Fields modification in high Al or In content III-nitrides

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Outlines

- Research background
- Theoretical methods & experimental details
- Fields modification
  - Control of crystal fields
    - Polarity in AlN
    - Inhomogeneity in InN
  - Compensation of anisotropy crystal field
    - Asymmetric (GaN)m/(AlN)n superlatices
  - Modification of internal electric field
    - Mg- and Si-δ codoped superlattices
  - Modification of misfit stress field
    - Ultrathin compressive strained InN/GaN MQWs
- Conclusions

Research background
Applications

- **Light Emitting Diodes**

  Blue, green, and white

- **Laser Diodes**

  Blue

- **Photo Detectors**

  Ultra Violet

- **High Power and High Temperature Transistors**

  Military, automobile and aircraft

LEDs are most widely used devices

Research background
LED applications

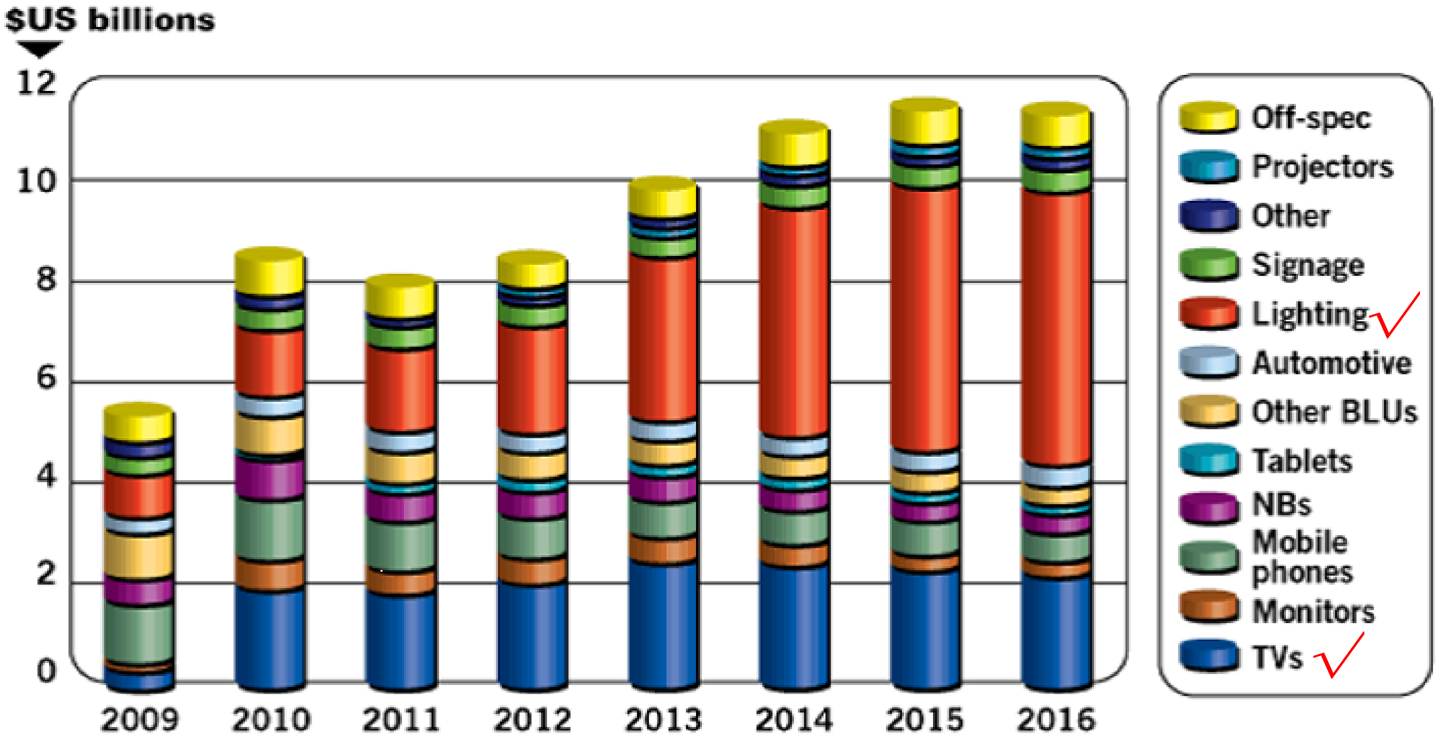


Figure. 2009-2016 packaged GaN LEDs by application. SOURCE: IMS Research.

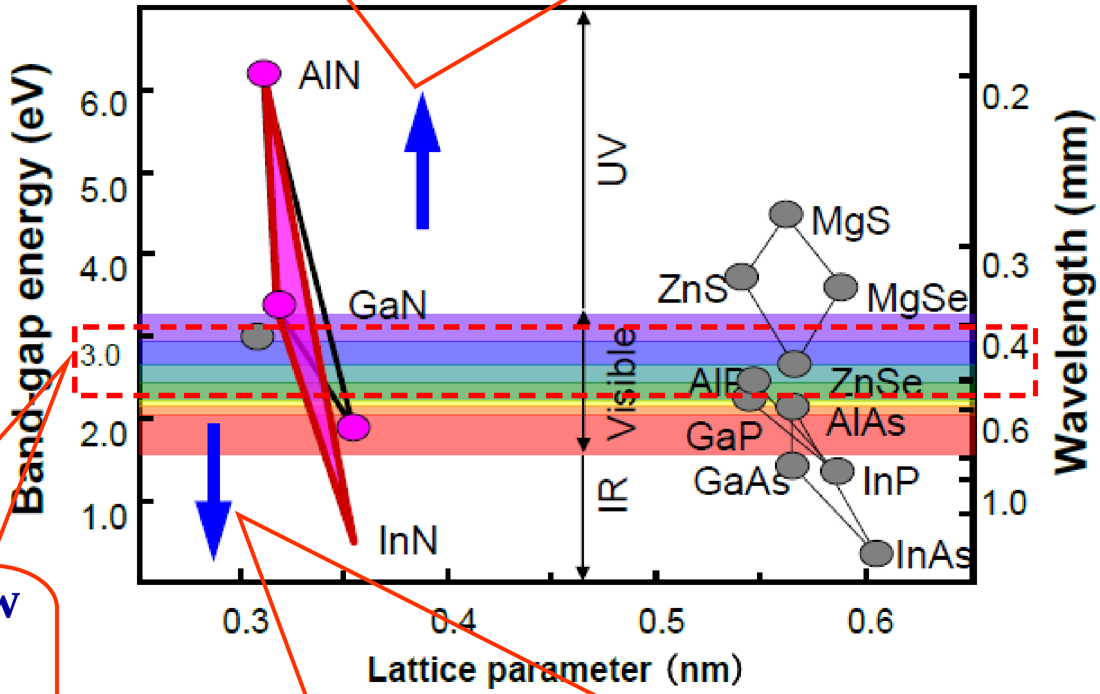
Most TVs are using III nitride LEDs as backlight
Lighting is expected to grow quickly in the near future

All of these are changing our lifestyle

Research background

Potentials of high Al or In content III nitrides

If high Al content III nitride materials and devices are developed, our manner would be profoundly changed.

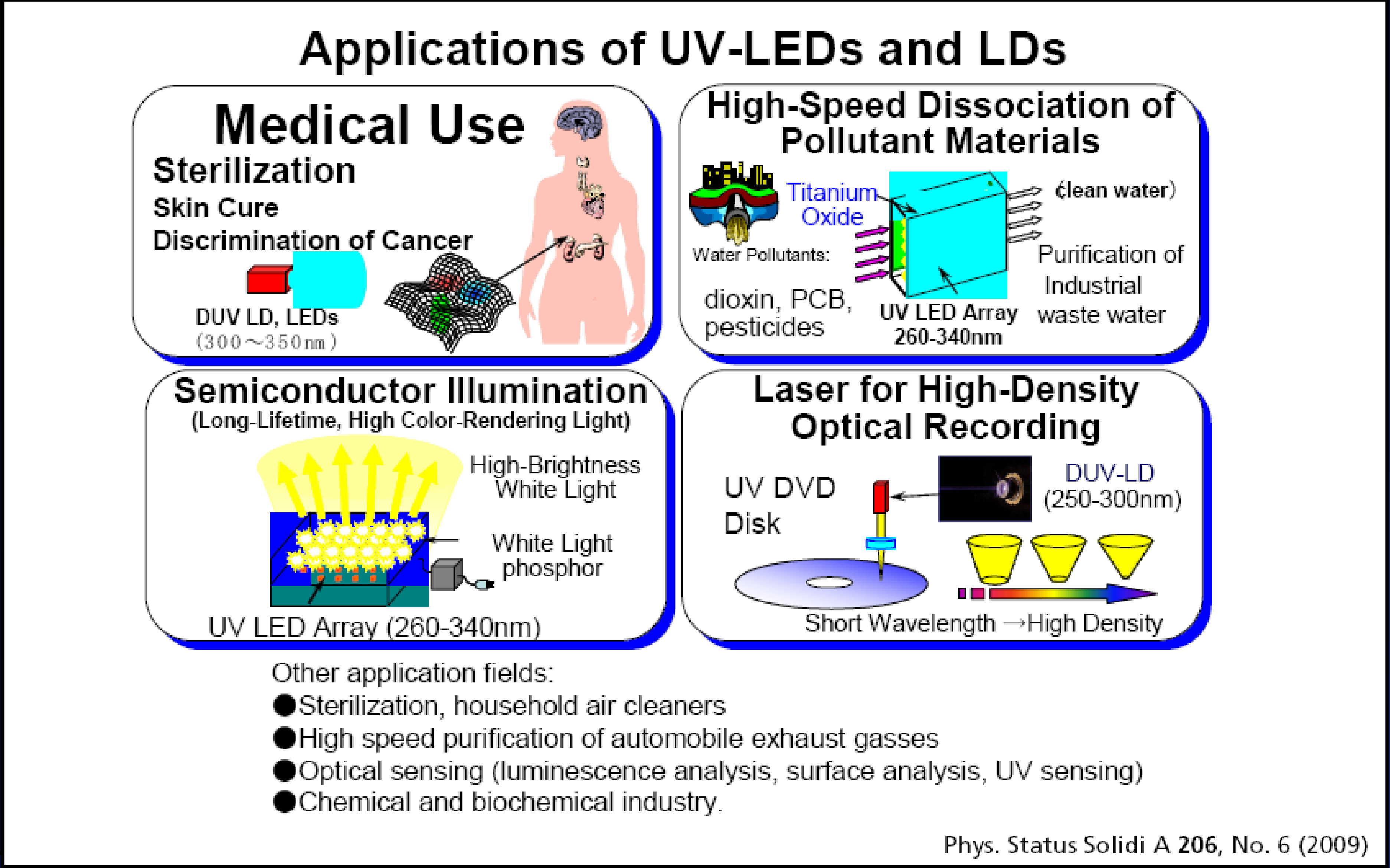


Only a narrow range of III nitrides has been used

If high In content materials can be grown well, III nitride devices would replace almost components made of other semiconductors.

Research background

Why high Al content III nitrides are so attractive ?



Applications of UV-LEDs and LDs

Medical Use

Sterilization

Skin Cure

Discrimination of Cancer

DUV LD, LEDs
(300～350nm)

High-Speed Dissociation of Pollutant Materials

Titanium Oxide

(clean water)

Water Pollutants:

dioxin, PCB, pesticides

UV LED Array
260-340nm

Purification of Industrial waste water

Semiconductor Illumination
(Long-Lifetime, High Color-Rendering Light)

High-Brightness White Light

White Light phosphor

UV LED Array (260-340nm)

Laser for High-Density Optical Recording

UV DVD Disk

DUV-LD
(250-300nm)

Short Wavelength →High Density

Other application fields:

- Sterilization, household air cleaners
- High speed purification of automobile exhaust gasses
- Optical sensing (luminescence analysis, surface analysis, UV sensing)
- Chemical and biochemical industry.

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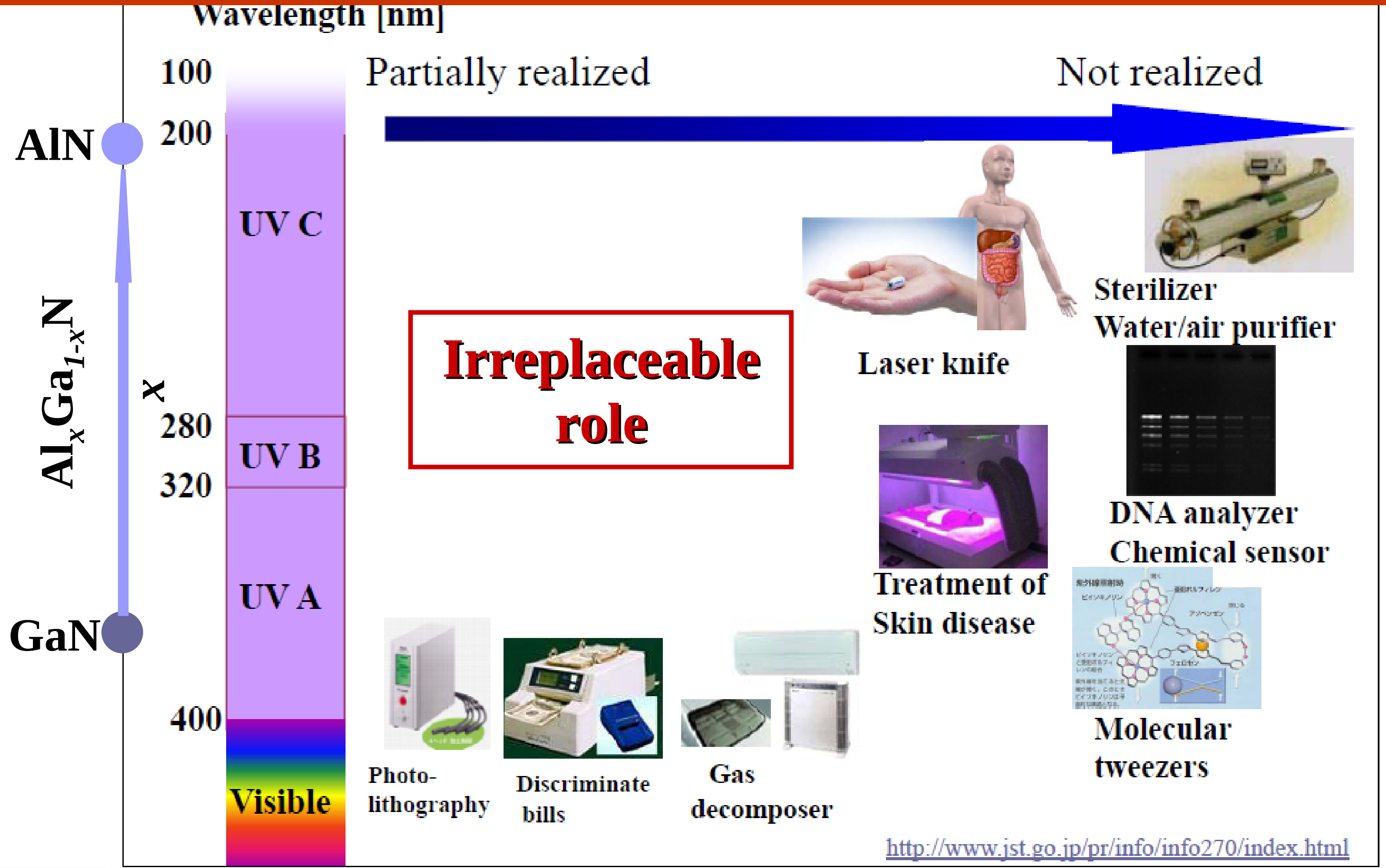
Research background

Potentials of high Al content III nitride

High Al content nitride is only one semiconductor system extending from UVA to UVC



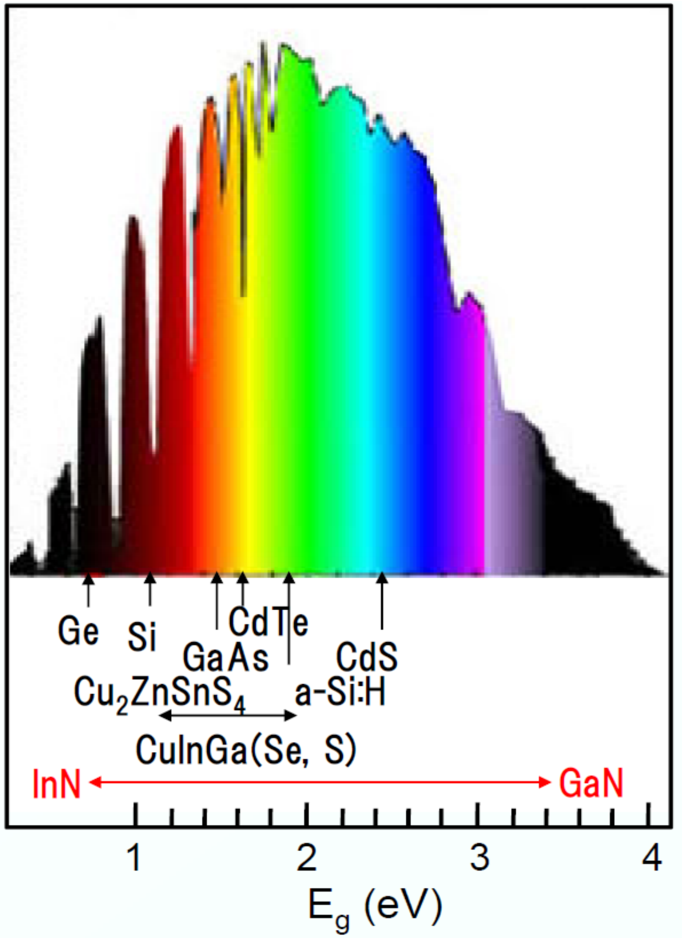
Irreplaceable role

http://www.jst.go.jp/pr/info/info270/index.html

Research background

Potentials of high In content III nitrides

High In content nitride is only one semiconductor system covering almost solar spectra



- **The direct band gap from 0.7 to above 2.4 eV allowing multiple junction solar cell fabrication using one material system.**
(Such wide band gap is not available in other established material systems)
- **High radiative efficiency even with high dislocation densities**
- **High mobility allowing good collection**
- **A large piezoelectric constant allowing control of surface recombination**
- **An existing industry centered around the nitrides**

