Short-range In-segregation in InGaN and InAIN. 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 InGaAIN 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



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

- Director: Izabella Grzegory
- Head of Semicondutors Lab: <u>T. Suski</u>
- 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

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



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%

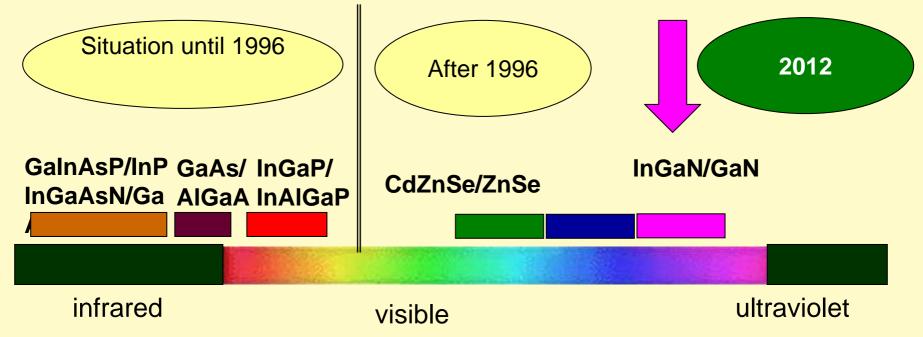
* applied research - 40%

* high pressure methods and instrumentation - 20%

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

Semiconductor Laser Diodes Semiconductor families used





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, AIN and their alloys for construction of green, blue and ulraviolet Light Emitting Diodes and Laser Diodes

Main Applications of nitride-based emitters





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

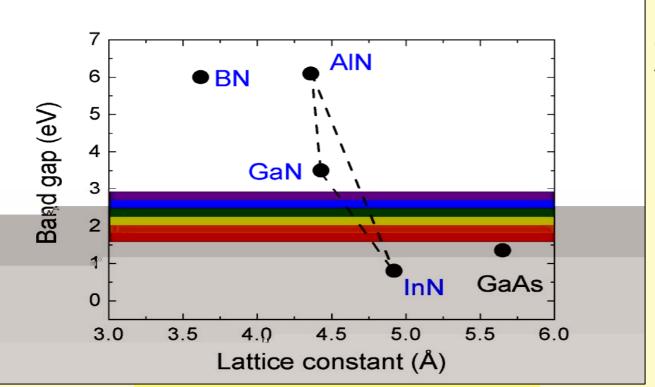
Second semiconductor system after Silicon

GaN-AIN-InN properties **Important aplications**



GaN-InN-AIN 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

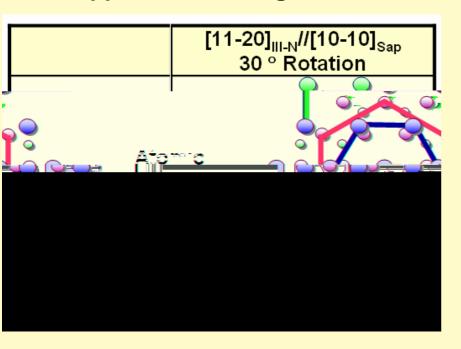
For visible range of the spectrum mostly InGaN alloy is used to construct active Quntum Wells

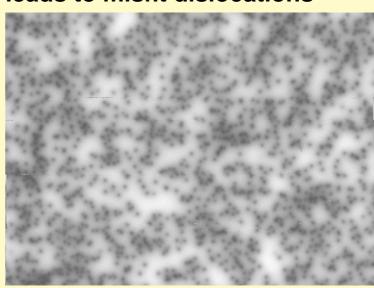
Heteroepitaxial growth of GaN; usually on sapphire

A BEST MOCVD GaN

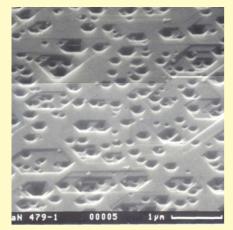
on sapphire Lai

Large lattice mismatch leads to misfit dislocations



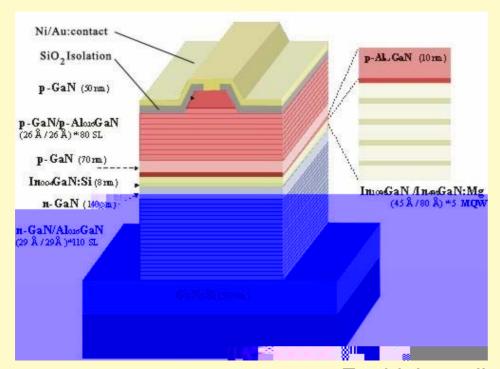


unipress



Importance of substrates





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:



Melting condition	Melting conditions of semiconductors					
crystal	T ^M , °C	p ^M , atm.				
Si GaAs GaP GaN AIN InN	1400 1250 1465 2500 2800 2200	< 1 15 30 45 000 >100 >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)

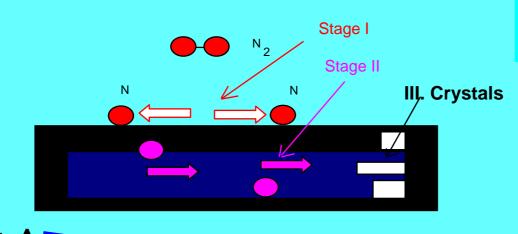
High Pressure Growth of GaN single crystals



Three stages of HPSG growth of GaN

- 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.

