Molecular Beam Epitaxy and p-type doping of InN

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Appreciation

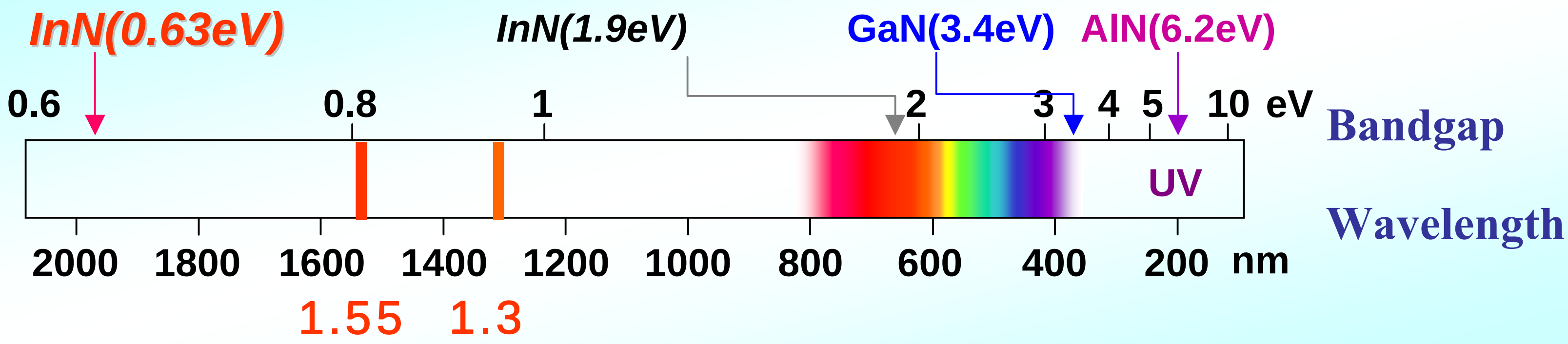
T. Mukai of Nichia Corporation for providing us GaN templates,

A. Majima and **M. Saitoh** of Nanometrics Japan LTD

T. Wolff of WEP LTD, Germany for ECV measurement

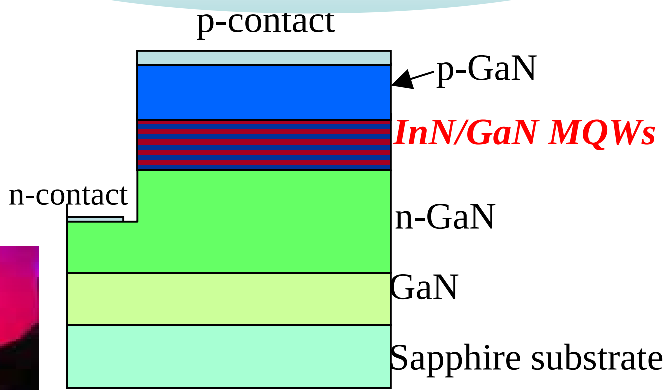
Outline

- Introduction
- Molecular Beam Epitaxy
- InN Epitaxy: Polarity effect and atomically flat surface
- Quality Improvement for InN epilayers
- Properties of InN epilayers
- P-type doping of InN
- Polarity Inversion InN:Mg
- Evidence of p-type
- InN based alloys and nanostructures
- Summary

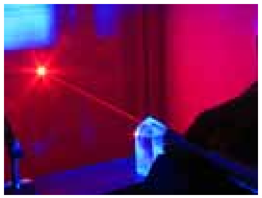


Emission wavelength coverage from 200nm to 2μm at RT

Wide-bandgap **III-nitrides** → ***"Wide"-emission range***

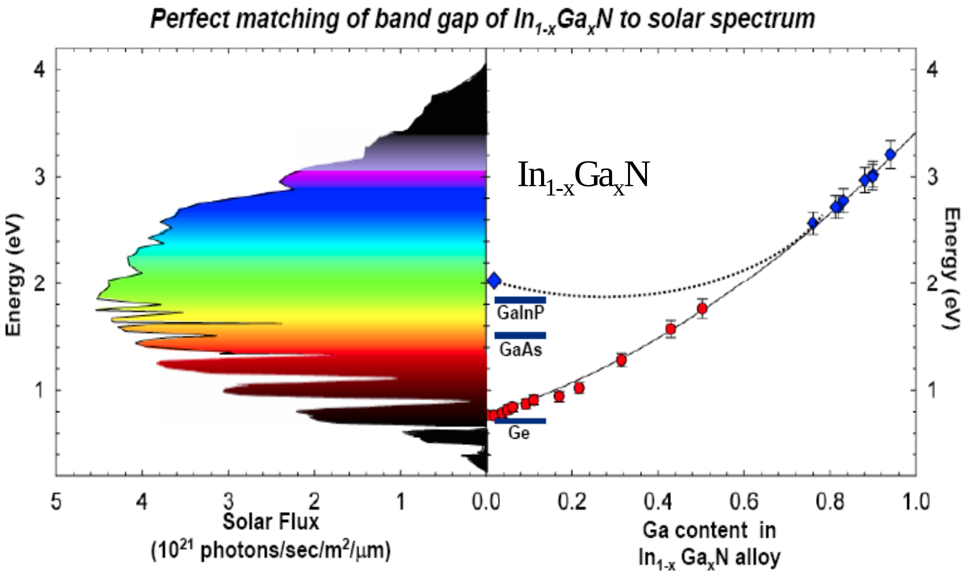


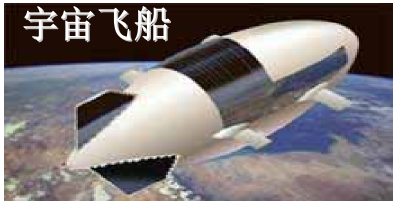
light emitting devices in visible and near infrared region, LEDs/LDs > 550nm/500nm (Free of As or P--healthy)

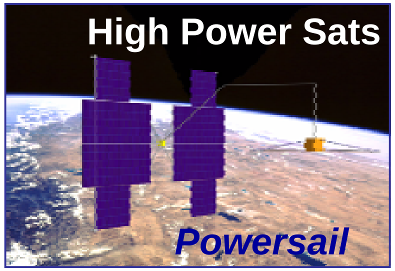


High Efficiency Solar Cell

Radiation-hard material-very suitable for using in space







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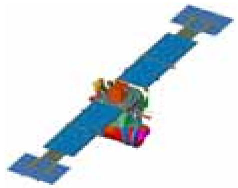
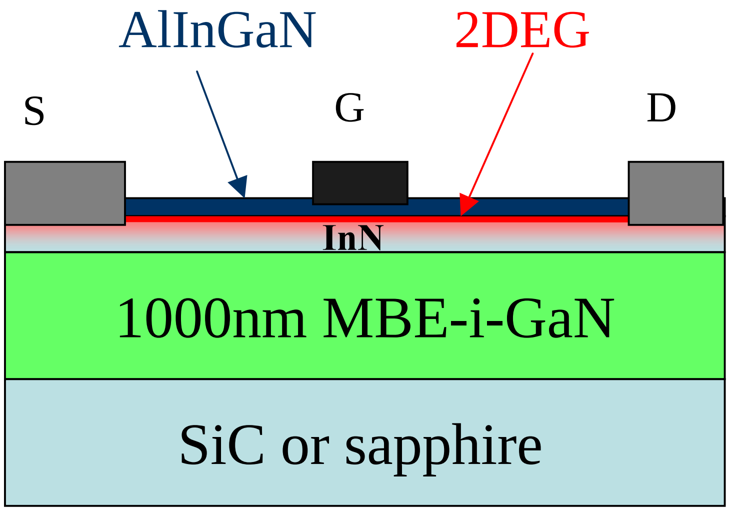
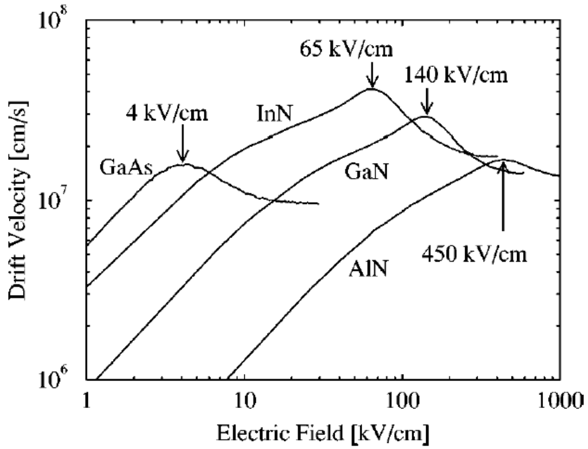


Theoretical Conversion Efficiency of InGaN Tandem Cell as a Function of Number of Junctions under AM 1.5.

High Electron Mobility Transistor HEMT

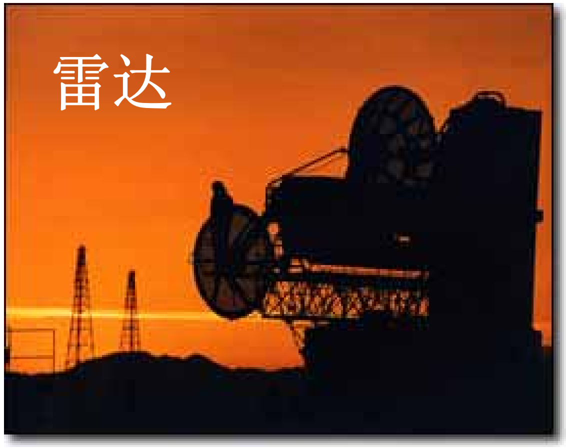
超高速AlInN/InN，InGaN/InN HEMT





主要半导体化合物的饱和速度

B.Foutz et.al, JAP, 85 (1999) 7727



InN: 高电子饱和速度~ **4.2×10^7cm/sec**，电子有效质量很小~**0.04 m_0**，超高电子迁移率，室温下理论预测的迁移率约为**14000 cm²/Vs**， 目前报道的**InN**薄膜的室温下迁移率超过**2000 cm²/Vs**， 非常适合于制作**HEMT**之类的高速电子器件。

Topics/Keypoints in InN research

- High Quality InN epilayers

  Low defect density, atomically flat surface, low residual carrier concentration

- Origin of high residual electron concentration

  InN-degenerate semiconductor

- P-type doping for InN

  Necessary for fabricating light emitting device

- InN based alloys

  High In content InGaN, InAlN

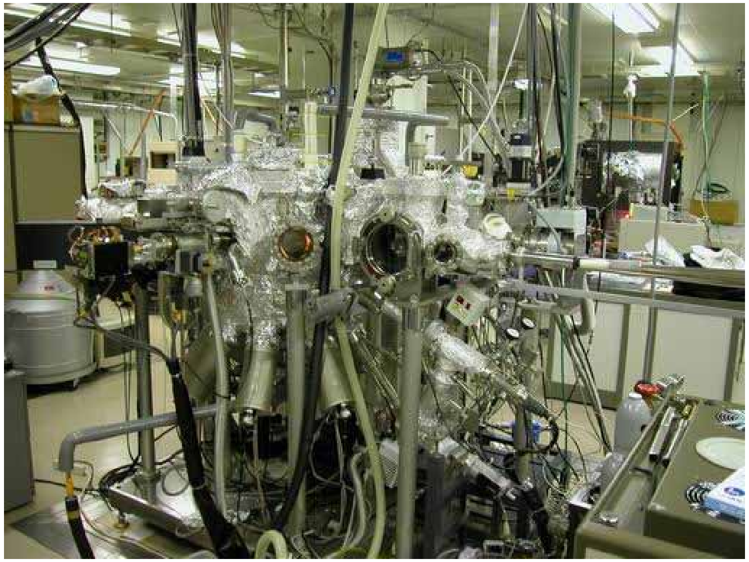
- InN based quantum structures, nanostructures

  InN well based quantum wells, InN quantum dots, nanowires

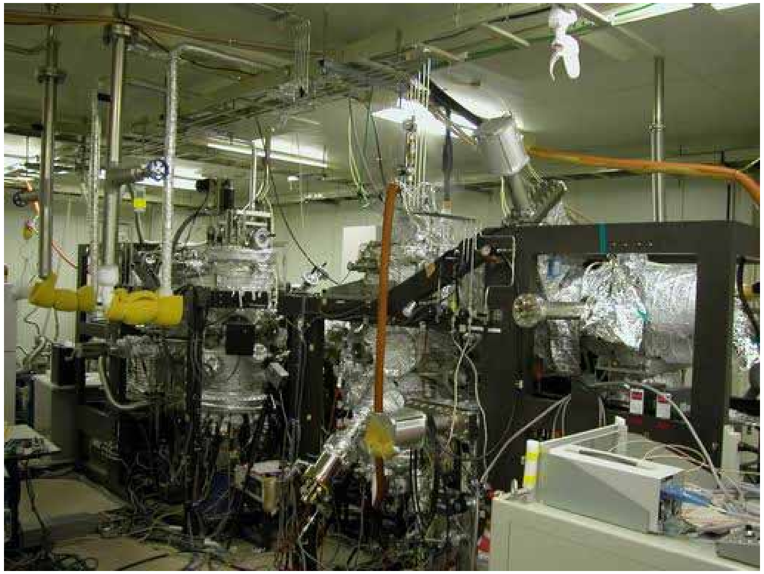
- Parameters/Physics for InN

  Several Parameters for InN are not clear yet.

