystals for laser substrates
- Band gap in InGaAlN ternary alloys. Absorption vs. Luminescence
- Modelling within the short-range In-fluctuation approach
  - Band gaps and their pressure coefficients
- Alternative results on InGaN layers and InGaN/GaN QWs
- Summary

Beijing, October, 25, 2012

unipress

UNIPRESS, Institute of High Pressure Physics of the Polish Academy of Sciences

- **Director: Izabella Grzegory**
- **Head of Semicondutors Lab: T. Suski**
- Prof. Sylwester Porowski – Director for 35 years

Polish Academy of Sciences is a corporation of famous professors and an „owner" of research institutions covering all fields. From humanistics to engineering and natural sciences.

UNIPRESS is one of 80 institutes of PAS

UNIPRESS is located in Warsaw (Warszawa) and consists of 7 Labs Largest - Semiconductor Laboratory

Beijing, October, 25, 2012

Institute of High Pressure Physics, UNIPRESS
Polish Academy of Sciences
One of about 80 research Institutes of PAS

unipress

Research areas:

* physics, optoelectronics: mainly in green-blue-violet spectral region
* electronics: mainly nitride epi-strucures for HEMTs and THz
* nanomaterials: ceramics, metals, superconductors
* biological materials

Untypical (for PAS) structure of research activity

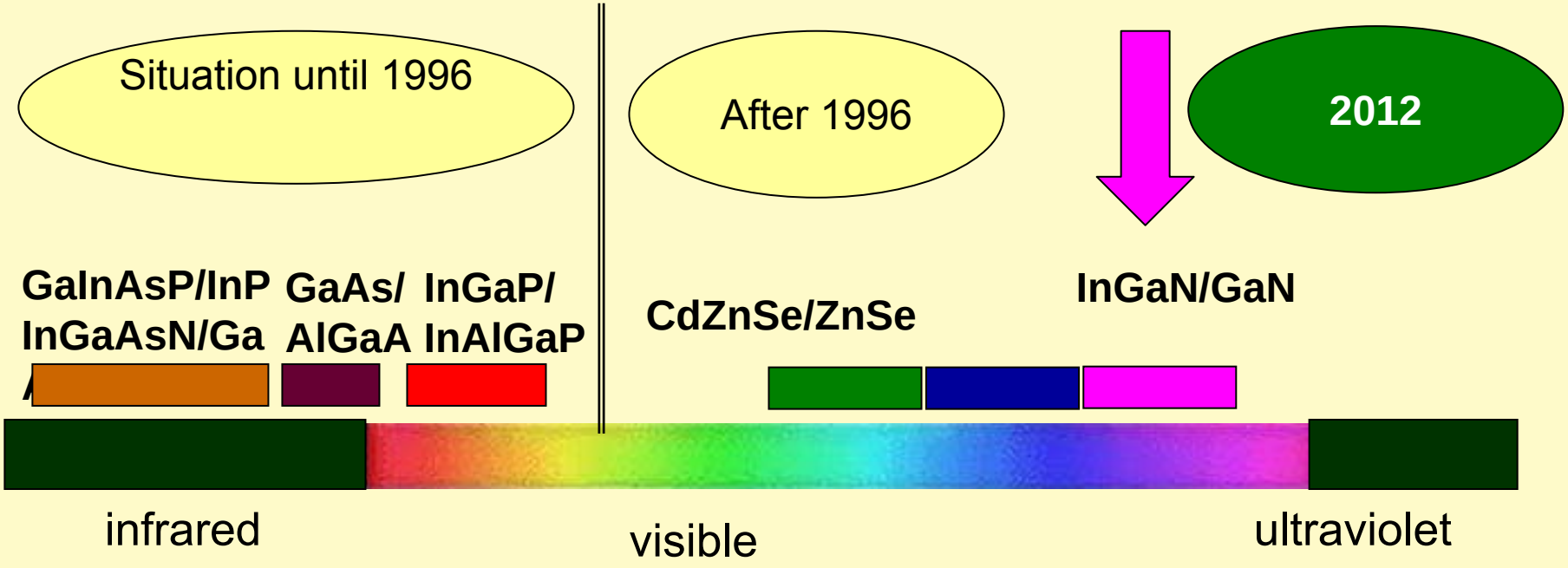
* basic research	- 40%
* applied research	- 40%
* high pressure methods and instrumentation	- 20%

150 employees, 75 researchers, 23 Ph.D. students, 6 spin-offs (the youngests TopGaN)

Beijing, October, 25, 2012

Semiconductor Laser Diodes
Semiconductor families used

unipress



Period 1980-1995 characterized by intensive search for semiconductors enabling the laser action in the spectral range from yellow (600nm) up to UV (400nm)

Choice of GaN, InN, AlN and their alloys for construction of green, blue and ulraviolet Light Emitting Diodes and Laser Diodes

Main Applications of nitride-based emitters

unipress

Laser Diodes;
BluRay, printing, medical applications
Projectors, thermal treatment of materials …

„Color" light emitting diodes;
Special lighting , transport signal,
telebeams

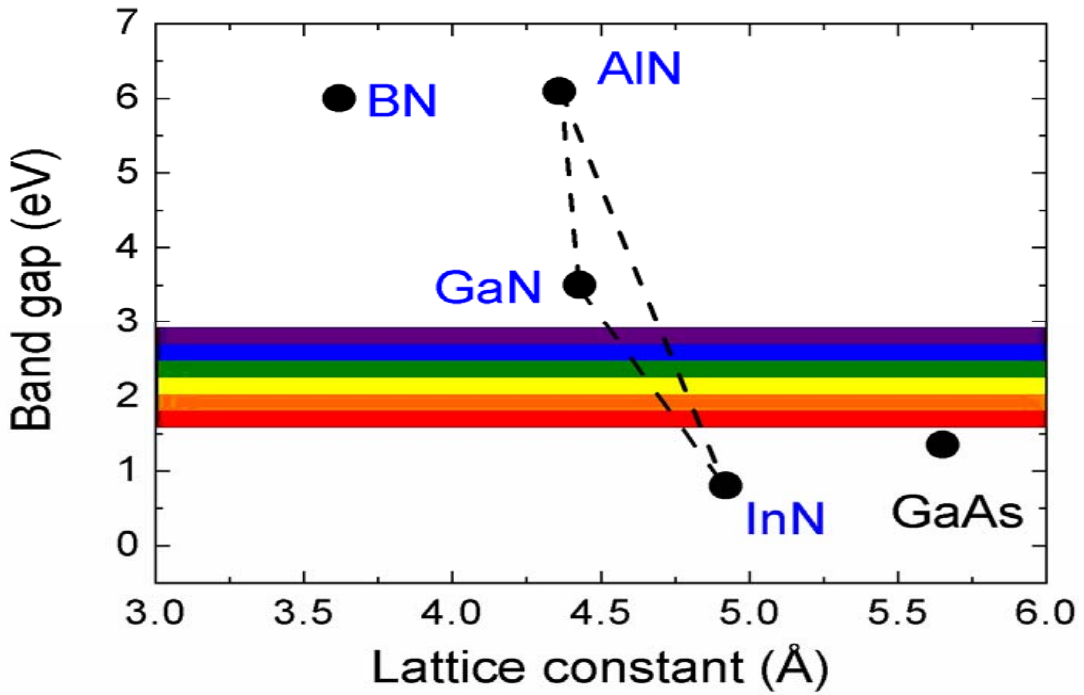
White LEDs:
General lighting,
replacement of bulbs
and fluorescent compact lamps

World Market 12.5 bln $ in 2011year
Second semiconductor system after Silicon

GaN-AlN-InN properties
Important aplications

unipress

GaN-InN-AlN short interatomic distances ⟹ strong chemical bonds
Large ionicity, wurtzite polar structure ⟹ spontaneous polarization, large piezoelectric tensor, ⟹ internal electric field in heterostructures & QWs
nonpolar and semipolar structures used to reduce internal electric field



Covered energy range:
from IR to deep UV
LEDs: 550 nm – 250 nm
LDs: 520 nm – 340 nm

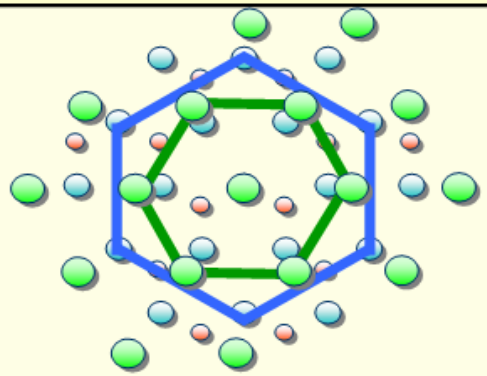
For visible range of the spectrum mostly InGaN alloy is used to construct active Quntum Wells

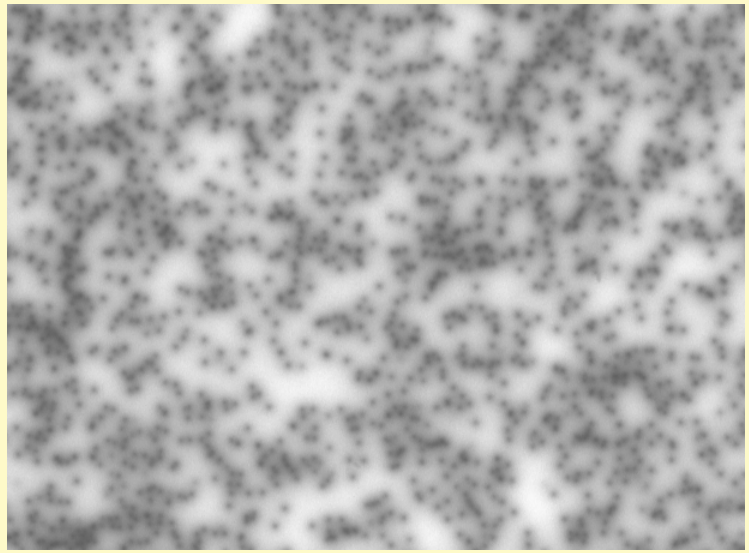
Heteroepitaxial growth of GaN; usually on sapphire

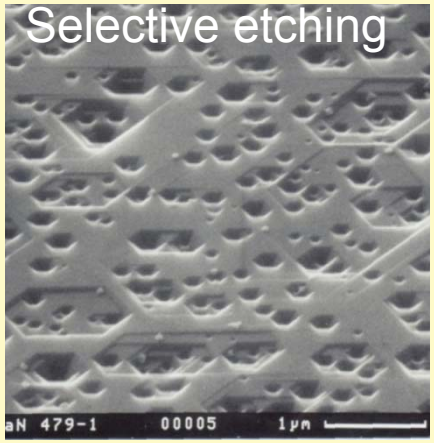
unipress

A BEST MOCVD GaN on sapphire

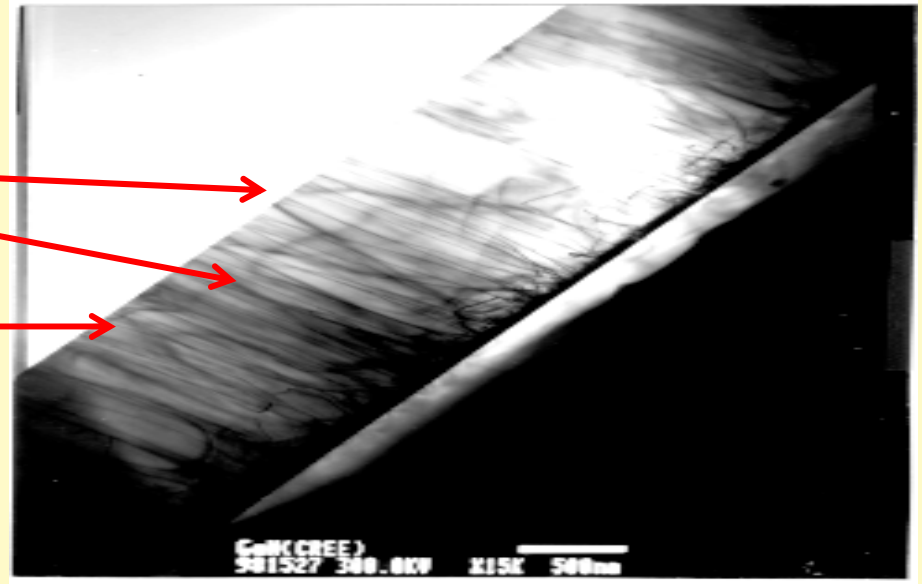
Large lattice mismatch leads to misfit dislocations

	$[11\text{-}20]_{III\text{-}N}//[10\text{-}10]_{Sap}$ 30 ° Rotation
Atomic arrangement	
GaN a=3.189 Å	+16.1%



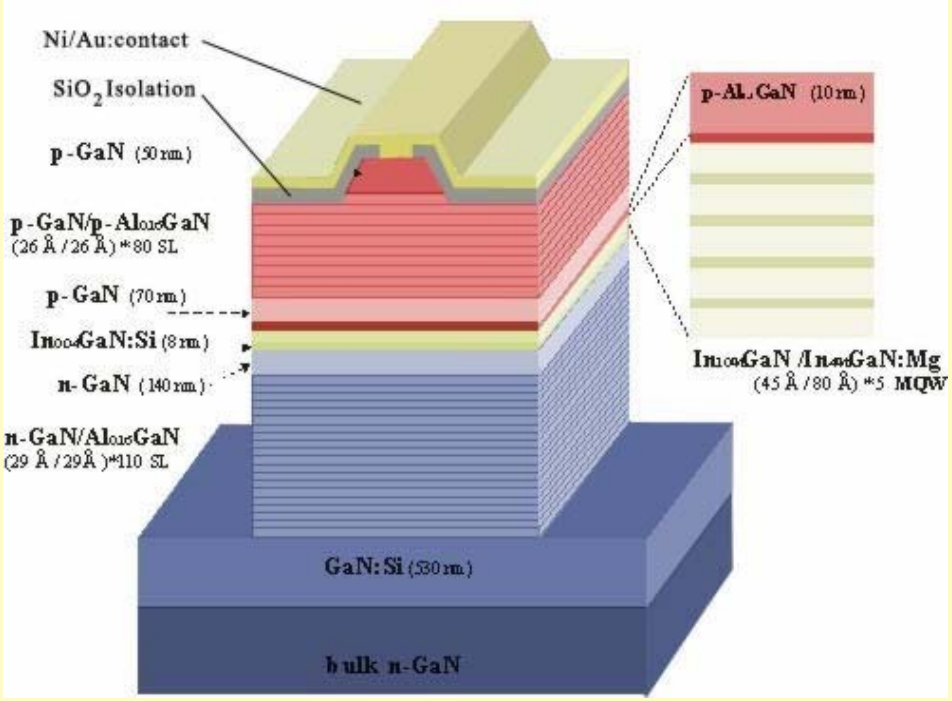


Misfit dislocations Density: 10^{8} -10^{10} cm^{-2}



Importance of substrates

unipress



For high quality laser structures
special GaN substrates necessary!!!
low defect (dislocation density), highly conductive

No conventional growth of nitride semiconductors possible
(i.e., by means of Czochralski or Bridgman methods)