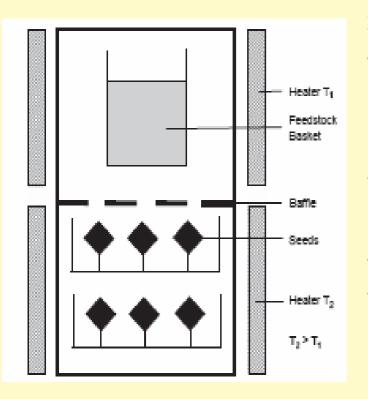




- Working volume 4500 cm³
- Max pressure 15 000 atm
- Temperature 1550°C
- Pressure stabilization 10 atm
- Temp. stabilization 0.1°C

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





High Pressure Autoclave

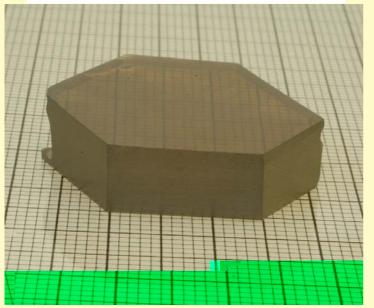
Ammonothermal method – analog of hydrothermal Where ammonia instead of water is used as a solvent. Temp. 400-600°C; Press. 0.1-0.3 GPa (1-3 kbar)

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.

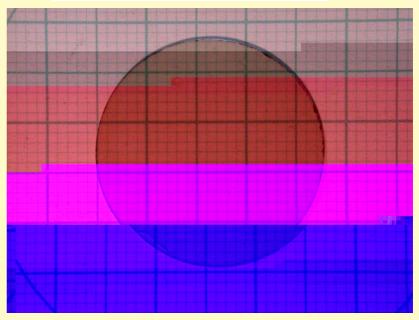
High Quality GaN Substrates for Laser Diodes





High Pressure Multi-feed -seed method





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

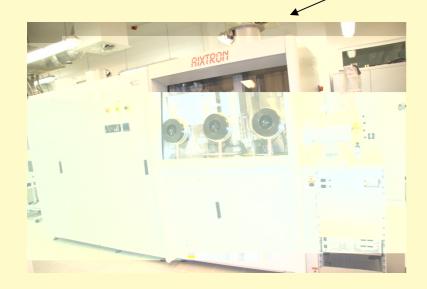


Surface preparation difficult.

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



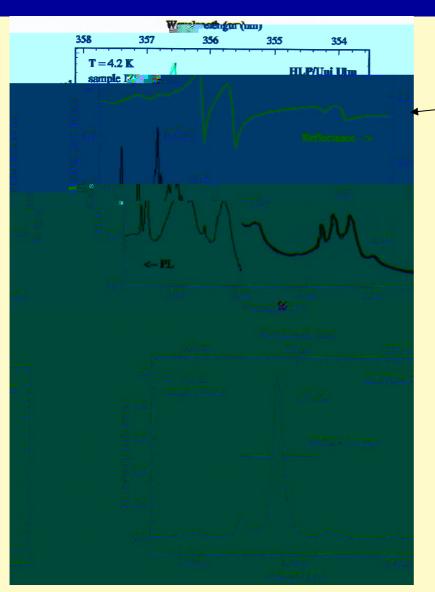
M. Leszczyński,



C. Skierbiszewski

Record optical properties Ultra-narrow emission/absorption lines



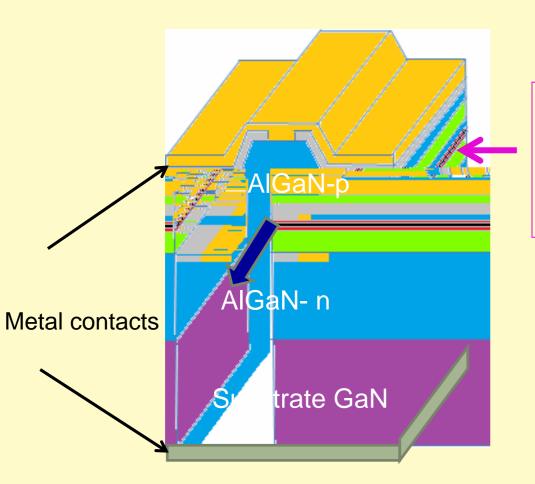


Very narrow lines Excitons clearly visible; FWHM = 0.11 meV

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

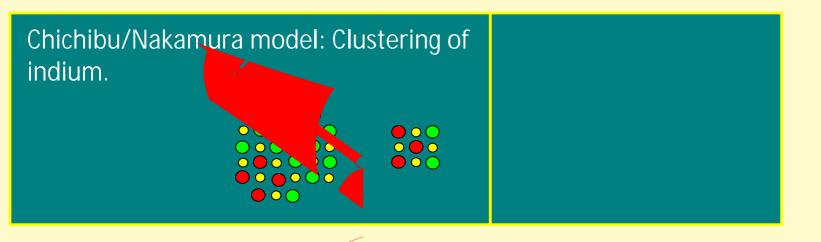
Multi-Quantum-Well Laser epi-structure





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 & AllnN. <u>Almost</u> commonly accepted concept