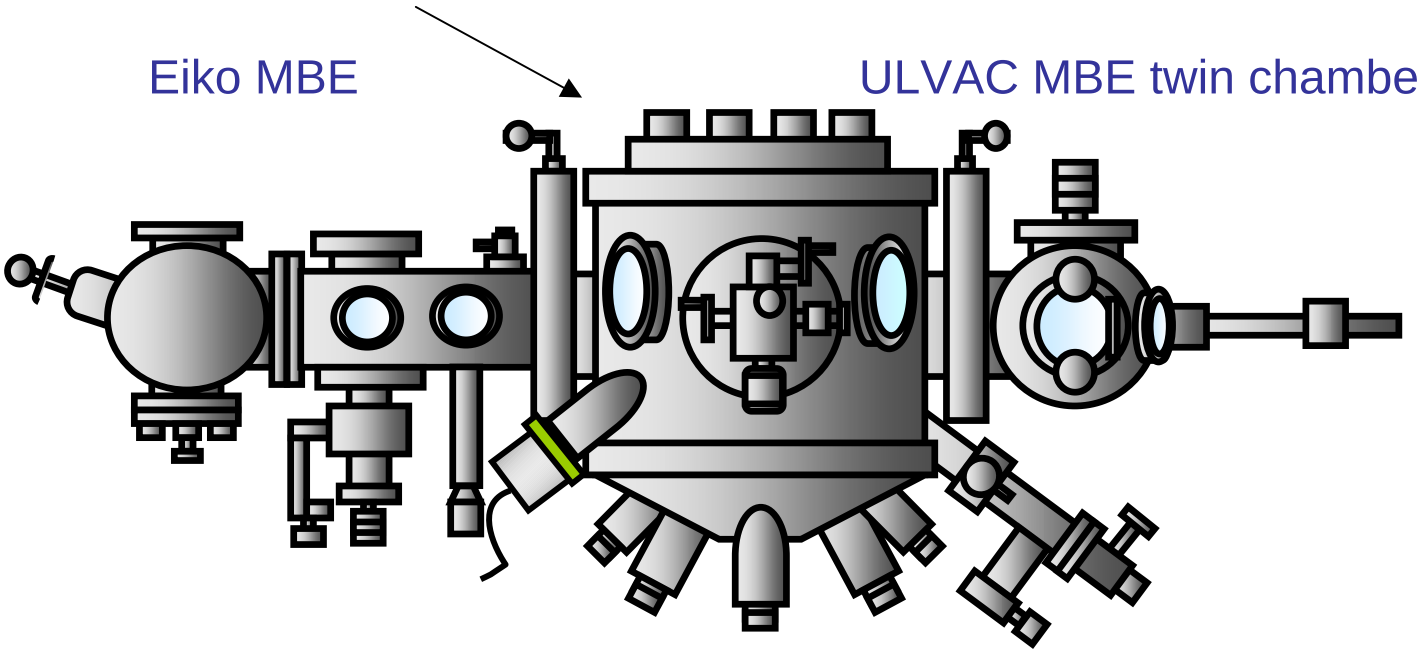
Molecular Beam Epitaxy



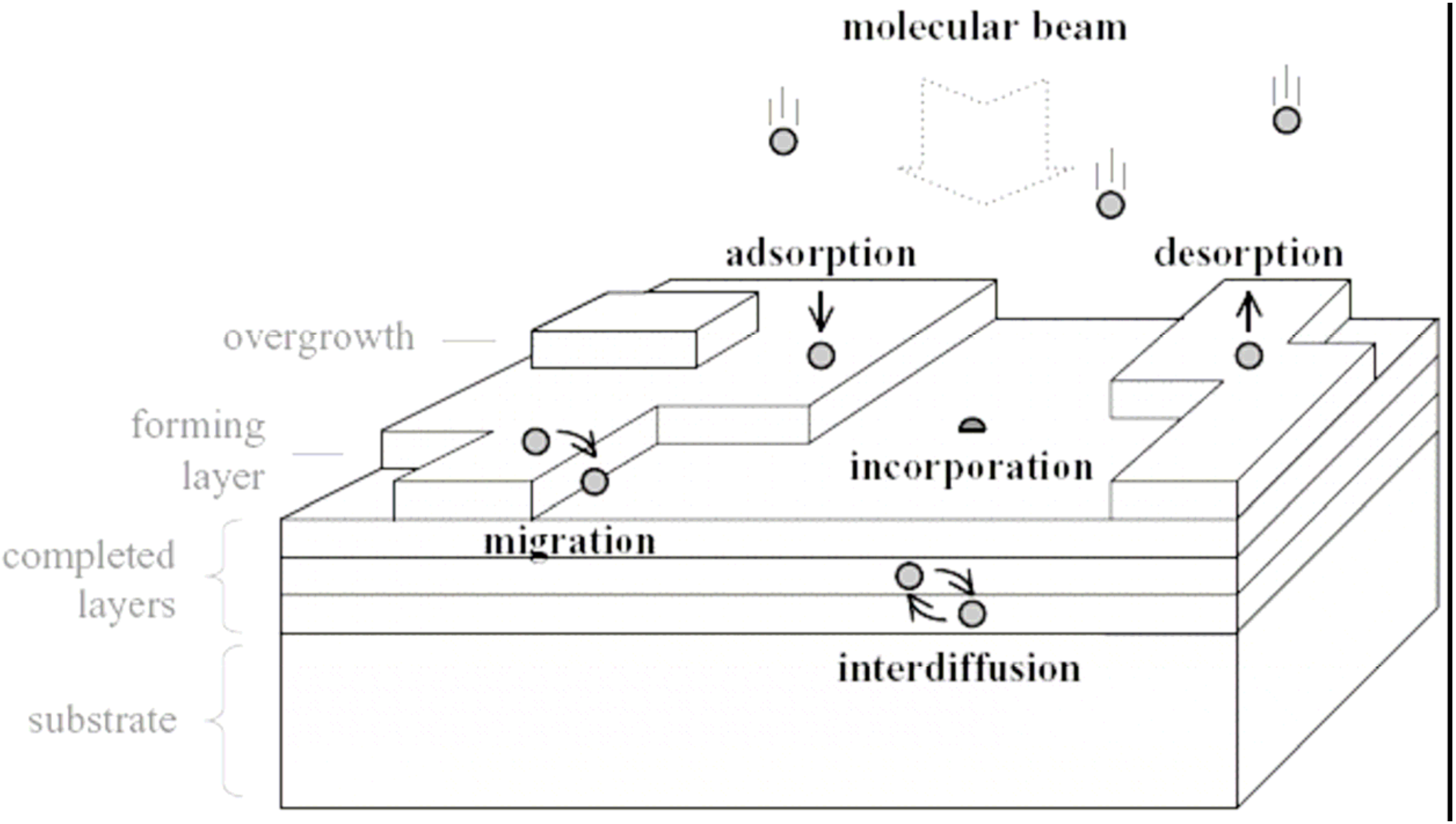
Eiko MBE



ULVAC MBE twin chamber



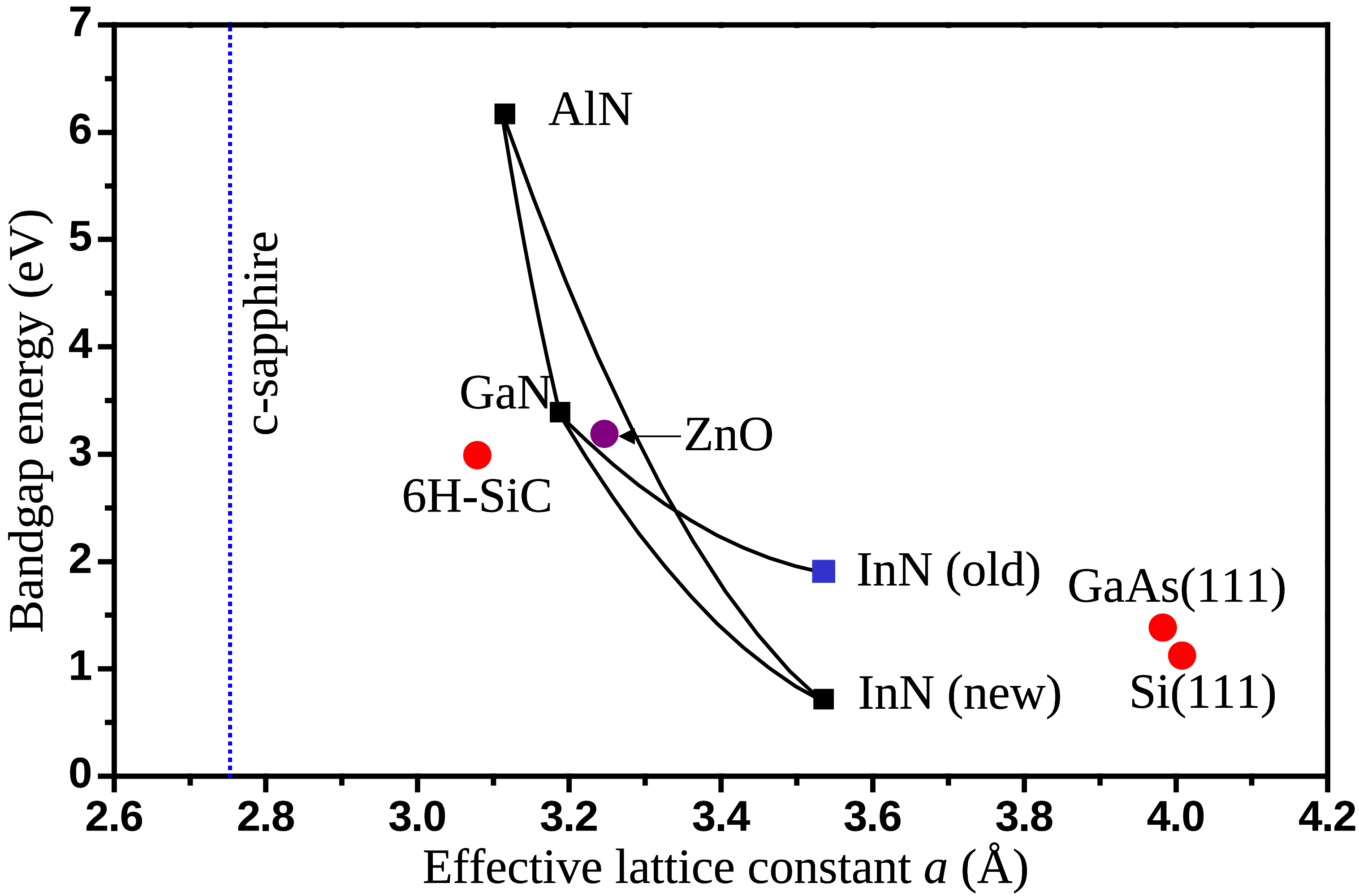
Epitaxy Mechanism



It is important to improve migration ability of surface atoms

Difficulty in InN Epitaxy

Large lattice mismatch leads to high defect density and poor quality



InN/sapphire 25%; InN/GaN~11%

X. Wang , A. Yoshikawa, *Prog. Cryst. Growth and Charact. Mater., 48/49 (2004) 42-103.*

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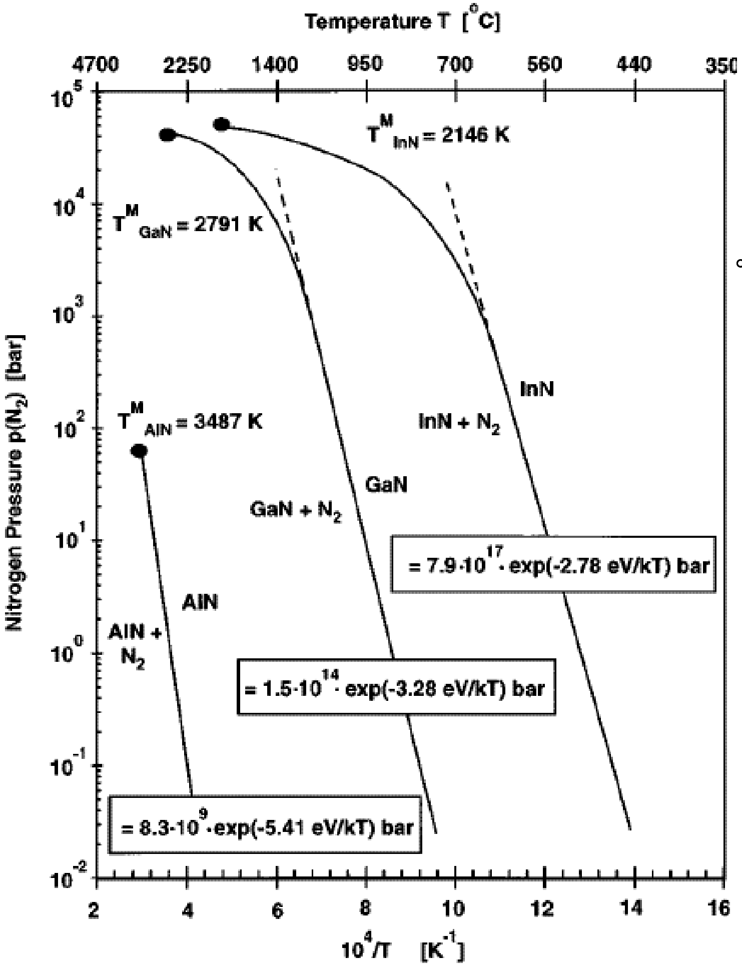
Difficulty in InN Epitaxy

high equilibrium N_2 vapor pressure over InN film

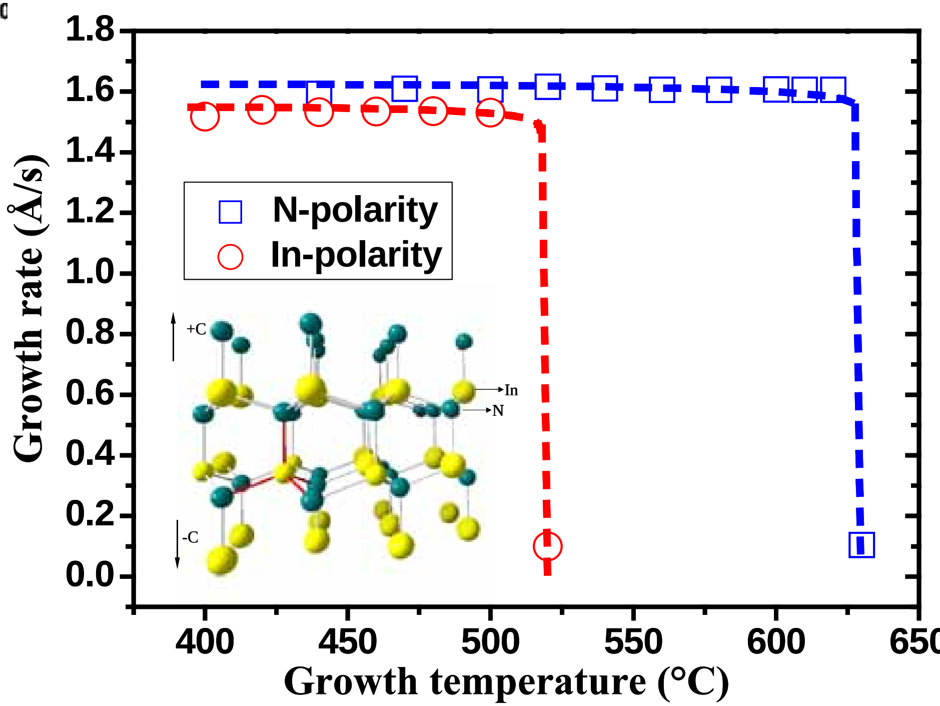
Low maximum growth temperatures much smaller than GaN and AlN



O. Ambacher, et al, J. Vac. Sci. Technol. B 14 (1996) 3532

Low Epitaxy Temperature

高饱和蒸汽压-热分解温度低-低外延温度



In Polarity $T_{InN} \leq 520°C$

N Polarity $T_{InN} \leq 620°C$

Very big growth Temperature mismatch between InN/GaN,AlN

MBE *vs* MOVPE on InN epitaxy

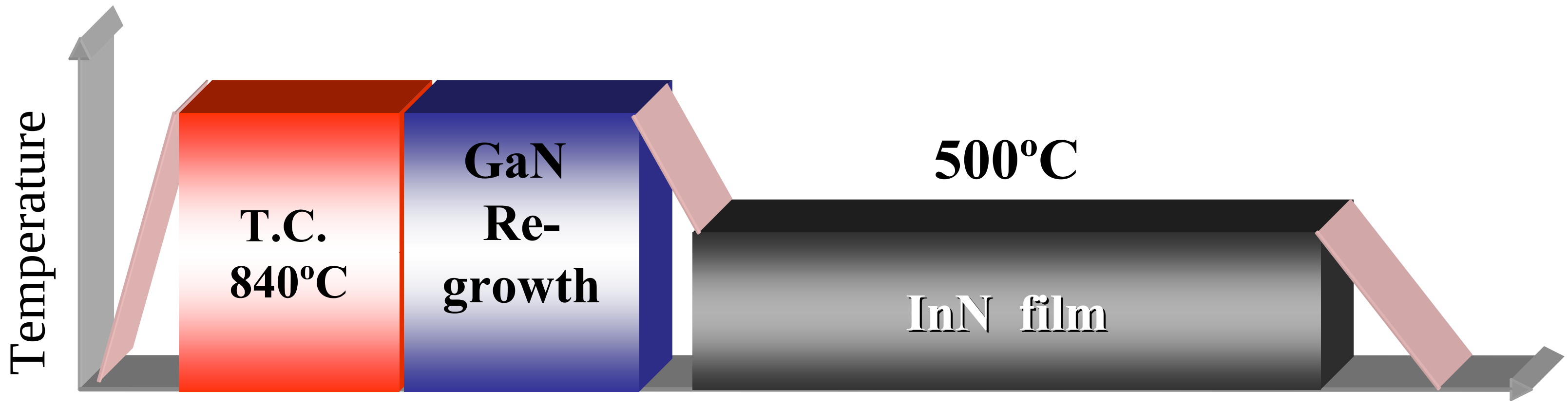
Problem for MOCVD: Low epitaxial temperature of InN

外延生长方法		MOCVD	MBE
源材料	In源	有机源(TMIn)	金属In
	N源	氨气-高温 有机氮源-碳污染	Plasma离化氮气
最大生长温度		≤ 520ºC/620ºC	≤ 520ºC/620ºC
生长速度		低	高
极性控制		难/N极性表面粗糙	容易
晶体质量		差	好
表面平整度		粗糙	平整
电子浓度n_e (cm^{-3})		~10^{18}	~10^{17}
迁移率(RT) cm^2/Vs		>1000	>2000

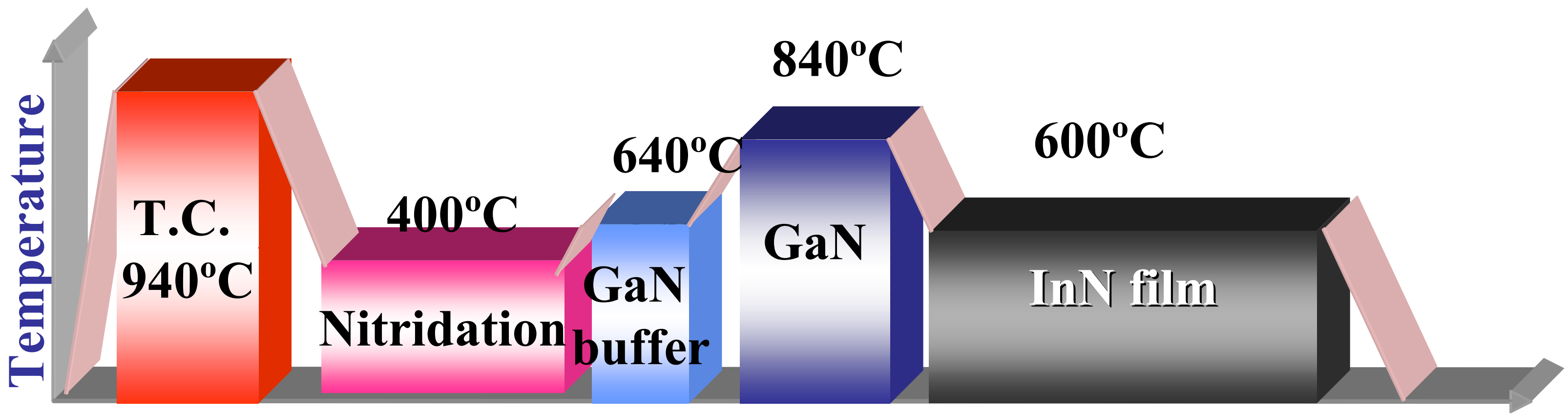
MBE shows advantage than MOVPE

Typical Growth Procedure

In-polar InN grown on Ga-polar GaN



N-polar InN grown on N-polar GaN



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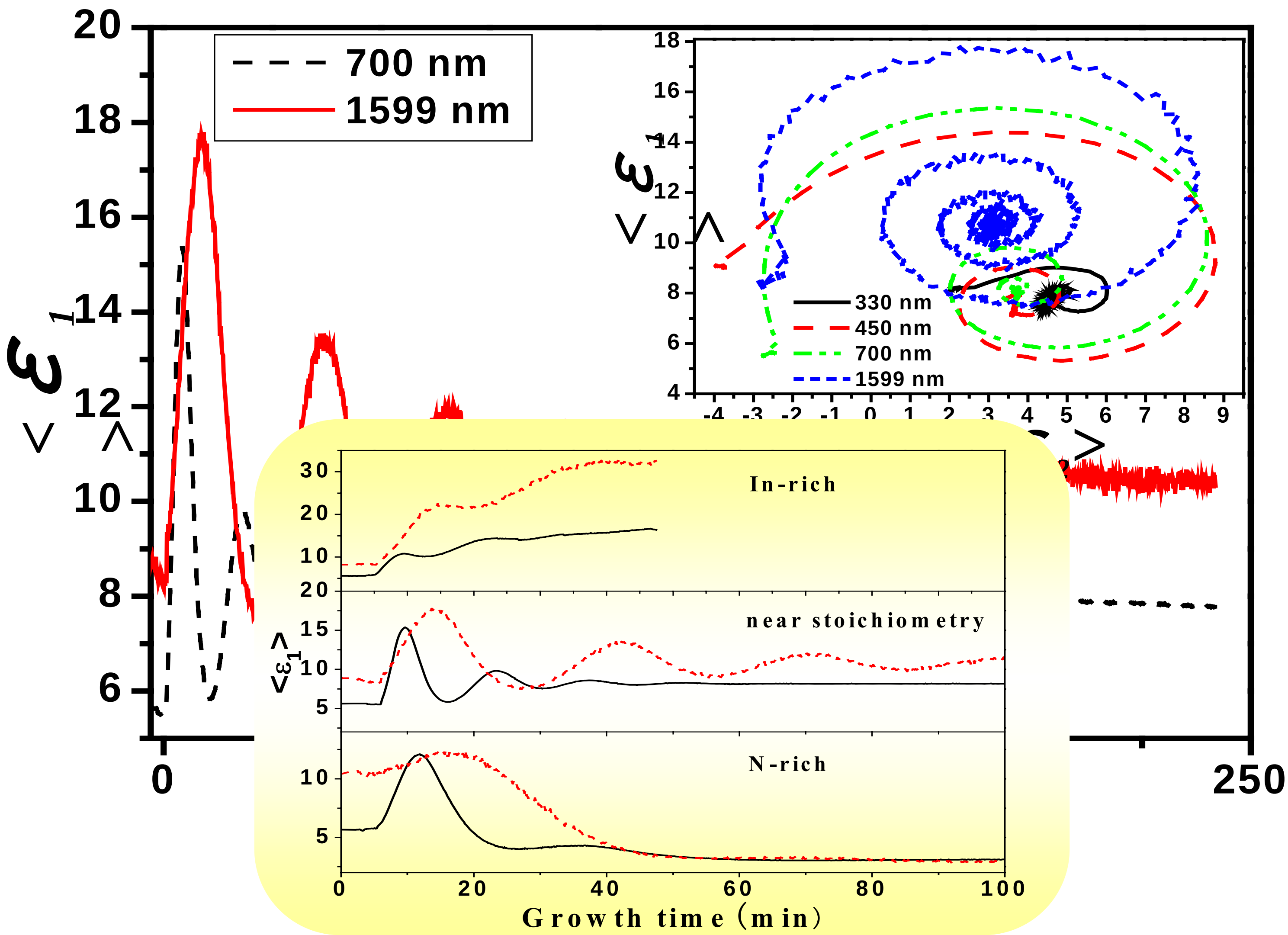
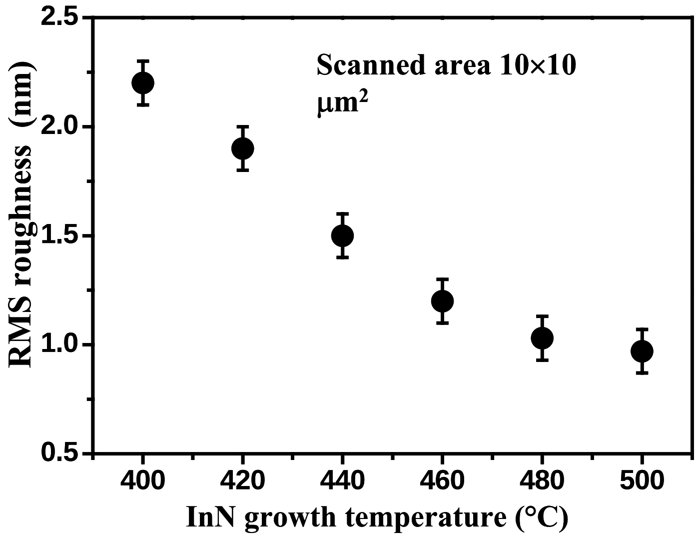
Epitaxy Behaviors/Stoichiometry