Research background

Problems

Fundamental and technologic problems

- **Lower crystalline quality**

  Strong misfit stress field

  Polar mixing

  Phase separation

- **Lower recombination efficiency**

  Strong polarization field

  Optical anisotropy

- **Lower *p*-type conductivity**

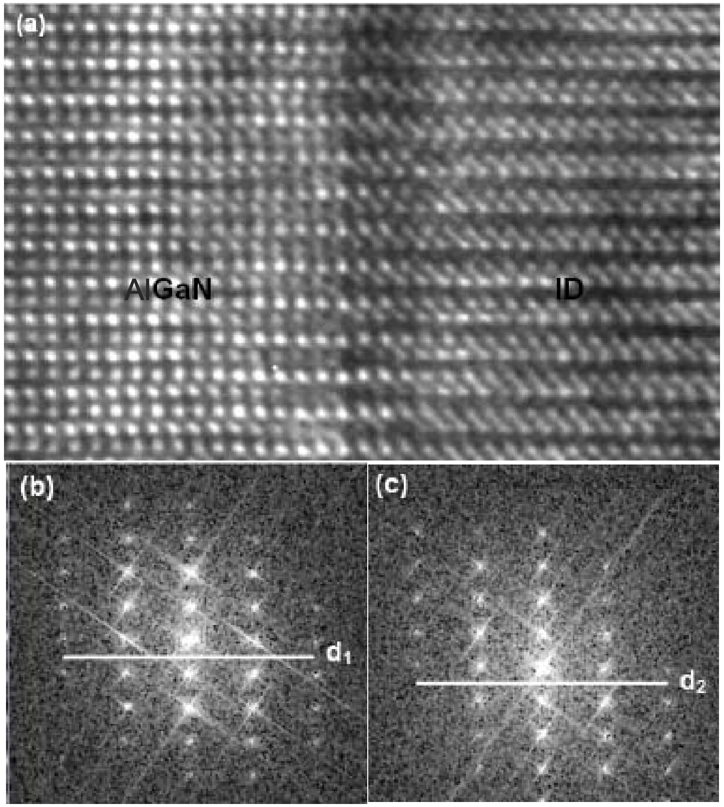
  Large thermal activation energy of acceptor in high Al content nitrides

Close relation with the fields in III nitrides

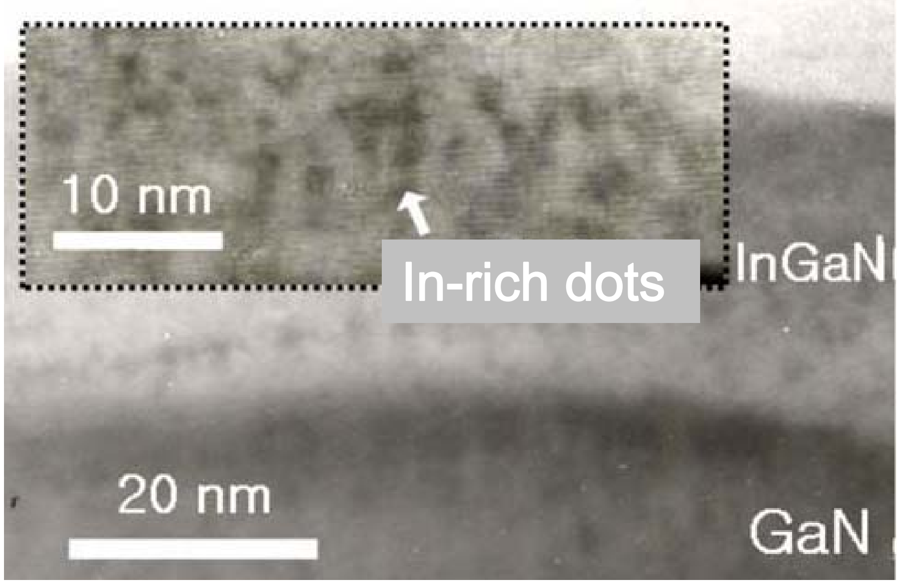
Research background

Problems

Lower crystalline quality is caused by inhomogeneous crystal field



(a) Cross-sectional HRTEM image of AlGaN layer at a **inversion domain** boundary. (b) and (c) inversion domain regions.



Cross-sectional TEM images of InGaN layer a grown on a GaN surface. The inset shows **In-rich dot** regions.

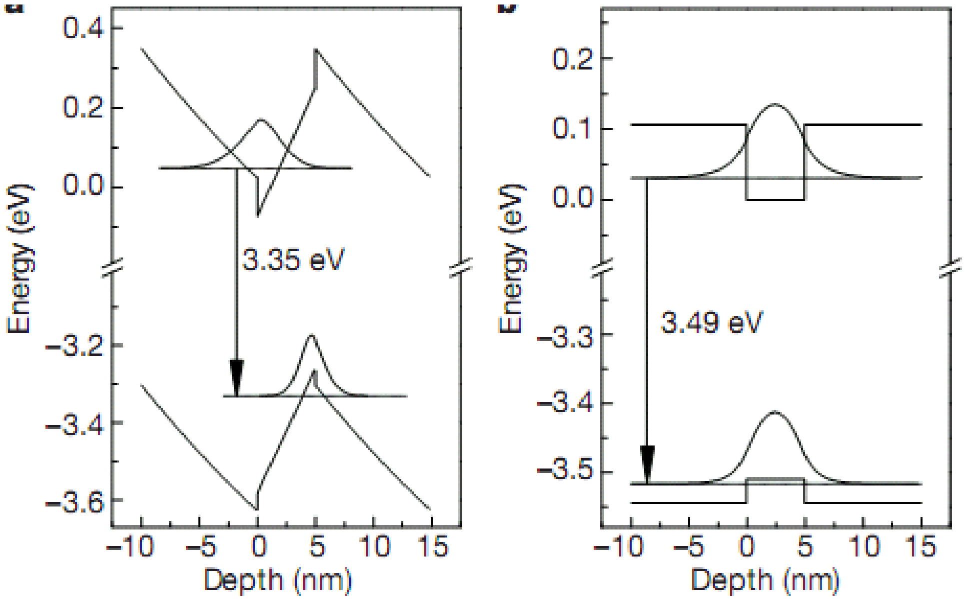
If people want to control the fields well

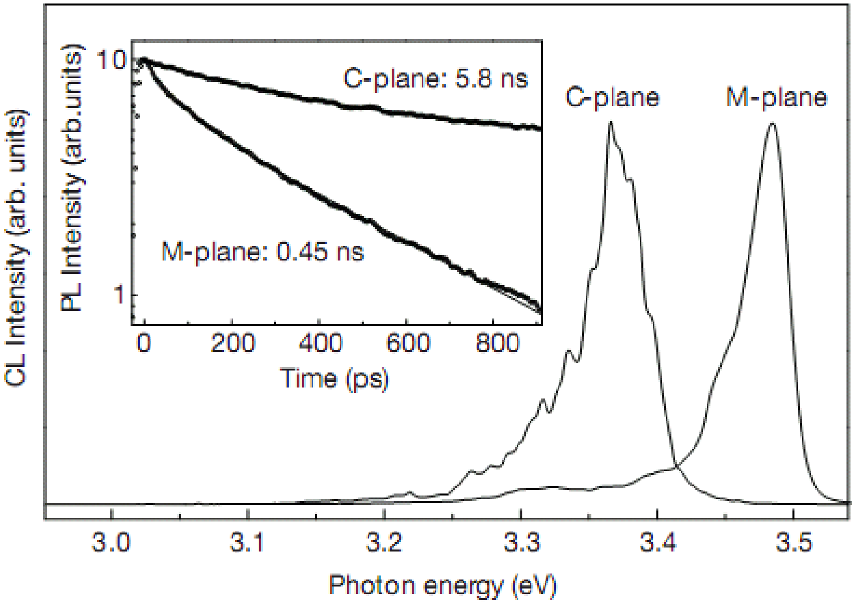
What happen during epitaxy ?
How to grow homogeneously ?

Research background

Problems

Lower recombination efficiency is caused by strong polarization field





Quantum confined Stark effect leading to carrier separation in quantum well.

The effect can be deminished by fabricating QW on non-polar plane, but it is difficult to grow.

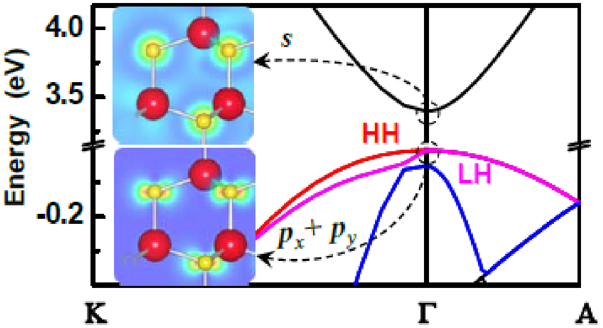
People should establish the methods

How to modify the polarization field ?
How to grow coherently under strong misfit stress field ?

Research background

Problems

Lower recombination efficiency is also caused by optical anisotropy

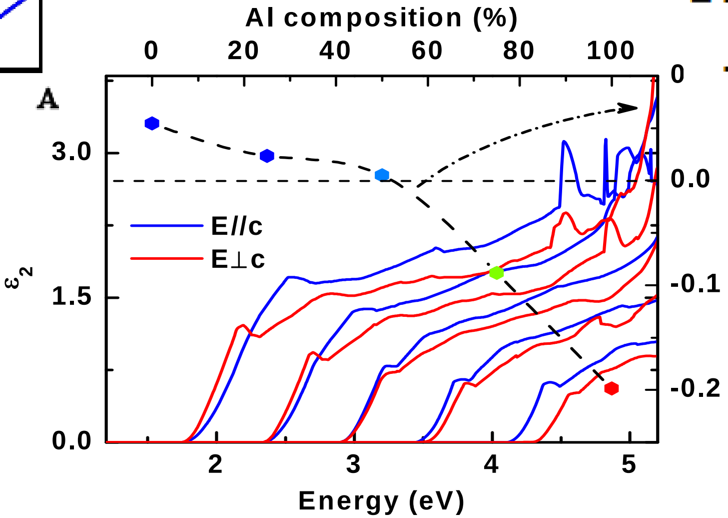


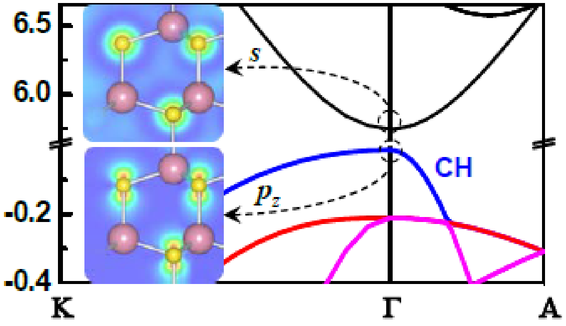
Heavy hole (HH) band Γ_6 （$x < 0.5$）

Favor for light extraction along *c* axis

(Ordinary light, E⊥*c*)

Top of valence bands in $Al_xGa_{1-x}N$





Crystal-field split hole (CH) band Γ_1 （$x > 0.5$）

Favor for light extraction vertical to c axis

(Extraordinary light, E//c)

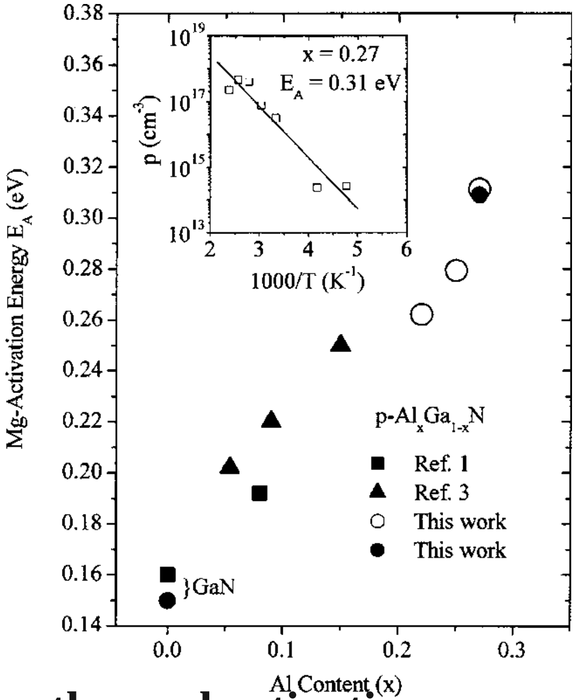
People are interested to know

Is it possible to change crystal field in high Al content nitride ?
How to realize optical isotropy to modify photon propagation ?

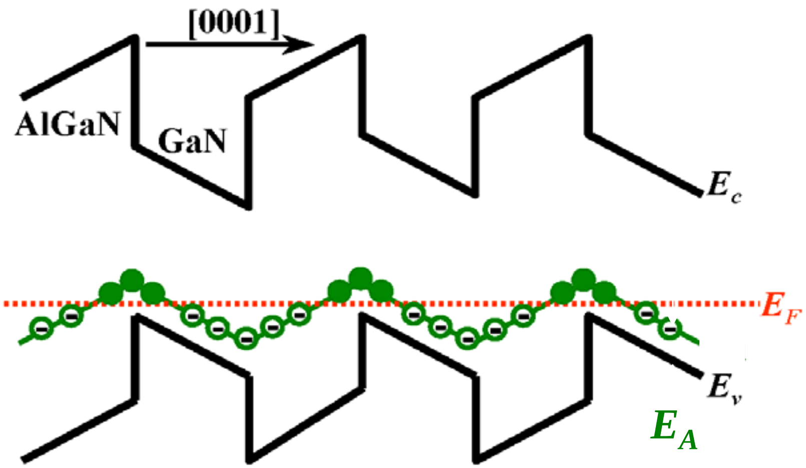
Research background

Problems

Lower p-type conductivity is caused by large thermal activation energy



Large thermal activation energy of Mg acceptor in high Al content AlGaN.



Conventional SL has be proposed to modify band bending so that part of Mg levels locate above Fermi level, but the modification is insufficient.

People like to develop method

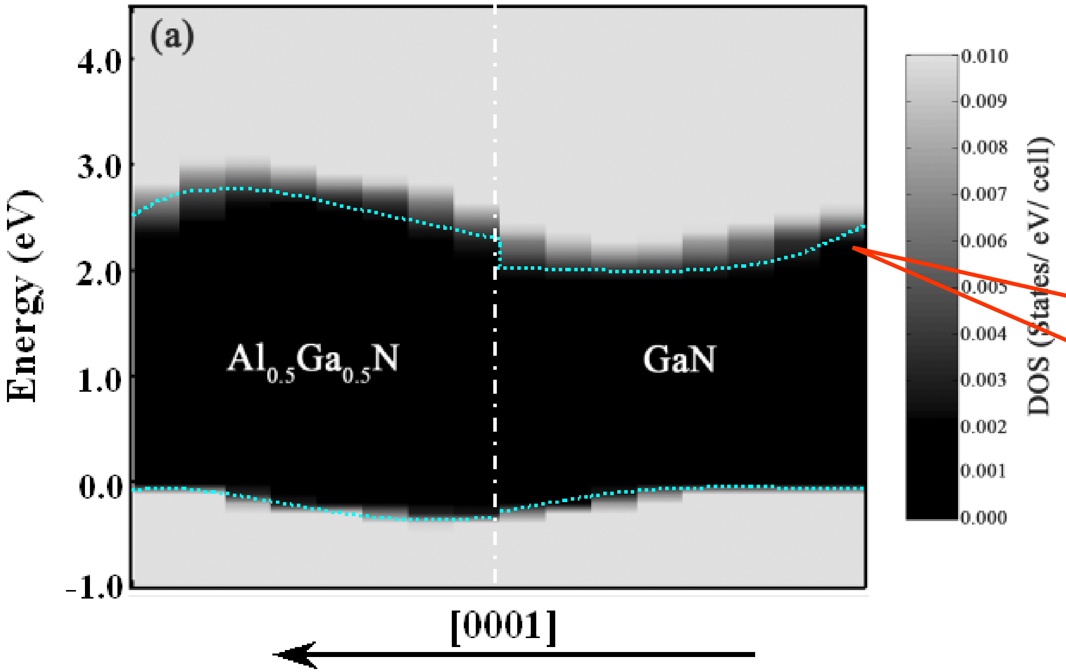
How to further modify internal field ?

Theoretical designs & experimental details

The first-principles calculation

Based on density function theory

- **Independence of experiential parameters**
- **Providing detailed information: atomic structure, wave function, charge density, potential, and energy**
- **Large system simulation: heterostructures, SLs, MQWs**

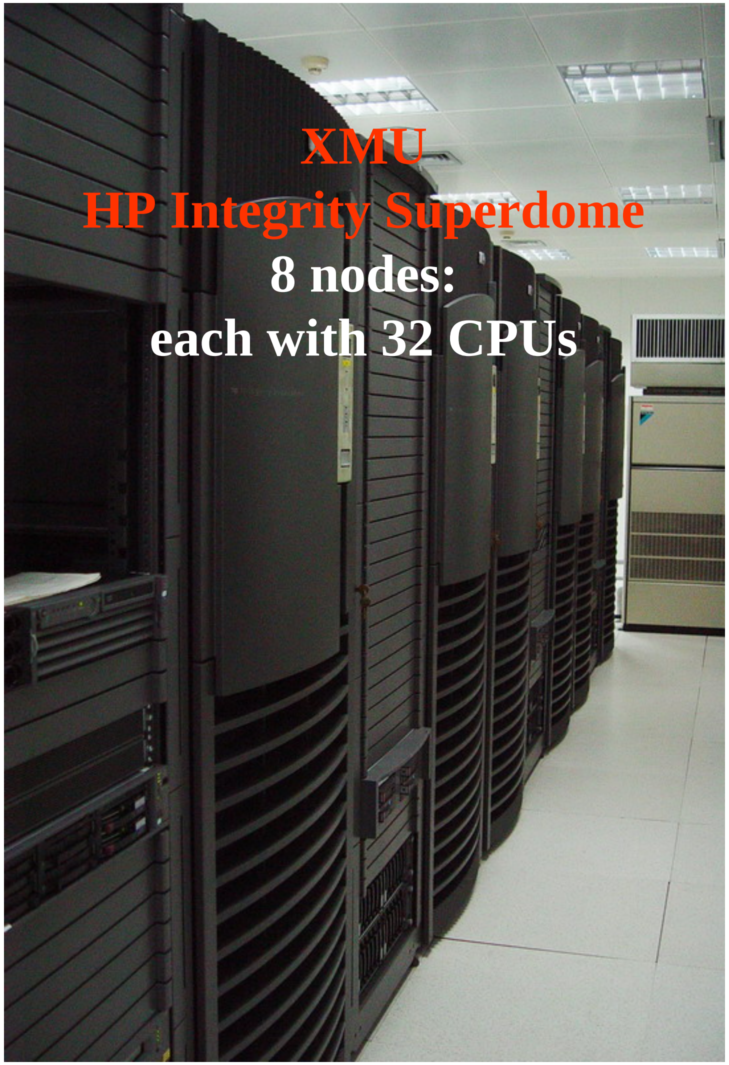


Band bending in the QWs

Calculated projected PDOS of different atomic layers are arranged along [0001] direction.