In- fluctuations

- clustering, spinodal decon
- -Chichibu et al. Appl. Phys.
- short range order/statisti
- Gorczyca et al.. Phys. Re
 There are results of optical spatial scale of below 50 10

ion, phase separation

<mark>?</mark>, 4188 (1996))

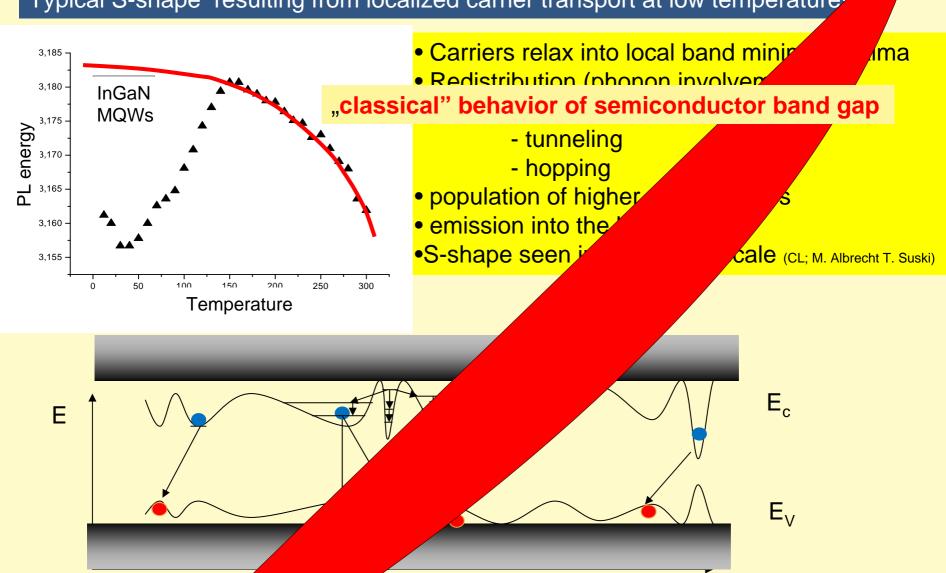
fluctuations

9, 2010), Bellaiche et al. **74**, 1842 (1999); emonstrating that potential fluctuations within portant 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



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



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

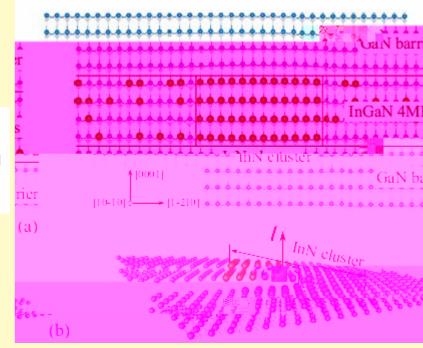
Strained and relaxed layers with different In concentration were observed when InGaN layers increased in thickness. Above the critical layer thickness stacking faults start to appear with increased density toward the surface.

Stacking faults cause an appearence of multipeak PL and CL.

JOURNAL OF APPLIED PHYSICS 108, 103503 (2010)

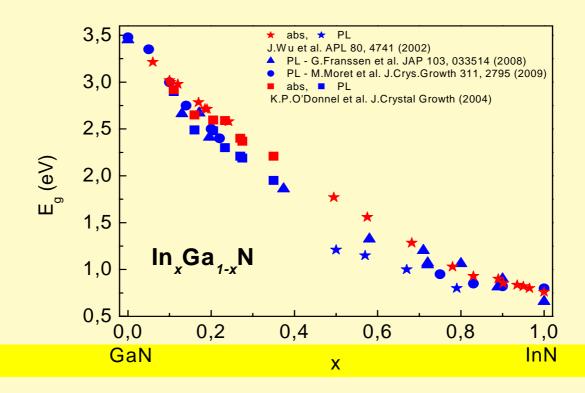
Influences of the biaxial strain and *c*-screw dislocation on the clustering in InGaN alloys