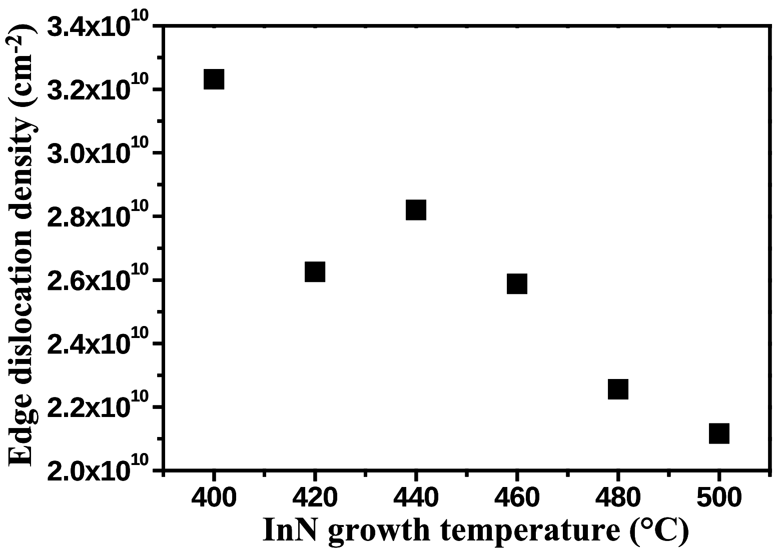
Outline
Introduction
MBE
InN epitaxy
Flat surface
Quality Up
InN Properties
P-type doping
Polarity Invers
P-type eviden.
InN Alloys
Nanostructure
Summary
Supplement

In-situ monitoring by spectroscopic ellipsometry

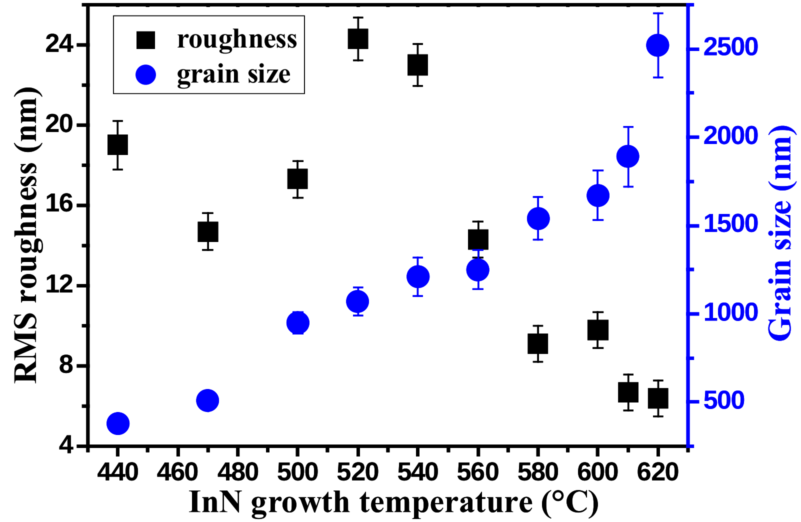


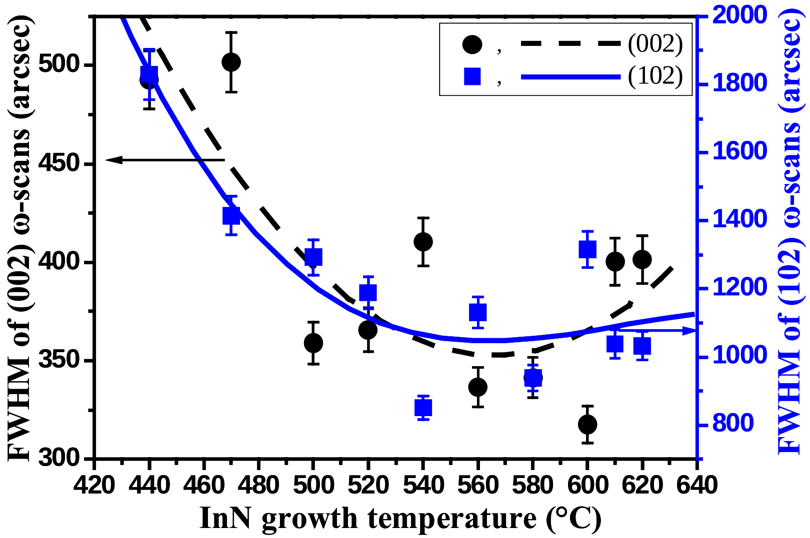
Effect of Growth Temperature





In-polarity





N-polarity

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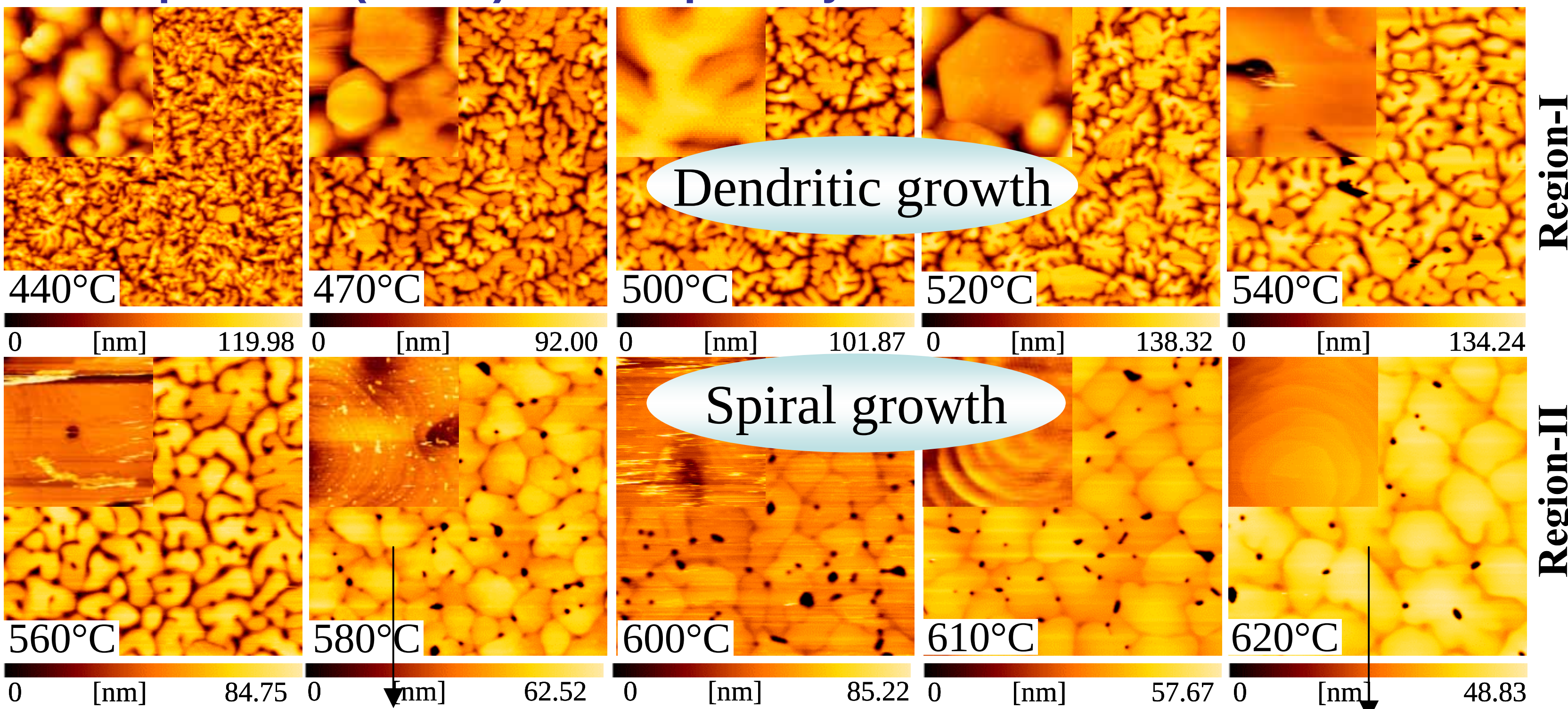
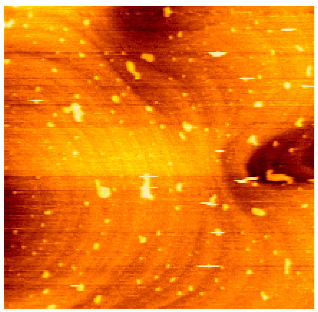
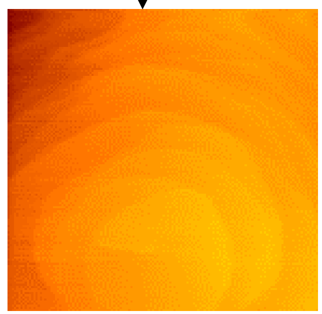
Typical Morphologies of N-polar InN

N-polarity epitaxy was studied first due to higher maximum epi-temperature (100°C) than In-polarity



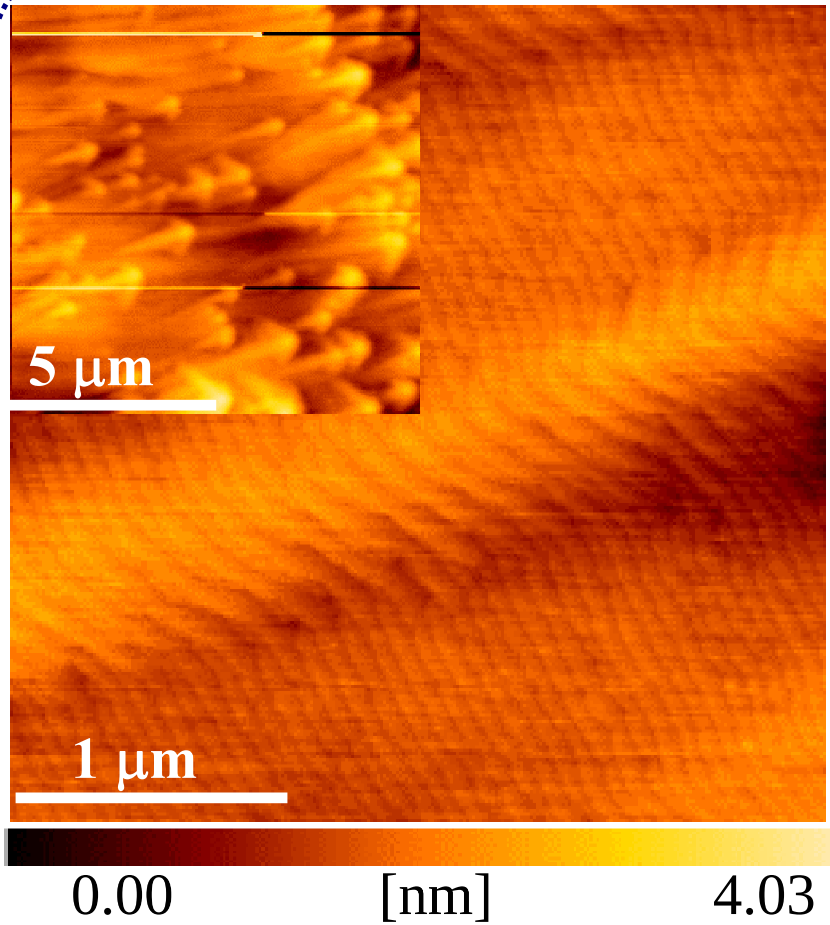


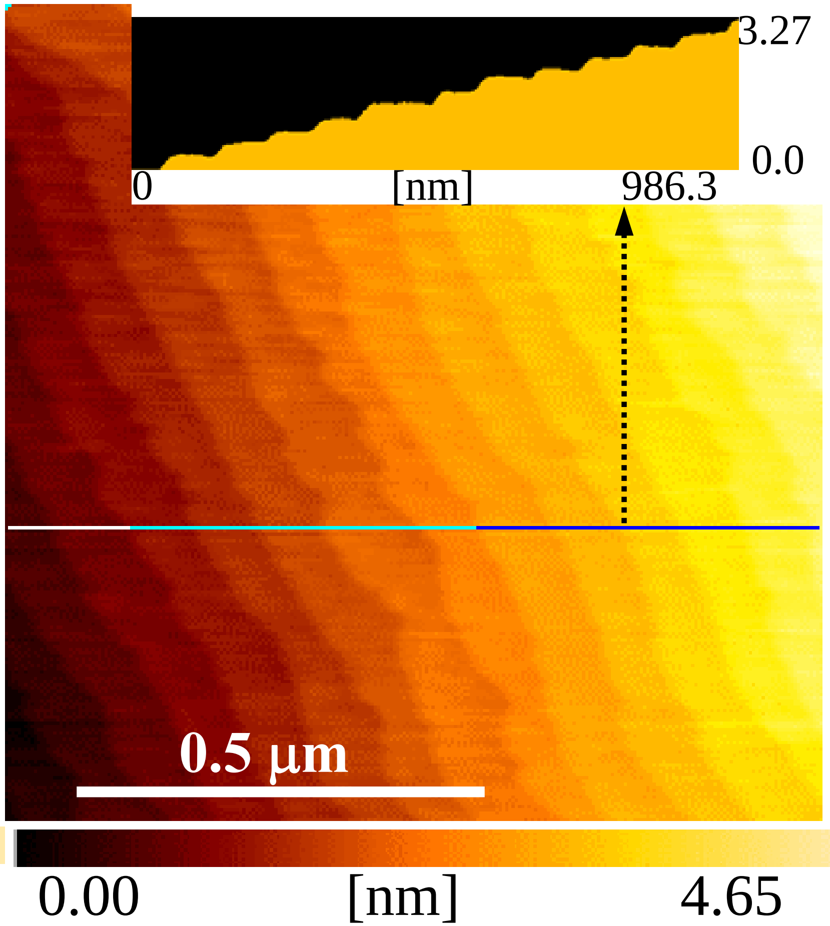
Enhanced migration of In adatoms with increasing growth temperature



X. Wang, et al, J. Appl. Phys. 99, 073512 (2006).

Atomically Flat Surface





Surface roughness is less than 1 nm in 10μm×10μm area

X. Wang, et al, Jpn. J. Appl. Phys. Part.2 Letter 45, L730 (2006).

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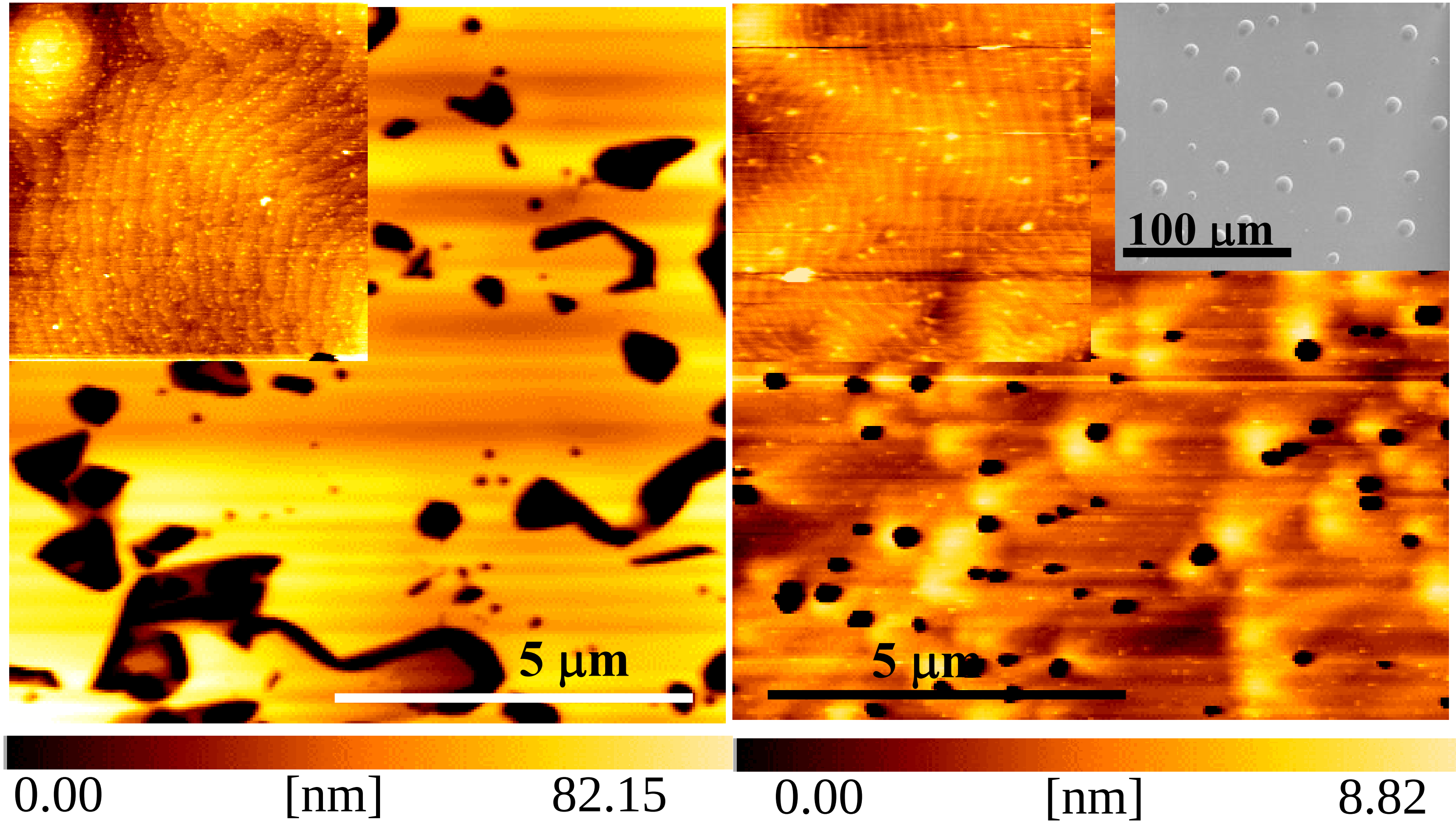
How to get atomically flat surface