III-N compounds thermodynamics:

unipress

Melting conditions of semiconductors

crystal	T^M, °C	p^M, atm.
Si	1400	< 1
GaAs	1250	15
GaP	1465	30
GaN	**2500**	**45 000**
AlN	**2800**	**>100**
InN	**2200**	**>60 000**
diamond (synthesis)	1600	60 000

Melting conditions of GaN very similar to diamond

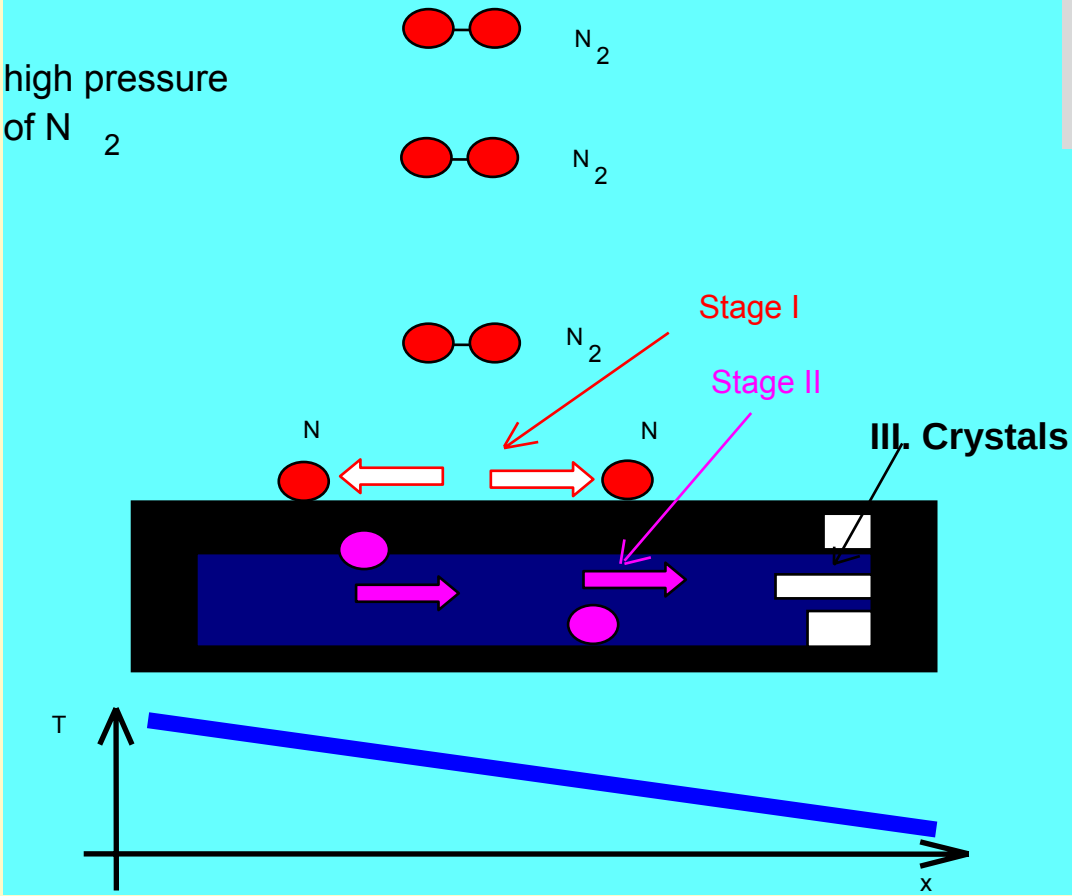
No conventional growth of nitride semiconductors possible (i.e., by means of Czochralski or Bridgman methods)

High Pressure Growth of GaN single crystals

unipress

Three stages of HPSG growth of GaN

I. Dissociative adsorption of nitrogen on liquid Ga surface
II. Dissolution and diffusion
III. Crystallization



From the solution of nitrogen in the liquid gallium

T=1500° C
P_{Nitrog}=15 000-20 000 atm

Method developed at Unipress by
I. Grzegory, S. Porowski,
M. Boćkowski, J. Karpiński

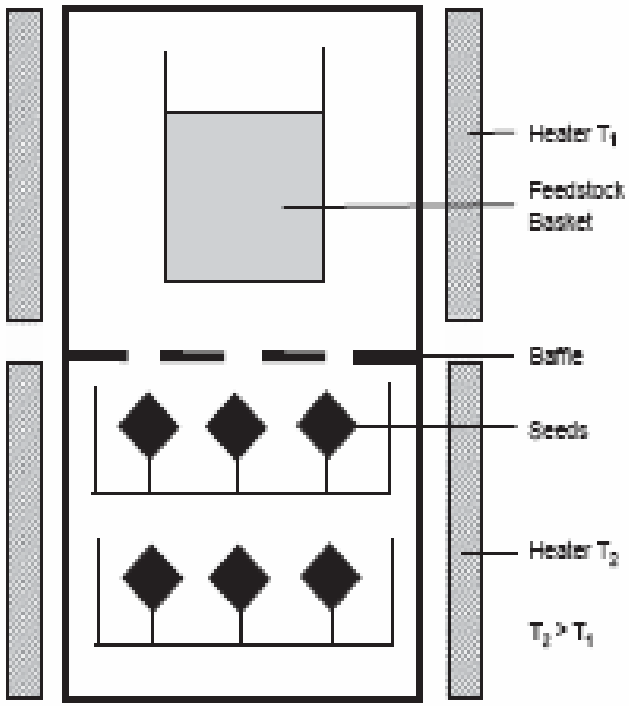
High pressure reactor for GaN Crystallization with the internal diameter of 100 mm.

unipress

- **Working volume 4500 cm^3**
- **Max pressure 15 000 atm**
- **Temperature 1550°C**
- **Pressure stabilization 10 atm**
- **Temp. stabilization 0.1°C**

Growth of GaN single crystals by ammonothermal method (Ammono Co , Warsaw, Poland)

unipress



High Pressure Autoclave

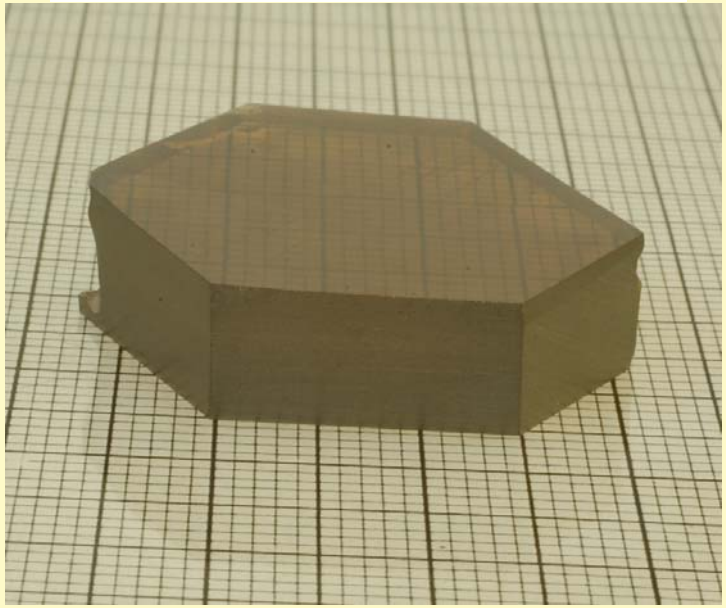
Ammonothermal method – analog of hydrothermal
Where ammonia instead of water is used as a solvent.
Temp. 400-600^{o}C; Press. 0.1-0.3 GPa (1-3 kbar)

Gan from feedstock is dissolved in 1 zone
and transported by convection in the temp gradient
to zone 2, where GaN is crystallized on native seeds
due to supersaturation of the solution.

The use of mineralizers is necessary in order
to enhance solubility of GaN in ammonia.

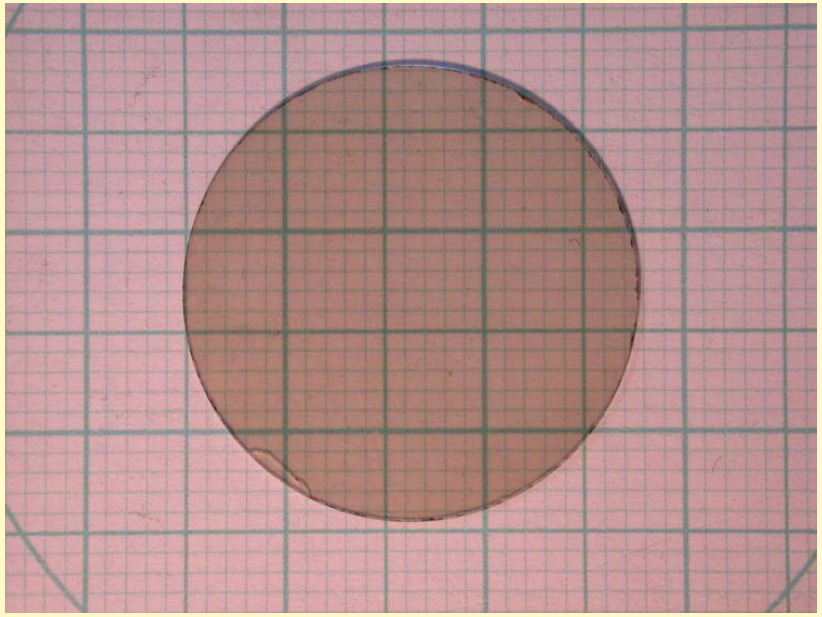
High Quality GaN Substrates for Laser Diodes

ammono



High Pressure
Multi-feed -seed method

unipress



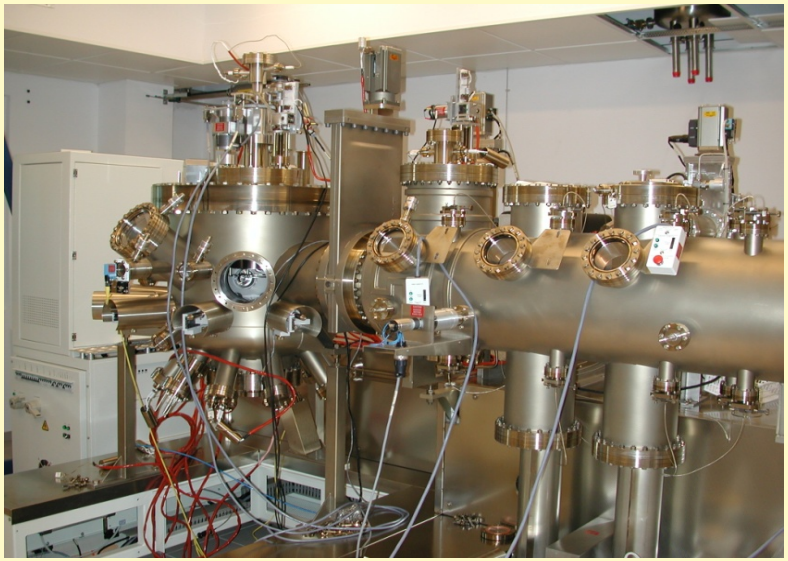
Growth of Nitride Layers, Quantum Structures and Devices on specially prepared surface of Bulk GaN crystal

unipress

Surface preparation difficult.
Mechano-chemical polishing

* * *

Metalorganic vapor phase epitaxy (3 MOVPE reactors) and molecular beam epitaxy (2 PA MBE reactors) growth of nitrides layers and structures in Unipress



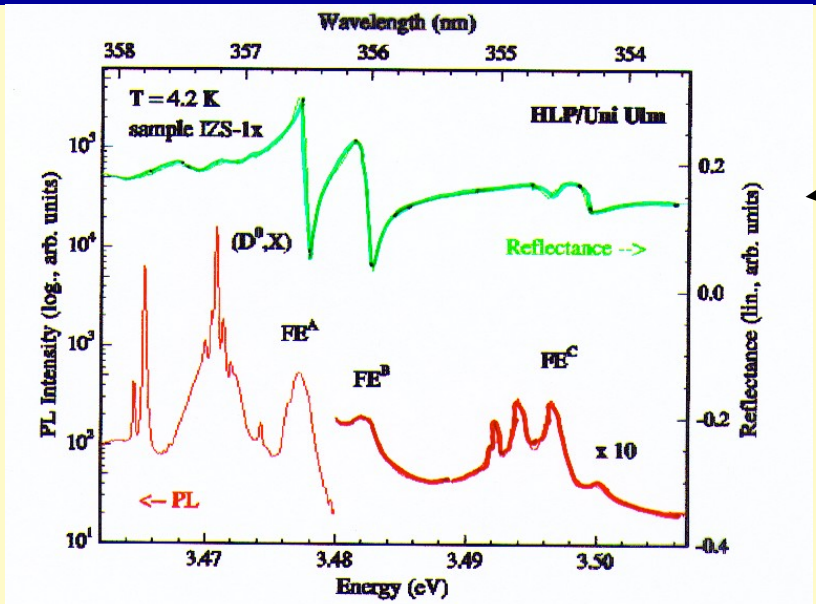
M. Leszczyński,

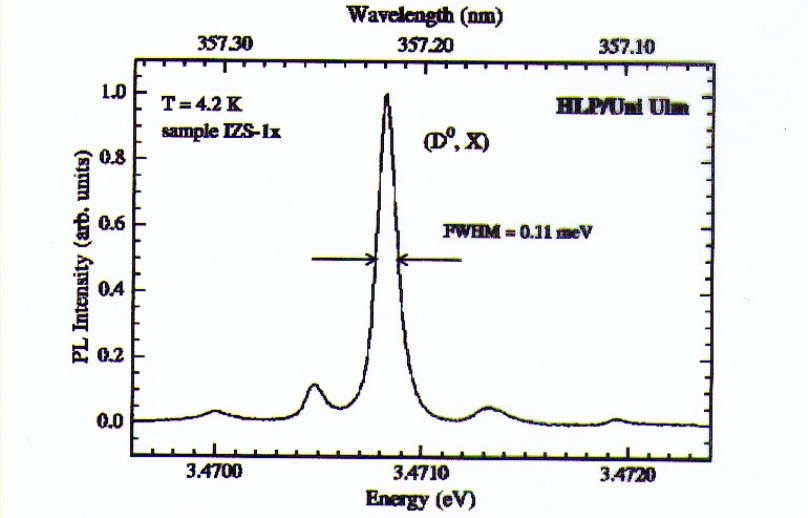
C. Skierbiszewski

Beijing, October, 25, 2012

Record optical properties
Ultra-narrow emission/absorption lines

unipress



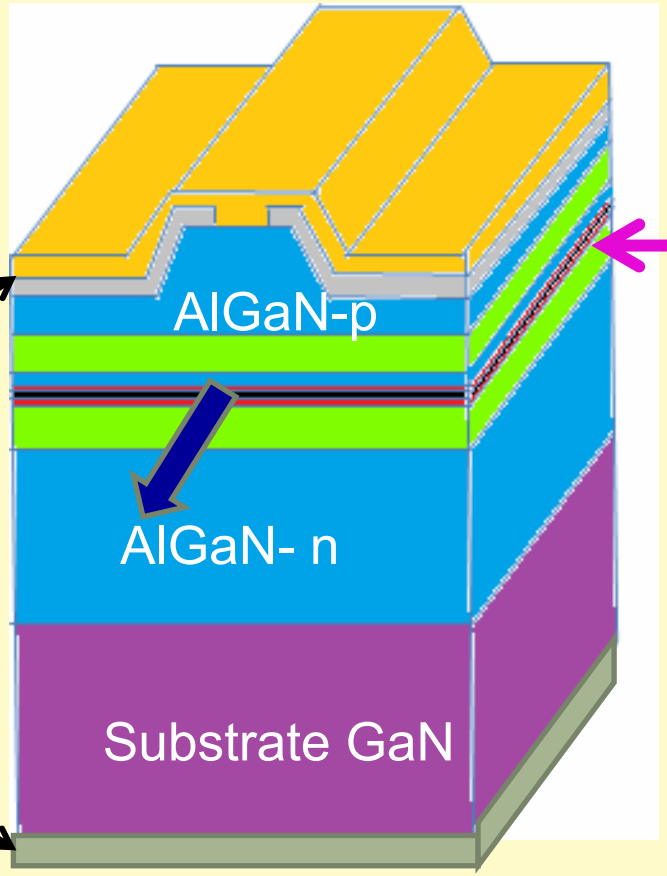


Very narrow lines
Excitons clearly visible;
FWHM = 0.11 meV

Comparable quality samples were grown on bulk GaN crystals both in MBE and MOVPE systems:

Multi-Quantum-Well Laser epi-structure

unipress

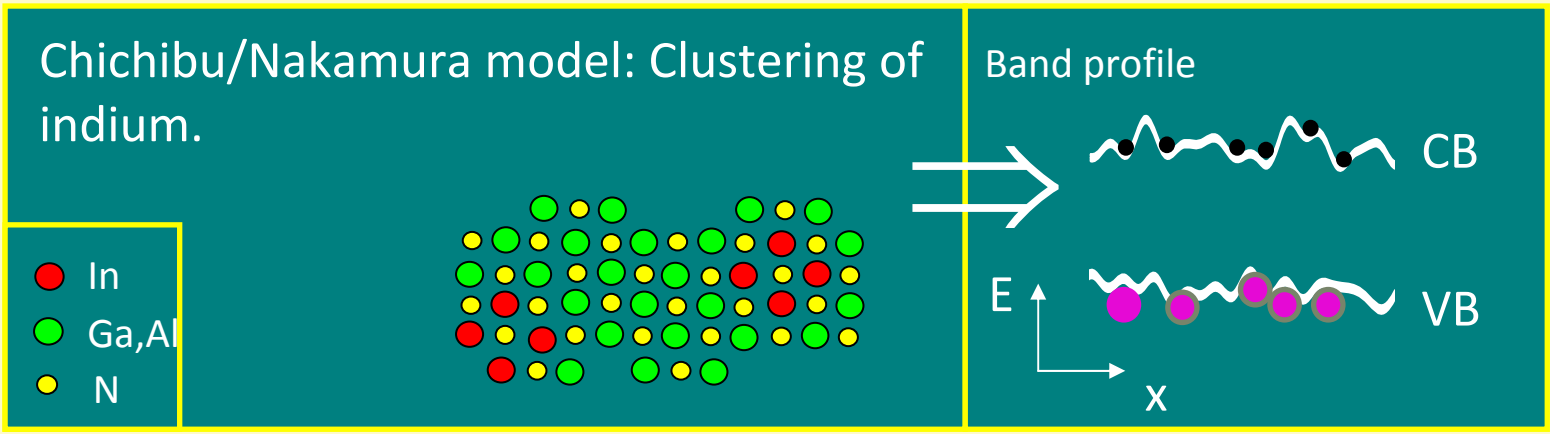


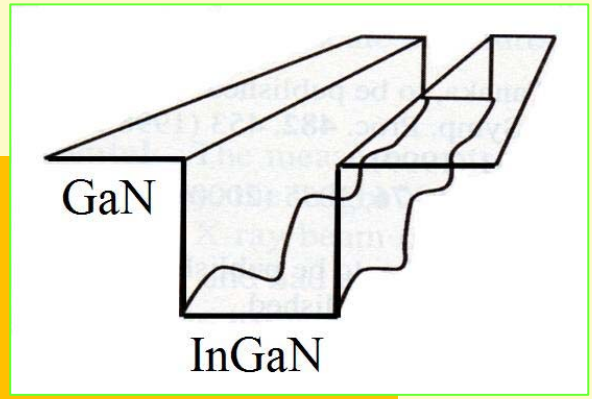
Metal contacts

Multi-Quantum Wells
of **$In_xGa_{1-x}N/GaN$** or **$GaN/In_yGa_{1-y}N$**
Radiative carrier recombination
leads to light emission
and eventually to lasing

Compositional inhomogeneities and carrier localization in InGaN & AlInN. Almost commonly accepted concept

unipress





In- fluctuations

- clustering, spinodal decomposition, phase separation
  *-Chichibu et al. Appl. Phys. Lett. **69,** 4188 (1996))*
- short range order/statistical alloy fluctuations
  *- Gorczyca et al.. Phys. Rev B (2009, 2010), Bellaiche et al. **74**, 1842 (1999);*

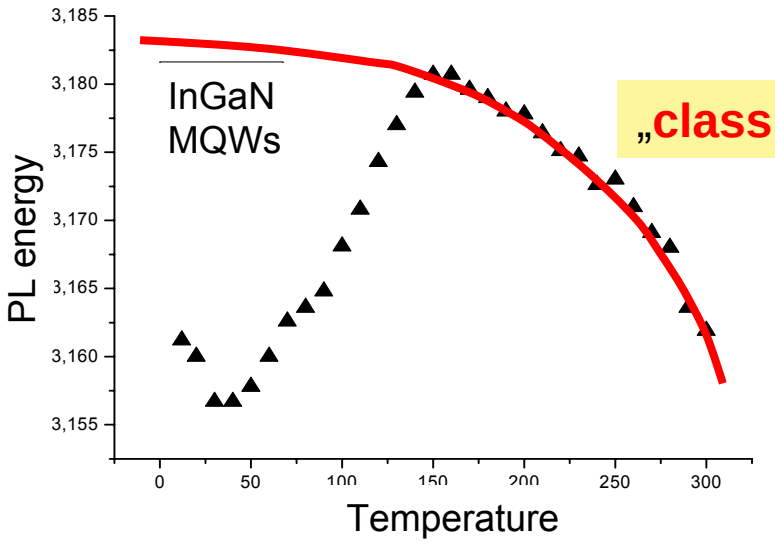
There are results of optical studies demonstrating that potential fluctuations within spatial scale of below 50-100 nm important for luminescence data (SNOM, CL)

What is a common understanding of the potential fluctuations contribution to the light emission in In-containing alloys.

Electron-hole pair or exciton transport before radiative recombination

unipress

Typical S-shape resulting from localized carrier transport at low temperatures

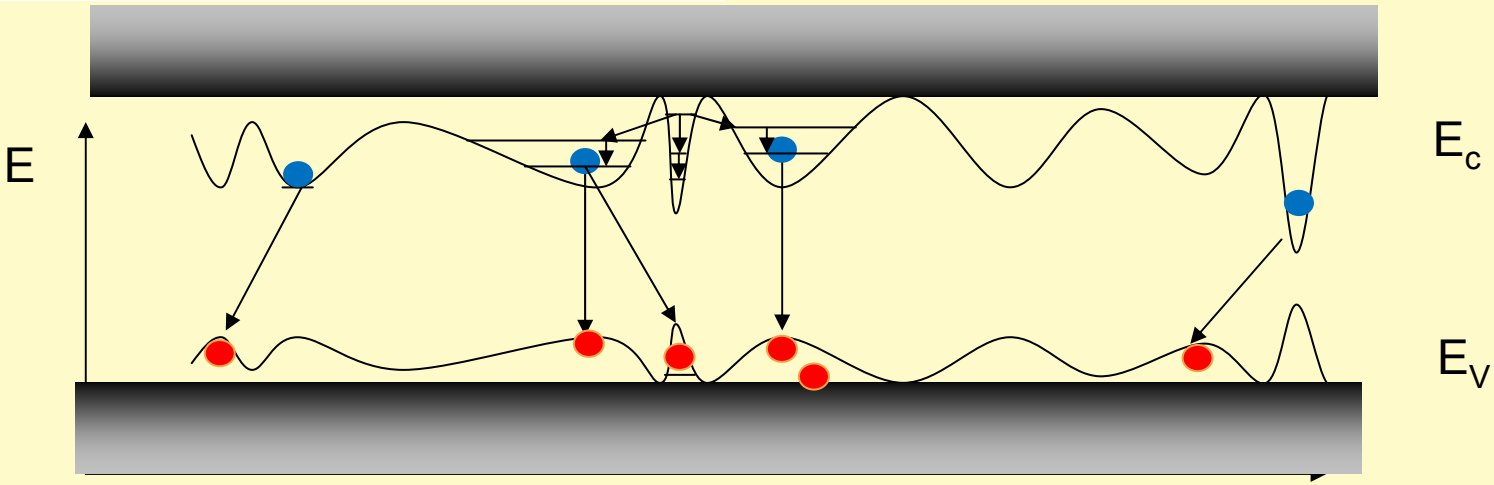


- Carriers relax into local band minima/maxima
- Redistribution (phonon involvement)

„classical" behavior of semiconductor band gap

- tunneling
- hopping

- population of higher energy states
- emission into the band
- S-shape seen in submicron scale (CL; M. Albrecht T. Suski)



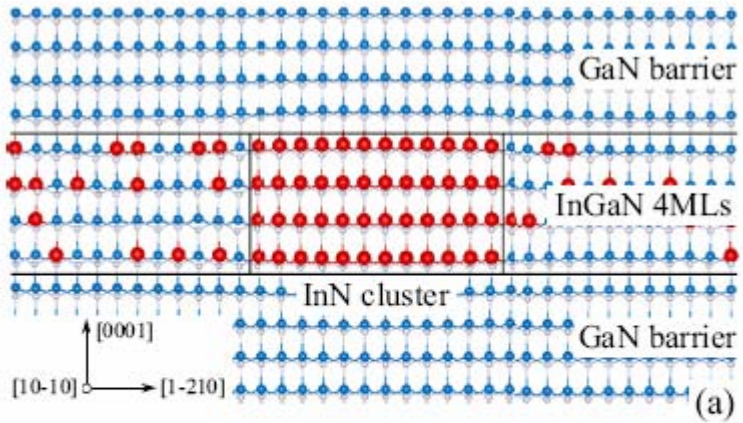
In-fluctuations are particularly enhanced when structural defects appear

Structural defects and cathodoluminescence of InGaN layers
Z. Liliental-Weber, et al. IWN 2010 (Tampa), in phys. stat. solidi
Strained and relaxed layers with different In concentration were observed when InGaN layers increased in thickness. Above the critical layer thickness stacking faults start to appear with increased density toward the surface. Stacking faults cause an appearence of multipeak PL and CL.

JOURNAL OF APPLIED PHYSICS 108, 103503 (2010)

Influences of the biaxial strain and *c*-screw dislocation on the clustering in InGaN alloys

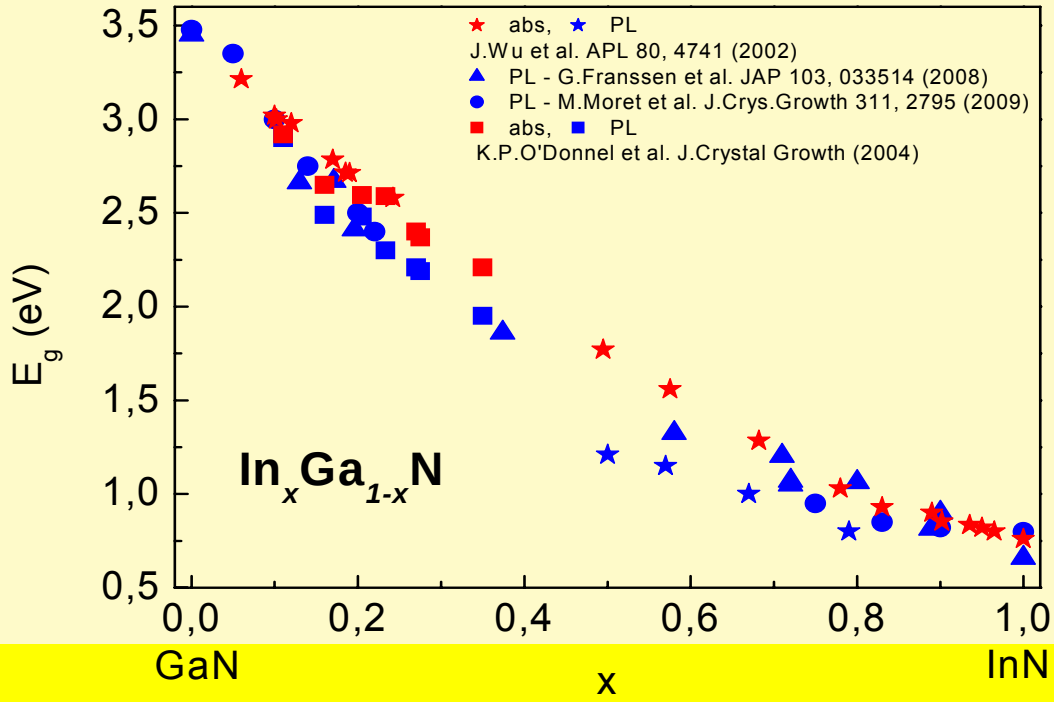
Huaping Lei,[1,a] Jun Chen,[2] and Pierre Ruterana[1]



Beijing, October, 25, 2012

$In_xGa_{1-x}N$ alloy „real" band gap determination
Differences between absorption-type and luminescence type of measurements

unipress

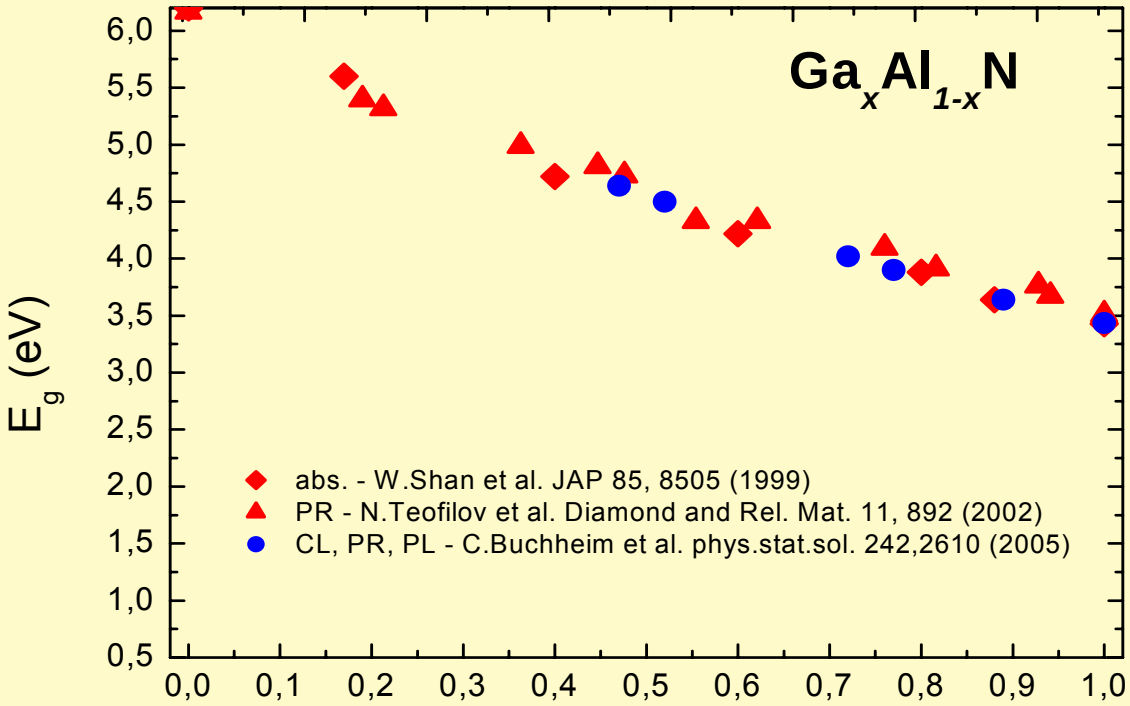


1. Large dispersion of data and significant bowing of E_g vs. x clearly seen
2. Higher magnitude of E_g measured by optical absorption in comparison with PL