Huaping Lei, 1,a) Jun Chen, 2 and Pierre Ruterana 1



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

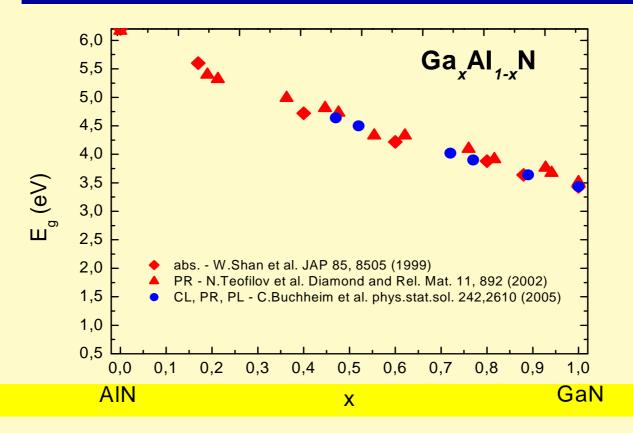




- 1. Large dispersion of data and significant bowing of E_q vs. x clearly seen
- 2. Higher magnitude of E_g measured by optical absorption in comparison with PL

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

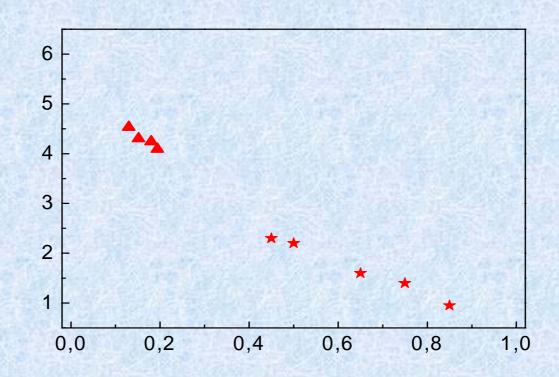




- 1. Small dispersion of data; almost linear dependence of E_{α} vs. x
- 2. Similar magnitude of E_g as measured by optical absorption and PL

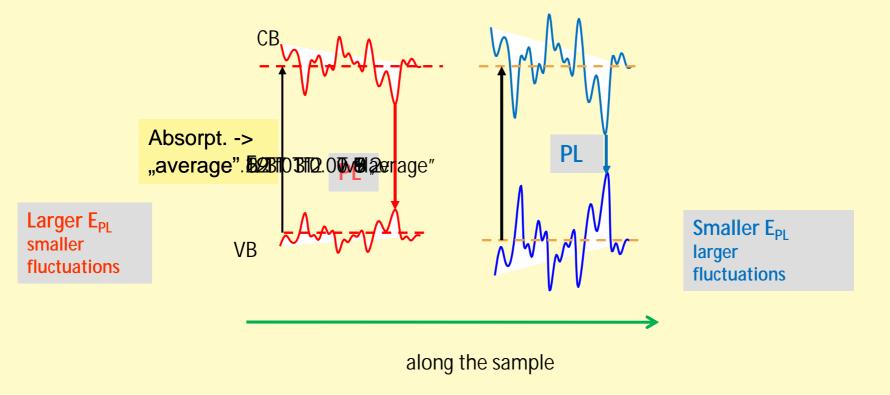
In_xAl_{1-x}N alloy band gap determination Differences between absorption-type and luminescence type of measurements





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)



Theoretical description



Method



Electronic band structures of wurtzite In_xGa_{1-x}N, In_xAI_{1-x}N, and Ga_xAI_{1-x}N by DFT with corrected band gaps

2 steps:

1. relaxed atomic positions

Pseudopotential method

S Vienna simulation package (VASP)

2. energy band structure

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

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

external potentials sharply peaked at the nuclear positions.