Theoretical designs & experimental details

Computers for theoretical designs

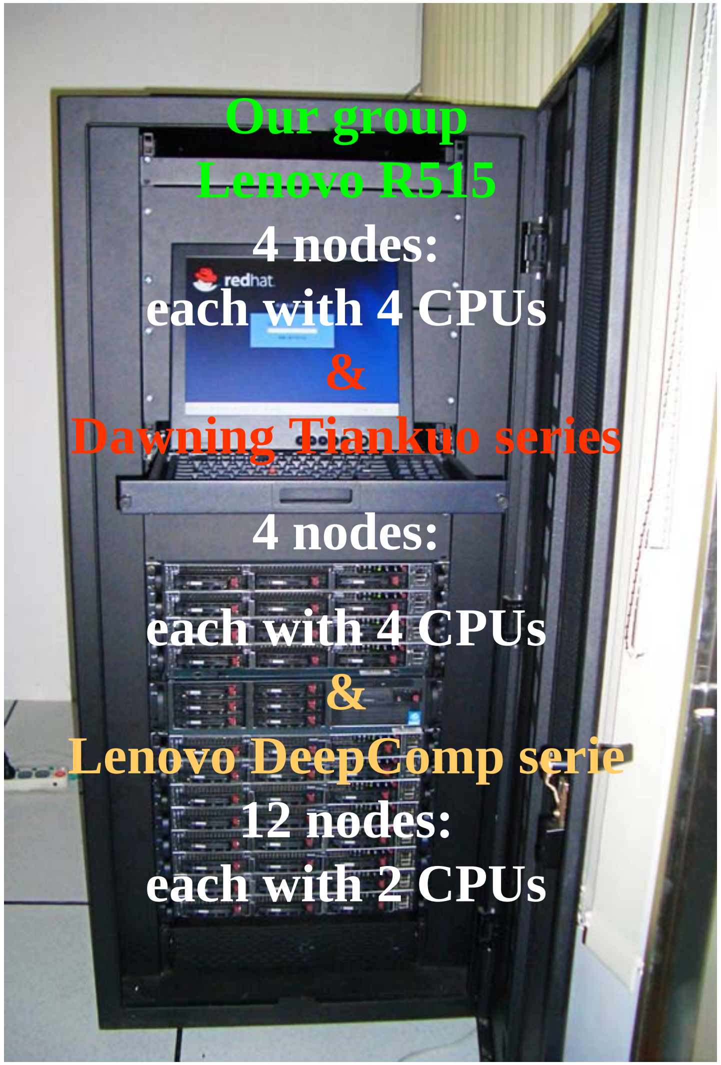


XMU

HP Integrity Superdome

8 nodes:

each with 32 CPUs



Our group

Lenovo R515

4 nodes:

each with 4 CPUs

&

Dawning Tiankuo series

4 nodes:

each with 4 CPUs

&

Lenovo DeepComp serie

12 nodes:

each with 2 CPUs

Theoretical designs & experimental details

Facility for epitaxy growth

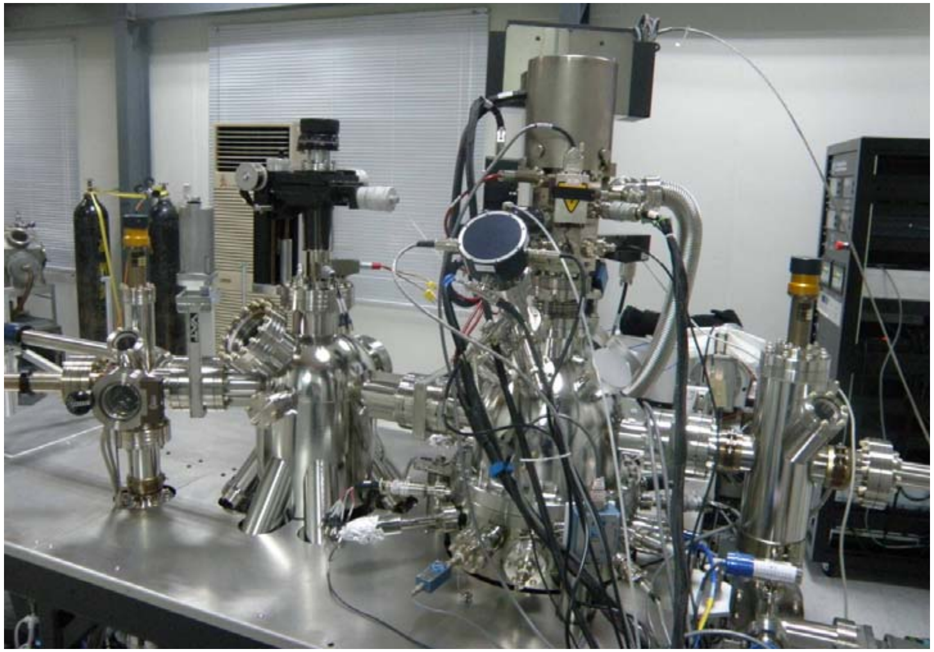
- **Growth system:** Thomas Swan MOVPE
- **Precursors:** TMG, TMI, TMA, NH_3, Cp_2Mg, and SiH_4

Thomas Swan 3×2 in. CCS

Theoretical designs & experimental details

Facilities for characterizations

in situ nano-structural comprehensive property measurement system



Functions

- SEM (spacial resolution 8.4 nm)
- CL (range 200-1000nm)
- STM & STS (atomic images)
- EL (carriers injection within structures smaller than 100nm)
- Temperature variation (in 6.6-1500K)
- Sample preparation

Theoretical designs & experimental details

Facilities for characterizations

Bede QC 200 XRD

Horiba Jobin Yvon UVISEL FUV Spectroscopic Ellipsometer

Accent HL5500 Hall system

Varian Cary 300

UV-visible spectrophotometer

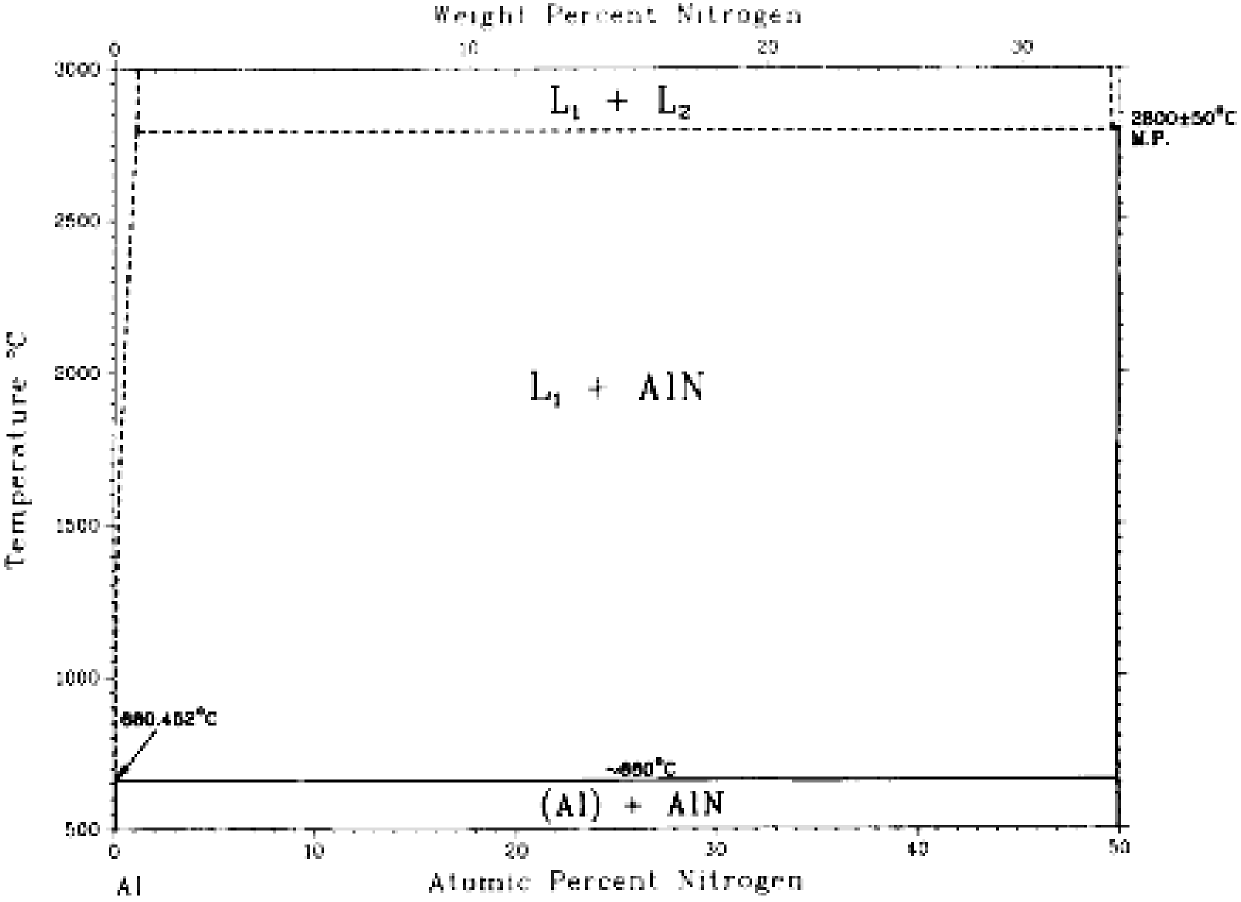
Control of crystal field

Polarity in AlN

High melting point
High pressure

by lower temperature epitaxy

Polarity mixture
Low crystalline quality

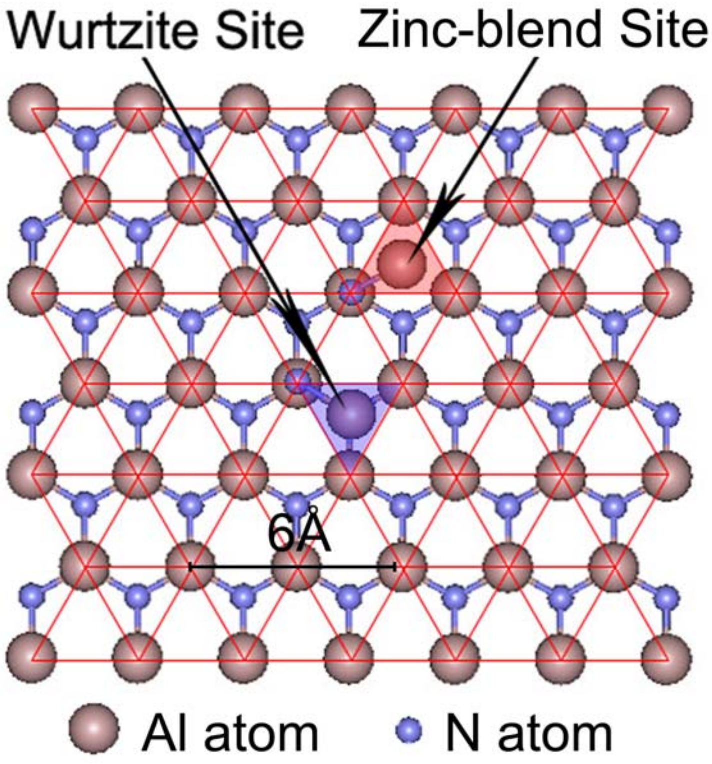


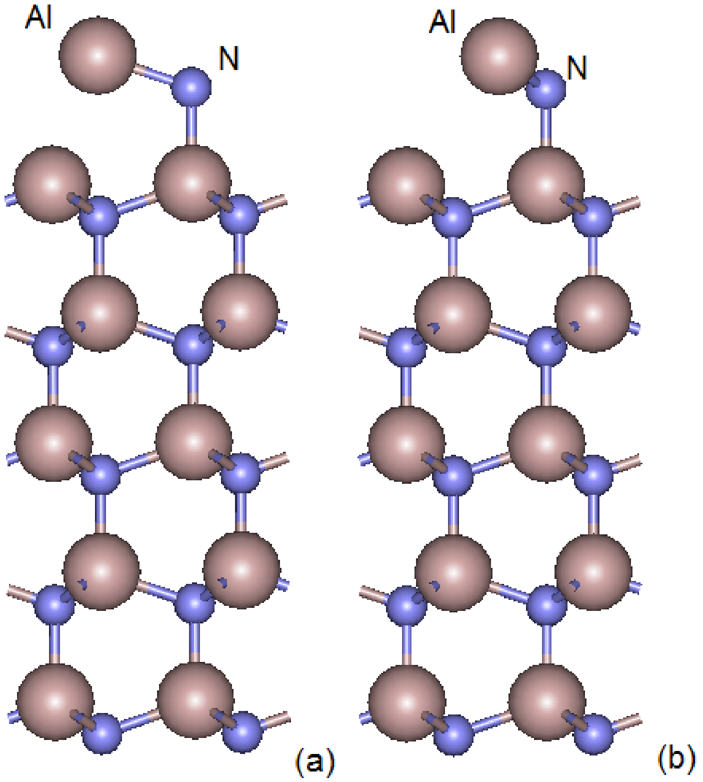
Influence on crystal field

Control of crystal field

Polarity in AlN

Monomer: AlN molecule





Because of severe pre-reaction between TMA and NH_3

Control of crystal field

Polarity in AlN

Ab initio calculation results

Al-polar surface

	Total Energy (eV)
E_{clean}	-364.385
E_{w1}	-377.533
E_{z1}	-377.448
E_{w2}	-393.284
E_{z2}	-389.11

N-polar surface

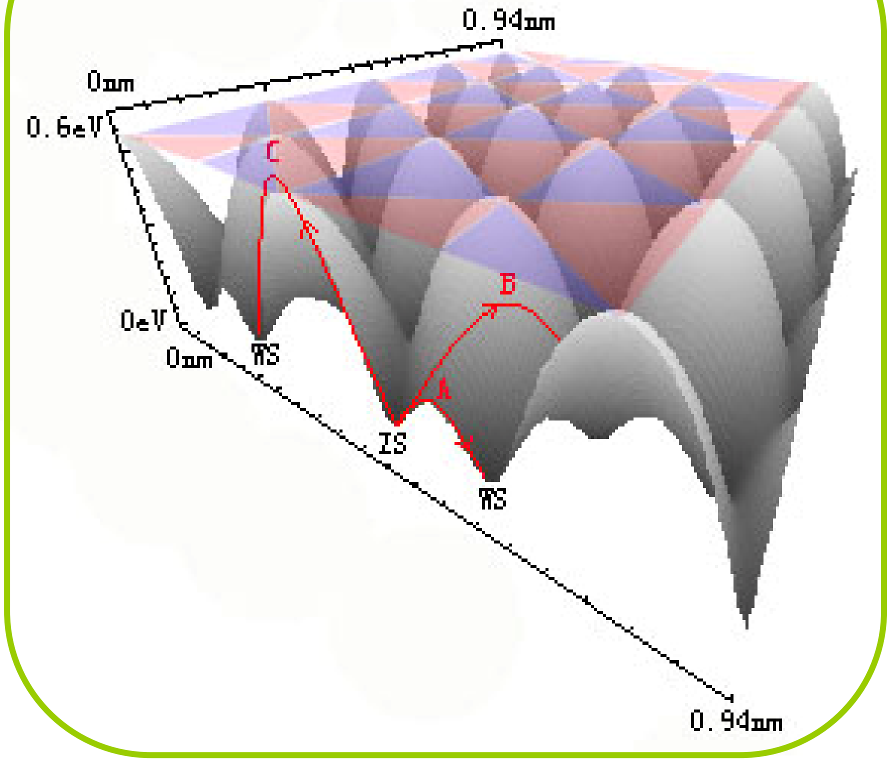
	Total Energy (eV)
E_{clean}	-359.599
E_{w1}	-371.857
E_{z1}	-369.838
E_{w2}	-380.676
E_{z2}	**-382.512**

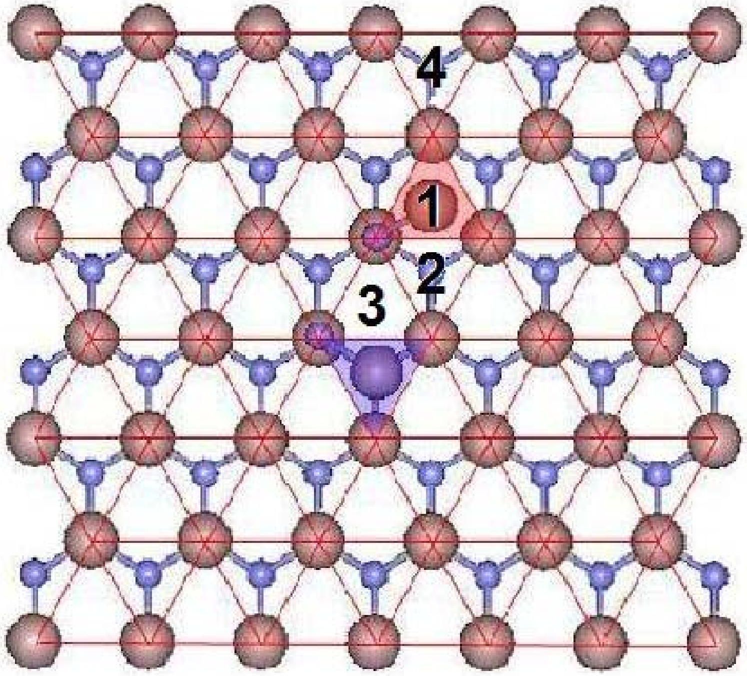
Control of crystal field

Polarity in AlN

Model for kinetic Monte Carlo simulation

Barrier heights of different paths





$$\upsilon = \upsilon_0 \exp\left(-\frac{\Delta E}{k_B T}\right)，\text{其中，}\ \Delta E = E_d^{w/z} + n_i E_b^{w/z} - n_j E_b^{w/z}$$