Beijing, October, 25, 2012

$Al_xGa_{1-x}N$ alloy band gap determination
Differences between absorption-type and luminescence type of measurements

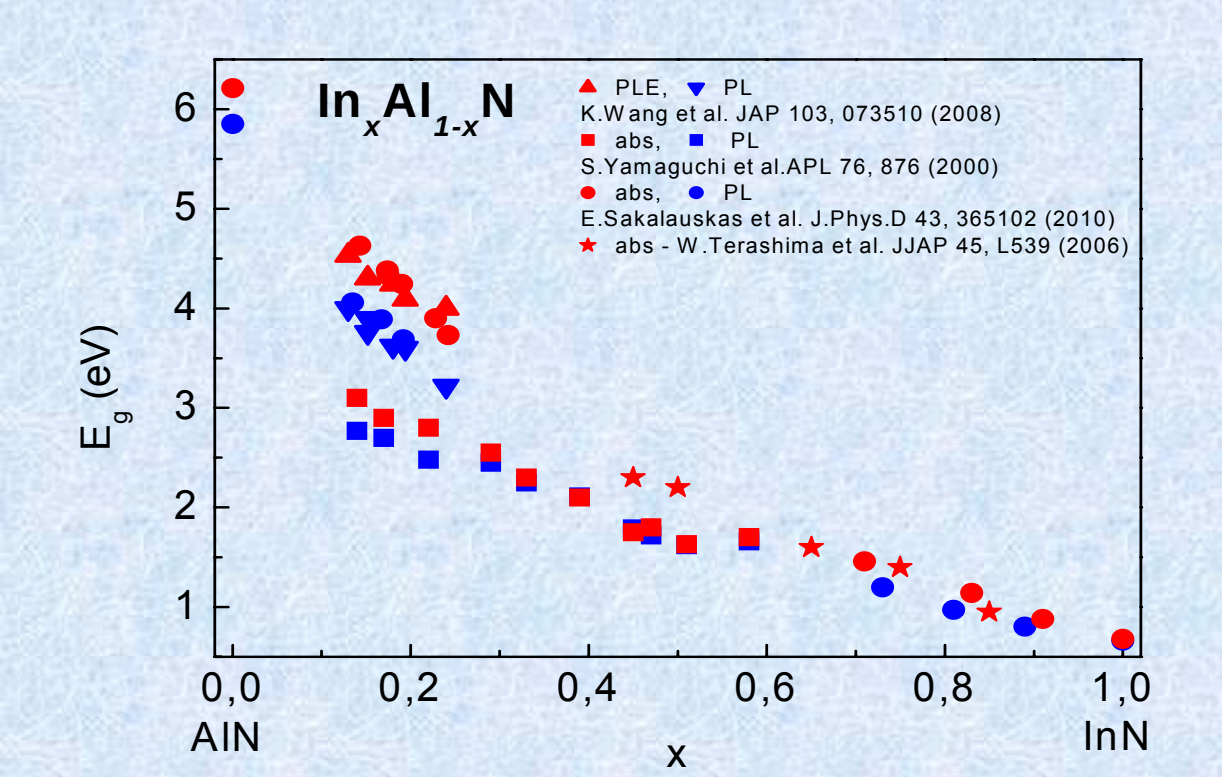
unipress



1. Small dispersion of data; almost linear dependence of E_g vs. x
2. Similar magnitude of E_g as measured by optical absorption and PL

$In_xAl_{1-x}N$ alloy band gap determination
Differences between absorption-type and luminescence type of measurements

unipress

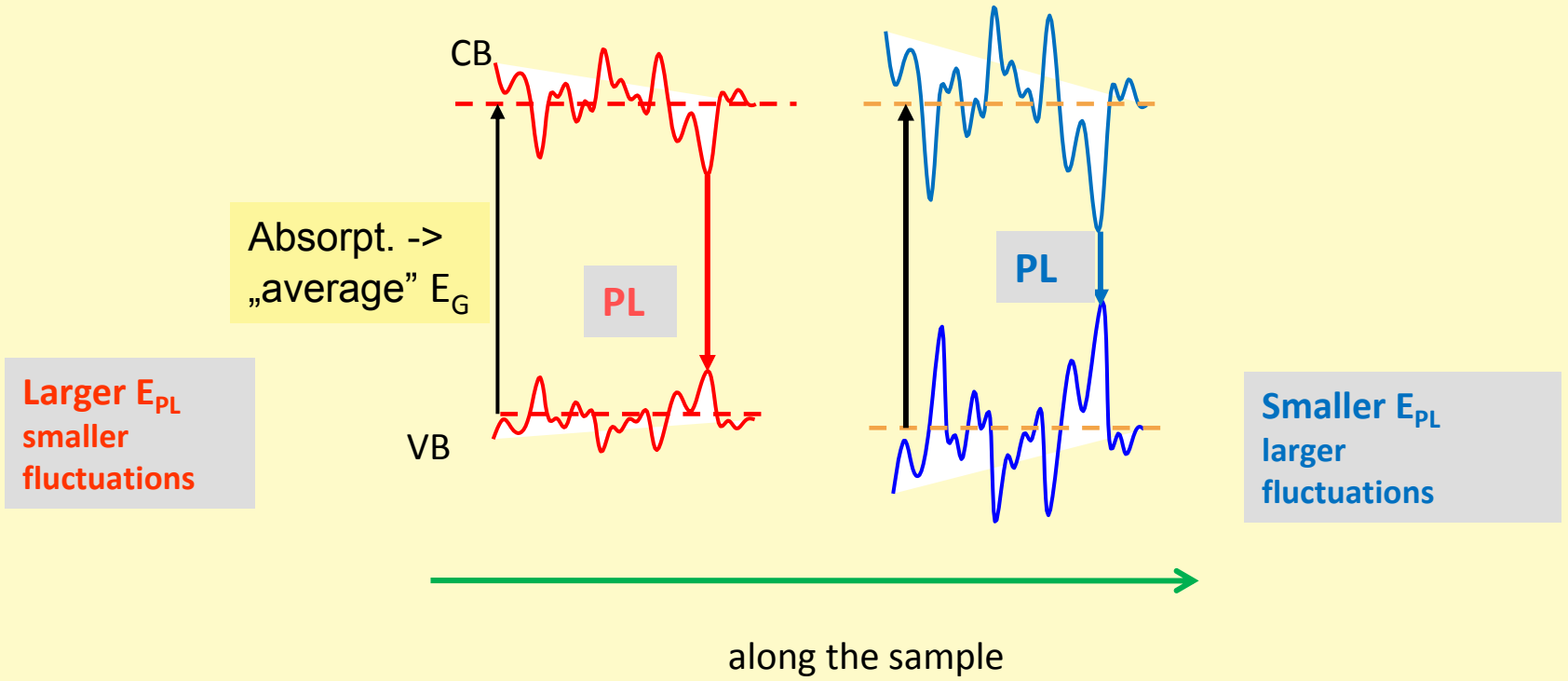


1. Very Large dispesion of data; strong bowing present
2. Two sets of results can be seen in the region of lattice match to GaN
3. Higher magnitude of E_g as measured by optical absorption in comparison with PL

Different E_G magnitude as determined by light absorption and luminescence measurements

unipress

Example: Two InGaN layers with ≈ the same „Average" Band Gap **E_G** but with diffrent luminescence energies.
Average Gap measured by absorption of light (requires large density of states)



Our hypothesis: Fluctuations correspond to local In-segregation, we simulate it by first principle calculations

Theoretical description

unipress

energy band structure
calculations of InGaN, InAlN, and AlGaN

with

simulation of
indium composition fluctuation
(In-clustering)

I. Gorczyca, T.Suski, N.E. Christensen, and A. Svane:
Phys. Rev. B. 2008,2009; Appl. Phys. Lett. (2009, 2010, 2011)

Beijing, October, 25, 2012

Method

unipress

Electronic band structures of wurtzite $In_xGa_{1-x}N$, $In_xAl_{1-x}N$, and $Ga_xAl_{1-x}N$

by DFT with corrected band gaps

2 steps :

1. relaxed atomic positions

Pseudopotential method

- **Vienna simulation package (VASP)**

2. energy band structure

Full-potential linear muffin-tin-orbital (FP-LMTO)

- **semicore cation-*d* states included as local orbitals**
- **band gaps correction**

external potentials sharply peaked at the nuclear positions.

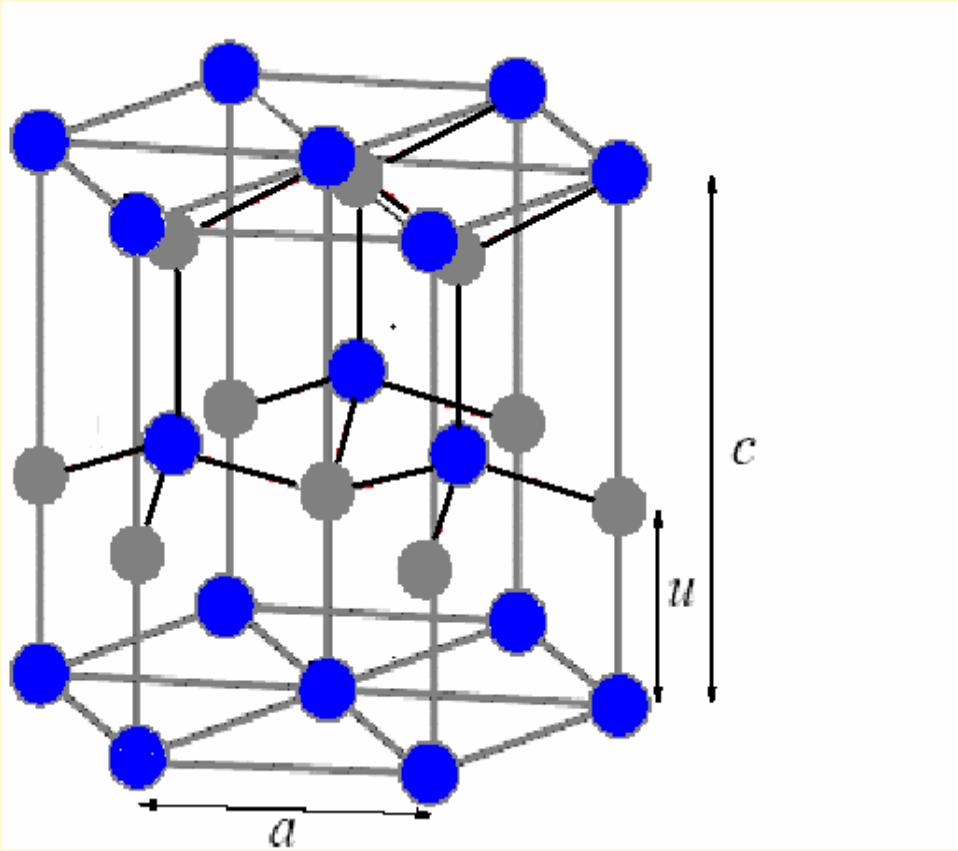
Method – superlattice like structure

unipress

$In_xGa_{1-x}N$, $In_xAl_{1-x}N$

32 atoms supercell
wurtzite structure

No of In atoms	x
2	0.125
3	0.19
4	0.25
6	0.375
8	0.50
10	0.625
12	0.75
14	0.875

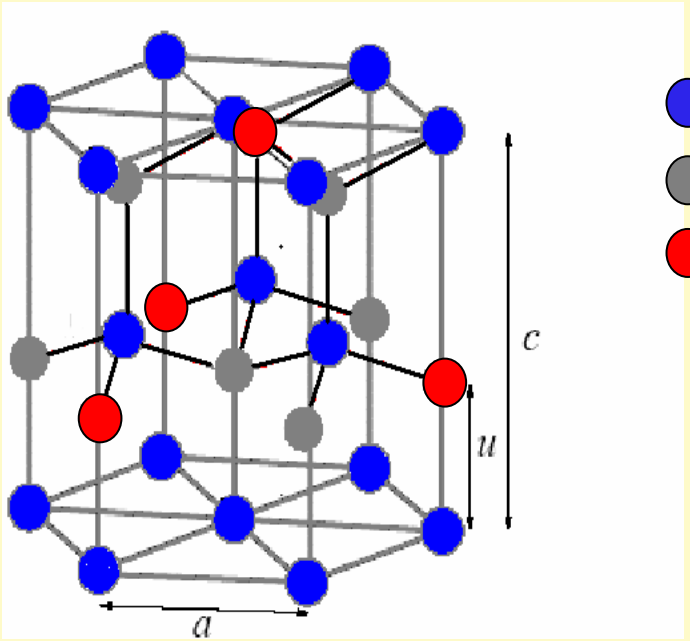


Assumed In-cation arrangements

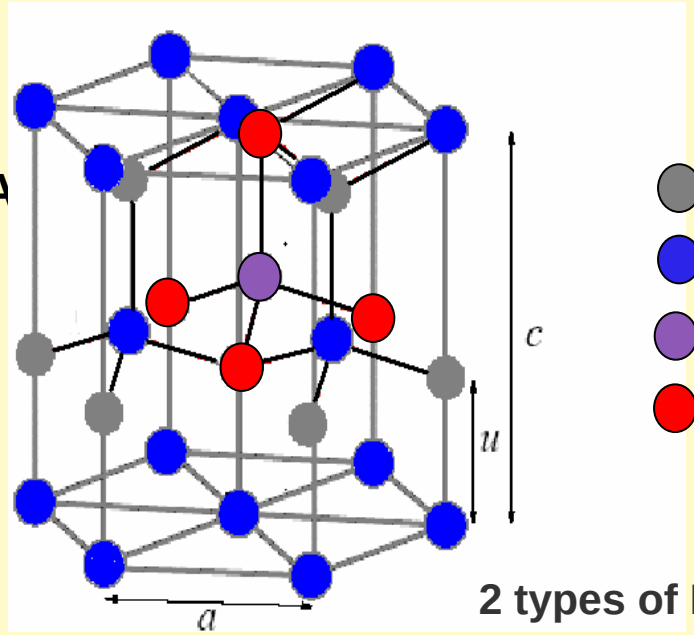
unipress

‘uniform’ arrangements of indium atoms

x=0.25



‘clustered’ arrangements of indium atoms



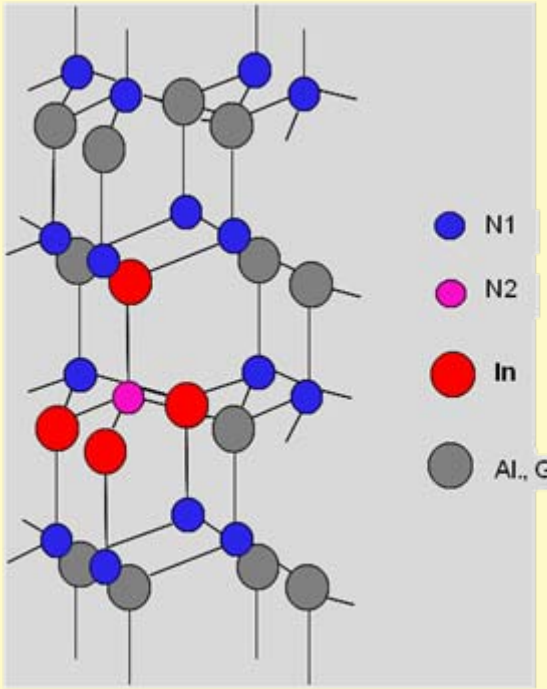
2 types of N atoms

What is the effect of different arrangements of indium atoms on the band structure?