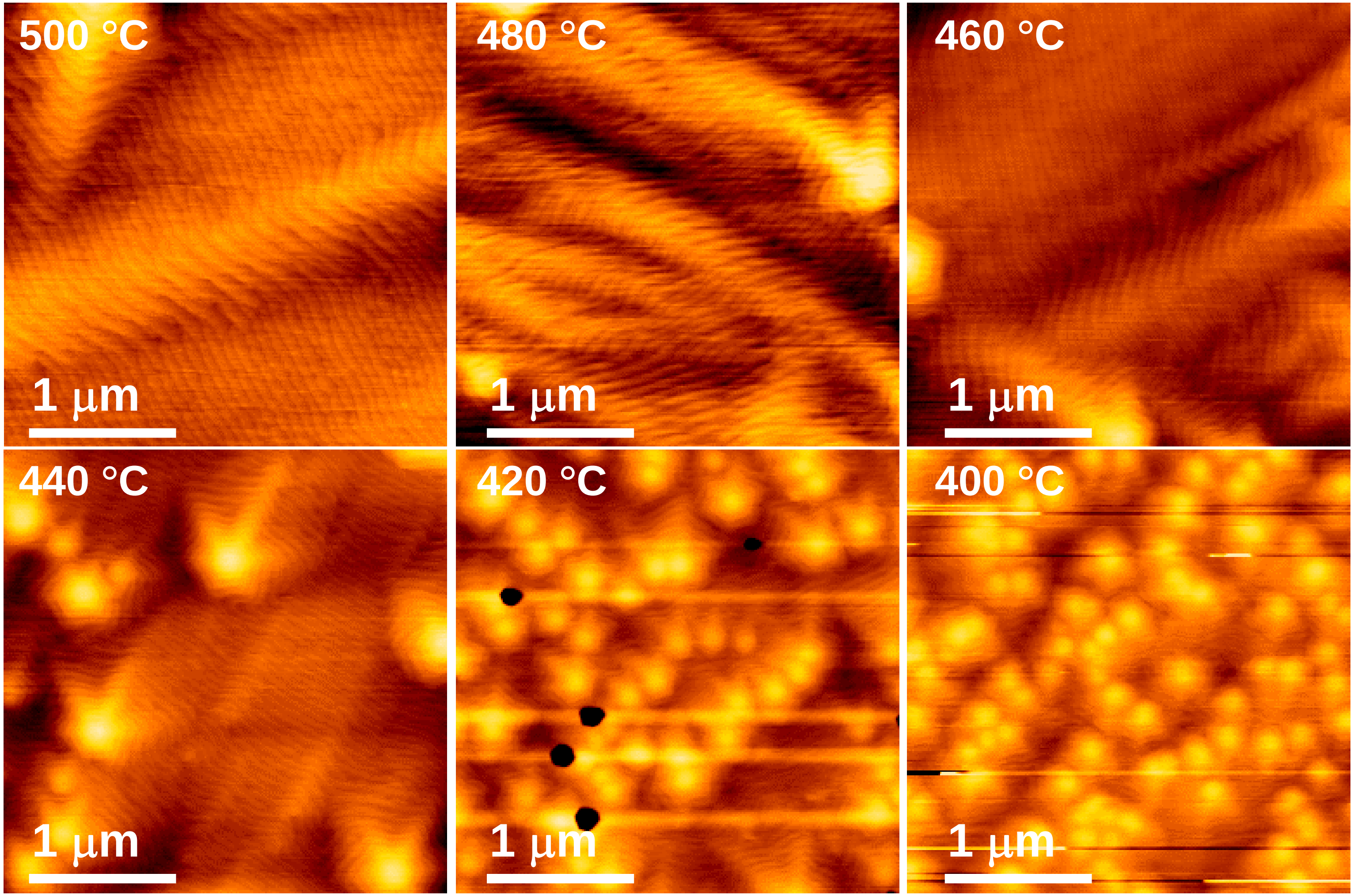


In/N=0.97

In/N=1.05

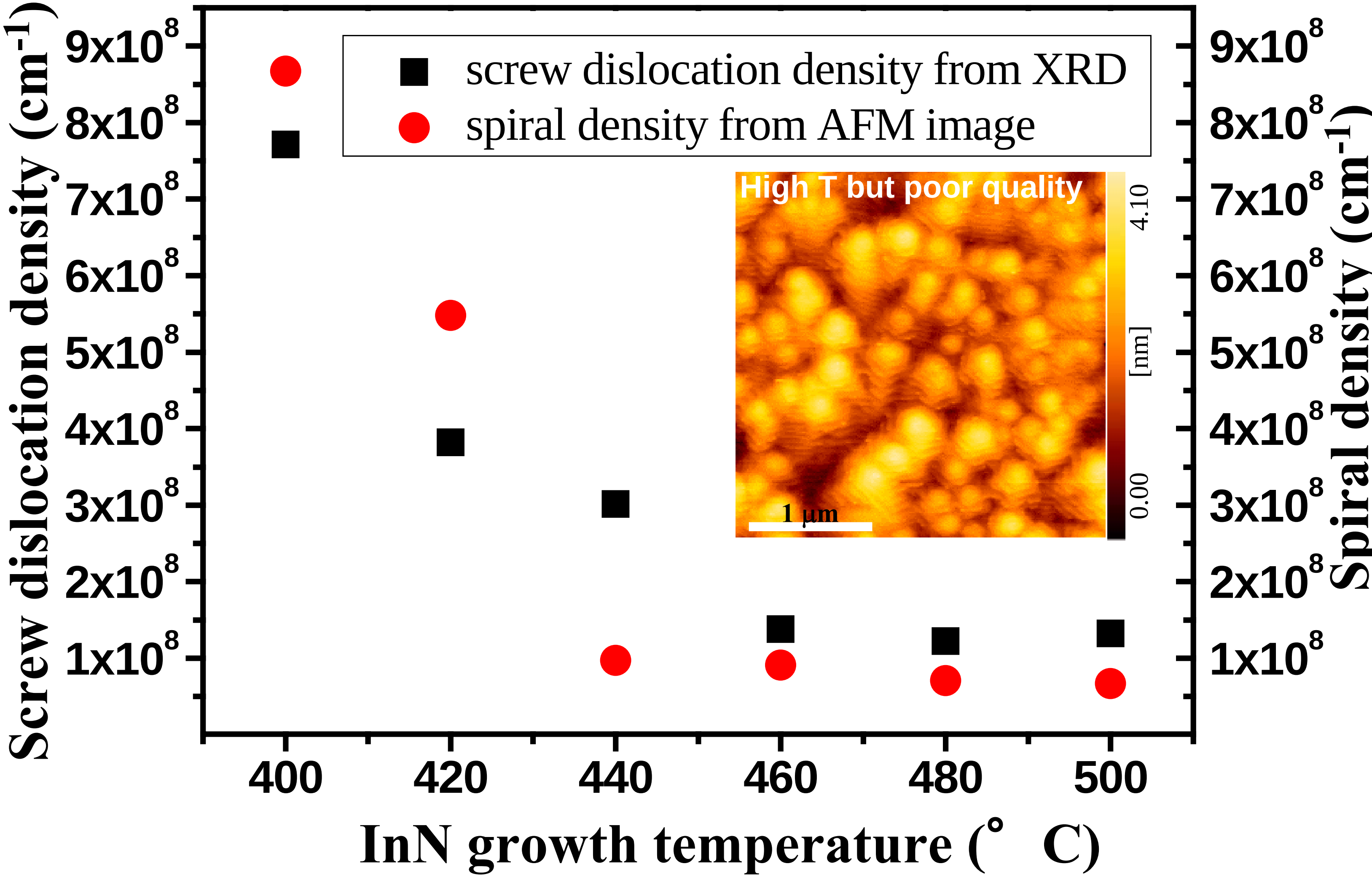
Slight In-rich condition is preferred

How to get atomically flat surface



High growth temperature is preferred

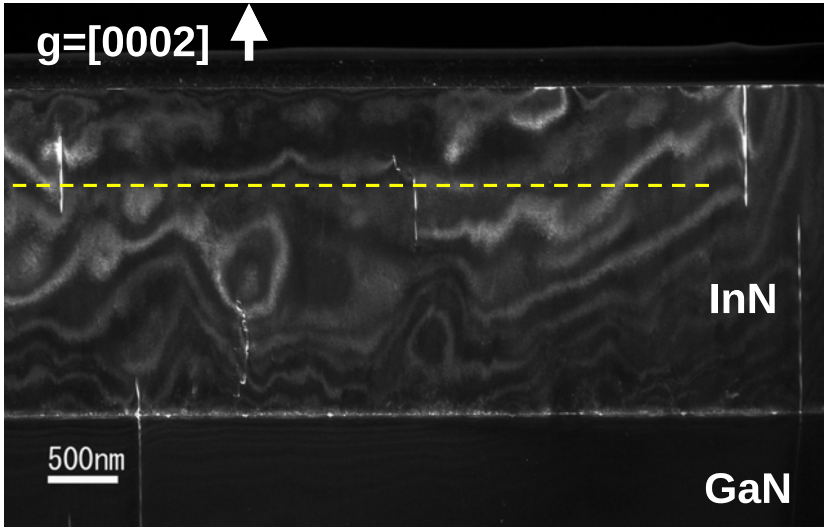
How to get atomically flat surface



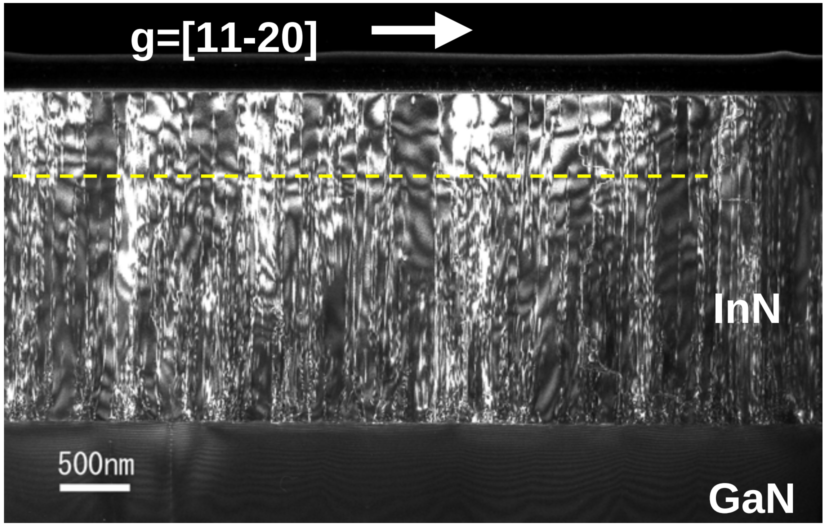
Low screw-type threading dislocation density

Crystalline Quality

Scew-type TD



Edge-type TD



	XRD		TEM	
TDs (cm^{-2})	Screw-	Edge-type	Screw-	Edge-
On GaN template	1.3×10^{8}	2.1×10^{10}	2.8×10^{8}	1.2×10^{10}

Crystalline quality was not good, in particular ETD density was still high

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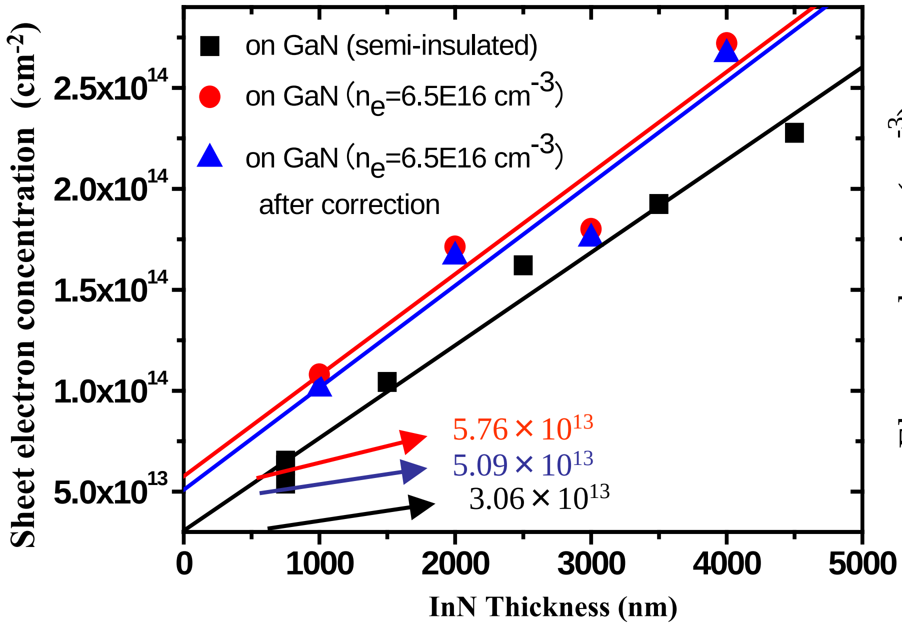
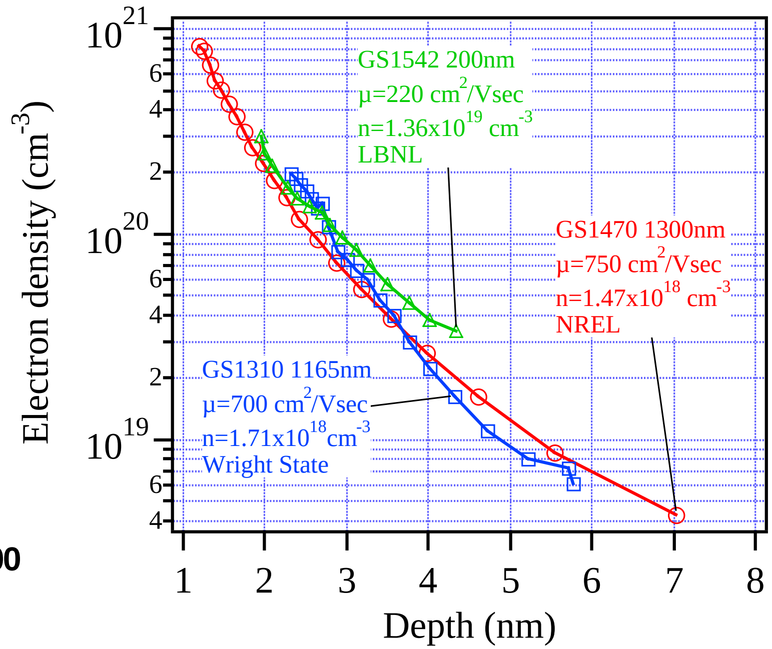
Surface Electron Accumulation

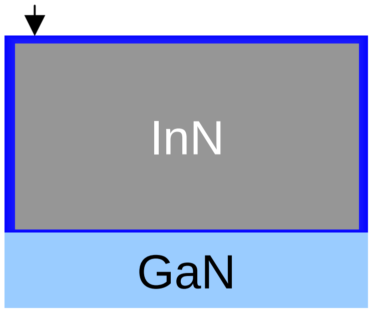




Sheet electron density at zero film thickness attributed to surface charge accumulation

High density surface electron was observed from ECV measurement.

Surface/interface electron accumulation



All metals form Ohmic contact on InN, also indicates surface accumulation, similar to InAs

Hai Lu, W. J. Schaff, L. F. Eastman, and C. E. Stutz, Appl. Phys. Lett. **82**, 1736 (2003)

W. J. Schaff, Hai Lu, L. F. Eastman, W. Walukiewicz, K. M. Yu, S. Keller, S. Kurtz, B. Keyes, L. Gevilas, Oct 2004 ECS meeting