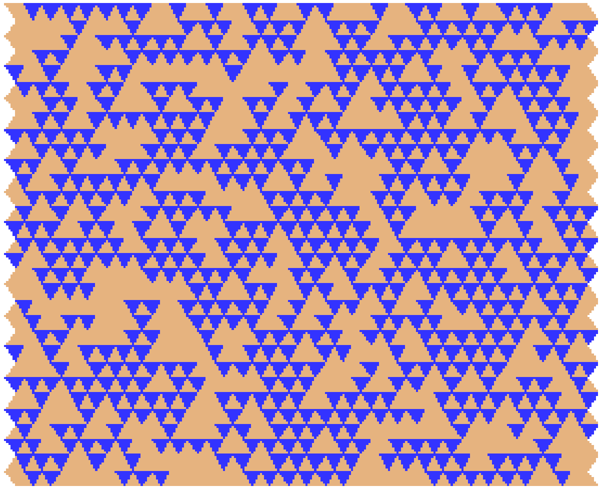
Control of crystal field

Polarity in AlN

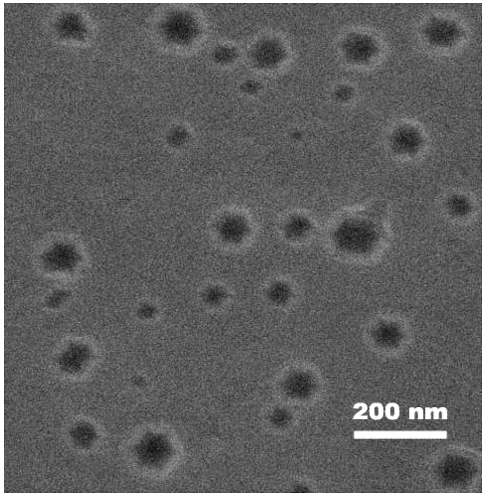
Monte Carlo simulations

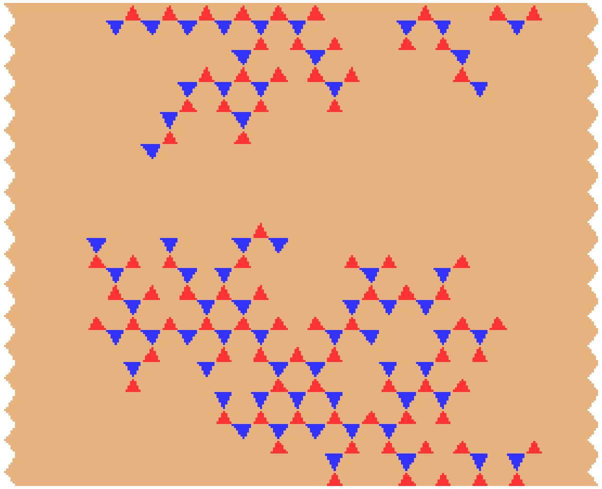
SEM images of epilayers

Structural phases

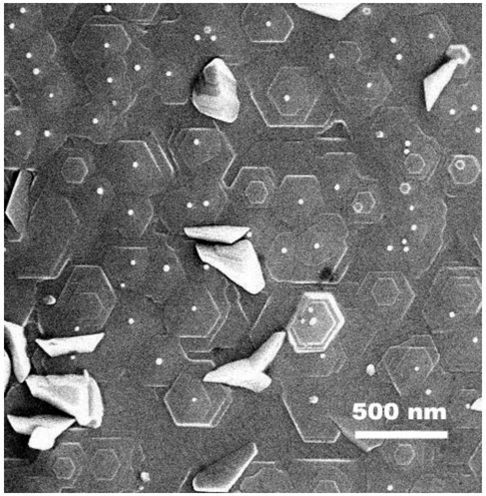


Pure wurtzite on Al-polar surface





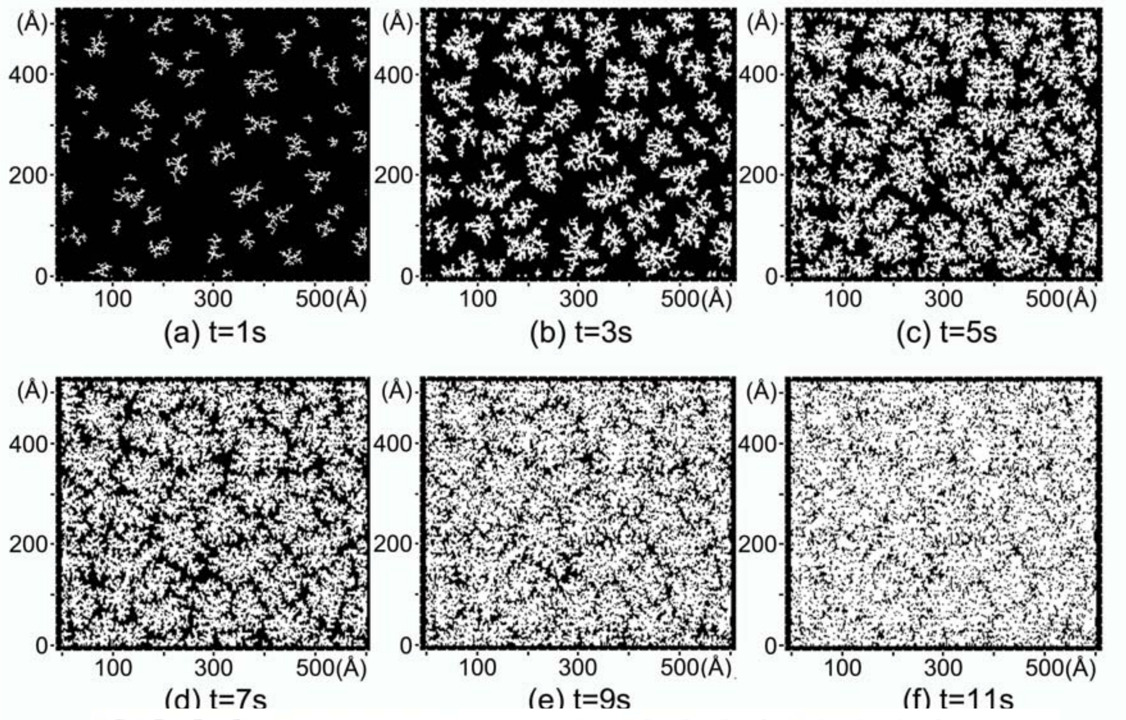
Mixed on N-polar surface



Control of crystal field

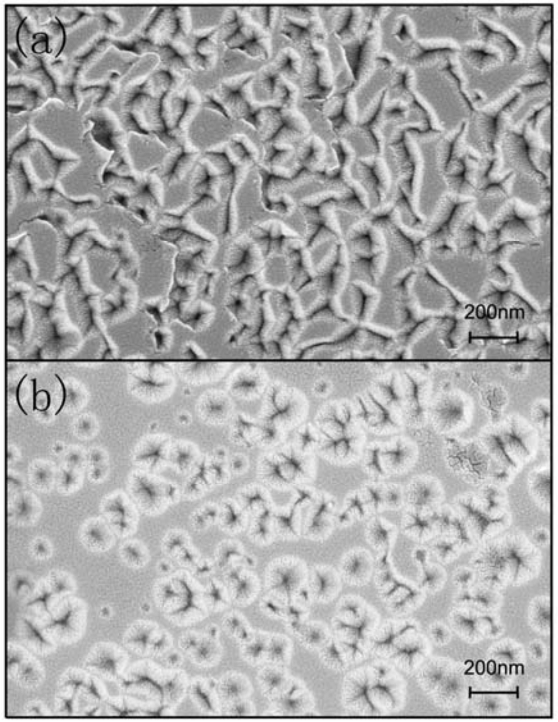
Polarity in AlN

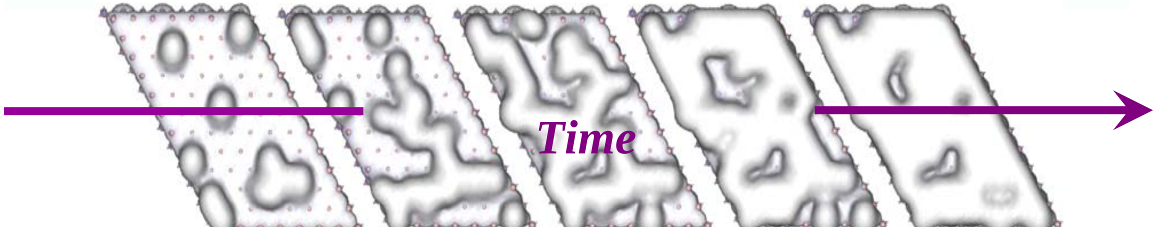
Kinetic process on Al-polar surface



(a) t=1s (b) t=3s (c) t=5s

(d) t=7s (e) t=9s (f) t=11s





Morphologies of Al-polar of different stages grown at 1373K.

Initiation from dendritic clusters → Adhesion forming continuous maze → Coalescence by fractal extension

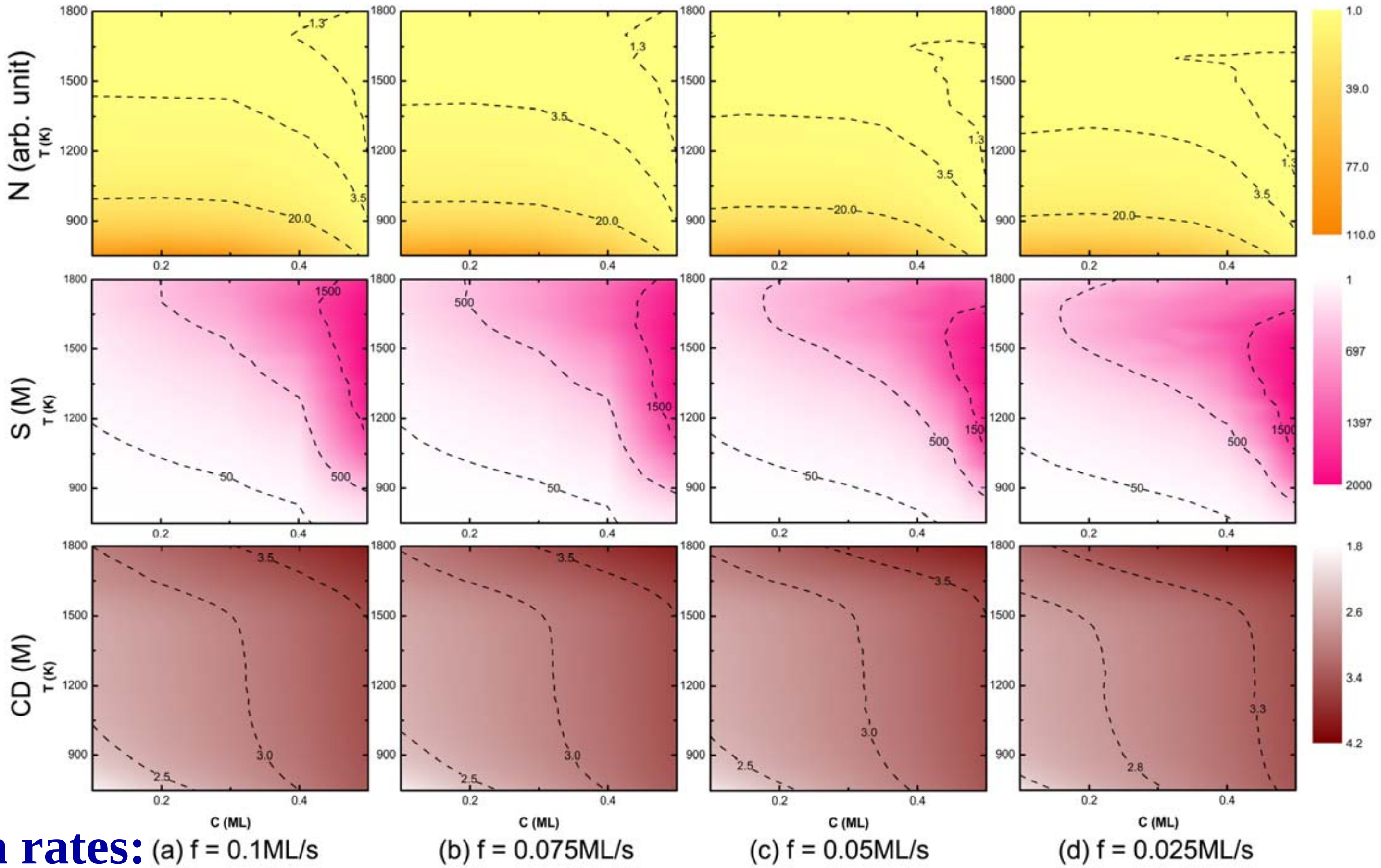
Control of crystal field

Polarity in AlN

Average cluster number

Average cluster size

Average cluster compact degree



Deposition rates: (a) f = 0.1ML/s (b) f = 0.075ML/s (c) f = 0.05ML/s (d) f = 0.025ML/s

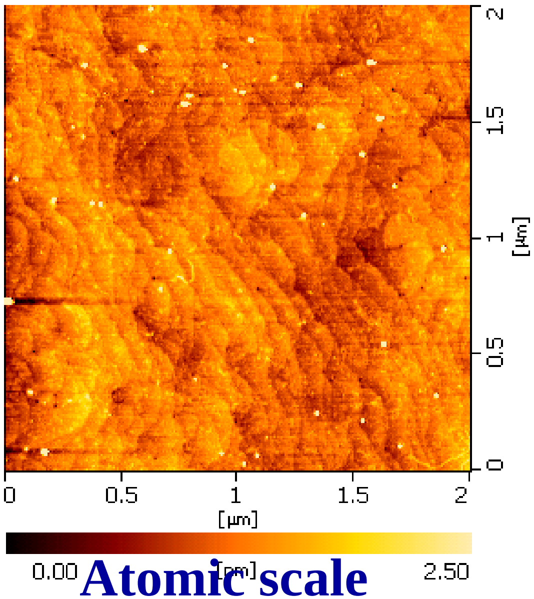
Coverage/temperature-kinetic phase diagrams

Change from fractal to compact mode: T>1650K

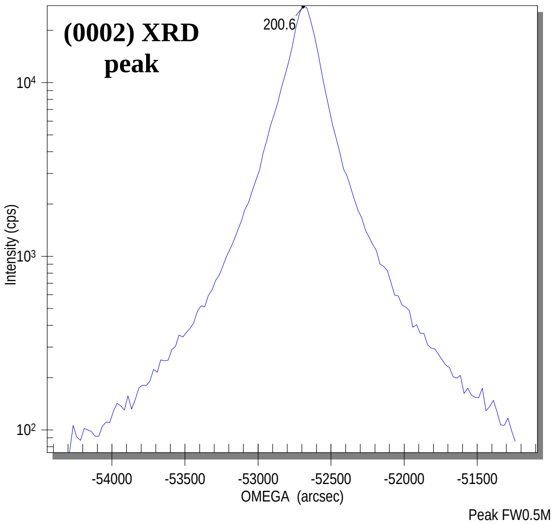
Control of crystal field

Polarity in AlN

AlN film grown at 1100^{o}C (1373K) with two step technique



Atomic scale surface step

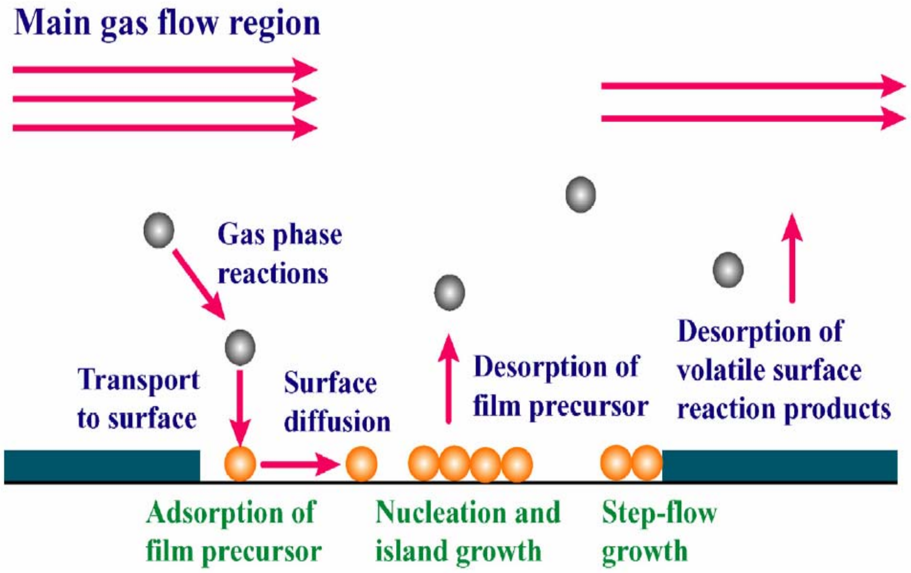


Lower dislocation density

Higher crystalline quality has been achieved in lower temperature

Control of crystal field

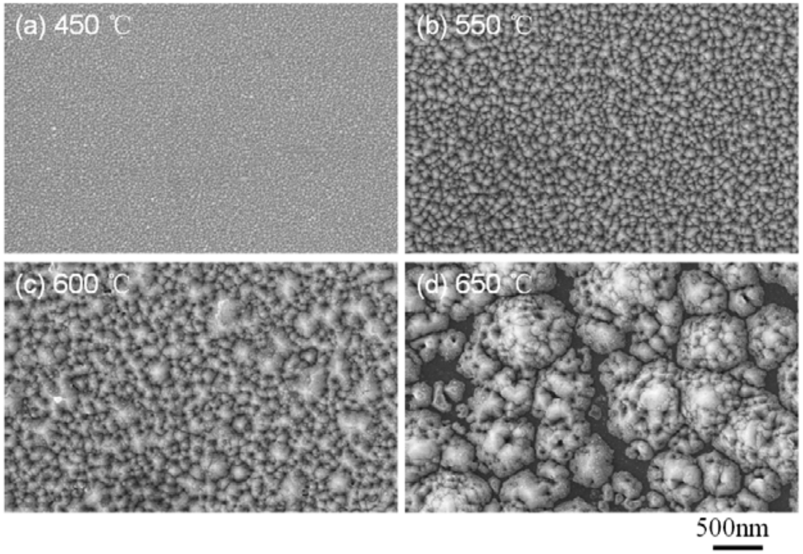
Inhomogeneity in InN



MOVPE depends on:

- Temperature
- Pressure
- V/III ratio

Inhomogeneity

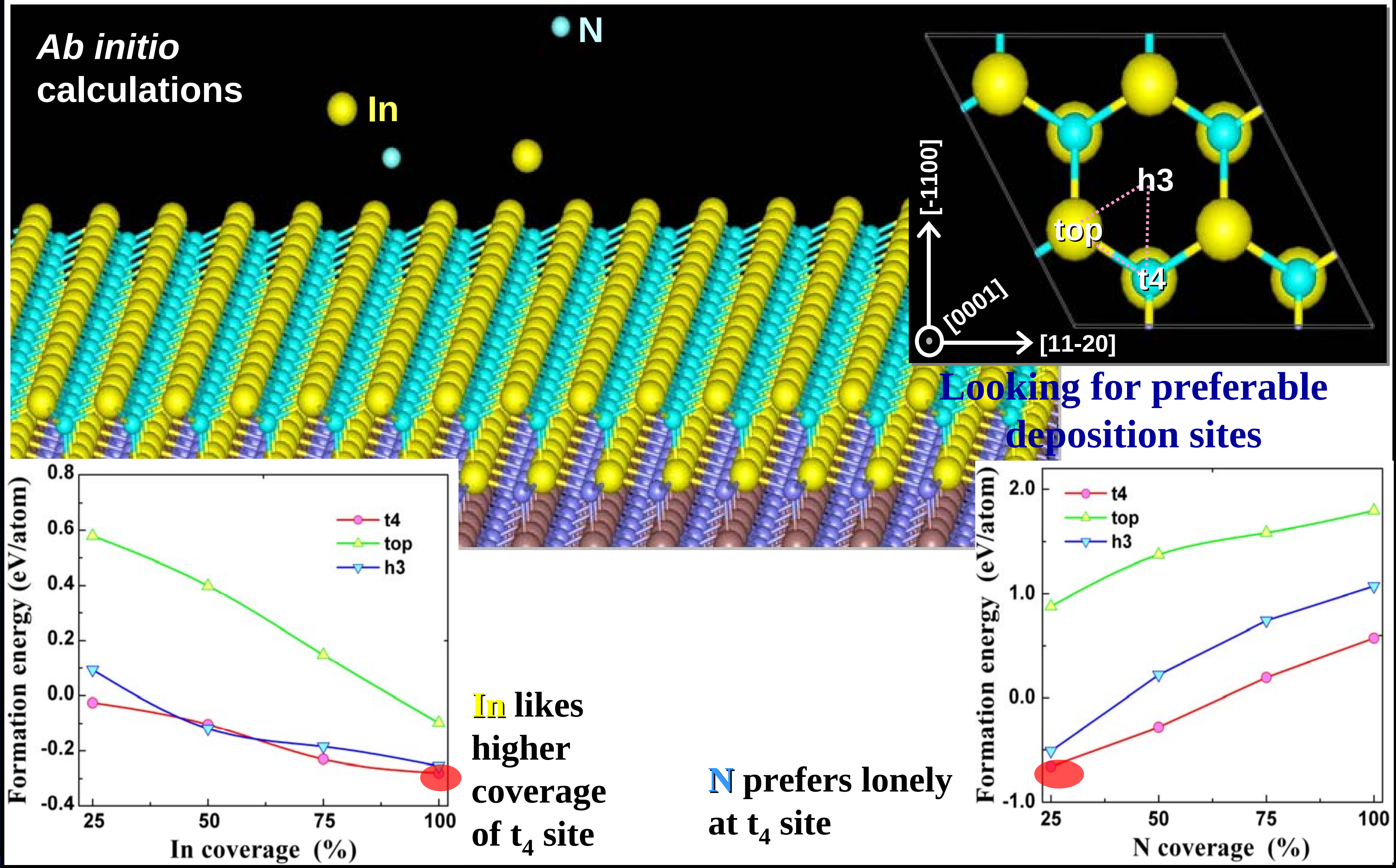


- Low InN dissociation temperature
- Extremely high equilibrium N vapor pressure over InN
- Low decomposition rate of NH_3 at low temperature

Severe influence on crystal field

Control of crystal field

Inhomogeneity in InN



Ab initio calculations

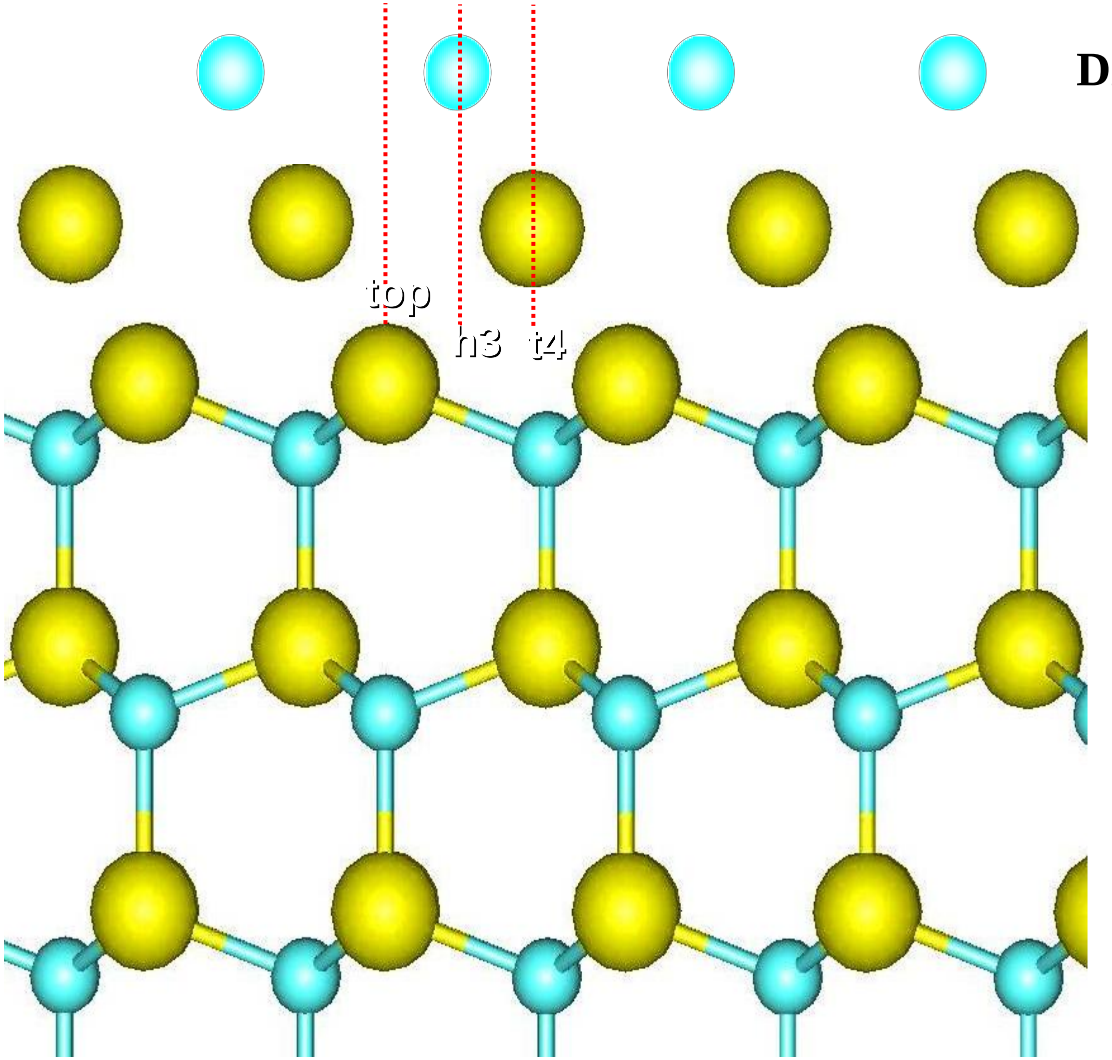
Looking for preferable deposition sites

In likes higher coverage of t_4 site

N prefers lonely at t_4 site

Control of crystal field

Inhomogeneity in InN



Diffusion path of N on In bilayer

E =

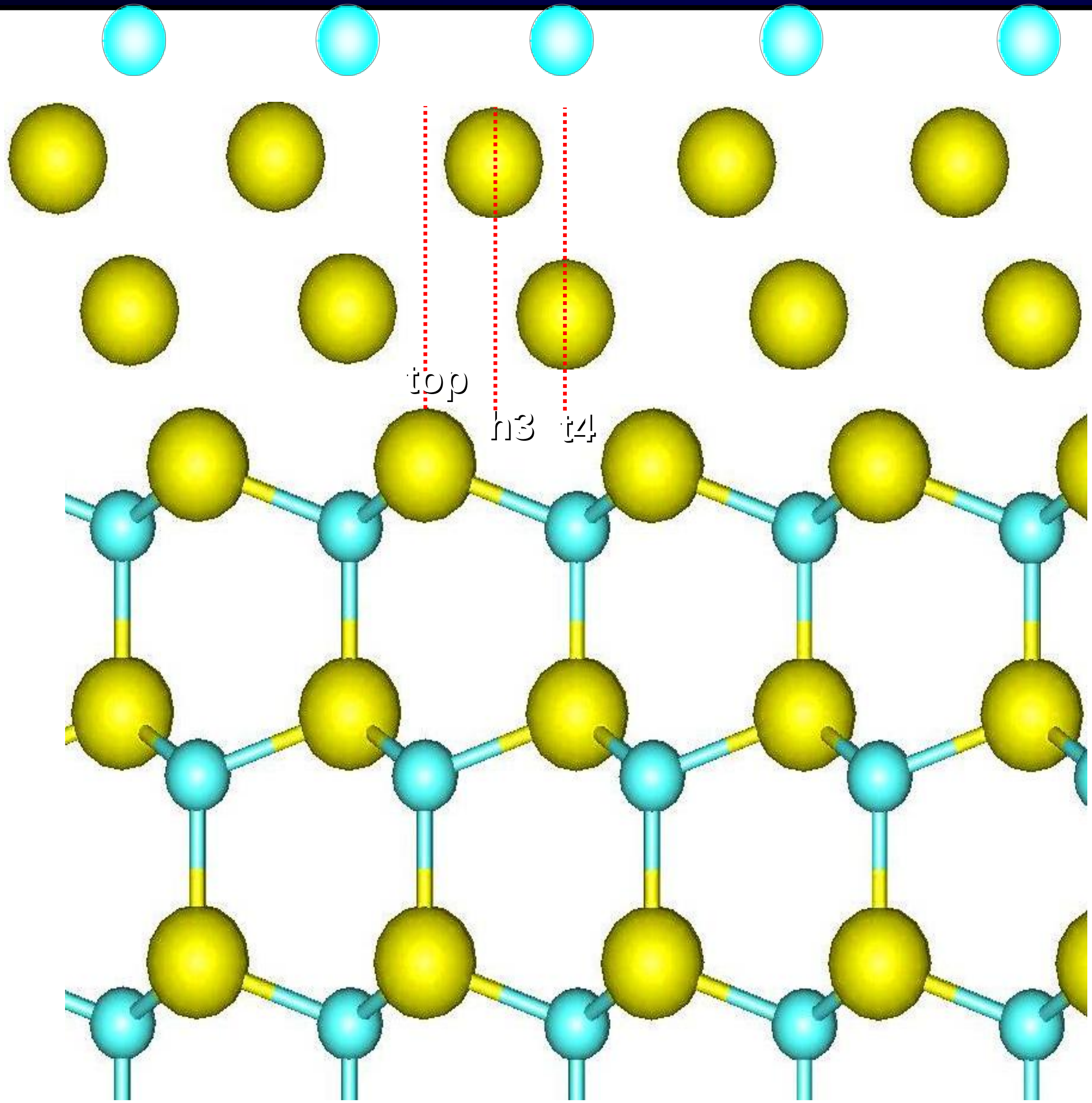
-313.0100 eV

N will penetrate into the interstitial space between In bilayer and

diffuse laterally to form tetrahedral coordination.

Control of crystal field

Inhomogeneity in InN



Nitrogen movement on In trilayer

E =

-321.5860 eV

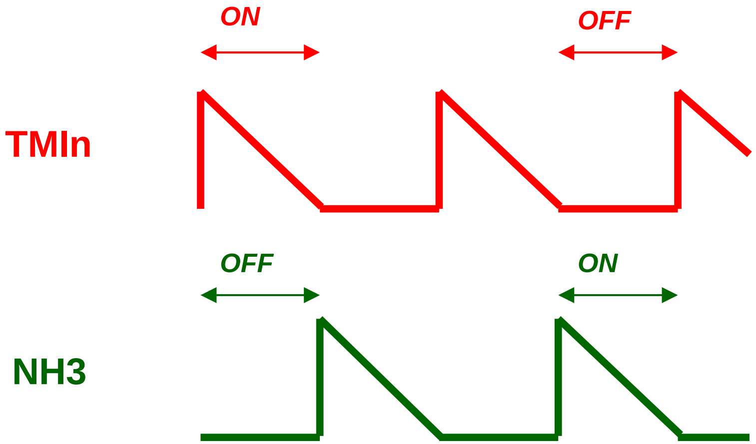
N can only pass through the top In layer !

Only In bilayer is helpful during epitaxy on In polar surface

Control of crystal field

Inhomogeneity in InN

Alternating supply technique to form the In bilayer

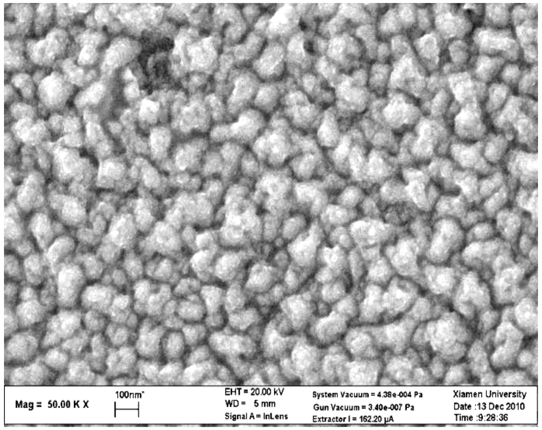


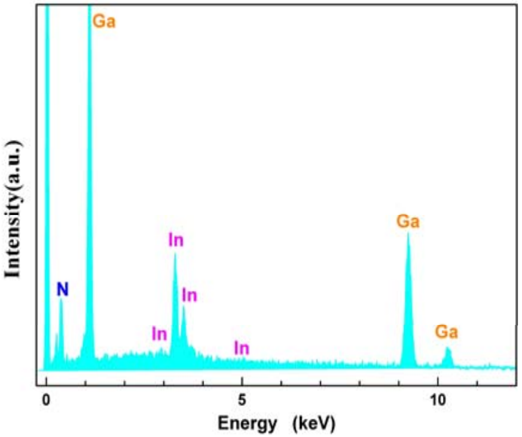
Sample	Time of TMIn(s)	Time of NH_3 (s)	T (℃)	P (Torr)
A	33	33	581.5	450
B	16	33	581.5	450
C	8	33	581.5	450
D	4	33	581.5	450