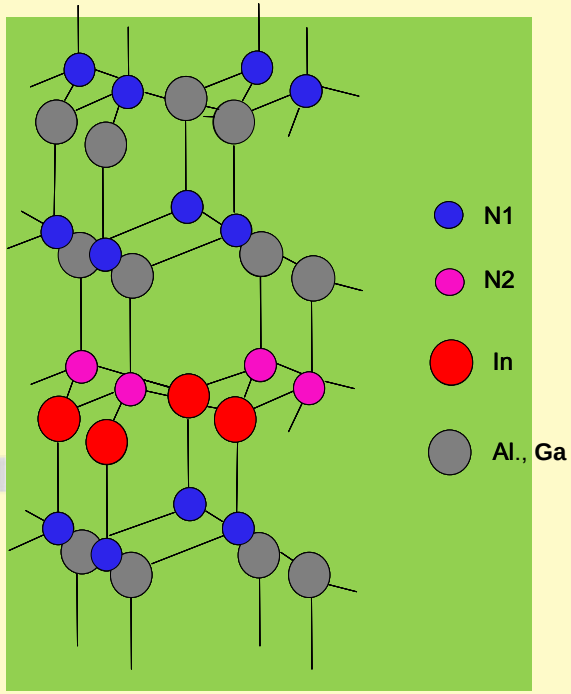
There is no unique definition of “least” or “most” clustered configuration of atoms for a given *x*.

unipress

Case 1



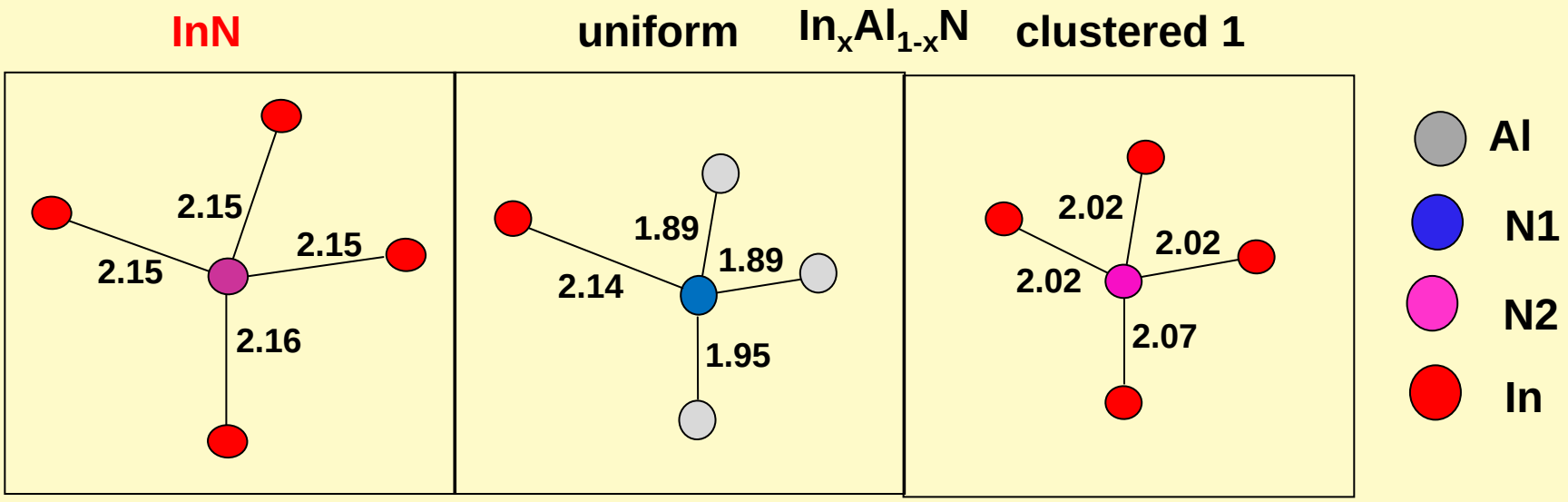
Case 2



What is the effect of different arrangements of indium atoms on the band structure?

Clustered $In_xAl_{1-x}N$ x=0.25
very short bond-length of In-N(2)

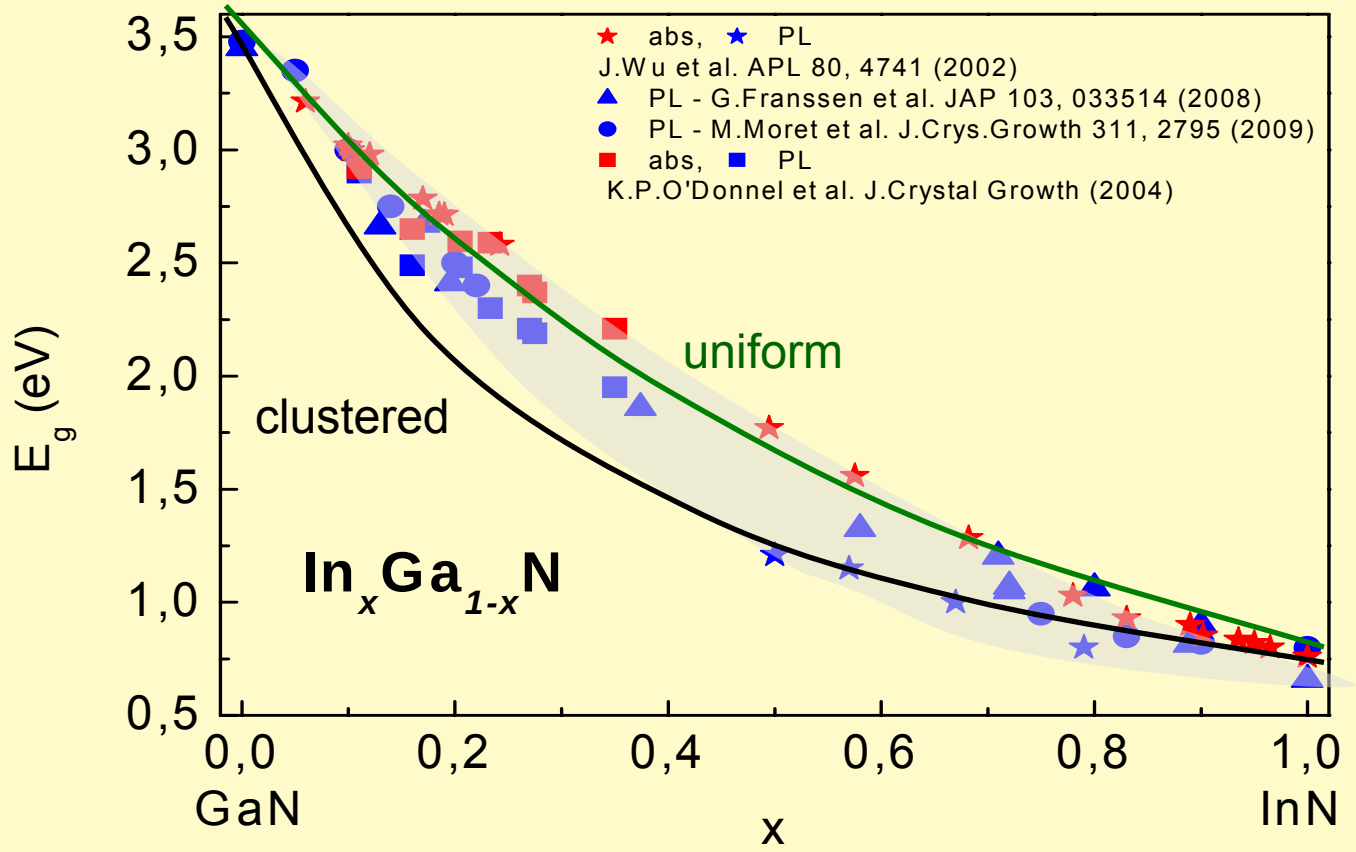
unipress



Shortening of the bond-length from 2.15 Å to 2.02 Å
Responsible for strong hybridization of In-N(2) bonds
What is even enhanced after applying pressure

$In_xGa_{1-x}N$ alloy band gap determination
Theory vs. experiment

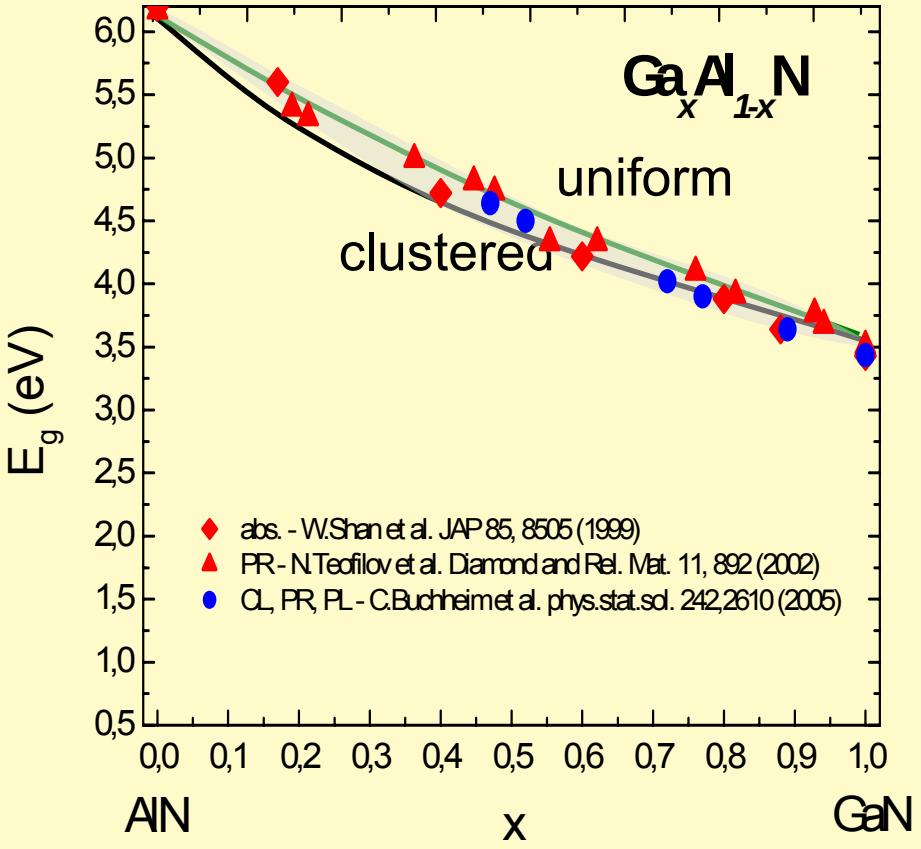
unipress

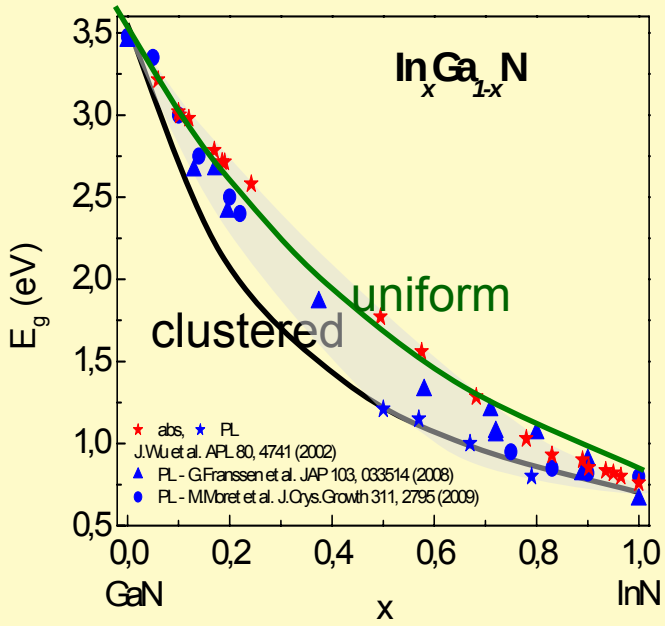


1. Significant bowing of E_g vs. x obtained by calculations with much more pronunced effect for clustered In-distribution
2. Calculations reproduce lage spreading of data suggesting presence of In-clustering

$Al_xGa_{1-x}N$ alloy band gap determination
Theory vs. Experiment, comparison with InGaN

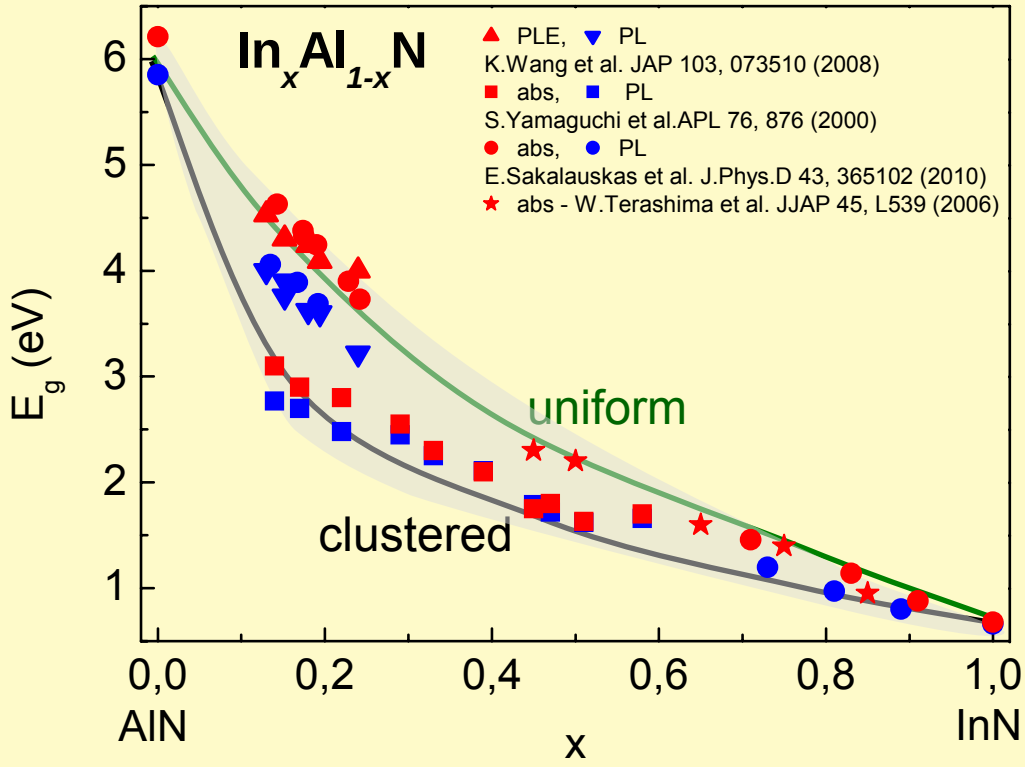
unipress





For **$Al_xGa_{1-x}N$** very small bowing of E_g vs. x obtained by calculations with slightly more pronounced effect for clustered Al/Ga distribution