Threading dislocation effect on n_e

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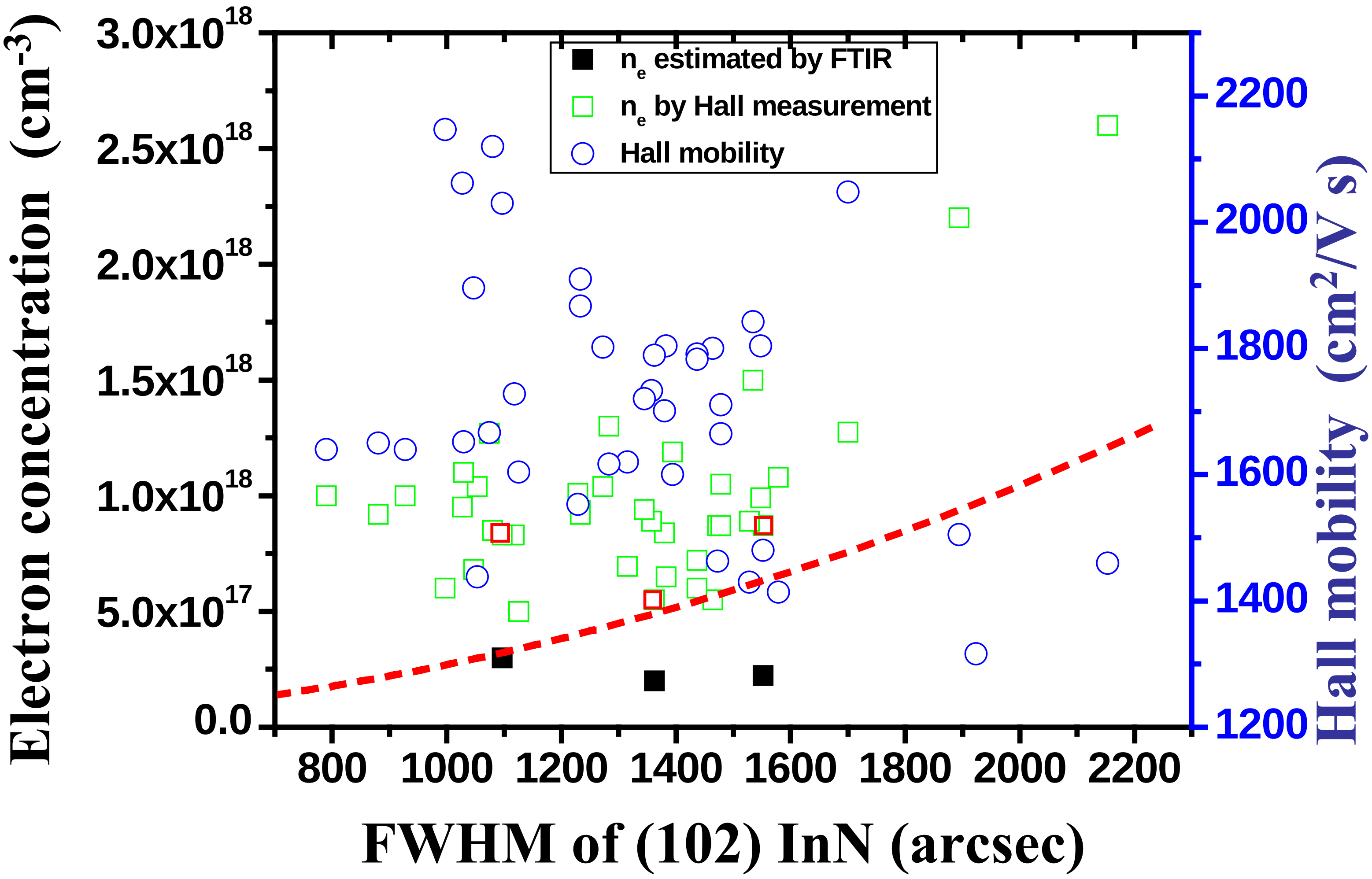
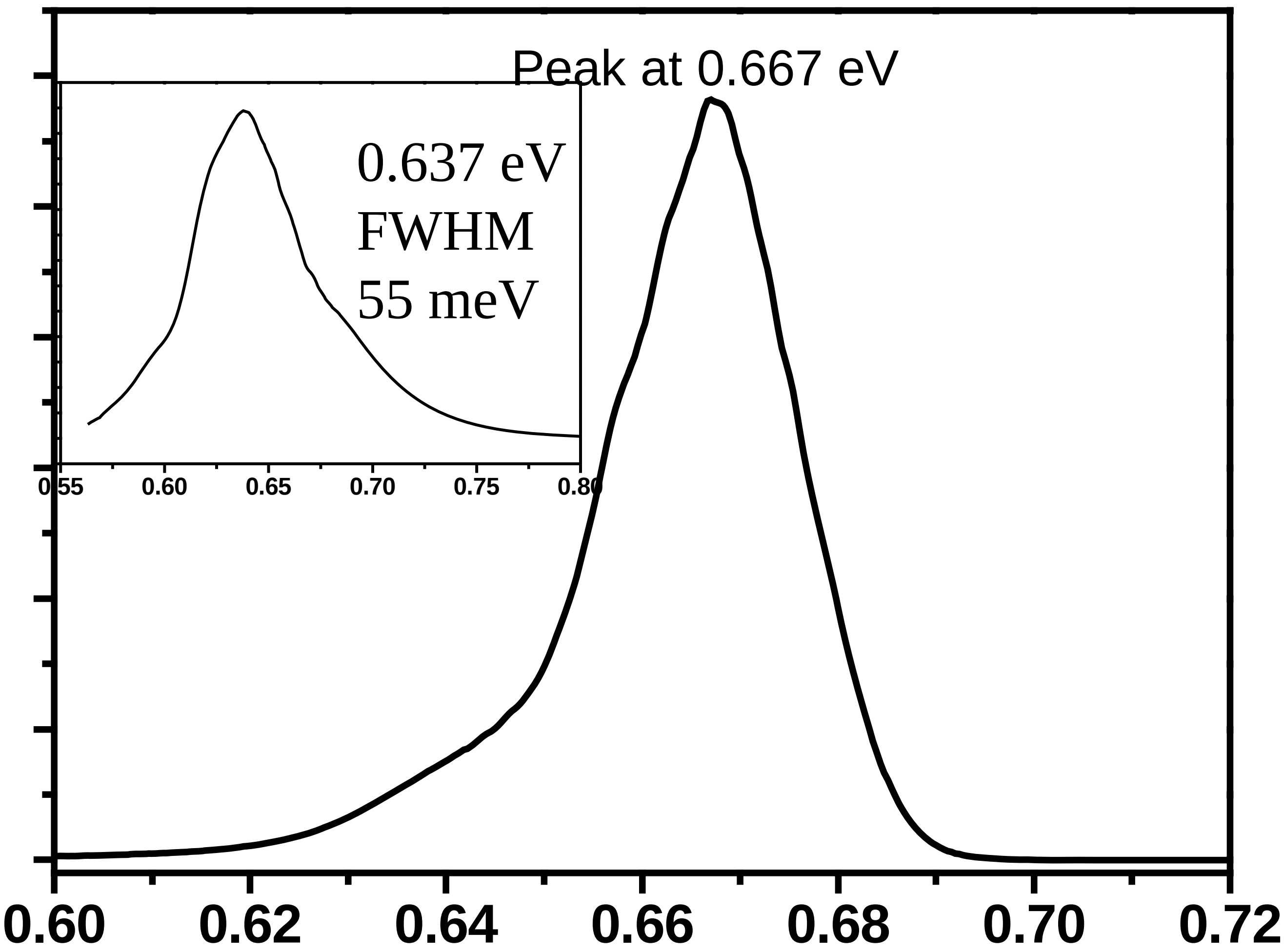


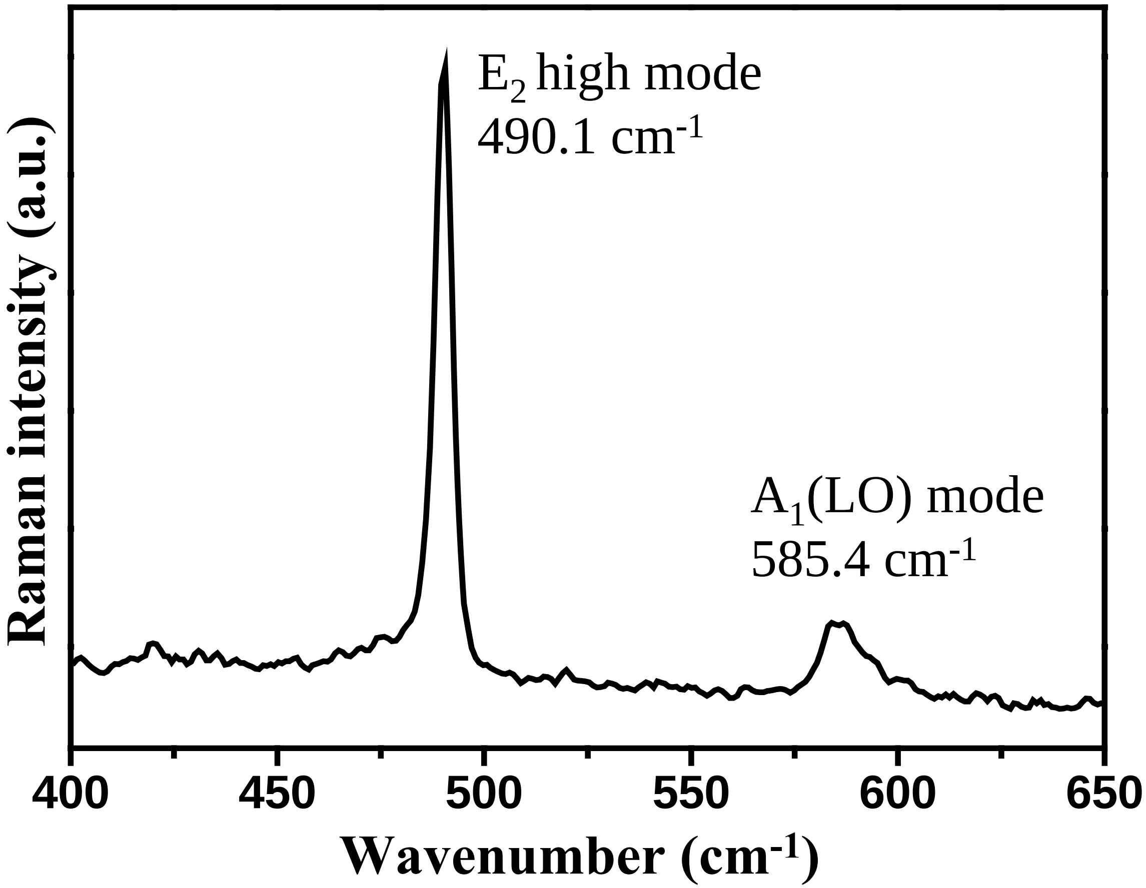
X Wang, S Che, Y Ishitani, A Yoshikawa, *Appl. Phys. Lett. 90 (2007) 151901*

PL Results



PL measurements show strong emission at 0.667 eV at 16 K and 0.637 eV at room temperature, absorption spectra also shows narrow band gap at around 0.63 eV at RT.

InN Parameters: Raman Scattering

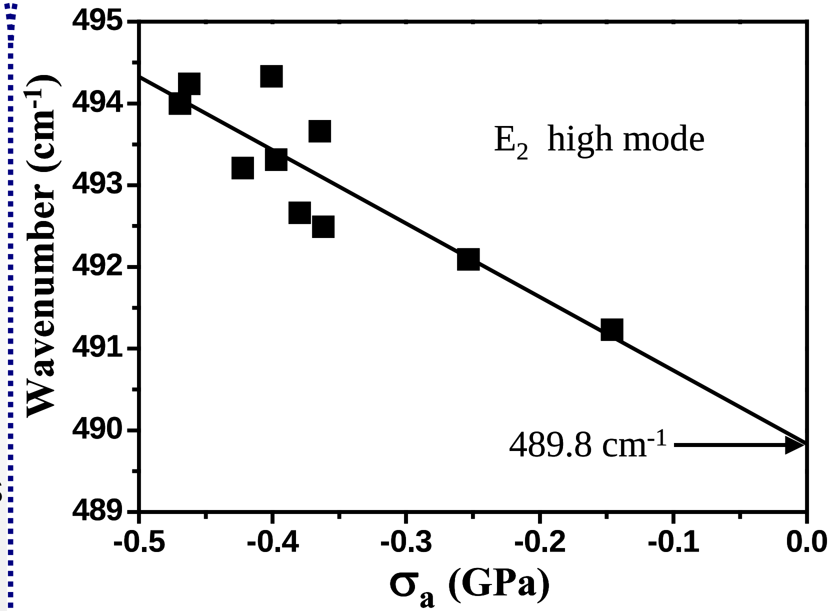


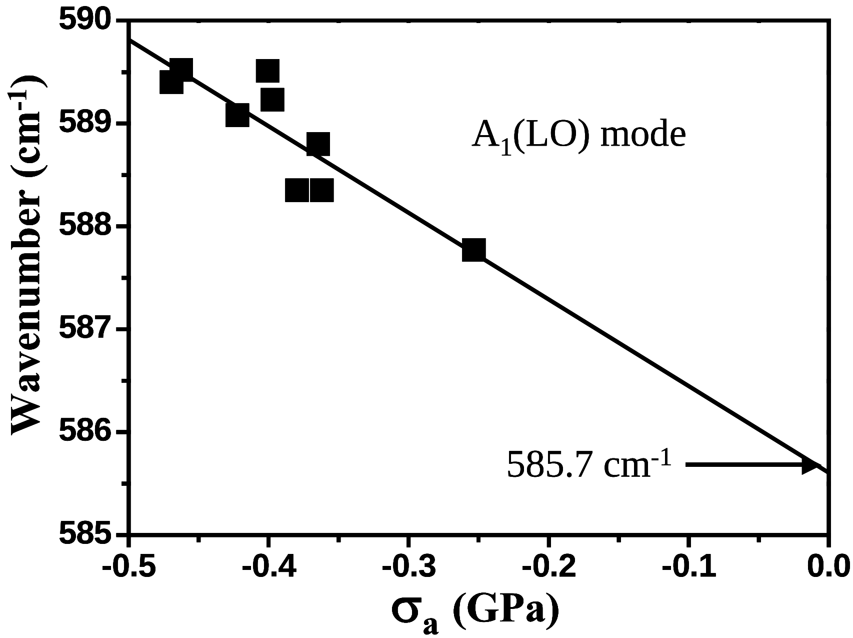
InN体材料

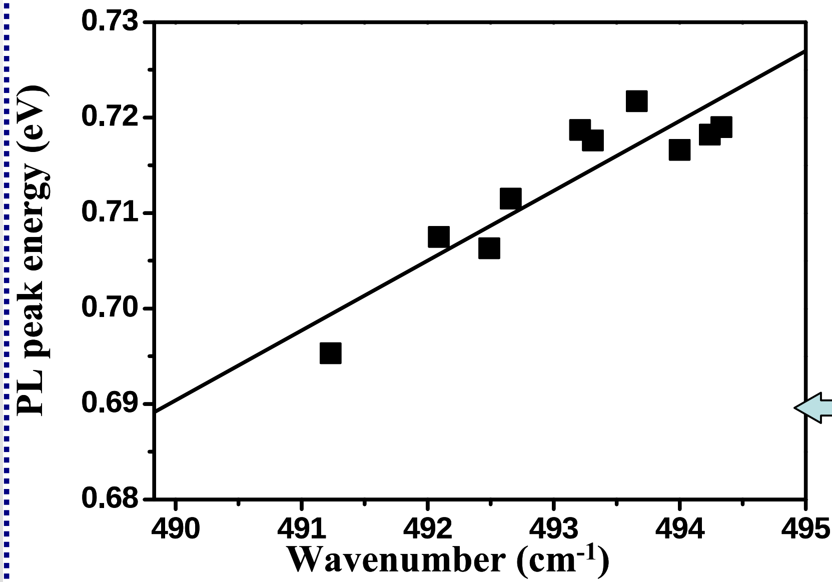
得到了无应变E_2和A_1(LO) 模的Raman散射峰的位置。

X Wang, S Che, Y Ishitani, A Yoshikawa, *Appl. Phys. Lett. 89 (2006) 261643.*

InN Parameters: Raman Scattering







Raman线性双轴应力系数（E2 模）$8.99 \pm 1.7\ cm^{-1}/Gpa$

Raman线性双轴应力系数（A1(LO) 模）$8.4 \pm 1.7\ cm^{-1}/GPa$

$\alpha E / \alpha\omega = 7.3 \pm 1.2\ meV/cm^{-1}$

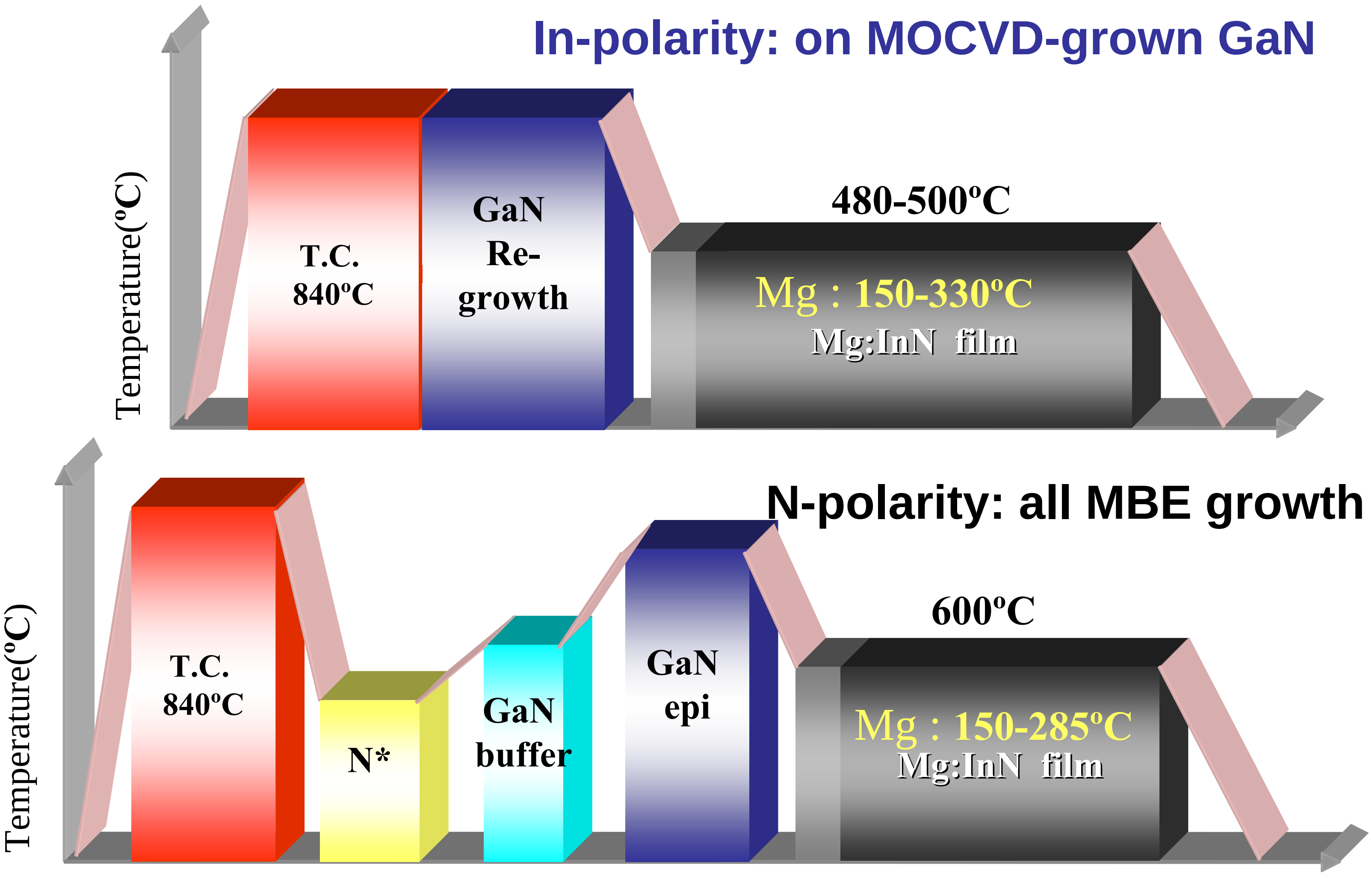
InN E_2 和A_1(LO)模式的形变势 (Deformation potentials)

Ref	C_{11}	C_{12}	C_{13}	C_{33}	a_{E_2} (cm^{-1})	b_{E_2} (cm^{-1})	$a_{A_1(LO)}$ (cm^{-1})	$b_{A_1(LO)}$ (cm^{-1})
[1]	190	104	121	182	–938±43	–407±101	–901±43	–587±101
[2]	223	115	92	224	–960±48	–489±82	–915±48	–642±82
[3]	271	124	94	200	–998±55	–635±56	–944±55	–750±56
[4]	204	85	72	217	–893±46	–236±87	–850±46	–395±87

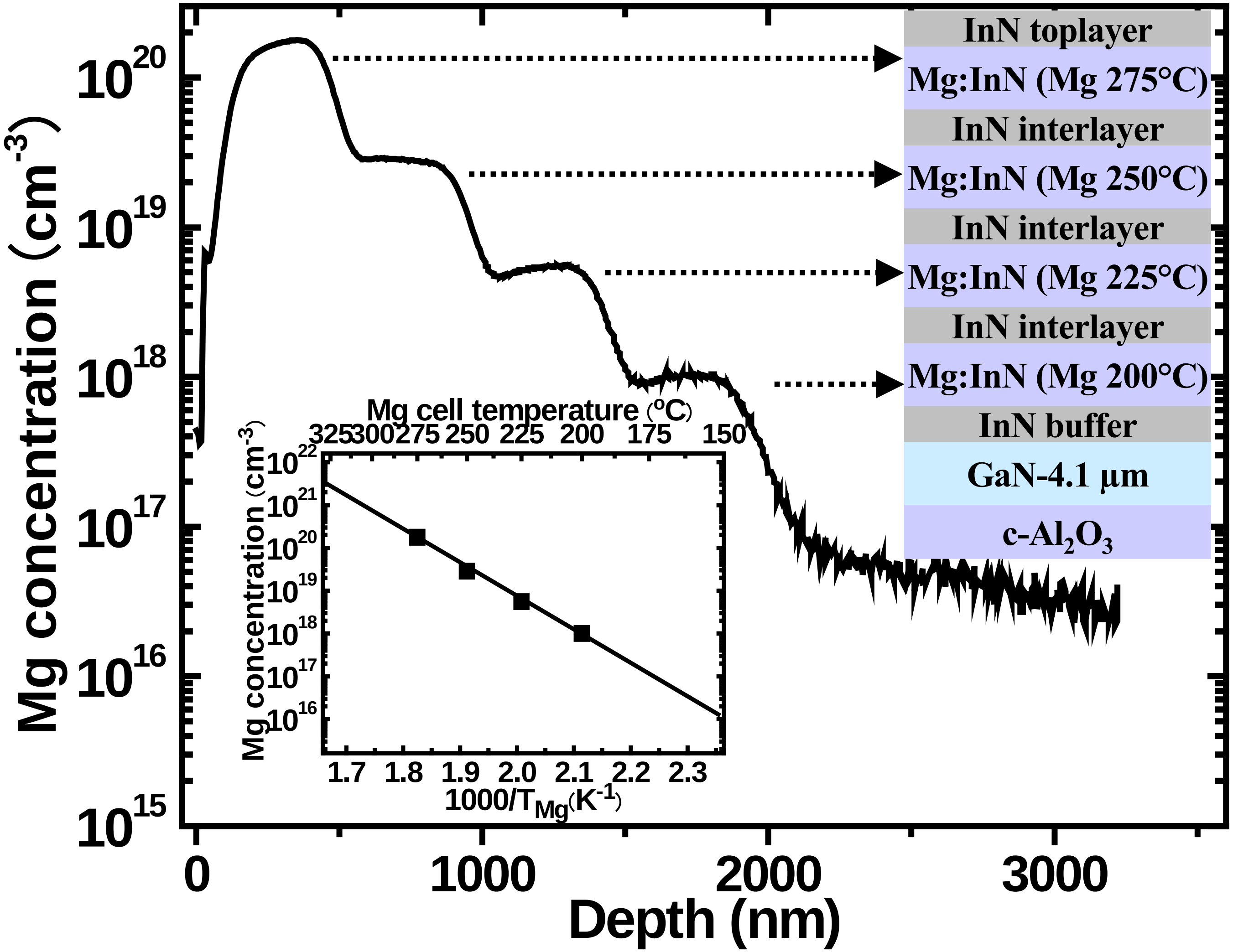
[1]V. S. Harutyunyan, P. Specht, J. Ho, and E. B. Weber, Defect and Diffusion Forum **226-228**, 79 (2004); A. U. Sheleg and V. A. Savastenko, Izv. Akad. Nauk SSSR, Neorg. Mater. **15**, 1598 (1979).
[2]A. F. Wright, J. Appl. Phys. **82**, 2833 (1997).
[3]K. Kim, W.R.L. Lambrecht, and B. Segall, Phys. Rev. B **82**, 2833 (1997).
[4]S.Yu. Davydov, Semiconductors **36**, 41 (2002).