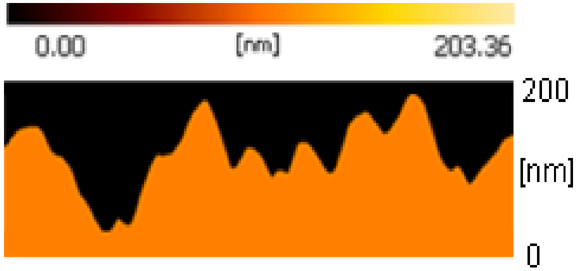
Control of crystal field

Inhomogeneity in InN

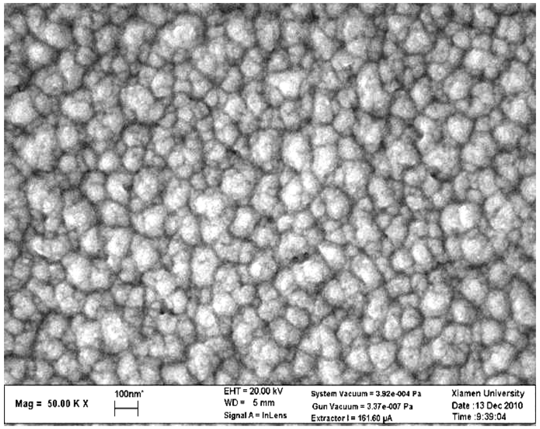
16 s

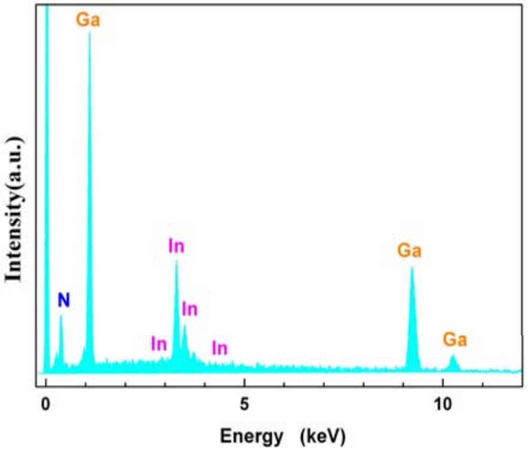


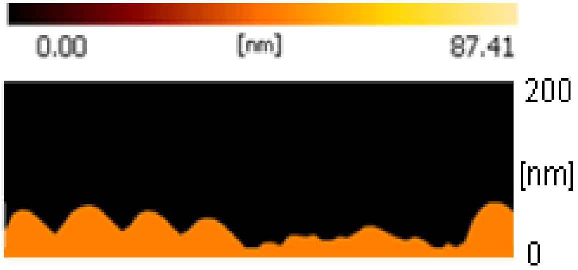




4 s





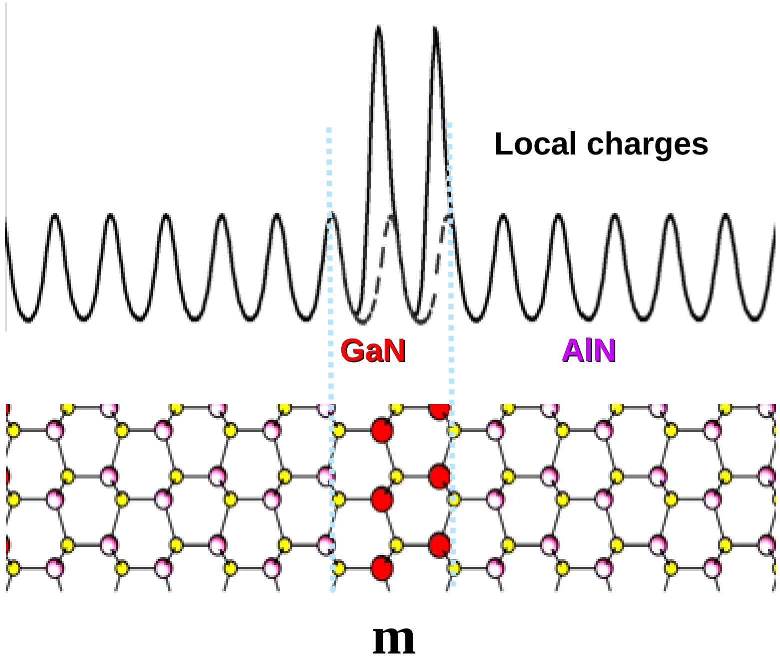


Higher quality InN films are available using the ultrathin In layer

Compensation of anisotropy crystal field

Asymmetric $(GaN)_m/(AlN)_n$ superlatices

Compensate asymmetric superlatices: Ultrathin GaN and thicker AlN

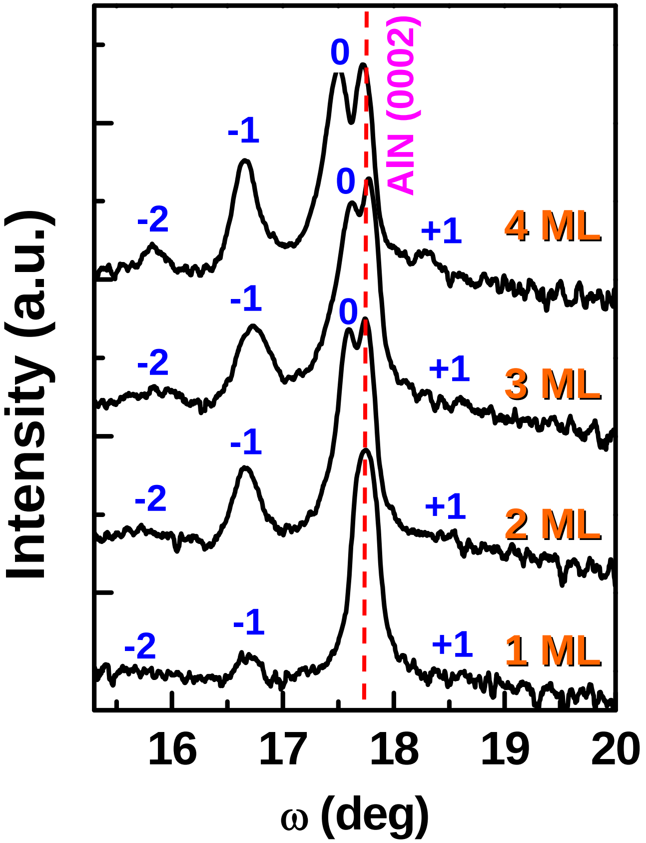


Compensation can be achieved !

The band edge anisotropy disappears when GaN well thickness becomes thinner than 6 MLs.

Compensation of anisotropy crystal field

Asymmetric $(GaN)_m/(AlN)_n$ superlatices



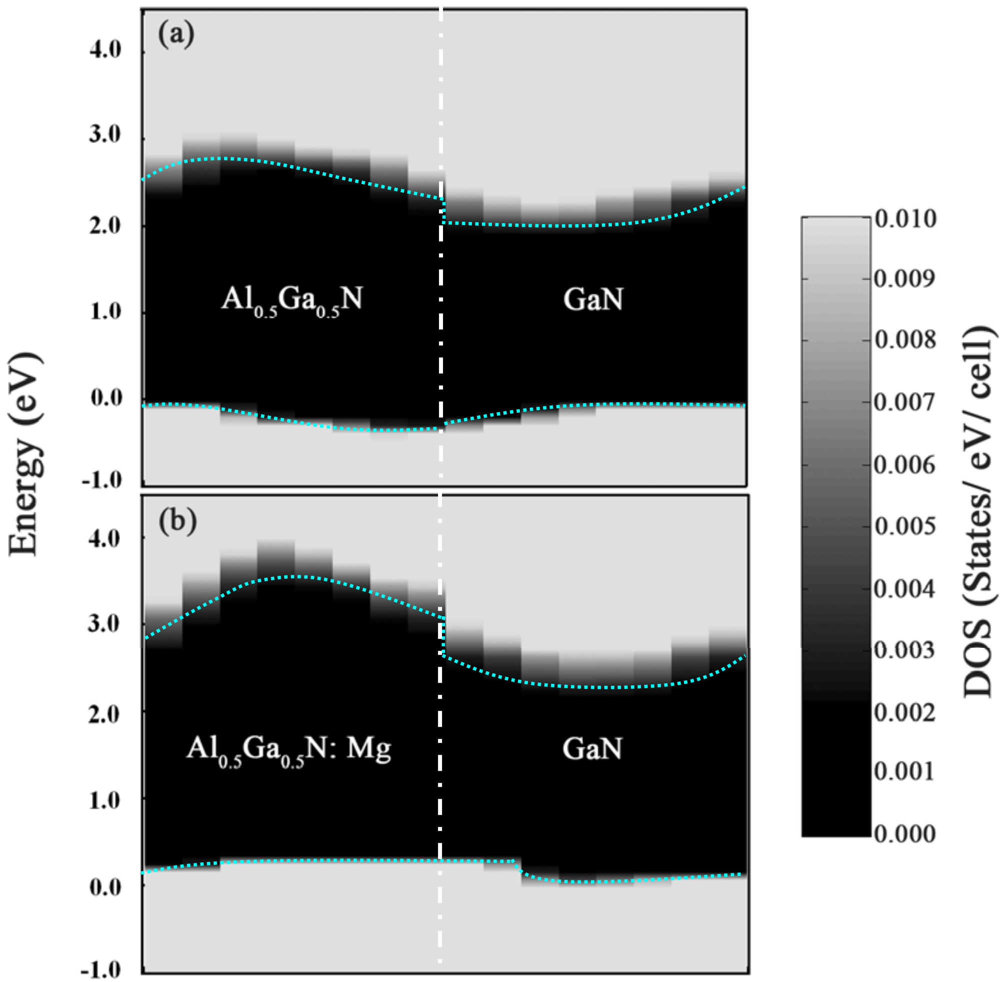
(0002) XRD rocking curves show that the superlattices have been fabricated.

Spectroscopic Ellipsometer spectra on two perpendicularly polarized directions.

Optical isotropization has been realized in high Al content AlGaN

Modification of internal electric field

Mg- and Si-δ codoped superlattices



Traditional Mg-modulation-doped AlGaN/GaN SL is still difficult to get low resistivity in high Al content nitrides !!

Band alignment changes from type-I to type-II when AlGaN is doped with Mg

J. Li, and J. Kang, Appl. Phys. Lett., 91, 152106 (2007)

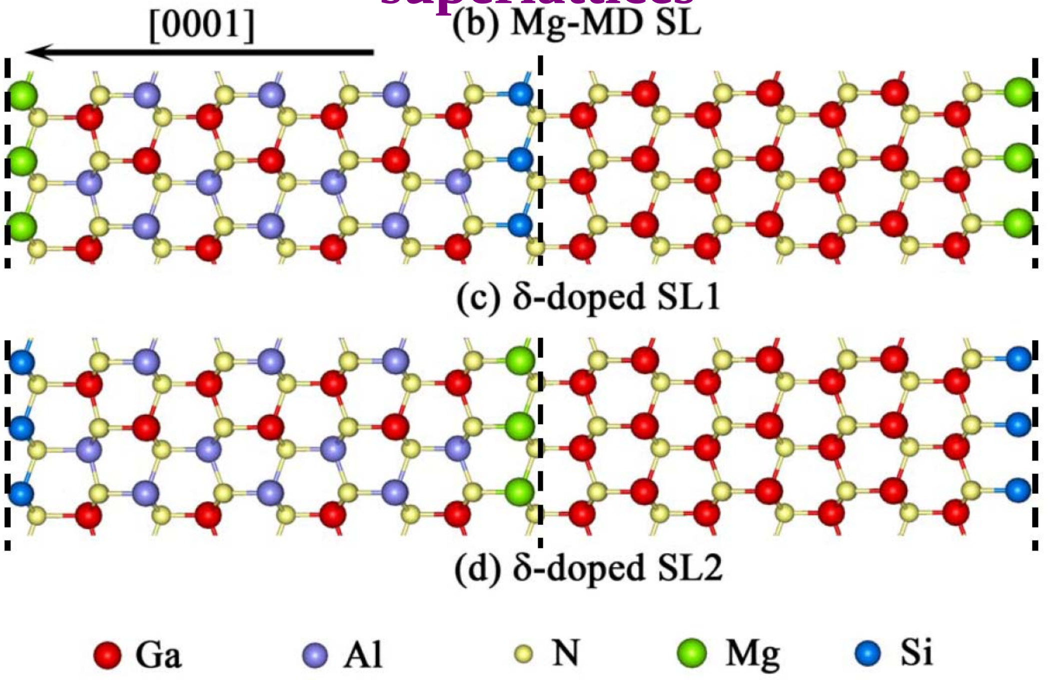
Modification of internal electric field

Mg- and Si-δ codoped superlattices

New structure: introducing an additional electrical field

A pair of Mg acceptor and Si donor sheets at the interfaces

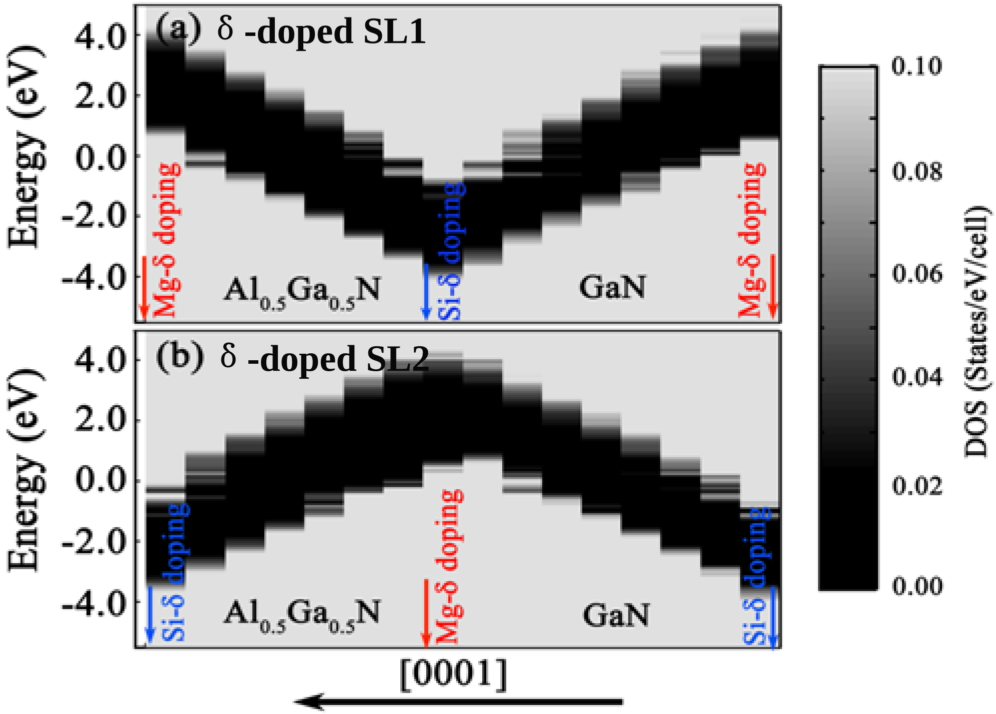
Mg- and Si-δ codoped superlattices



- **δ-doped layer:** **Mono-atomic layer of Mg or Si at the interfaces**
- **Potential:** **PAW_GGA;**
- **K-mesh:** **8X8X2;**

Modification of internal electric field

Mg- and Si-δ codoped superlattices

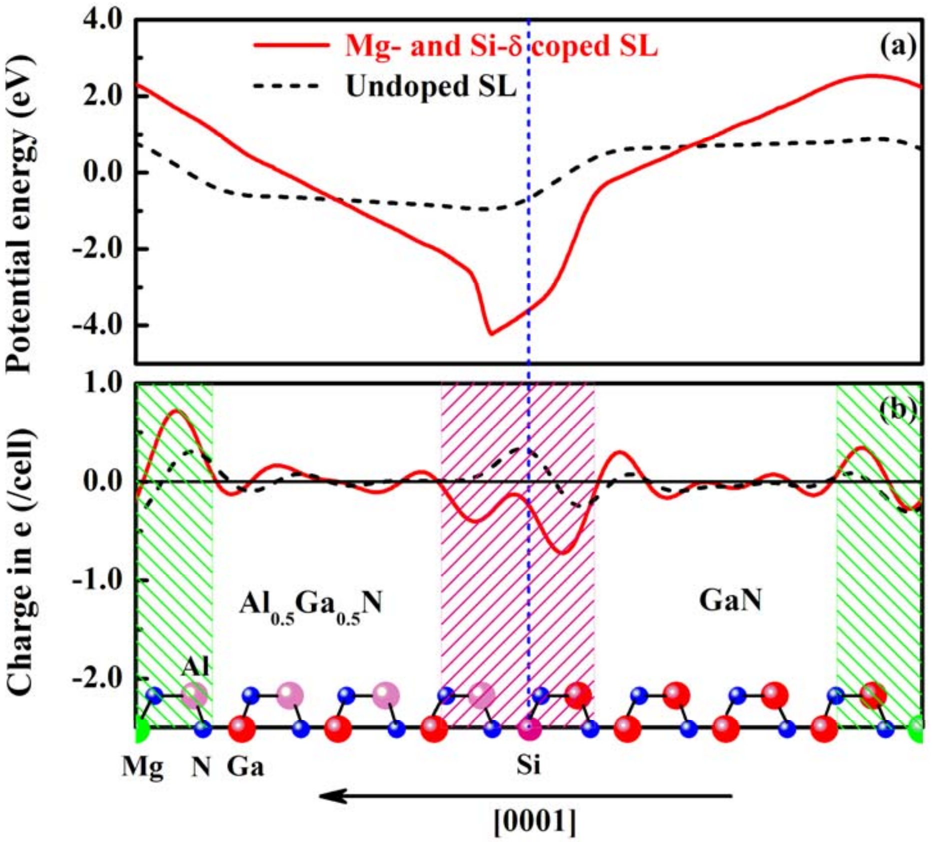


- Remarkable band bending in both δ-codoped SLs
- Opposite trend for SL1 and SL2

Modification of internal electric field can be achieved!