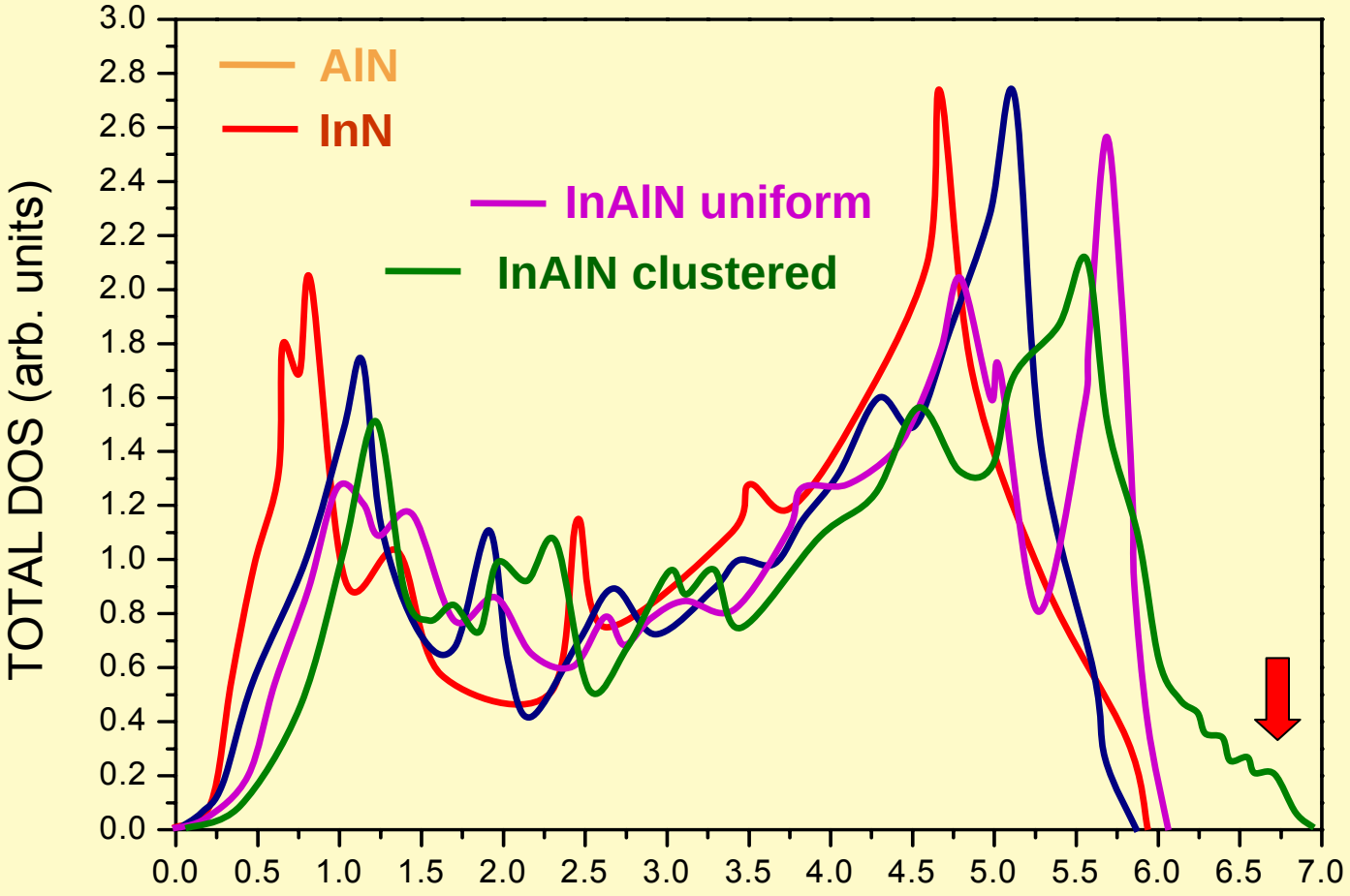
$In_xAl_{1-x}N$ alloy band gap determination
Theory vs. Experiment,



1. For **$In_xAl_{1-x}N$** - huge bowing of E_g vs. x obtained by calculations with much more pronunced effect for clustered In-distribution
2. Calculations reproduce lage spreading of data suggesting presence of In-clustering.
3. Role of In (In-N bonds) seems to be crucial

Valence-band density of states (VB DOS)

Comparison for various nitrides

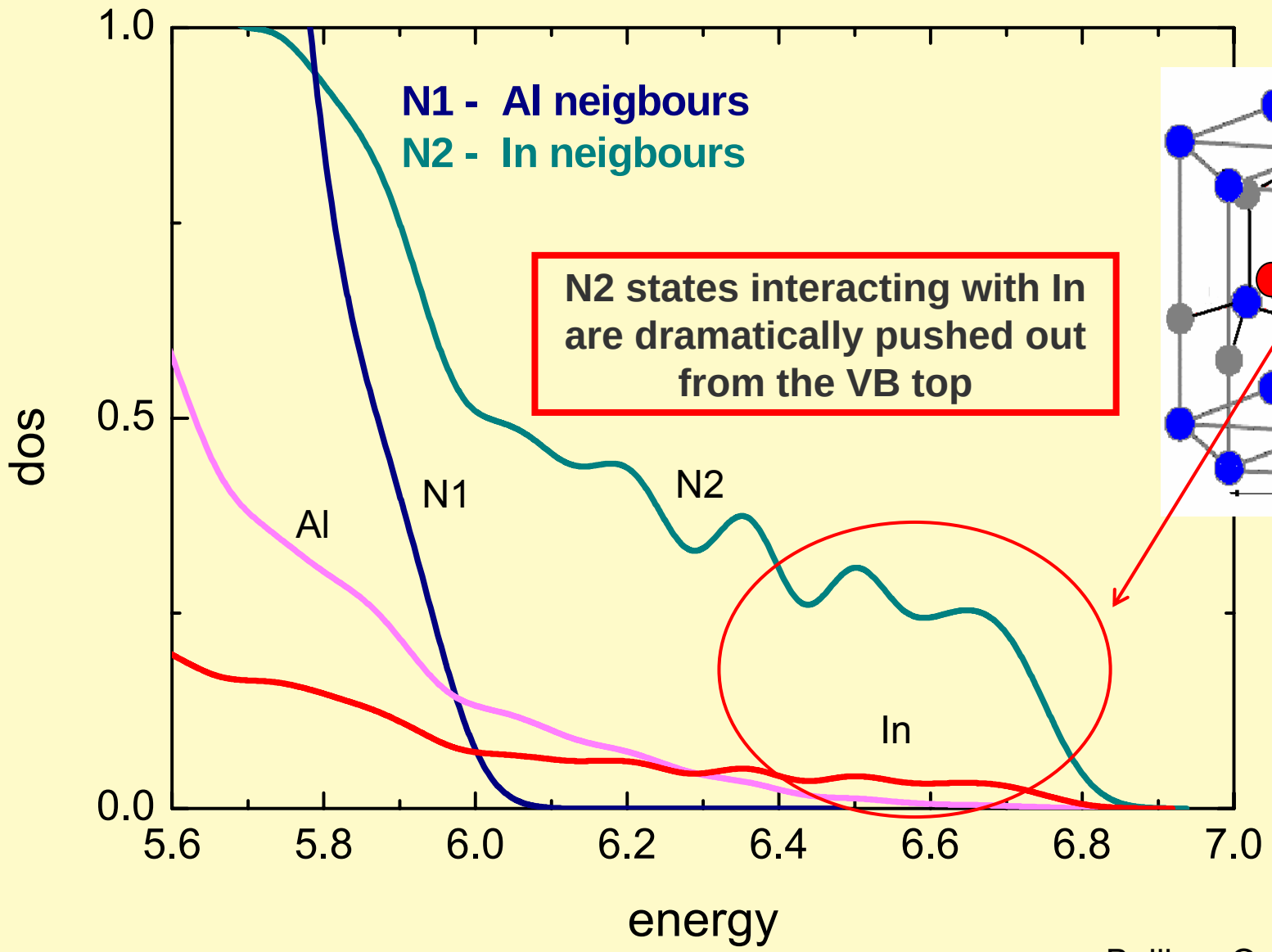


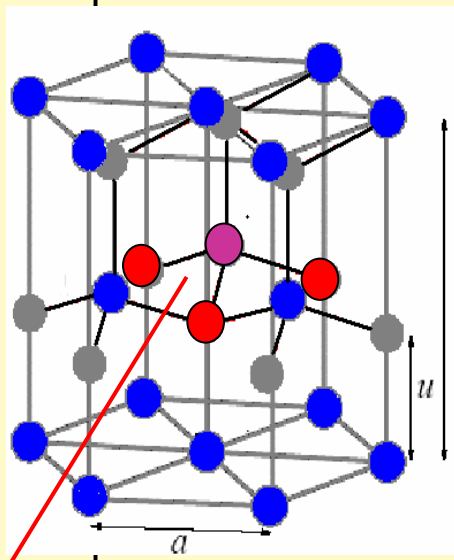
bottom of the valence band as energy reference level

ΔE about 1eV

Which atomic states are responsible for the valence band width expansion? Partial DOS