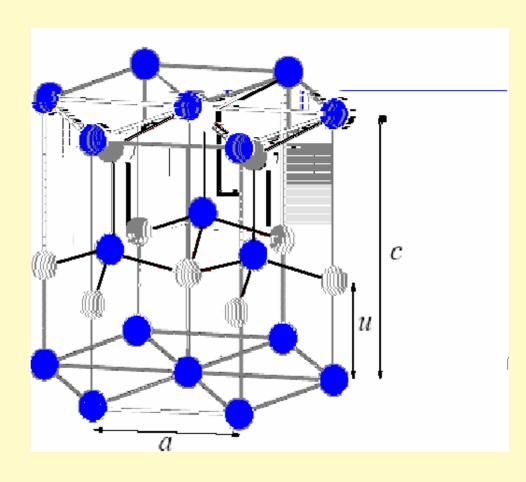
Method – superlattice like structure

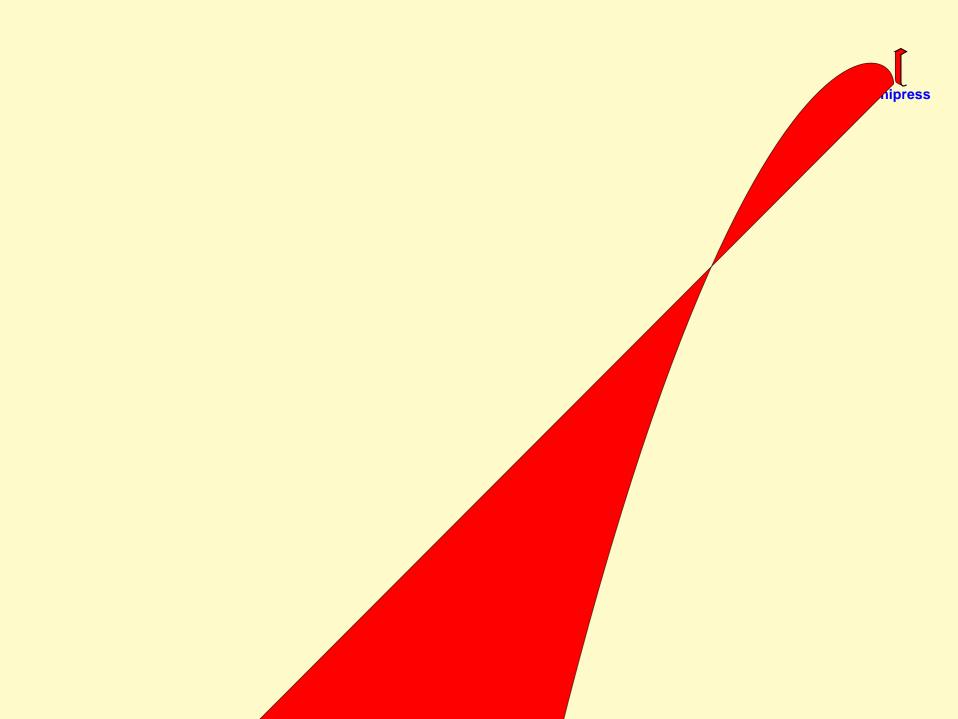


 $In_xGa_{1-x}N$, $In_xAI_{1-x}N$

32 atoms supercell	
wurtzite structure	

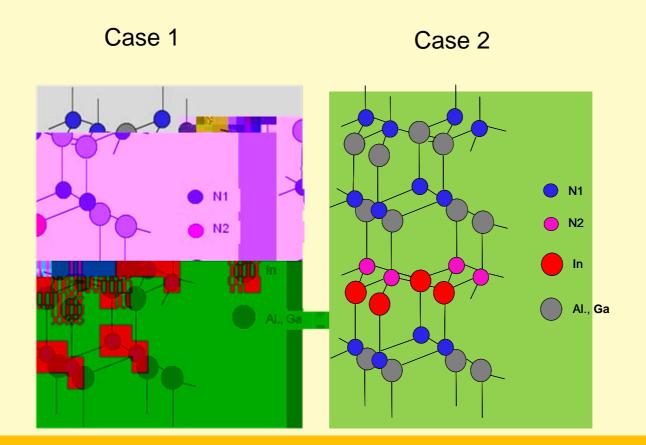
No of In atoms	x
2	0.125
3	0.19
4	0.25
6	0.375
8	0.50
10	0.625
12	0.75
14	0.875





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

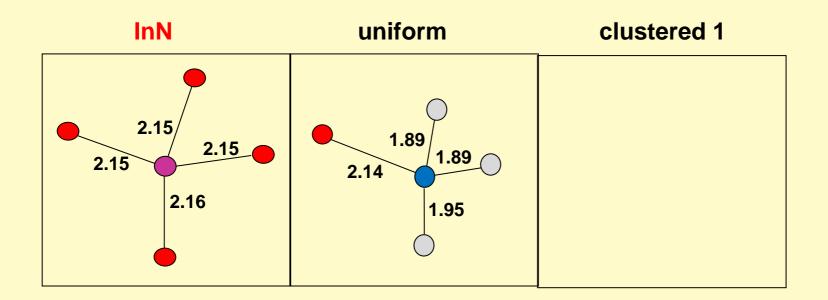




What is the effect of different arrangements of indium atoms on the band structure?

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

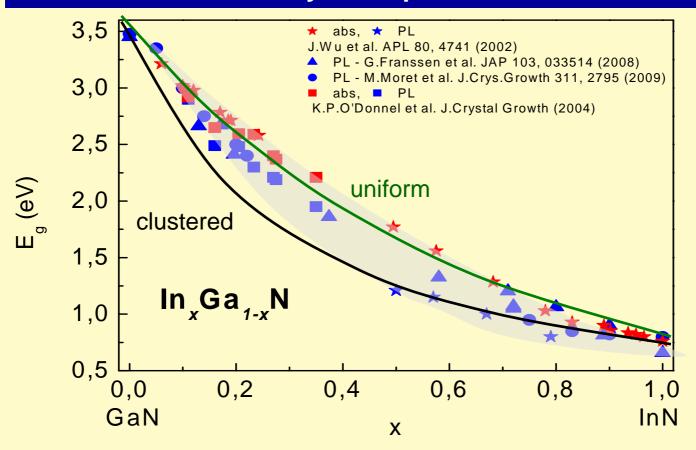




Shortening of the bond-length from 2.15 Å to 2.02 Å Responsible for strong hybridization of In-N(2) bonds What is even enhanced after applying pressure