Modification of internal electric field

Mg- and Si-δ codoped superlattices

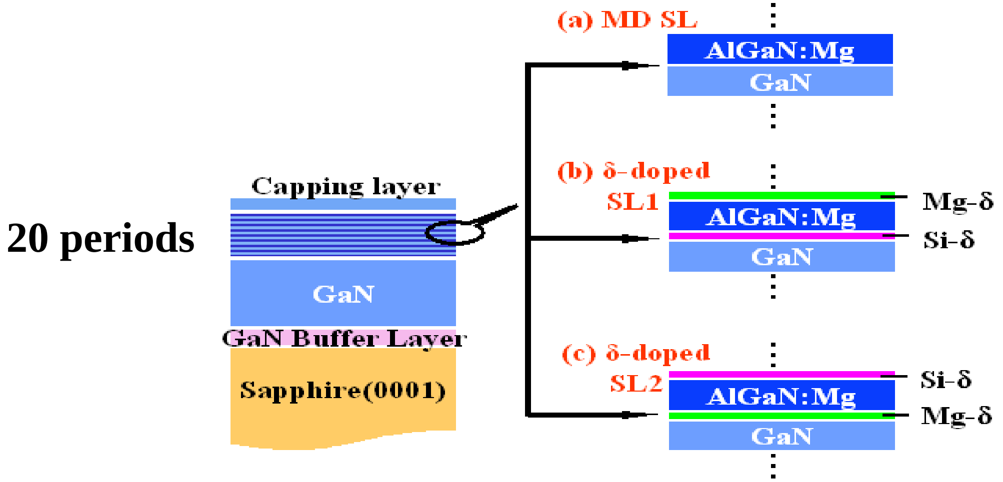


- Electrons transfer from Si-doped interface to Mg-doped interface

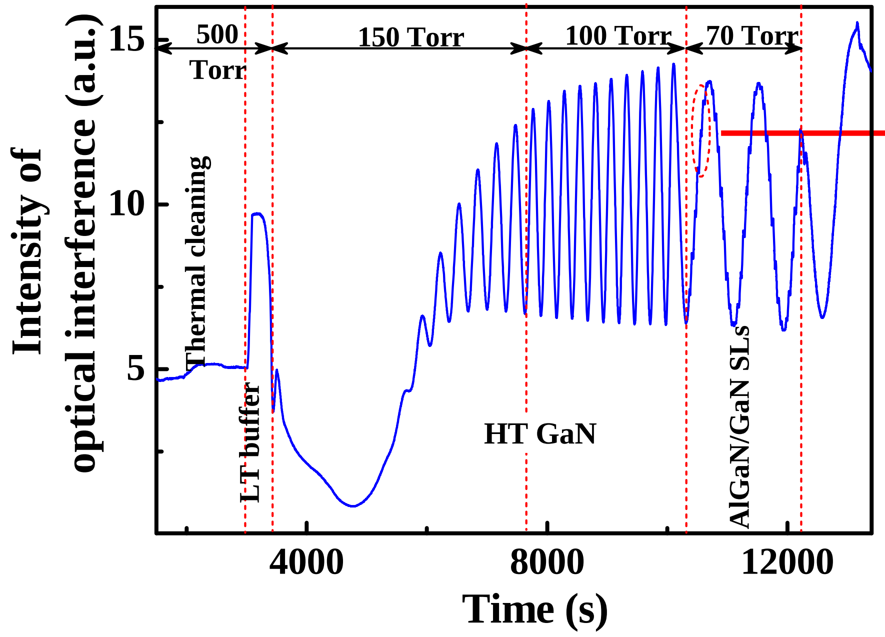
Increase the internal electric field and the band bending

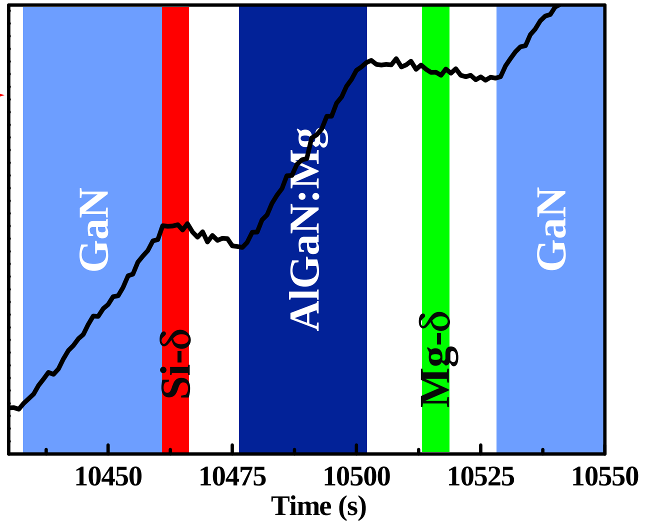
Modification of internal electric field

Mg- and Si-δ codoped superlattices



- On high quality thick-GaN layer
- δ-doped layers: Closing TMG & TMA and keeping on NH_3 and Cp_2Mg or SiH_4
- Growth interruption to smooth interface

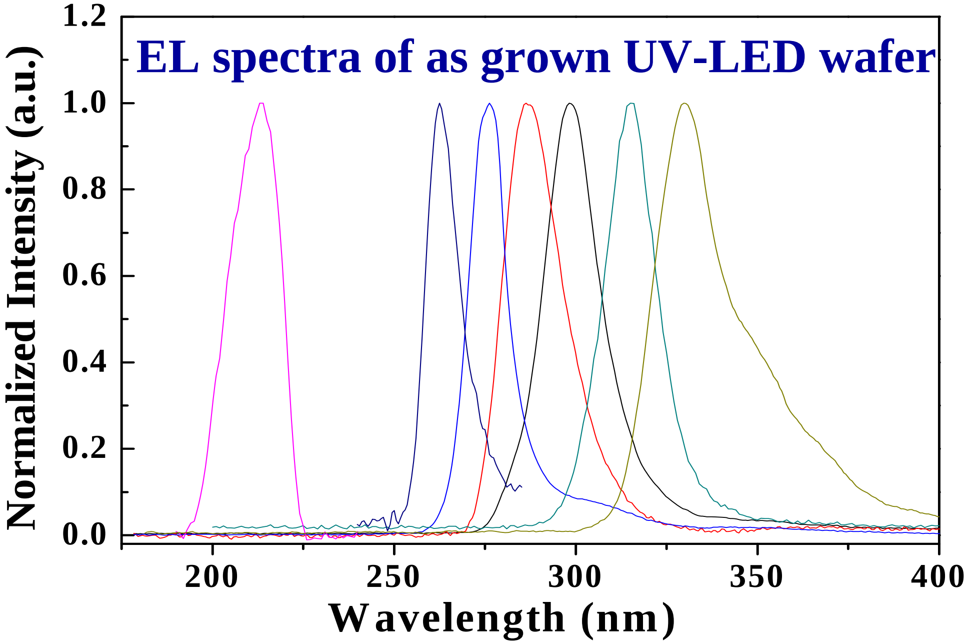


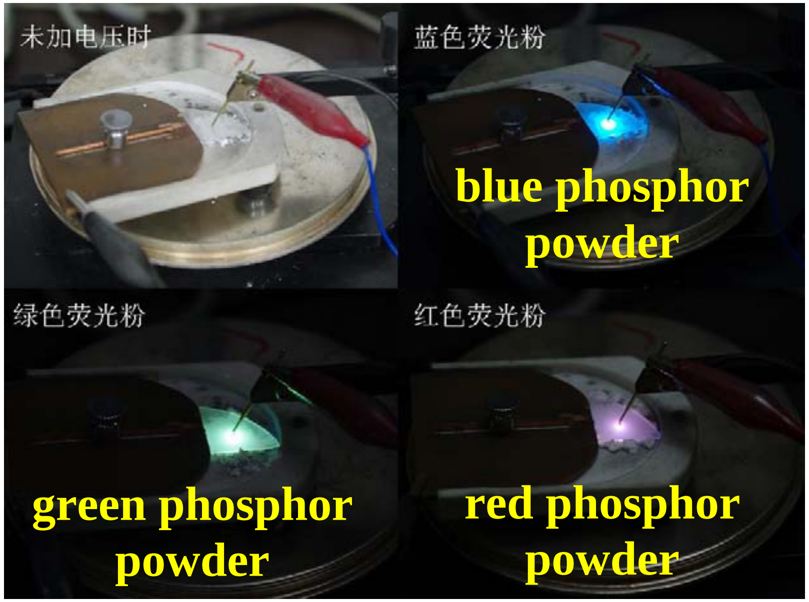


Modification of internal electric field

Mg- and Si-δ codoped superlattices

Application for DUV-LED





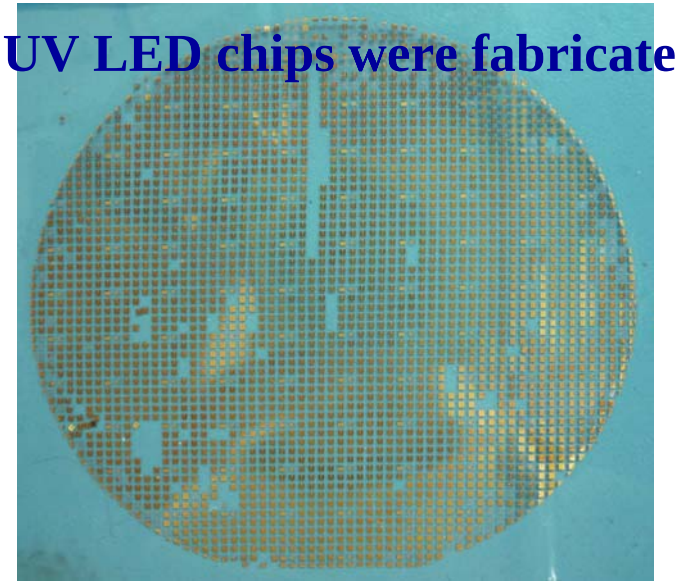
As grown wafer with peak-wavelength up to 213nm is easy to light up

δ-codoped structure is superior in *p*-type conductivity for high Al content AlGaN

Modification of internal electric field

Mg- and Si-δ codoped superlattices

DUV LED chips were fabricated

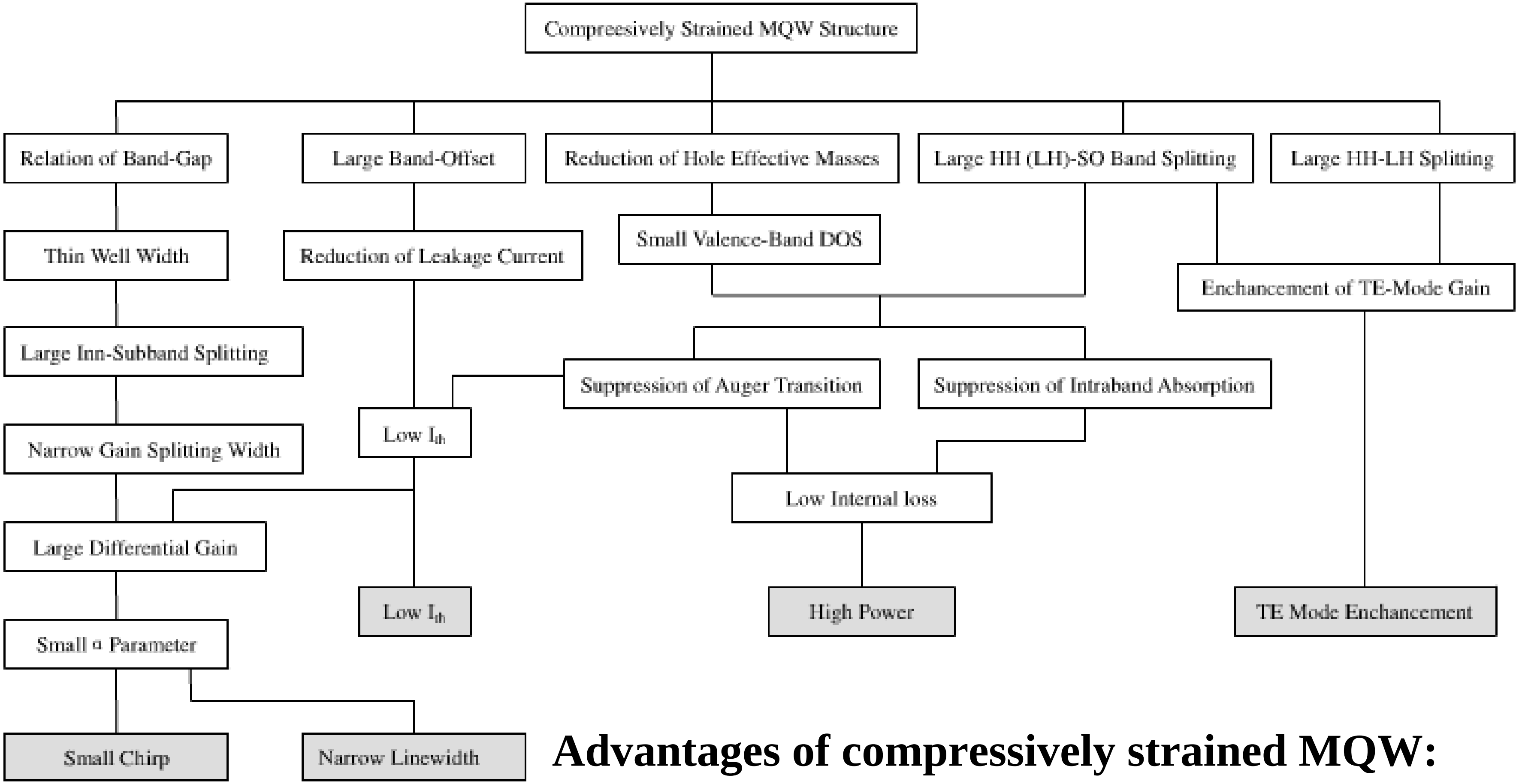


Position	V_f @ 1mA	V_f @ 20 mA	V_f @ 100mA
Up	3.68	5.08	6.08
	3.98	5.21	6.43
Middle	3.53	4.96	6.20
	3.69	4.98	6.08
Down	3.82	5.00	6.26
	3.83	5.02	6.28
Left	3.92	5.13	6.39
	3.68	4.70	5.80
Right	3.87	5.09	6.37
	3.90	5.11	6.35

The relevant turn-on voltages are smaller than those of MD SL structure

Modification of misfit stress field

Ultrathin compressive strained InN/GaN MQWs



Compreesively Strained MQW Structure

Relation of Band-Gap

Large Band-Offset

Reduction of Hole Effective Masses

Large HH (LH)-SO Band Splitting

Large HH-LH Splitting

Thin Well Width

Reduction of Leakage Current

Small Valence-Band DOS

Enchancement of TE-Mode Gain

Large Inn-Subband Splitting

Suppression of Auger Transition

Suppression of Intraband Absorption

Low I_{th}

Narrow Gain Splitting Width

Low Internal loss

Large Differential Gain

Low I_{th}

High Power

TE Mode Enchancement

Small α Parameter

Small Chirp

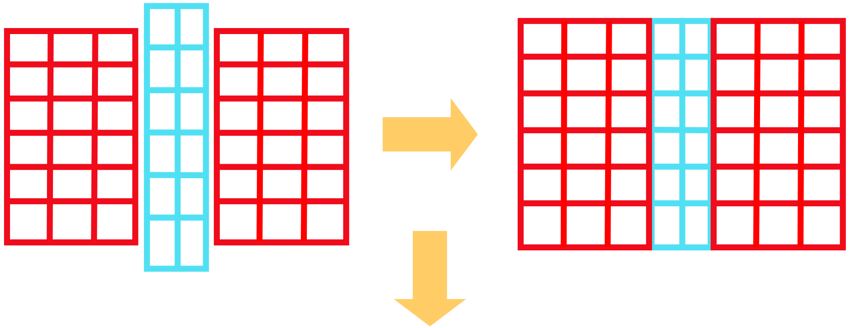
Narrow Linewidth

Advantages of compressively strained MQW:

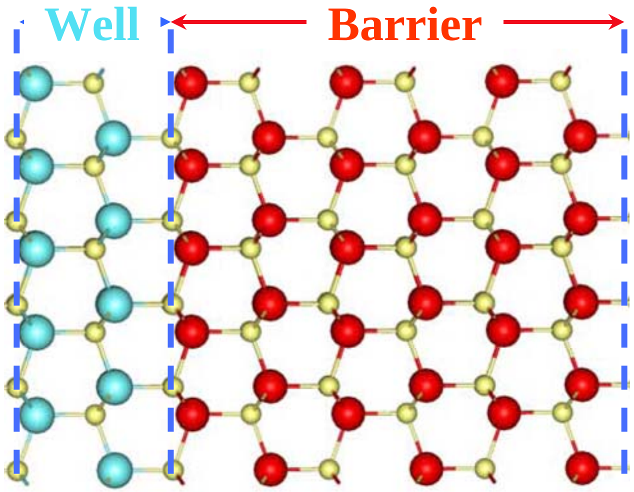
- **Narrow line-width**
- **High power**
- **Low threshold current, and so on**

Modification of misfit stress field

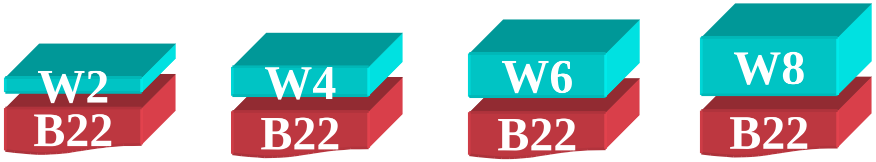
Ultrathin compressive strained InN/GaN MQWs



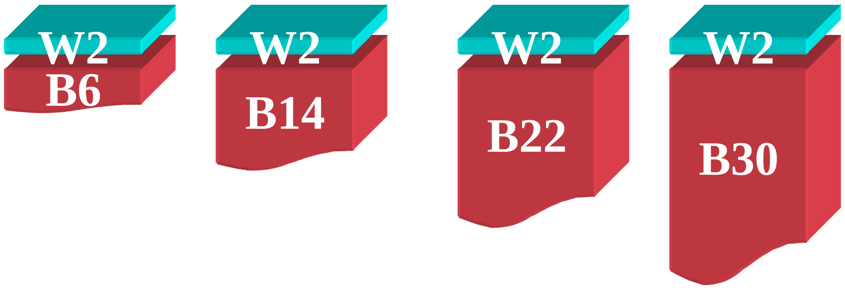
- ➢What will happen in the strained QWs with strong piezoelectric effect.
- ➢How to achieved coherent QWs with strong stress field.