Density of states for $In_xAl_{1-x}N$ x=0.25
clustered

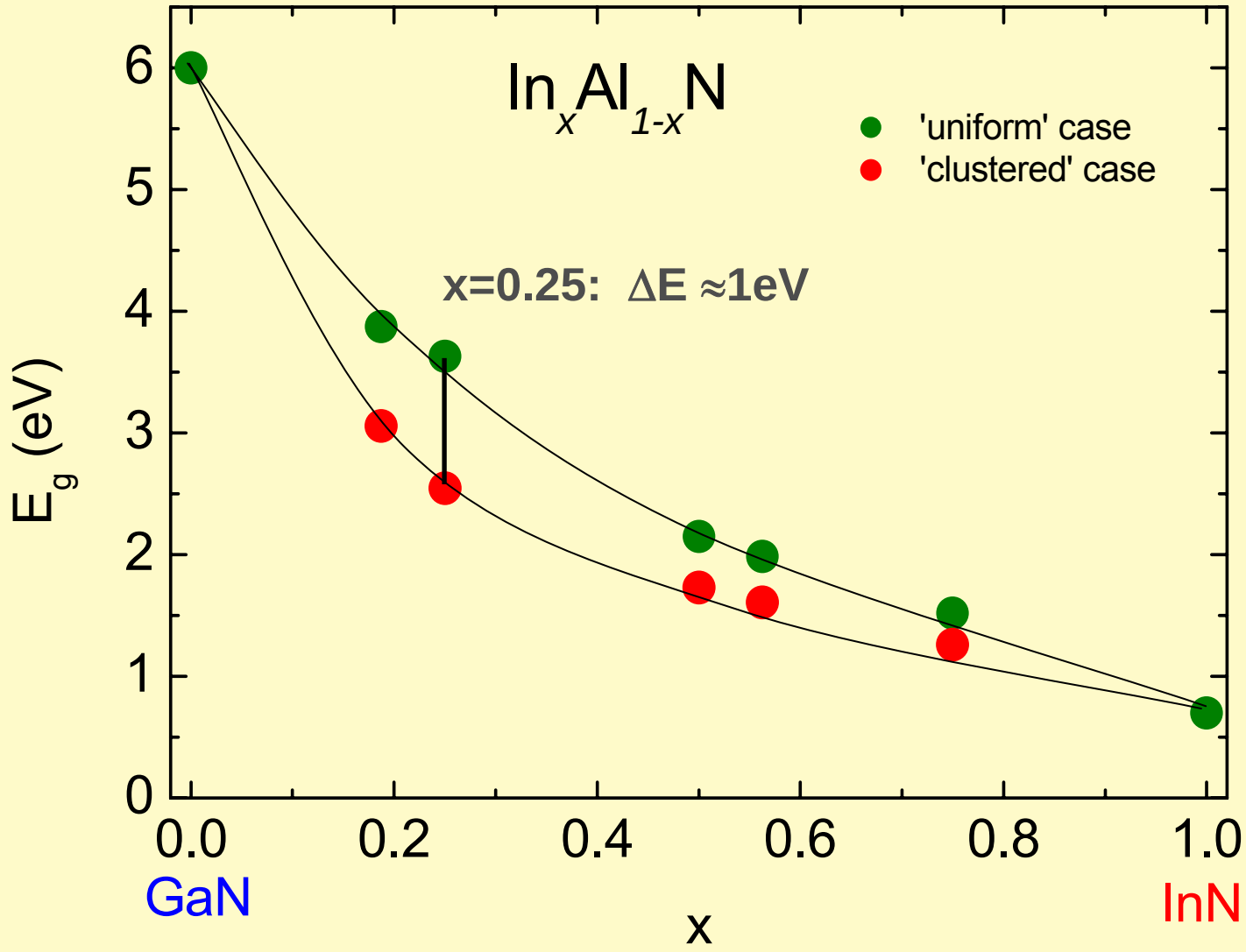




unipress

Beijing, October, 25, 2012

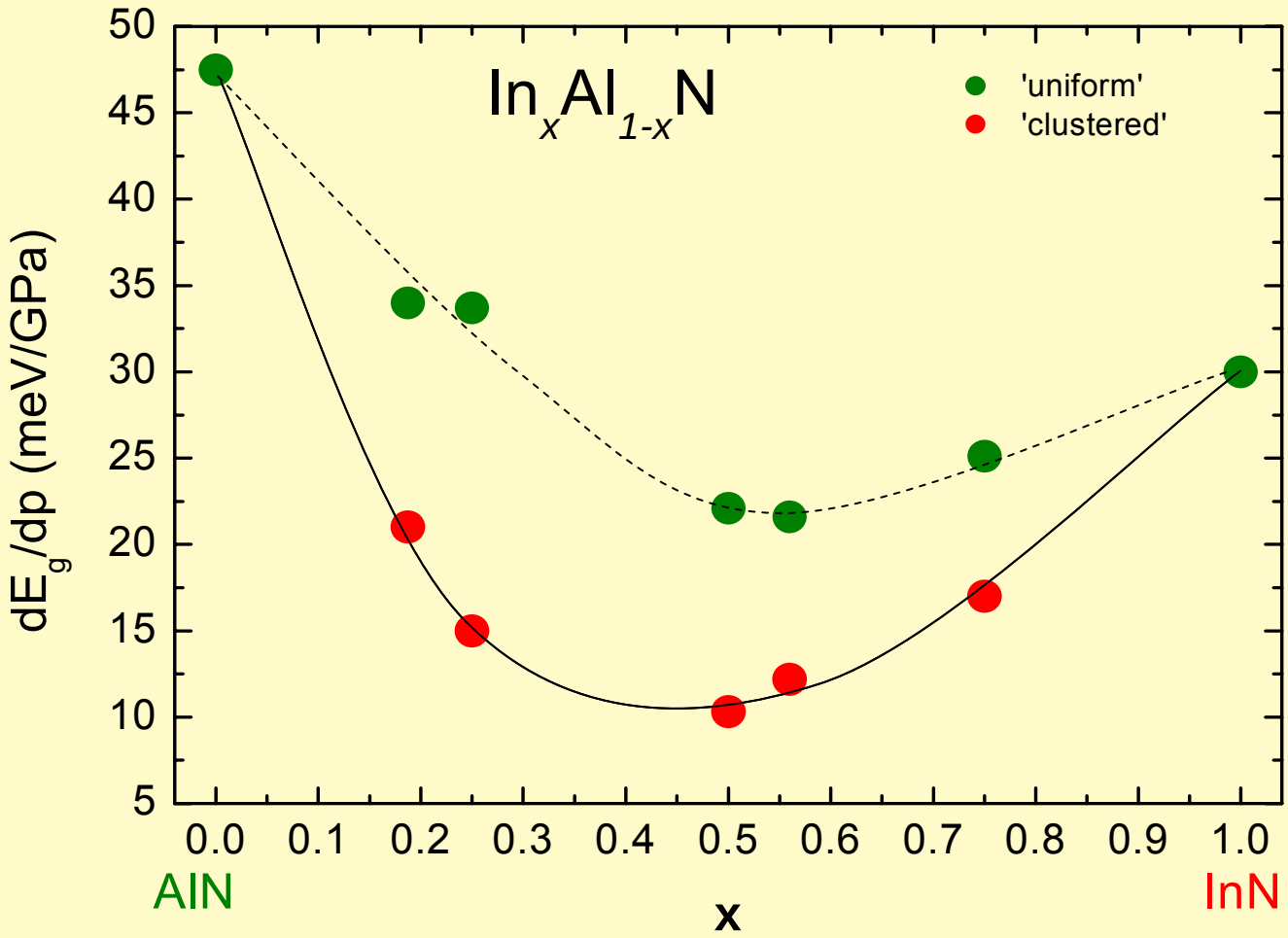
Bandgap bowings – results od calculations



Decrease of the band gap comes from the valence band width reduction

Pressure coefficients of bandgap – calculations
Sensitive tool to detect In-segregation?

unipress

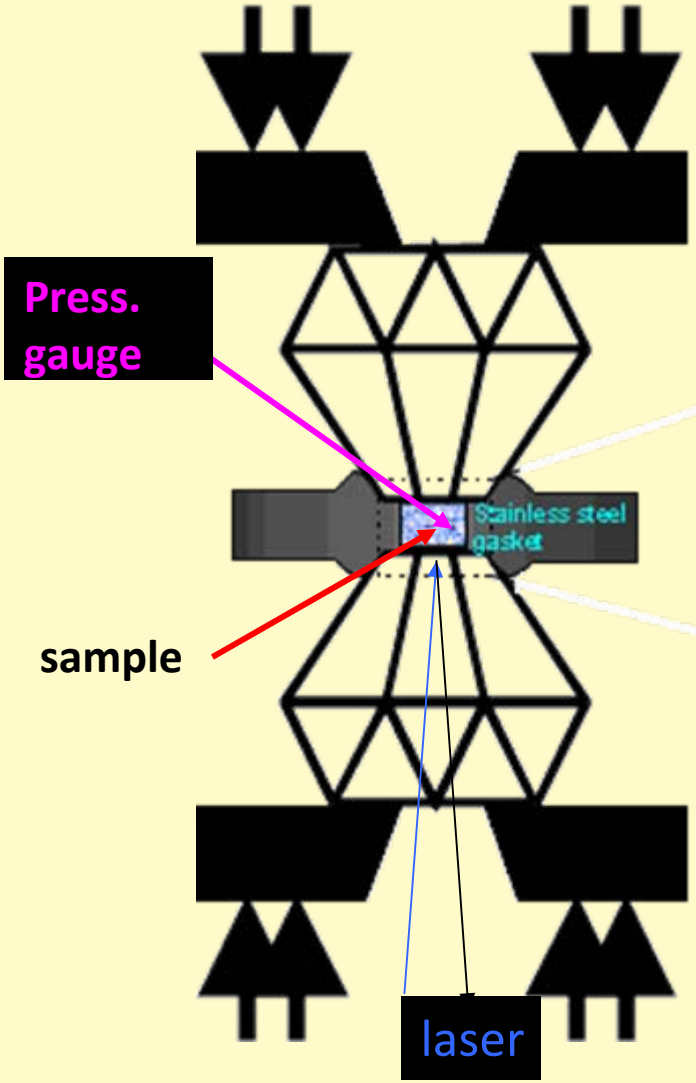


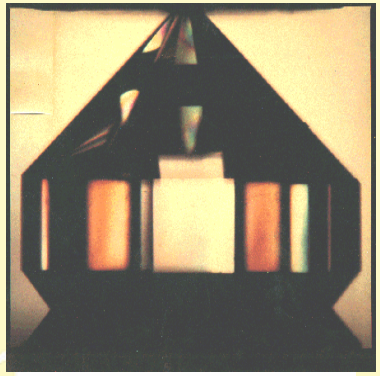
Predicted magnitude of pressure coefficient for clustered case much lower than for binary compounds. A chance for verification.

Experimental techniques in high-pressure studies of the optical properties of semiconductors.

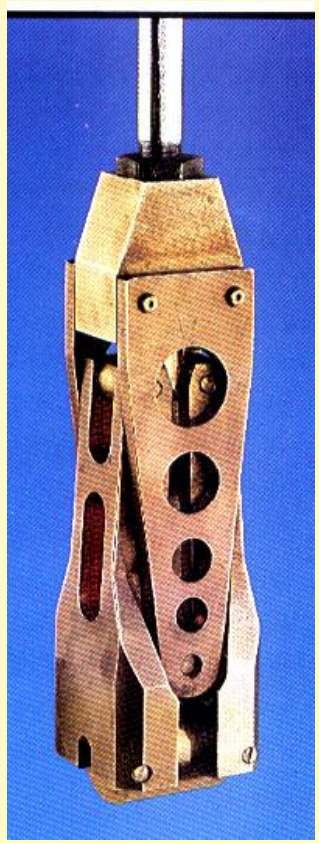
unipress

Diamond Anvil Cell





Solid argon as pressure transmitting medium



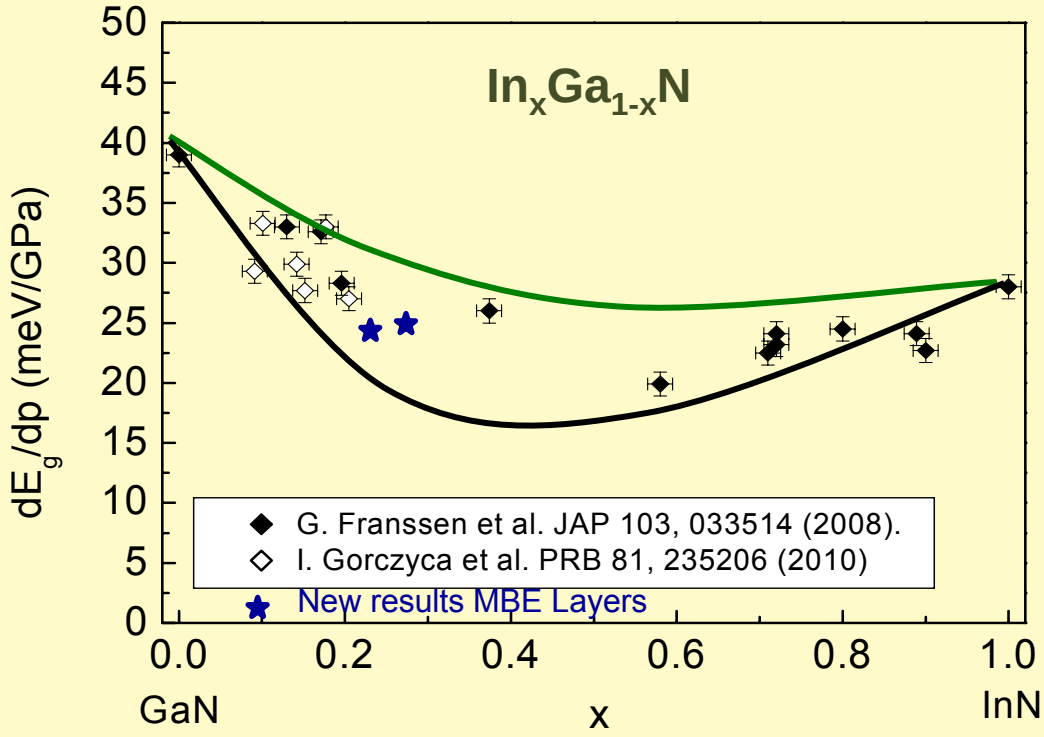
Pressure units: 1 atm = 1 bar; 10 kbar=1 GPa

$In_xGa_{1-x}N$ alloy band gap dependence on pressure

Theory vs. experiment

unipress

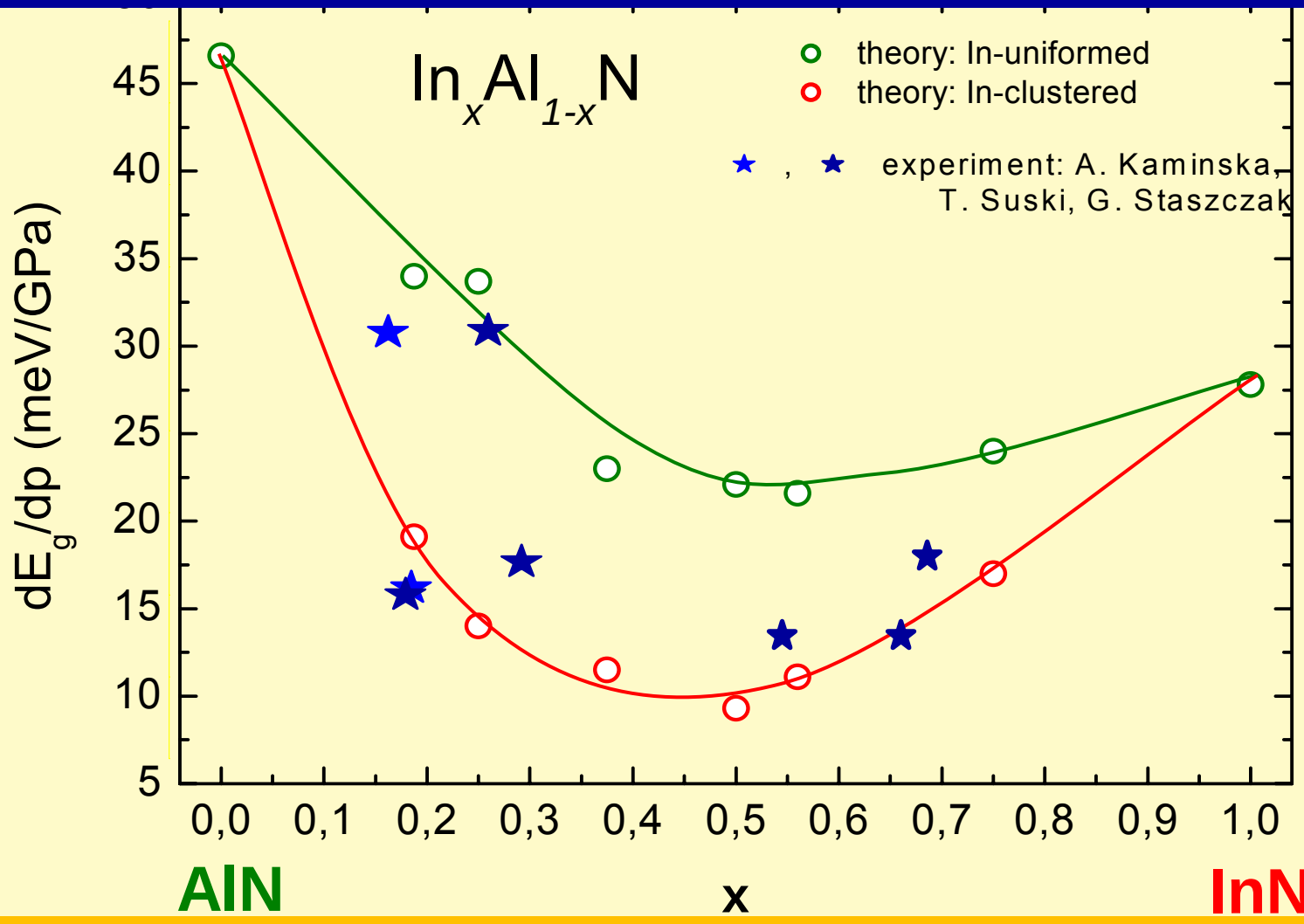
dE_g/dp bowing



1. Significant bowing of dE_g/dp vs. x obtained by calculations with much more pronunced effect for clustered In-distribution
2. Calculations reproduce lage spreading of data suggesting presence of In-clustering