C_{ij}--Elastic stiffness constants; a and b --deformation potentials

Growth Process of Mg-doped InN

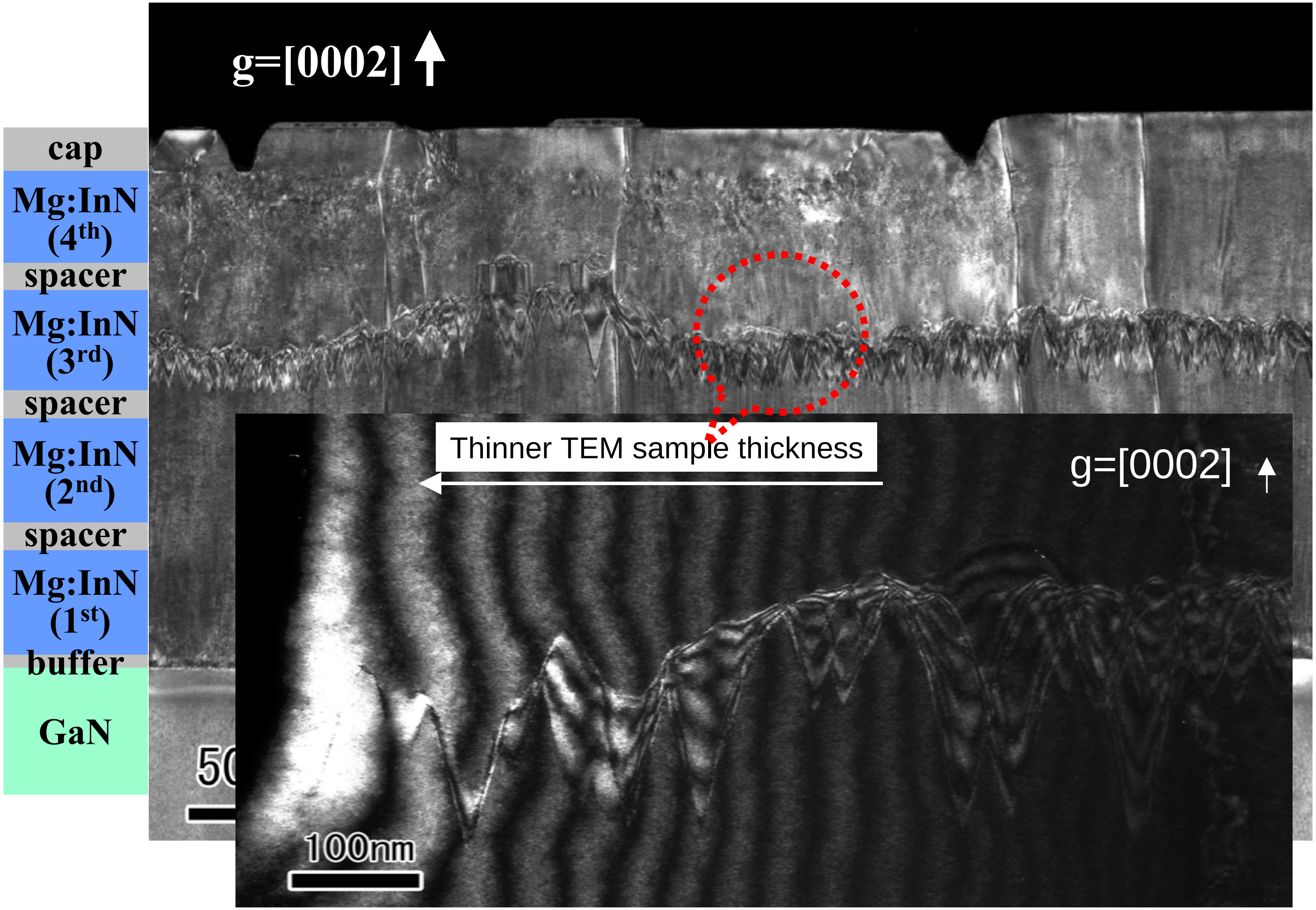


Mg concentration in InN:Mg



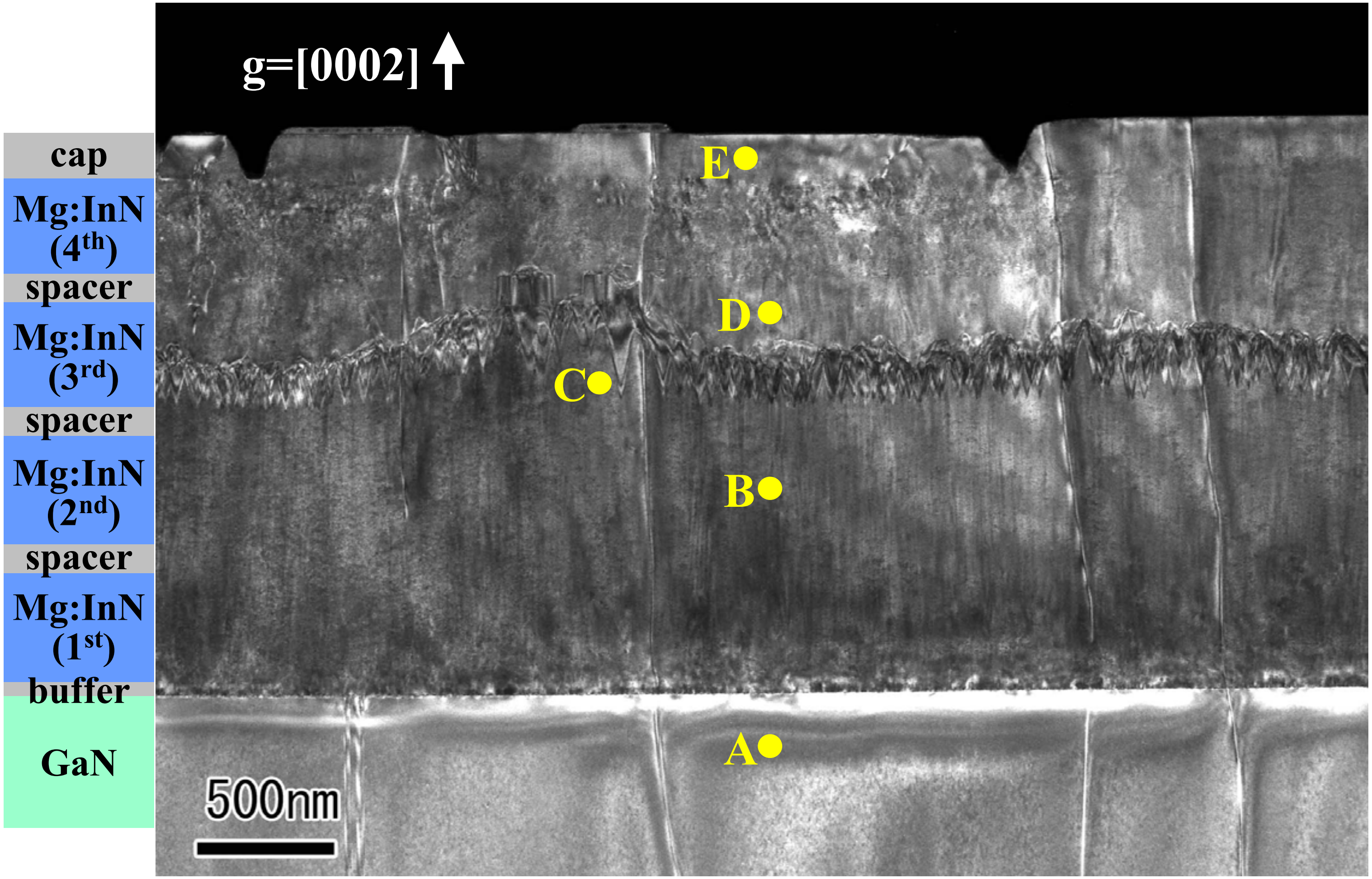
The Mg-doping level in each Mg:InN layer is almost constant and the boundary at the different doping levels is sharp; The Mg concentration changes exponentially with T_{Mg},. The sticking coefficient of Mg on In-polarity InN is almost unit.

Domain structure in InN:Mg



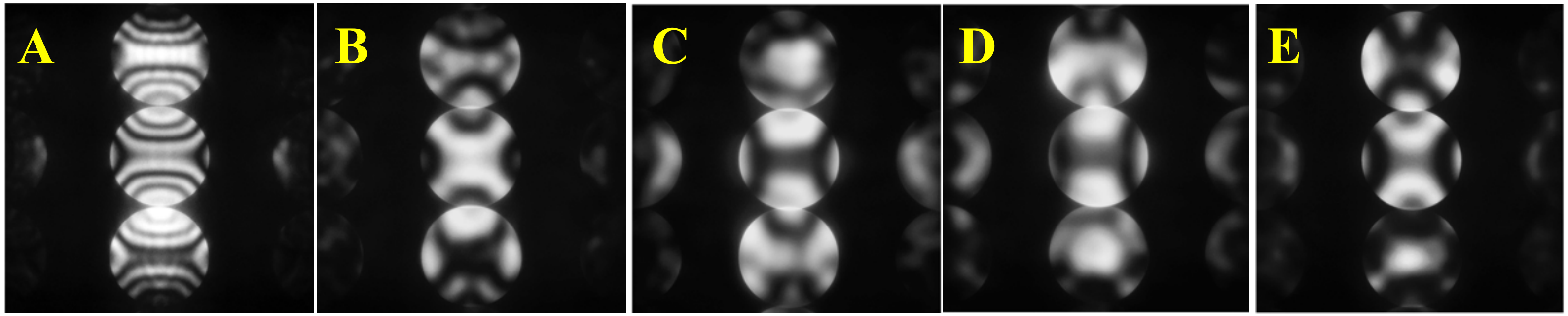
A layer with domain structure is observed at 3rd Mg:InN layer with Mg concentration of 2.9×10^{19} cm^{-3}. Are these domains inversion domains?

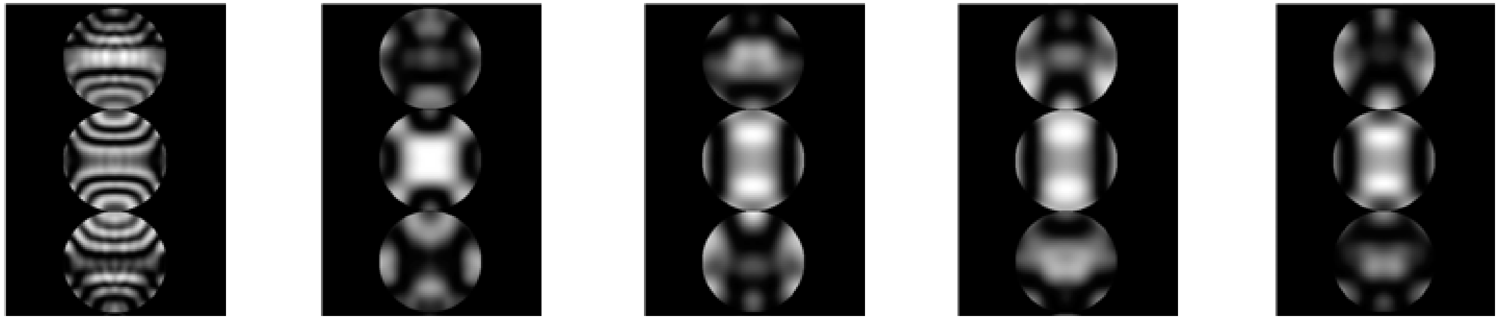
Polarity Investigation



Several points were chosen to check polarity by convergent beam electron diffraction (CBED) in TEM measurement.

CBED Results in TEM Measurement



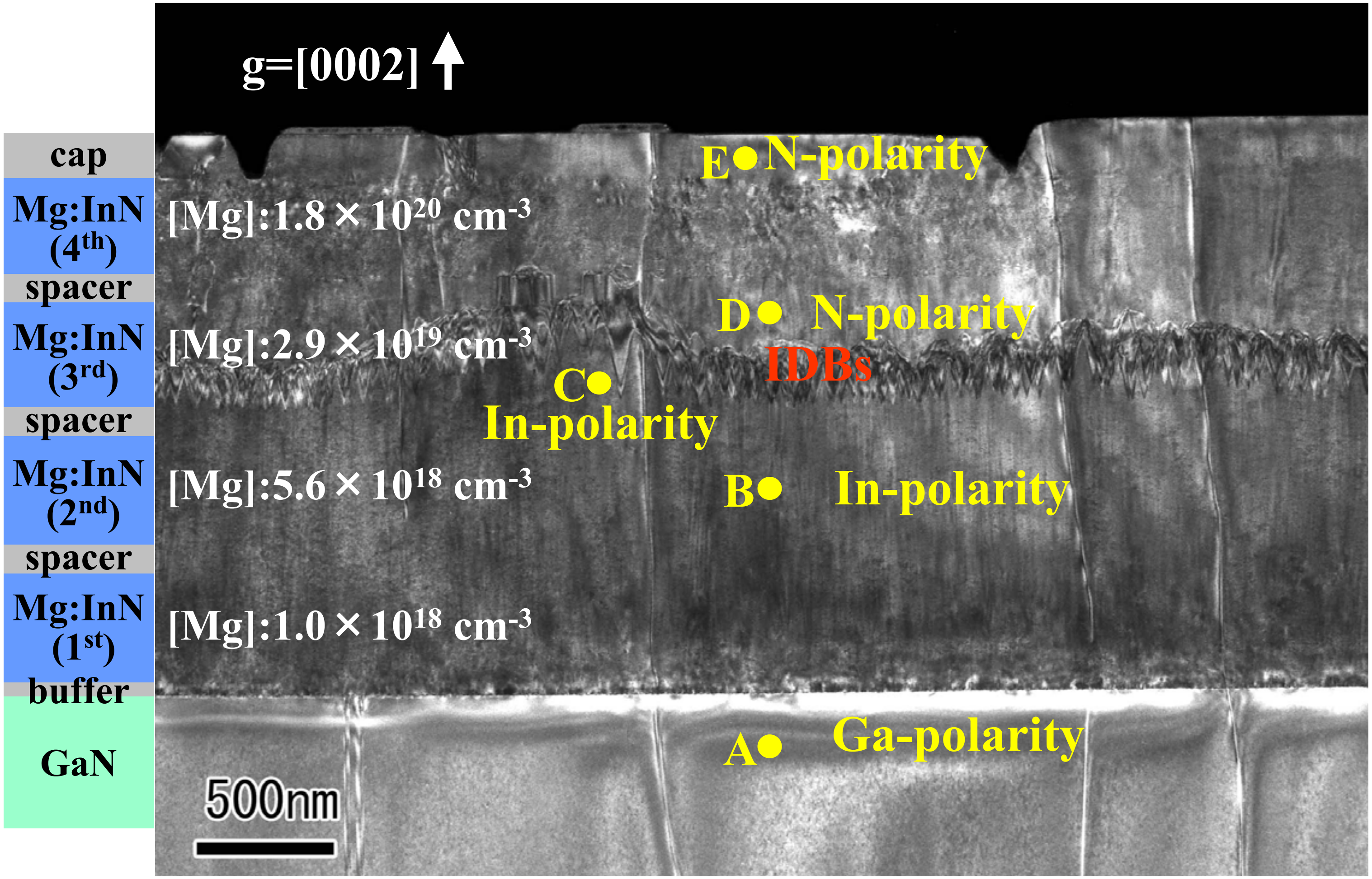


Ga-polar GaN (*t*=205 nm) | **In-polar InN (*t*=90 nm)** | **In-polar InN (*t*=68 nm)** | **N-polar InN (*t*=64 nm)** | **N-polar InN (*t*=73 nm)**

Simulation

Polarity was determined by comparison between measured CBED patterns and simulated patterns

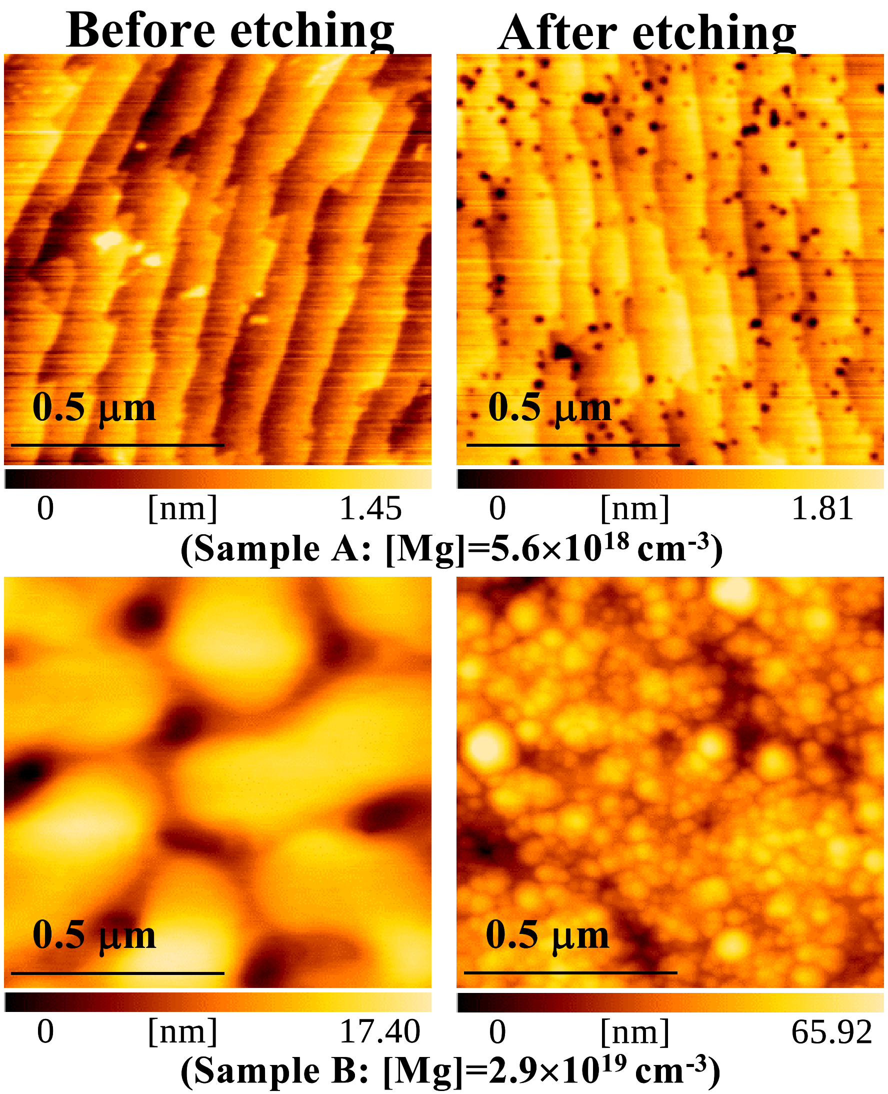
Polarity Inversion in InN:Mg



Polarity was inverted from In-polarity to N-polarity, confirming domains are inversion domains.