Tuning strain



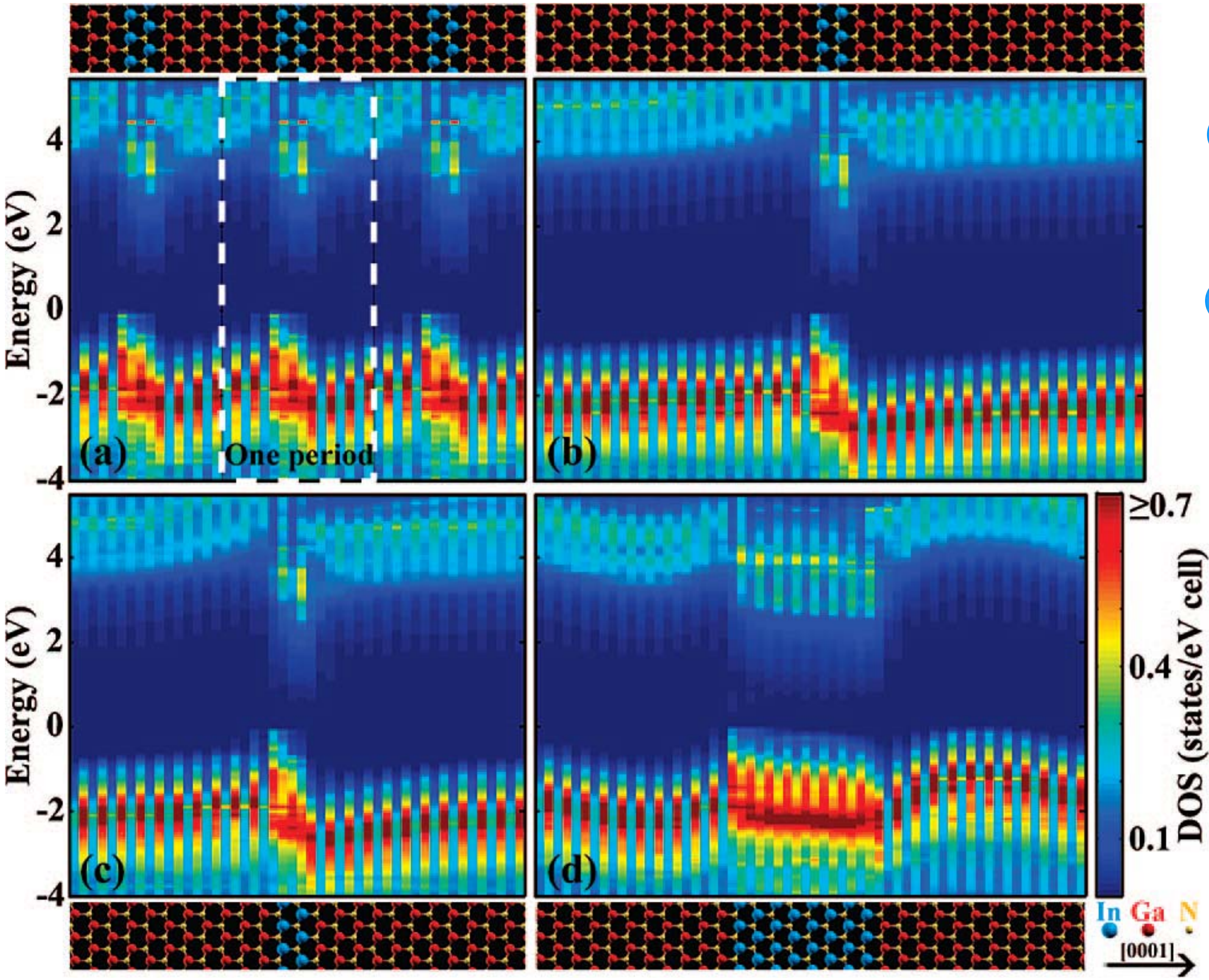
❖ Different well widths: 2, 4, 6, 8 MLs
Barrier thickness: 22 MLs



❖ Different barrier thickness: 6, 14, 22, 30 MLs
Well width: 2 MLs

Modification of misfit stress field

Ultrathin compressive strained InN/GaN MQWs



Electronic structures depend on barrier and well thickness

Band bending

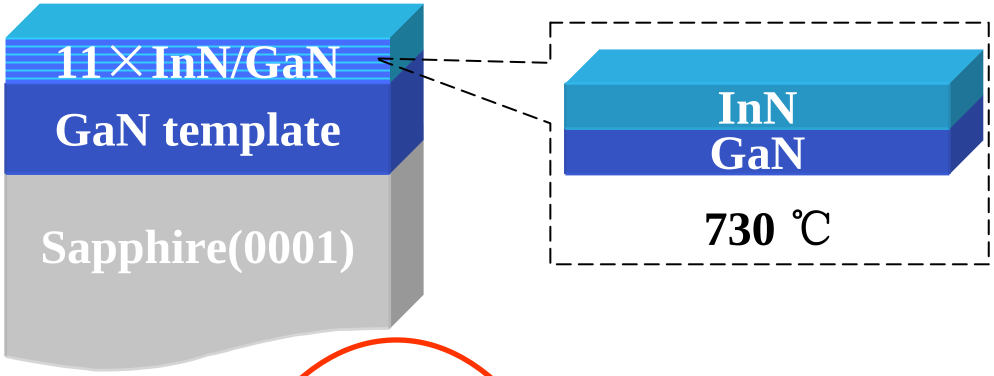
- Slightly enhanced as barrier thickness increases
- Markedly reduced as well width increases

Well width > 6 MLs
New VB extremum appear

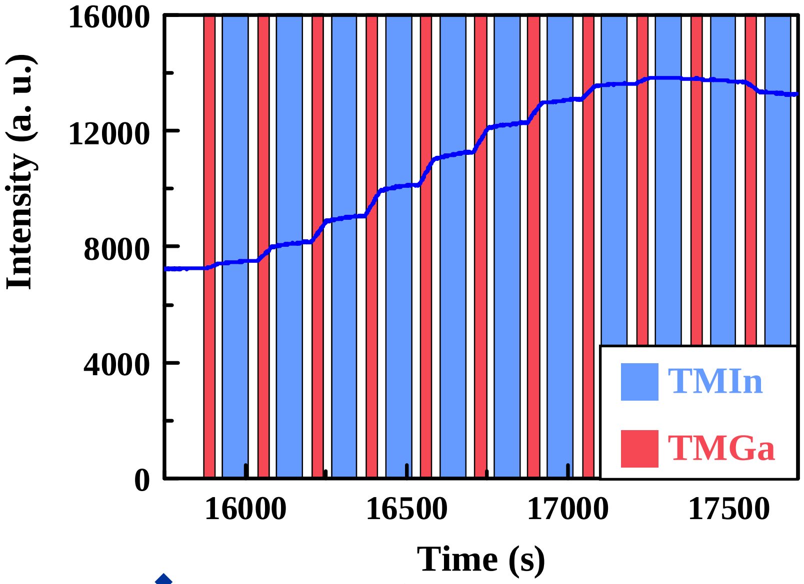
Ultrathin InN/GaN QW will be better

Modification of misfit stress field

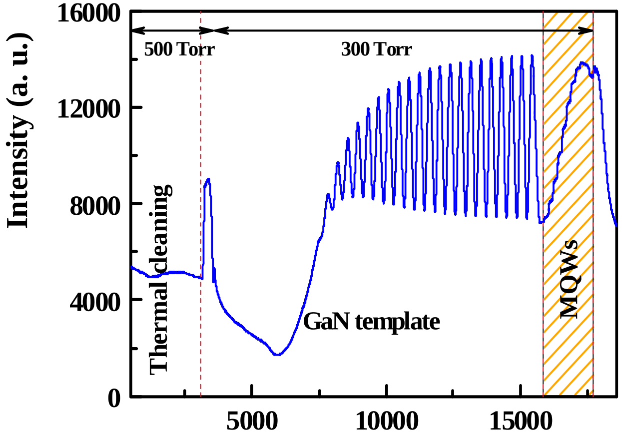
Ultrathin compressive strained InN/GaN MQWs



Sample	TMG (s)	TMI (s)	Well Width (ML)	Barrier Thickness (ML)
BI	24	90	4	11
BII	48	90	4	23
BIII	96	90	4	45
WI	48	45	2	23
WII	48	90	4	23
WIII	48	180	8	23

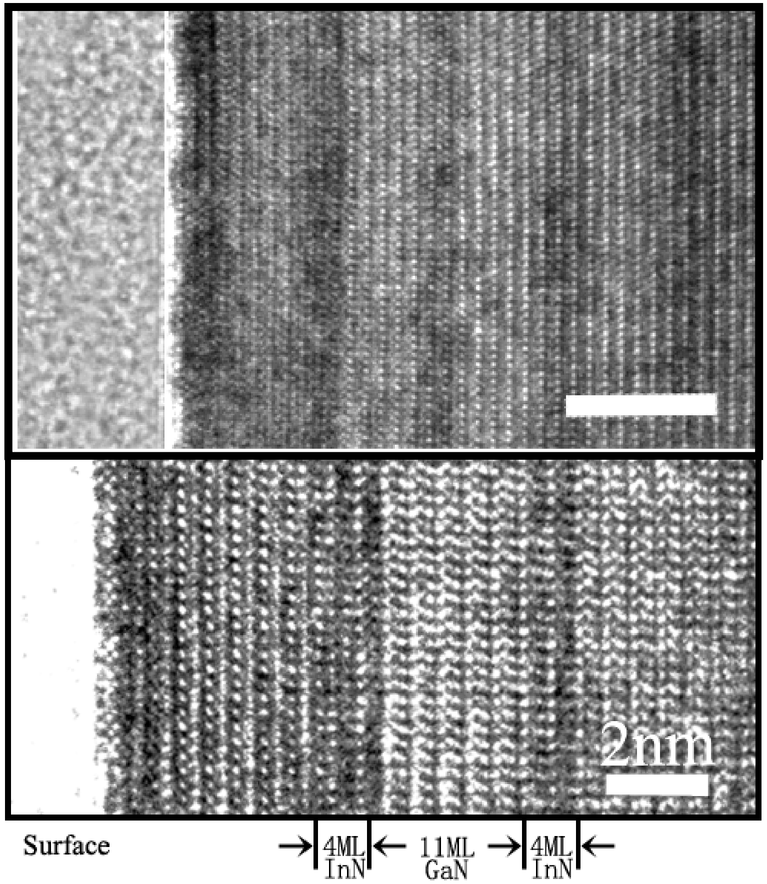


- **Interruption at InGaN/GaN interface**

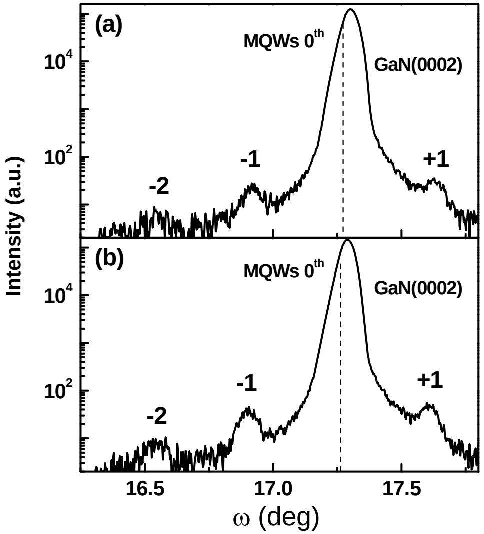


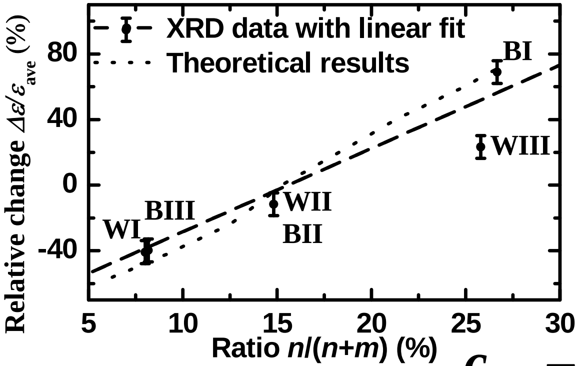
Modification of misfit stress field

Ultrathin compressive strained InN/GaN MQWs



Coherent lattice and atomically sharp interfaces in HRTEM image



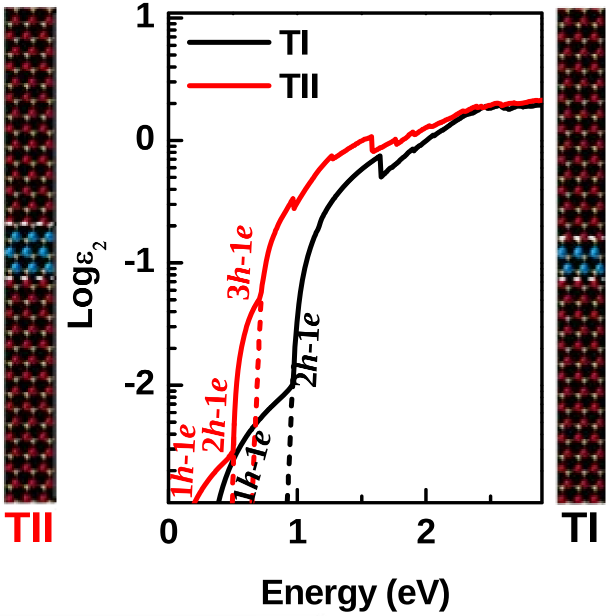


The average strain $\varepsilon = \dfrac{c_{ave} - c_0}{c_0}$

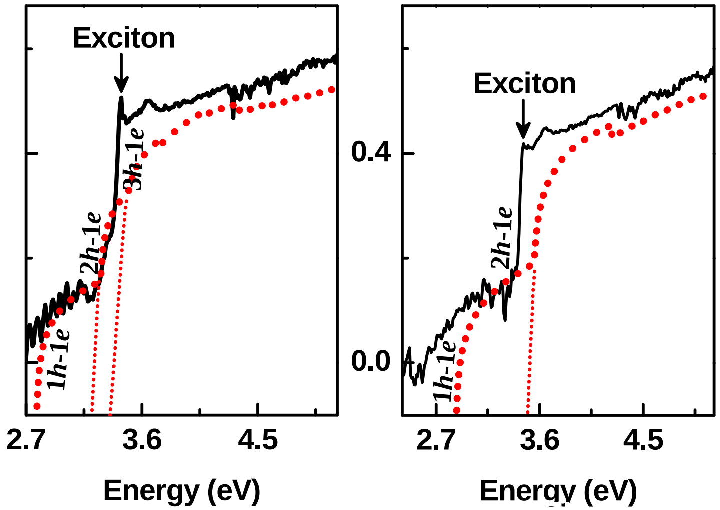
Coherent growth and strained control have been achieved

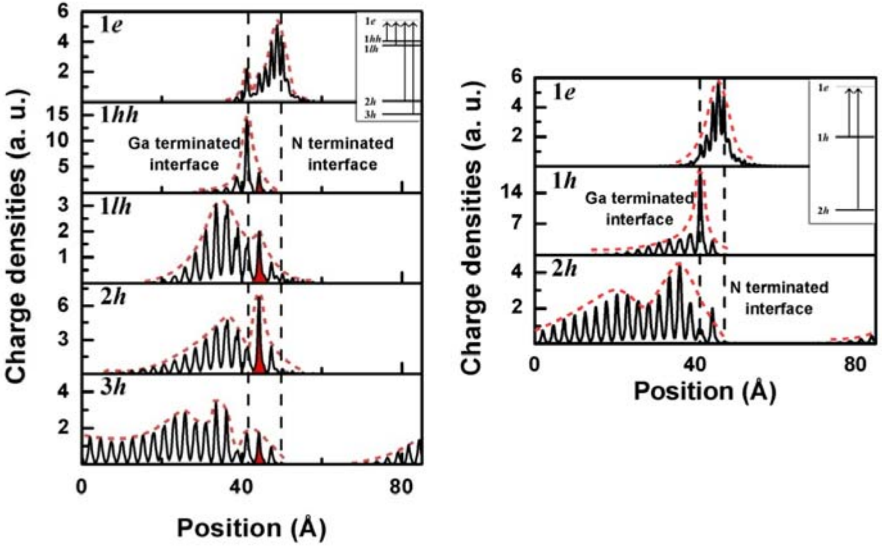
Modification of misfit stress field

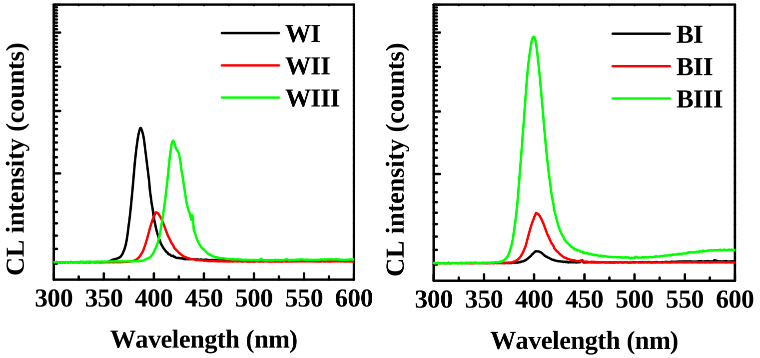
Ultrathin compressive strained InN/GaN MQWs



$$\frac{\omega}{nc}\varepsilon_2 = \alpha$$





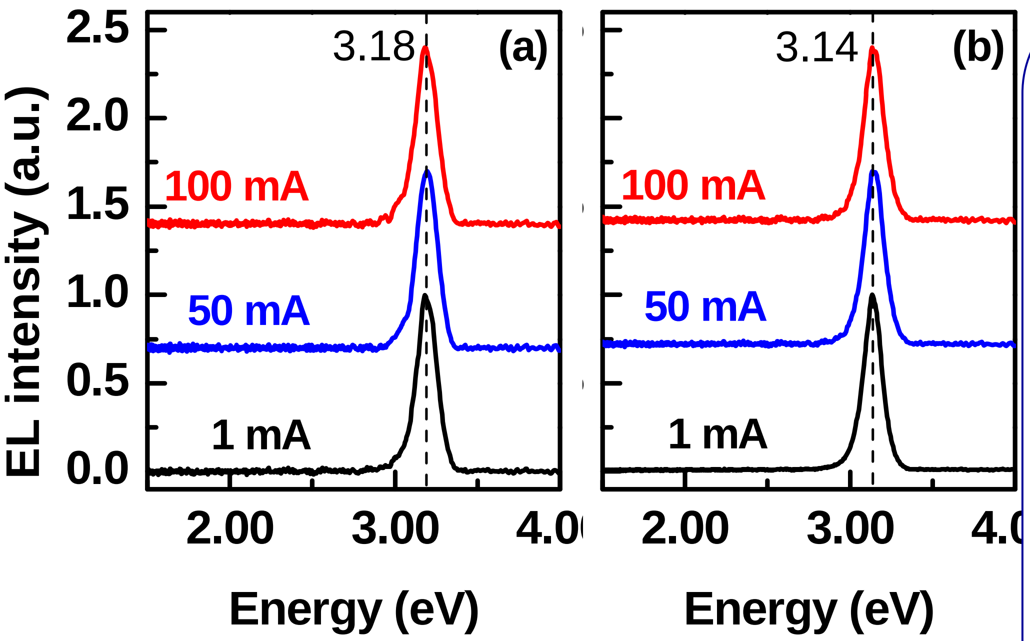


Agreement between the experiment results and the simulations indicates that the strain-dependent quantized levels have been realized.

Modification of misfit stress field

Ultrathin compressive strained InN/GaN MQWs

Application for UV-LEDs



Peak wavelength < 400nm

EL spectra under different injection currents are free from

- **Yellow band**

  Reduction in defect recombination outside QW

- **Red shift**

  Reduction in many body effect, such as Auger transition

- **Blue shift**

  Reduction in band-filling effect caused by phase separation

  Reduction in QCSE induced by the screening of the piezoelectric fields

Ultrathin compressive strained MQW structure is superior in LEDs

Conclusions

- Higher quality nitride films have been grown based on their dynamic/kinetic properties
- Anisotropy of wurzite structure has been compensated in high Al content nitrides by introducing GaN/AlN superlattices
- Modification of internal electric field has been achieved by using Mg- and Si-δ codoped superlattices
- Modification of misfit stress field has been realized in ultrathin compressive strained InN/GaN MQWs

Fields modification is the most important for III-nitride applications

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Fields modification in high Al or In content III-nitrides

Xiamen University

Thank you!