$In_xAl_{1-x}N$ alloy band gap dependence on pressure

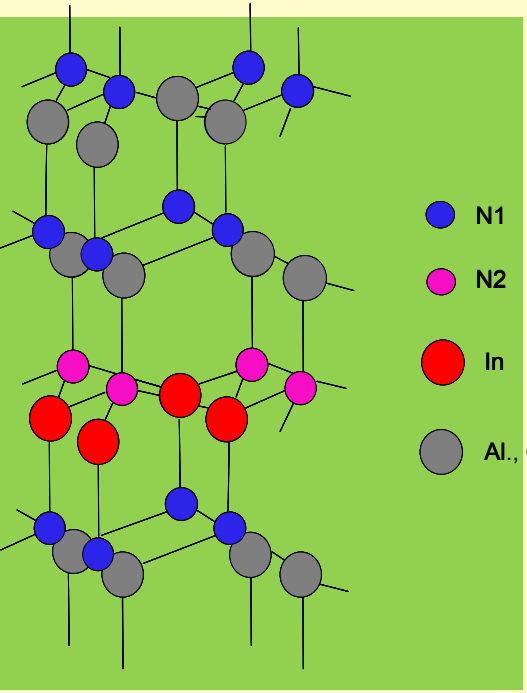
Theory vs. experiment



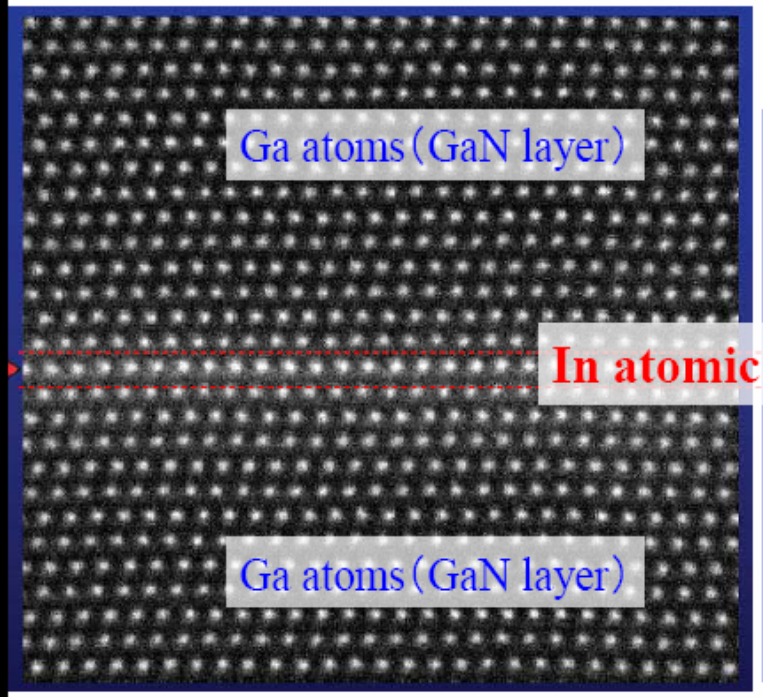
1. Drastic bowing dE_g/dp vs. x obtained by calculations with much more pronounced effect for clustered In-distribution.
2. Experiment - again two sets of data for very similar samples

Our studies of In-segregation very useful for description of real (artificial) structures _ Short Period Superlattices of InN/GaN

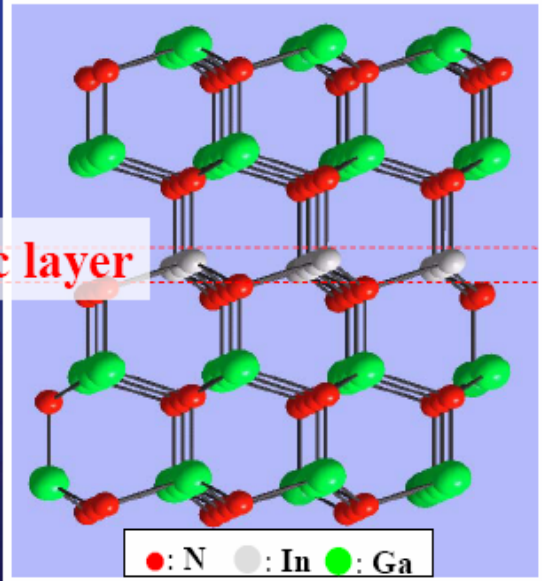
unipress



Fundamental structure of the proposed symmetrical structure 1ML-InN/GaN matrix quuntum well



Δa (InN/GaN)=11%



Ultimately thin InN wells (~1 monolayer)

Coherent growth of 1ML-thick InN wells on GaN, High quality in principle

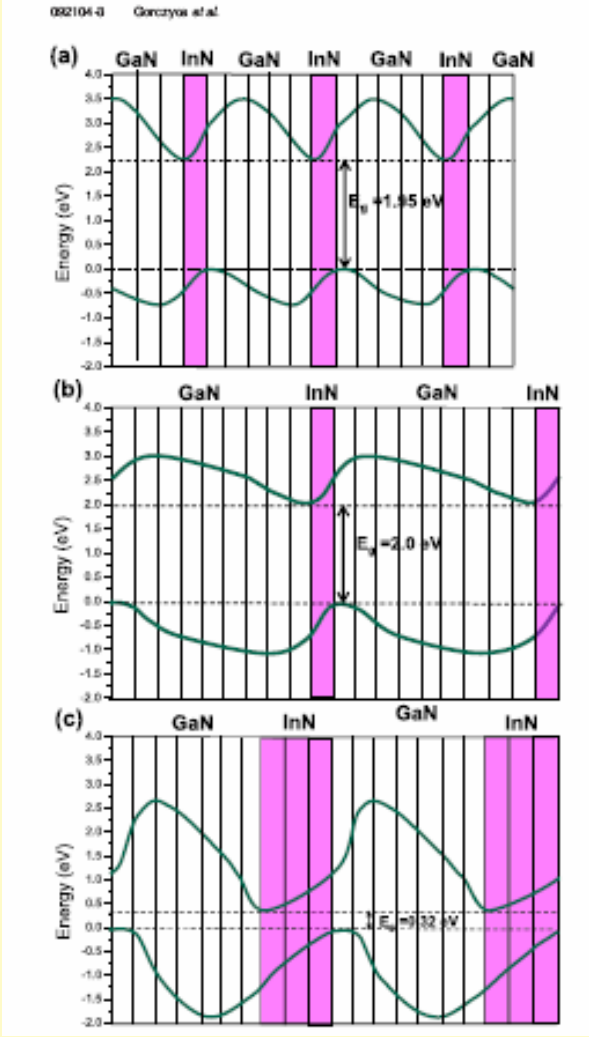
Idea Prof. Yoshikawa (Chiba University); Growth Prof. Wang (PKU)

Theory and pressure studies UNIPRESS; Cryst. Growth and Design (2012), APL (2012)

Very fruitful collaboration with School of Physics Peking University

2. Band-gap-engineerig within green-amber -red spectral range

unipress



Band structure calculations (ab initio)
Optical studies using hydrostatic pressure

InN/GaN Superlattices: Band Structures and their Pressure Dependence

I. Gorczyca, T. Suski, G. Staszczak, N. E. Christensen, A. Svane, X.Q. Wang, E. Dimakis and T.D. Moustakas

IWN2012-Sapporo
oral presentation

Summary: Results of „superlattice” approach

unipress

- Using a simplified modelling a significant (very large in the clustered materials) composition dependent bowings of the gaps and their pressure coefficients were found in In-containing nitride alloys.

- Strong interaction of In and N2 is related to shorter bonds

- Applying pressure enhances all the effects observed.

In-N bonds becoming even shorter lead to stronger interaction between In and N states at the top of the VB and cause further widening of the VB.

- The two models ‘uniform’ and ‘clustered’, represent extreme cases - the results show the scatter that can reflect different segregation of indium atoms depending on growth conditions.

- „Real” structures with In-segregation along atomic planes are produced and studied.

Summary

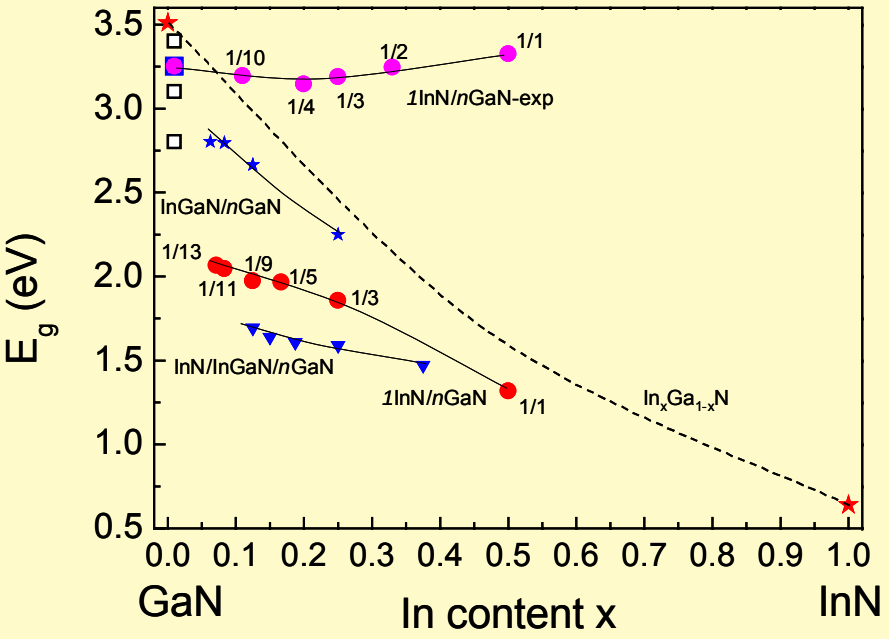
unipress

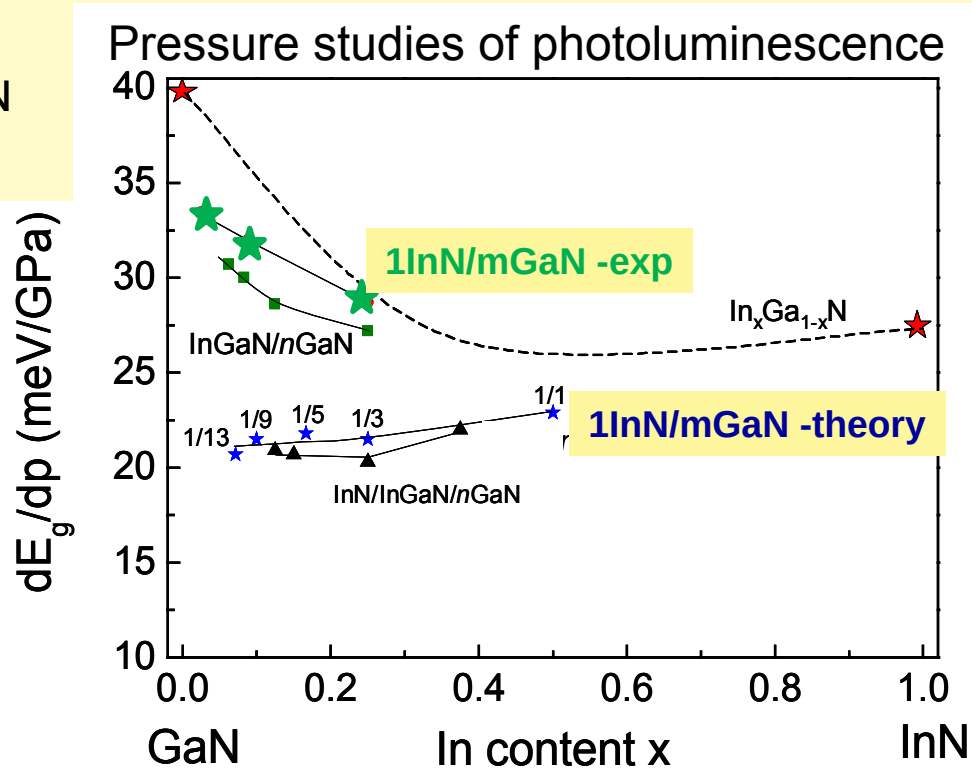
There is a tendency to In-segregation even in ***perfect*** InGaN and InAlIN layers/structures

A simplified approach („Superlattice”) describes well observations concerning band gap and their pressure coefficients in samples originating from different labs grown by MOVPE and MBE techniques.

There is a tendency to In-segregation but in ***imperfect*** InGaN and InAlIN layers/ Structures (dislocations, grain boundaries, Precipitates, role of local strain important)

A sophisticated approach (Monte Carlo simulations etc.) describes well decrease of band gaps in InGaN incoherent alloy.


3.5
3.0
2.5
2.0
1.5
1.0
0.5
E_g (eV)
0.0 0.1 0.2 0.3 0.4 0.5 0.6 0.7 0.8 0.9 1.0
GaN
In content x
InN
1/10
1/2
1/1
1/4
1/3
1InN/nGaN-exp
InGaN/nGaN
1/13
1/9
1/11
1/5
1/3
InN/InGaN/nGaN
1InN/nGaN
1/1
$In_xGa_{1-x}N$


Pressure studies of photoluminescence
40
35
30
25
20
15
10
dE_g/dp (meV/GPa)
1InN/mGaN -exp
$In_xGa_{1-x}N$
InGaN/nGaN
1/1
1/9
1/5
1/3
1/13
1InN/mGaN -theory
InN/InGaN/nGaN
0.0 0.2 0.4 0.6 0.8 1.0
GaN
In content x
InN

Incoherent alloys (InGaN) demonstrate strong decrease of band gap - sophisticated calculations

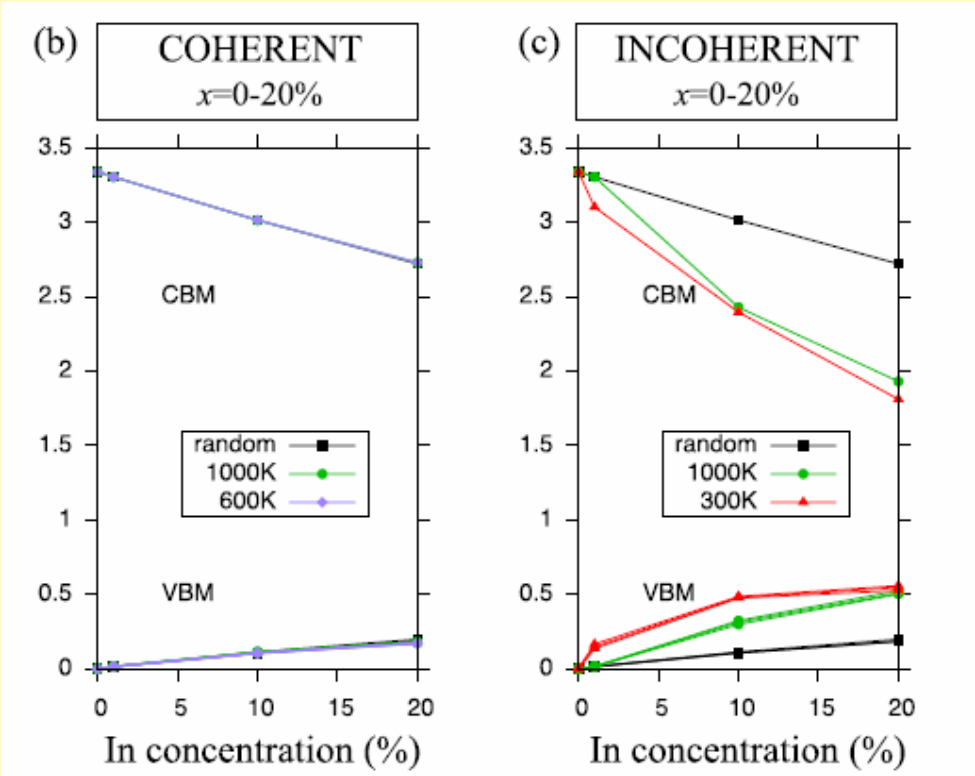
unipress

Bridging the gap between atomic microstructure and electronic properties of alloys: The case of (In,Ga)N

J.A. Chan, J.Z. Liu, and Alex Zunger - Phys. Rev. B82, 045112 (2010)

Authors consider lattice **coherent alloys – precipitates having continuous crystal planes across the phase boundary between them and the crystal matrix**

incoherent alloys – precipitates having the dislocations, grain boundaries Leading to disengaging them from the matrix



Incoherent alloys demonstrate A strong decrease of band gap with respect to coherent and random alloys