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

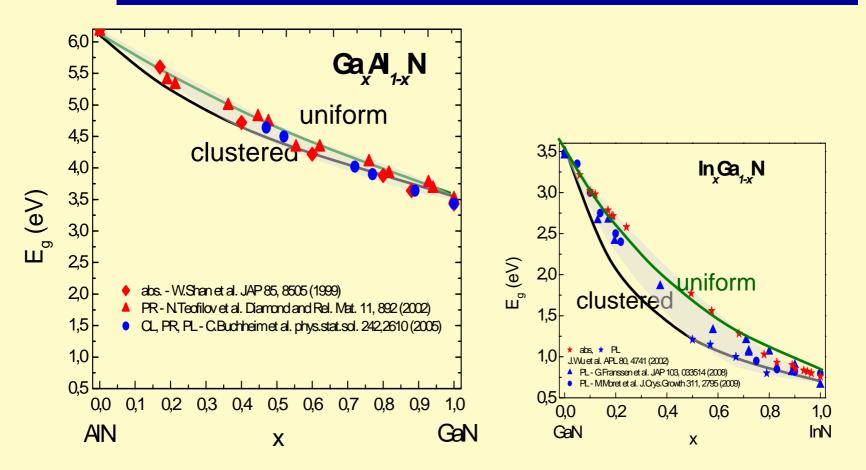




- 1. Significant bowing of E_g vs. x obtained by calculations with much more pronunced effect for clustered In-distribution
- 2. Calculations reproduce lage spreading of data suggesting presence of In-clustering

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

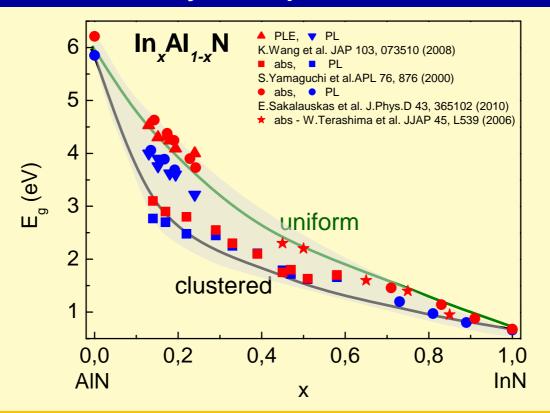




For $Al_xGa_{1-x}N$ very small bowing of E_g vs. x obtained by calculations with slightly more pronunced effect for clustered Al/Ga distribution

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



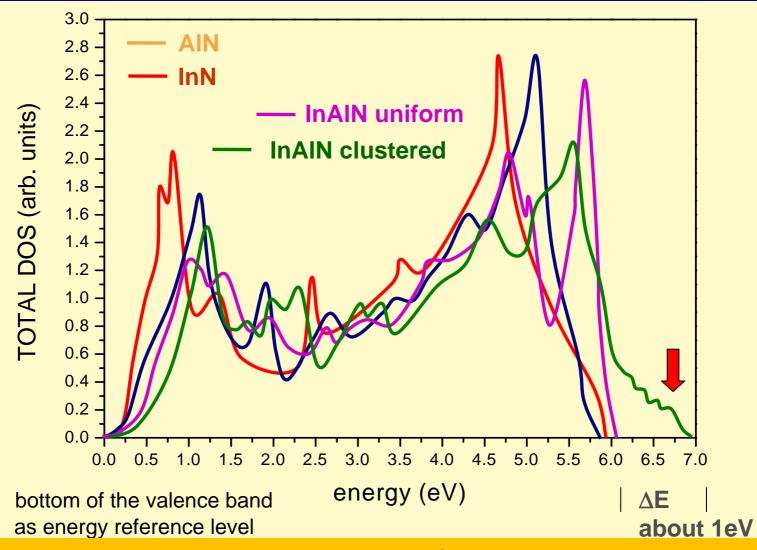


- 1. For $In_xAI_{1-x}N$ huge bowing of E_g vs. x obtained by calculations with much more pronunced effect for clustered In-distribution
- 2. Calculations reproduce lage spreading of data suggesting presence of In-clustering.
- 3. Role of In (In-N bonds) seems to be crucial

Valence-band density of states (VB DOS)



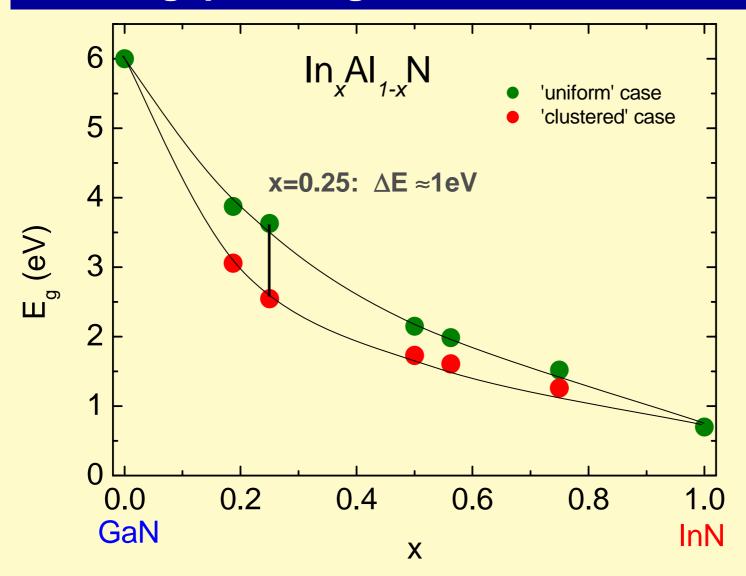
Comparison for various nitrides

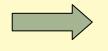


Which atomic states are responsible for the valence band width expansion? Partial DOS