X Wang, S Che, Y Ishitani, A Yoshikawa, *Appl. Phys. Lett. 91 (2007) 081902*

Polarity Investigation by Chemical Etching



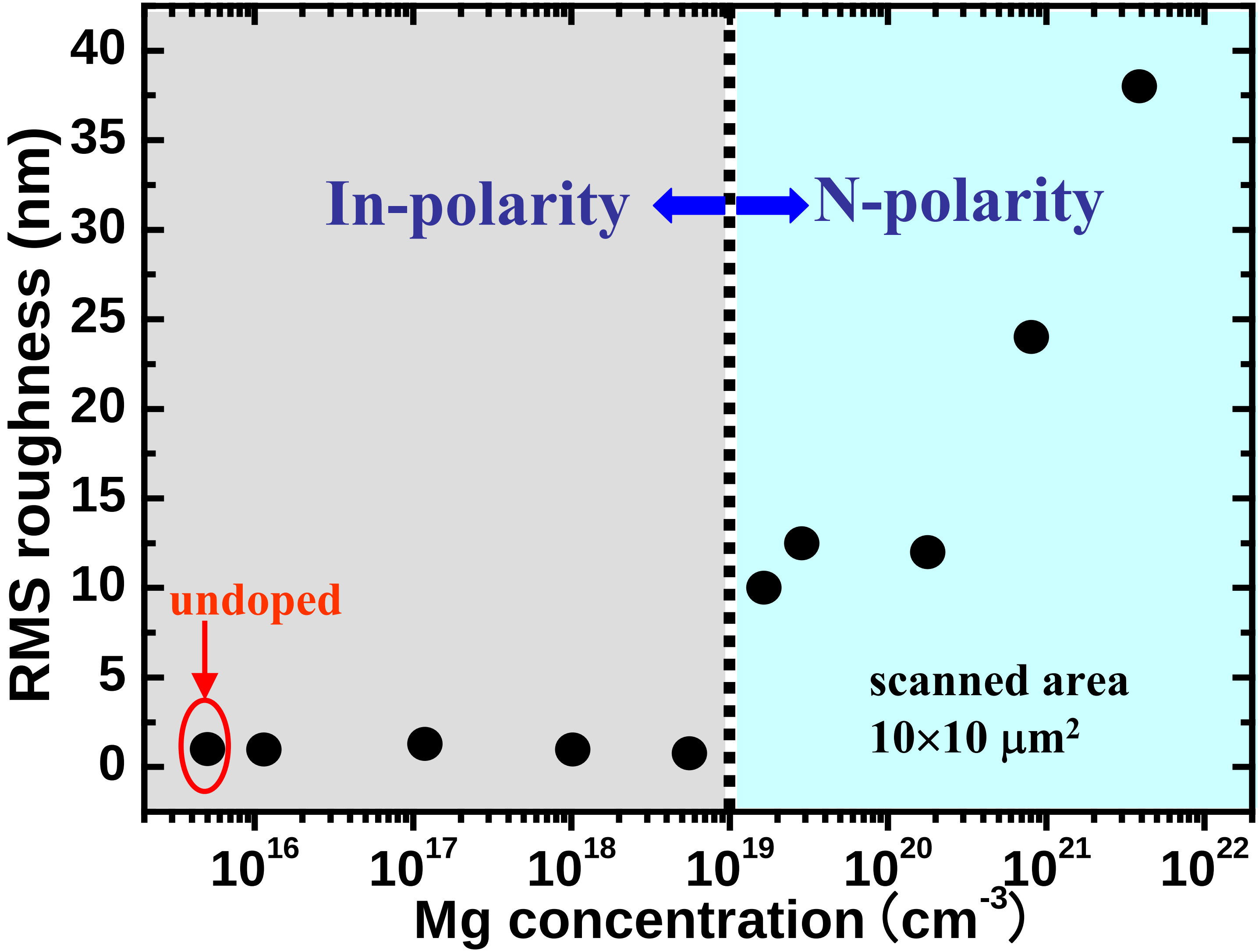
In-polarity

N-polarity

10M KOH
for 2h at RT

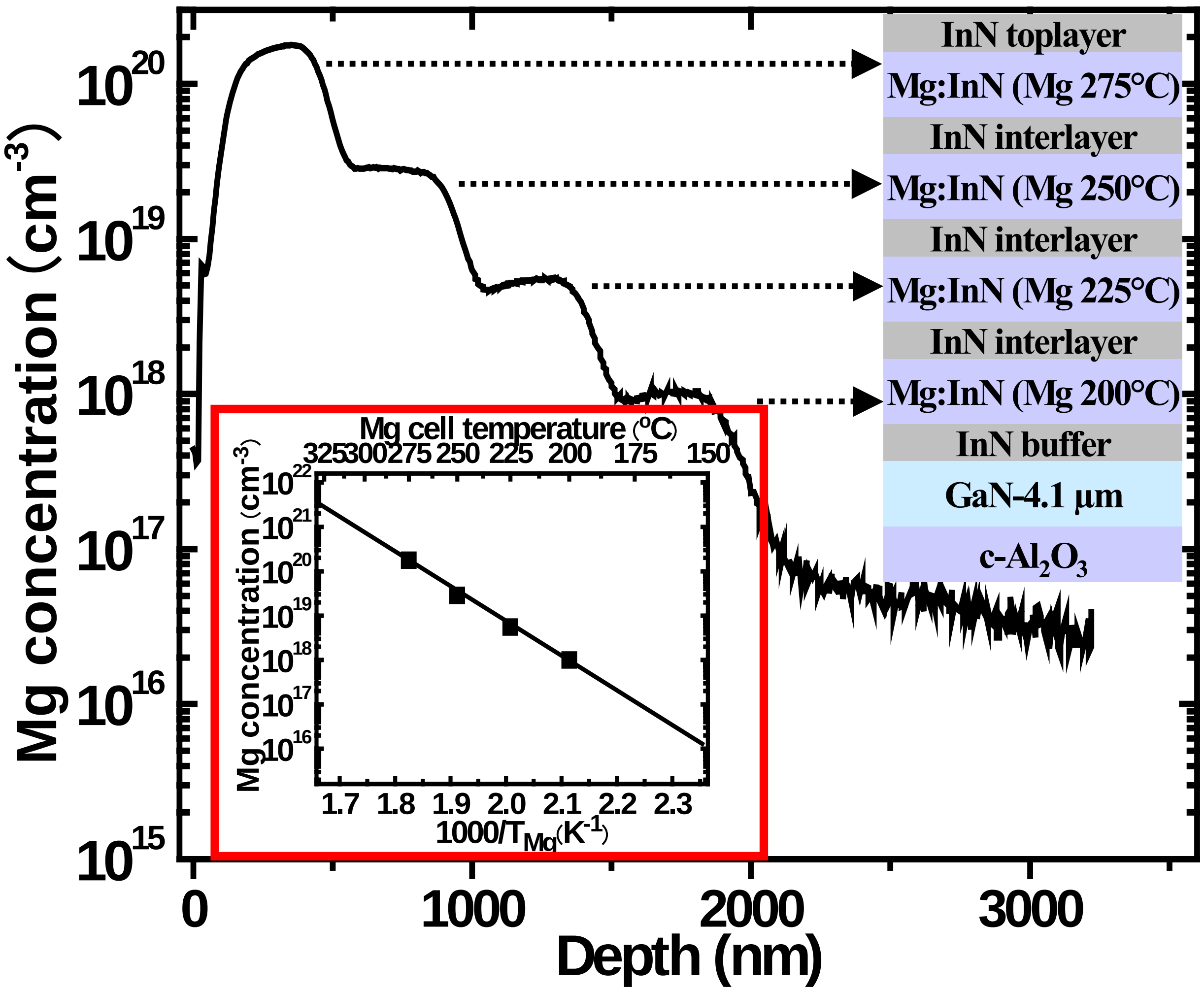
In-polarity InN was difficult to be etched, and step-flow feature was kept after etching.
N-polarity InN was easily etched, surface became rougher and small island-like structure was observed on surface.

Polarity Investigation by Chemical Etching



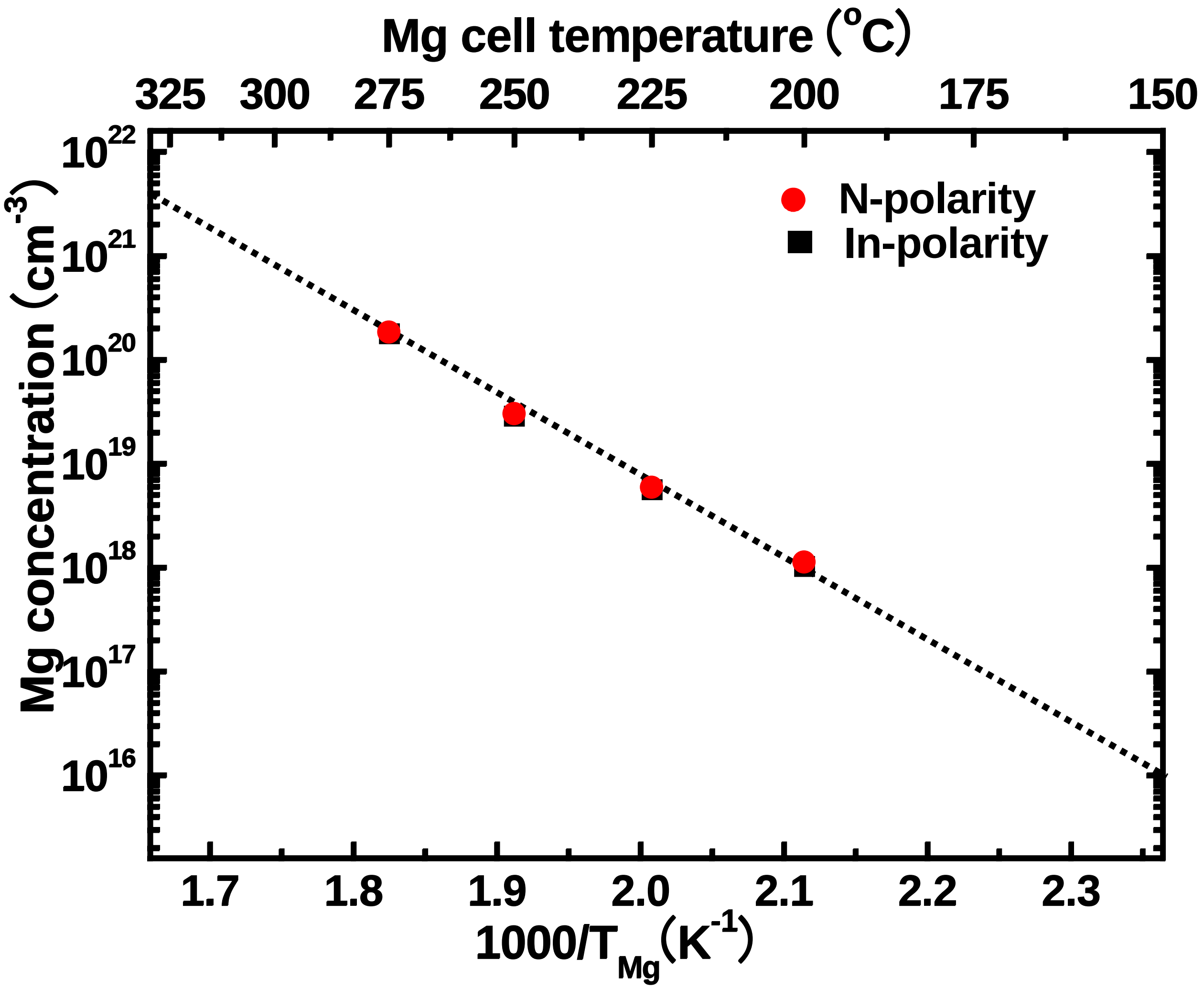
Further investigation on several samples with different [Mg]s shows polarity inversion happened at [Mg]~10^{19} cm^{-3}.

Mg concentration in InN:Mg



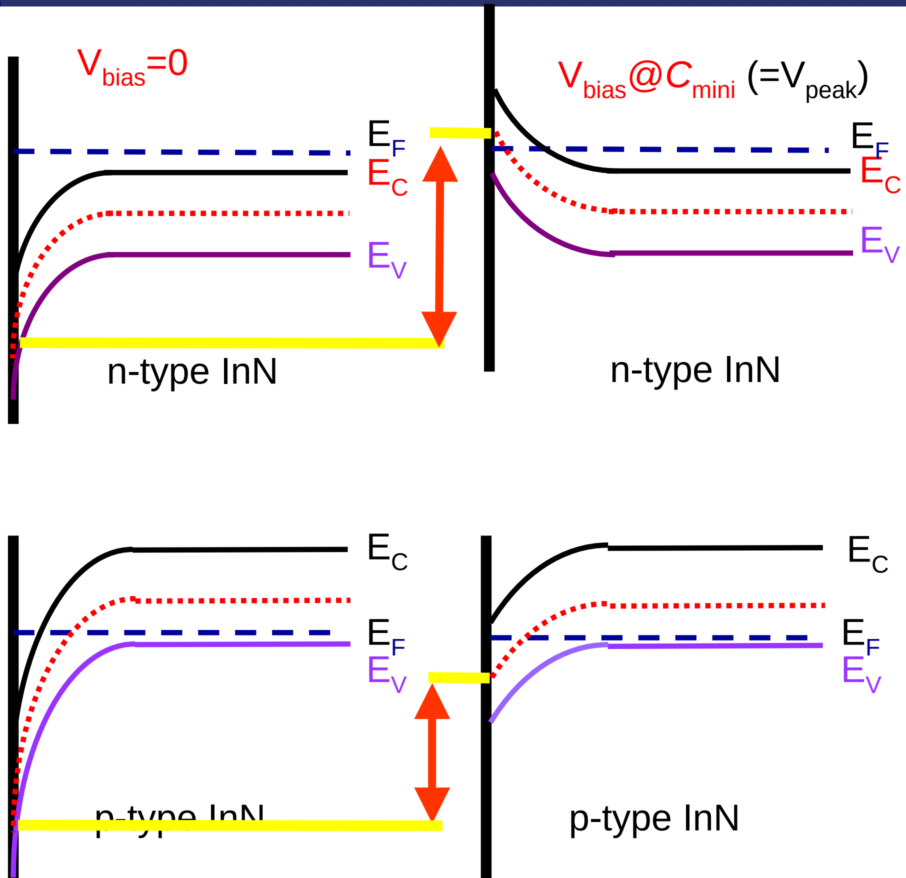
Return to Mg concentration at different Mg cell tempeature.

[Mg] Comparison between In and N polarities

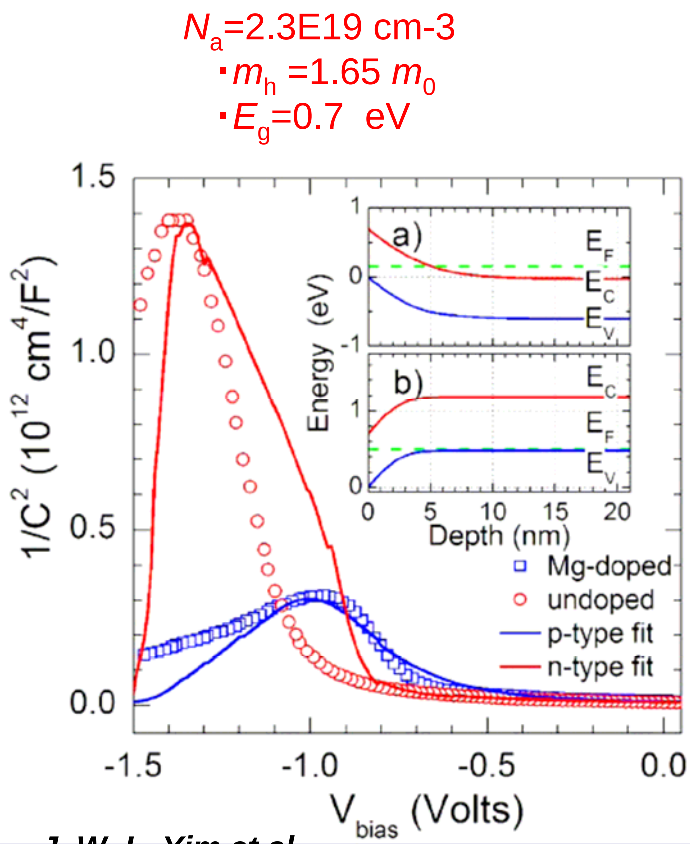


[Mg] shows almost the same value at the same supplied Mg beam flux, independent of polarity, probably due to the low growth temperature.