Bandgap bowings – results od calculations



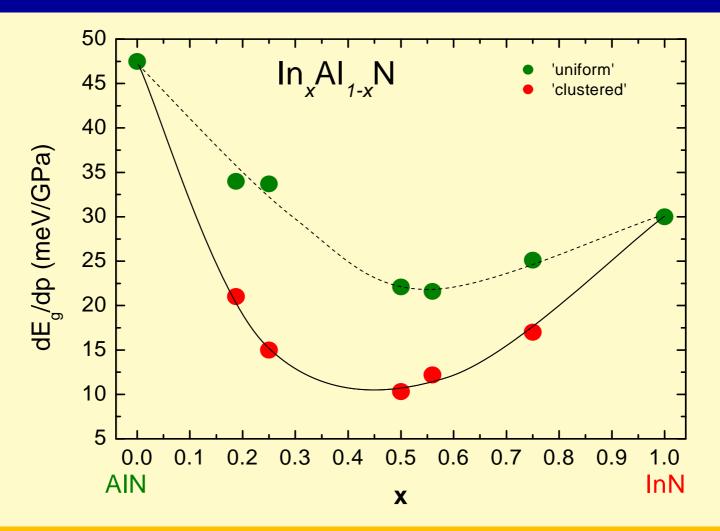




Decrease of the band gap comes from the valence band width reduction

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



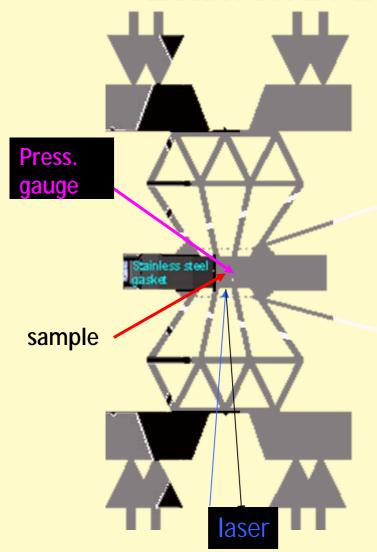


Predicted magnitude of pressure coefficient for clustered case much lower than for binary compounds. A chance for verification.

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



Diamond Anvil Cell

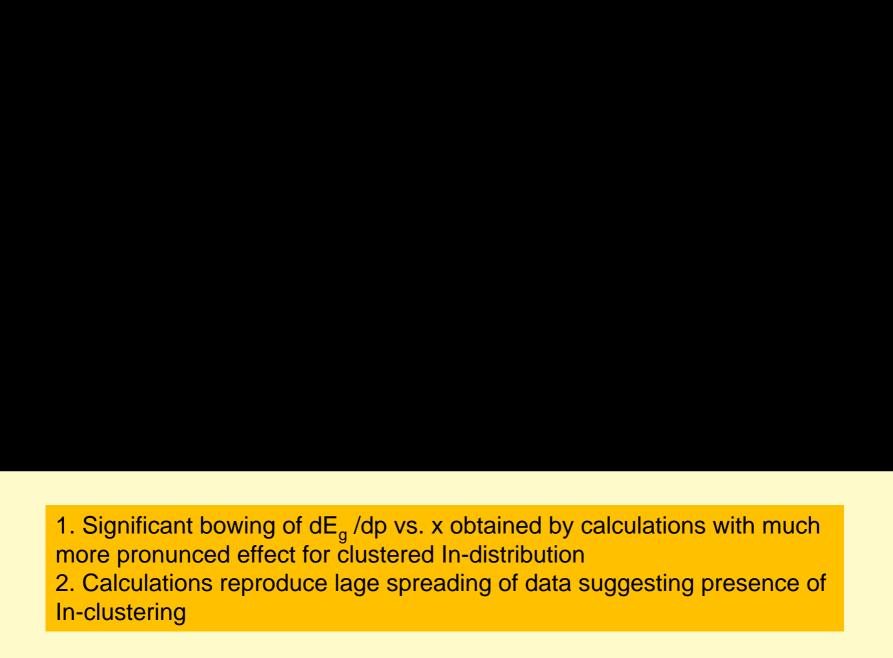


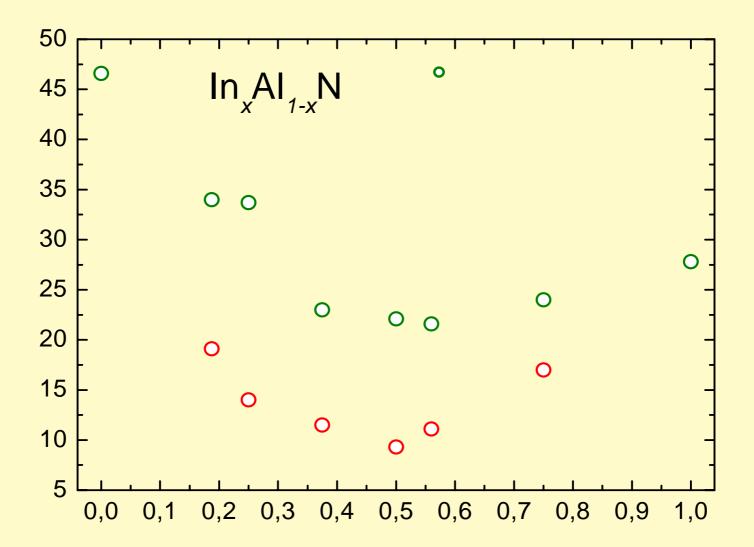


Solid argon as pressure transmitting medium



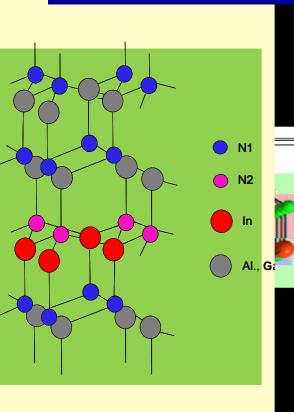
Pressure units: 1 atm = 1 bar; 10 kbar=1 GPa



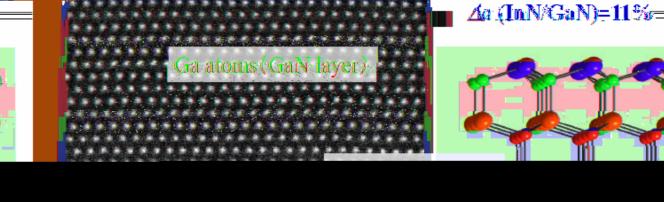


Our studies of In-segregation very useful for description of real (artificial) structures _ Short Period Superlattices of InN/GaN





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

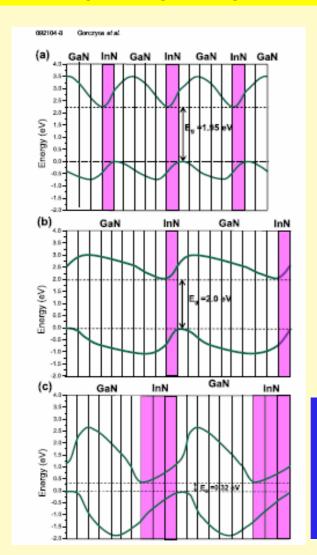


Idea Prof. Yoshikawa (Chiba University); Growth Prof. Wang (PKU)
Theory and pressure studies UNIPRESS; Cryst. Growth and Design (2012), APL (2012)

Very fruitful collaboration with School of Physics Peking University

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





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

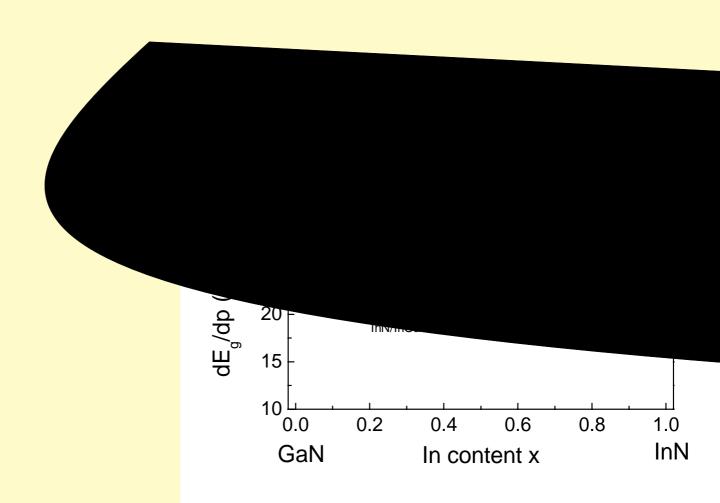


There is a tendency to In-segregation even in *perfect* InGaN and InAllN layers/structures

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 <u>imperfect</u> InGaN and InAllN 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.



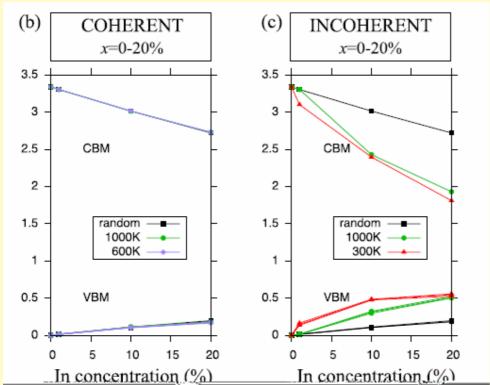
Incoherent alloys (InGaN) demonstrate strong decrease of band gap - sophisticated calculations



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



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