P-type Mg:InN-ECV measurement



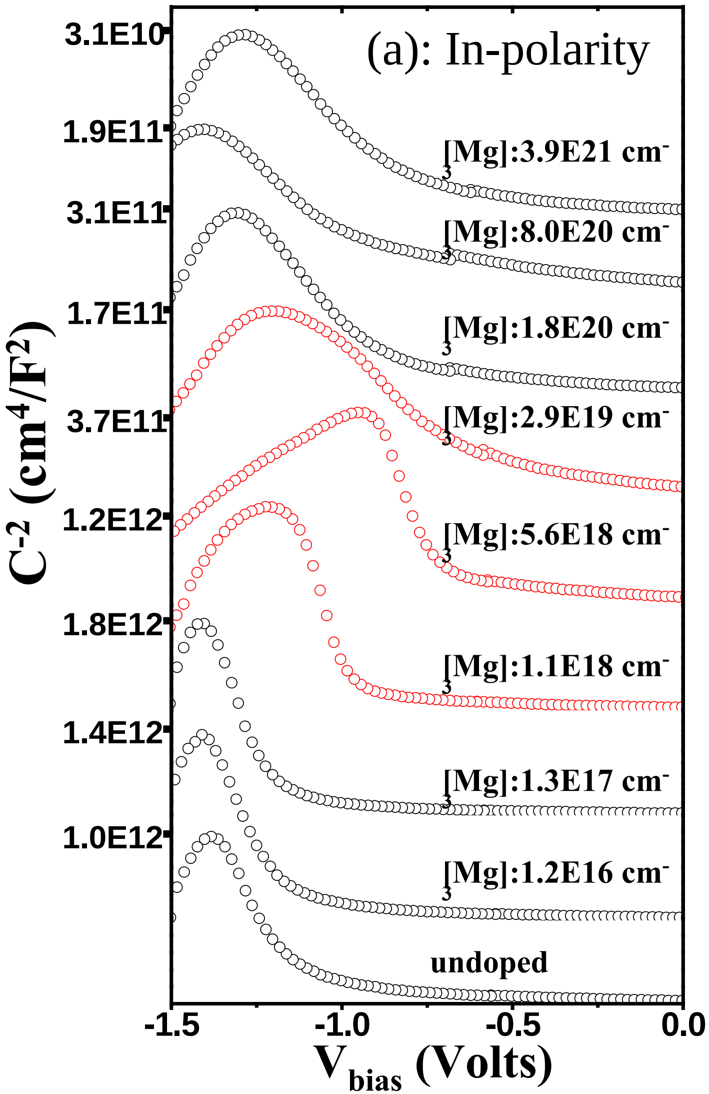
MIS structure C-V properties

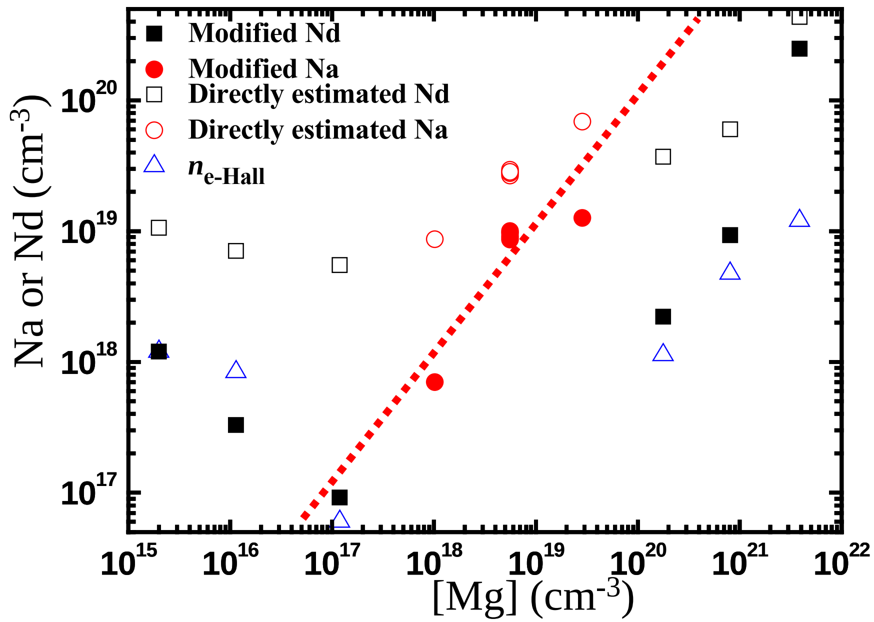


J. W. L. Yim et al., Phys. Rev. B 76, 041303 (2007)

C^{-2}-Vbias spectra can be simply understood as follows: 1) under thermal equilibrium, i.e., under zero Vbias, the surface Fermi levels for both p-type and n-type InN samples are pinned at about 0.9 eV high above the conduction band bottom. 2) the surface Fermi level or surface potential can be modified by the applied voltage and the surface Fermi level position inside the forbidden band corresponding to the C^{-2} peak is different in magnitude of 0.35 to 0.45 eV between p-type and n-type InN samples, and then 3) Vbias values when detect-ing C^{-2} peaks are different for p-type and n-type conduction InN.

P-type conduction - ECV measurement In-polarity





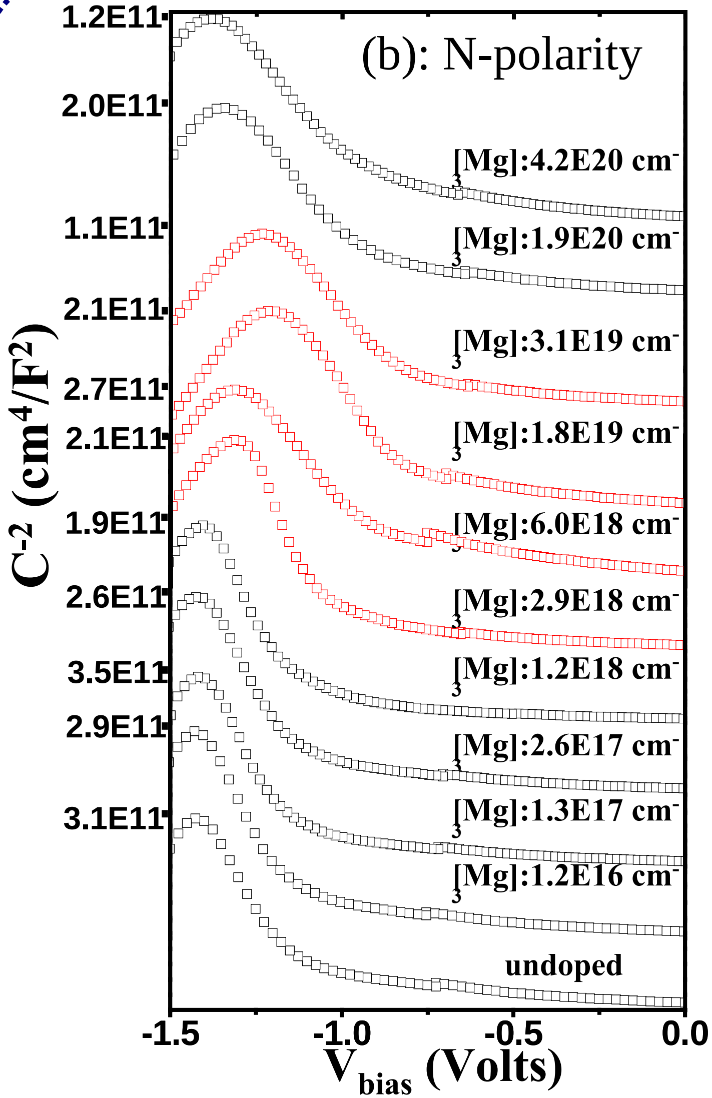
Sample	$n_{e\text{-Hall}}$ (cm^{-3})	$N_{d\text{-ECV}}$ (cm^{-3})	$C_{min\text{-cal.}}$ (nF/cm^2)	$C_{min\text{-exp.}}$ (nF/cm^2)	$\Delta C.$ (nF/cm^2)
E861	5.08E17	6.9E18	254	834	580
E868	5.17E17	8.9E18	256	938	682
E863	5.08E17	6.6E18	254	816	562
E671	6.01E17	1.2E19	274	1067	793
E920	9.08E17	7.8E18	330	885	555

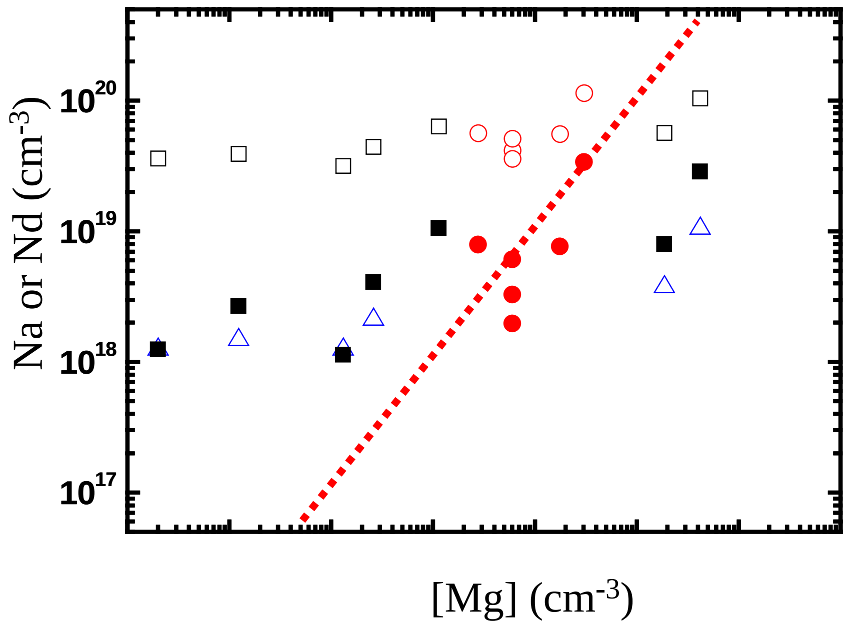
▪ $m_h = 0.42\ m_0$ ▪ $E_g = 0.63$ eV $\varepsilon_r = 9.3\varepsilon_0$

In-polarity regime

X Wang, S Che, Y Ishitani, A Yoshikawa, *Appl. Phys. Lett. 91 (2007) 242111*

P-type conduction - ECV measurement N-polarity

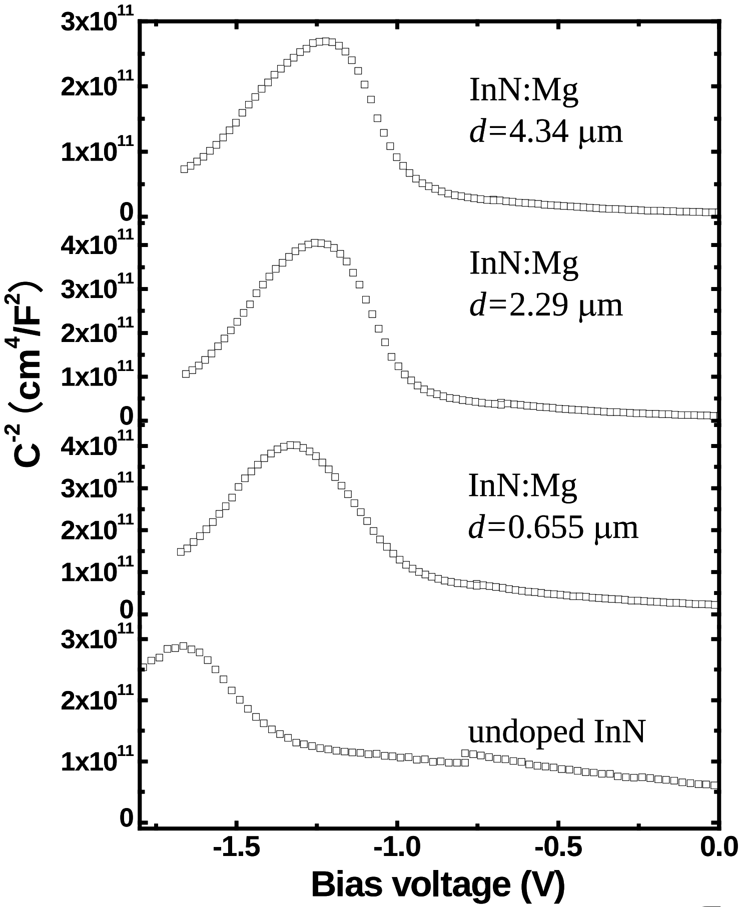


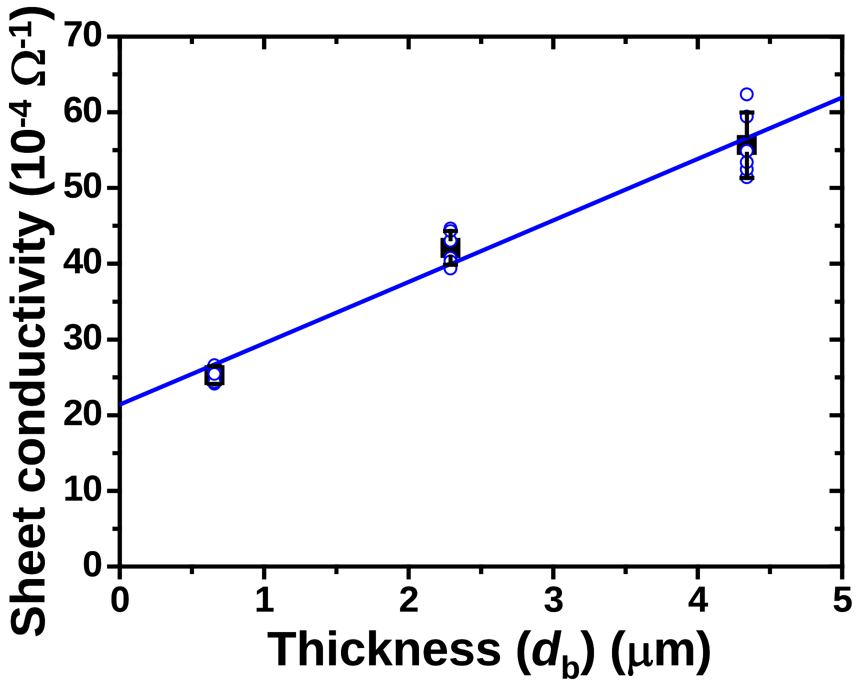


Sample	$n_{e\text{-Hall}}$ (cm^{-3})	$N_{d\text{-ECV}}$ (cm^{-3})	$C_{min\text{-cal.}}$ (nF/cm^2)	$C_{min\text{-exp.}}$ (nF/cm^2)	ΔC. (nF/cm^2)
E812	1.25E18	3.8E19	382	1763	1381
E814	1.25E18	3.0E19	382	1650	1268
E970	1.30E18	3.6E19	389	1794	1405
E974	1.25E18	2.8E19	382	1603	1221

N-polarity

Mobility of hole in p-type InN





$$\sigma_{st} = \sum_i \sigma_i d_i$$

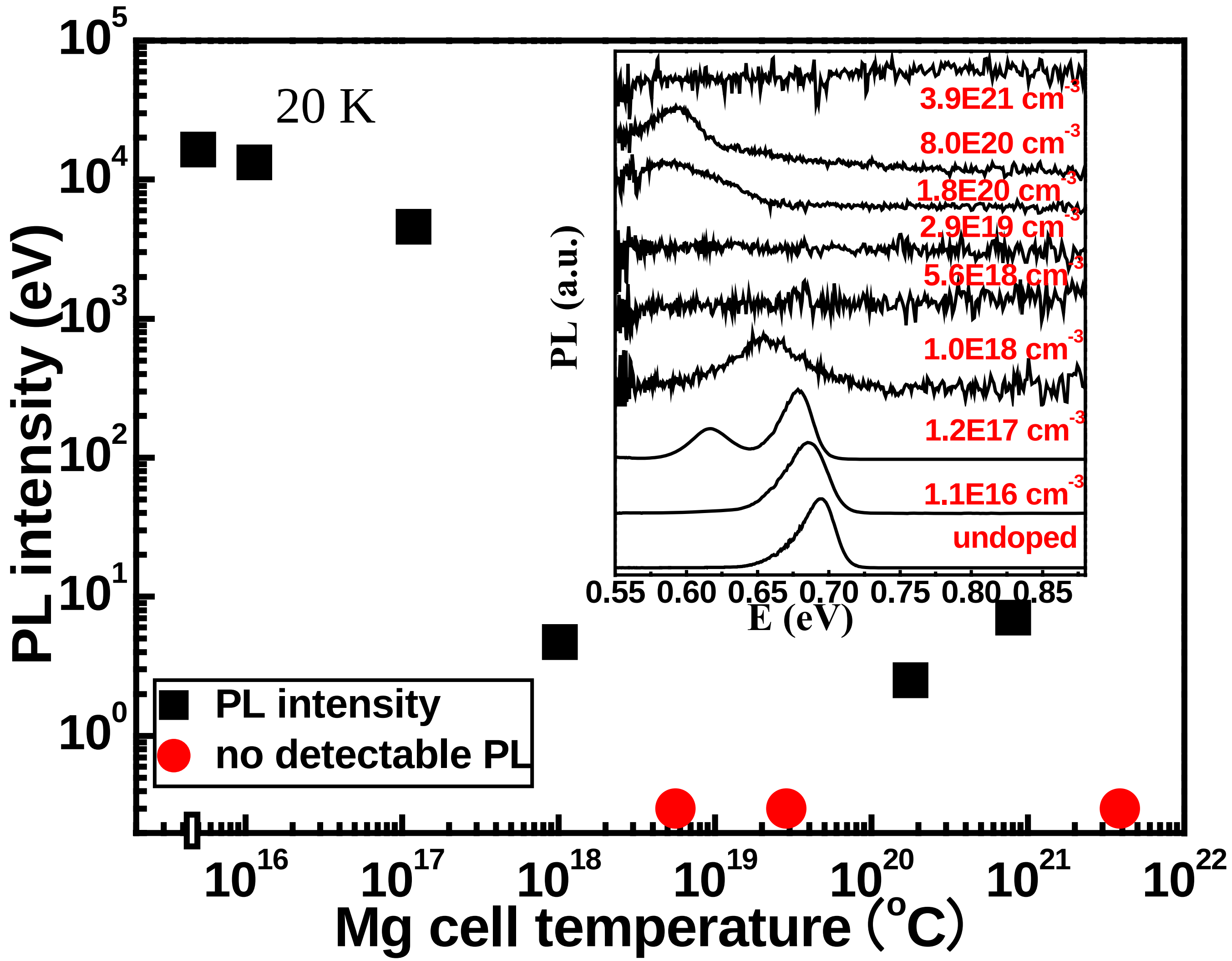
$$\sigma_{st} = \sigma_b d_b + (\sigma_{ss} + \sigma_{si} + \sigma_{su}) = \sigma_b d_b + \sigma_{s-others}$$

$$\sigma_b = pq\mu_h$$

Mobility of holes was estimated to be around 23 cm2/Vs.

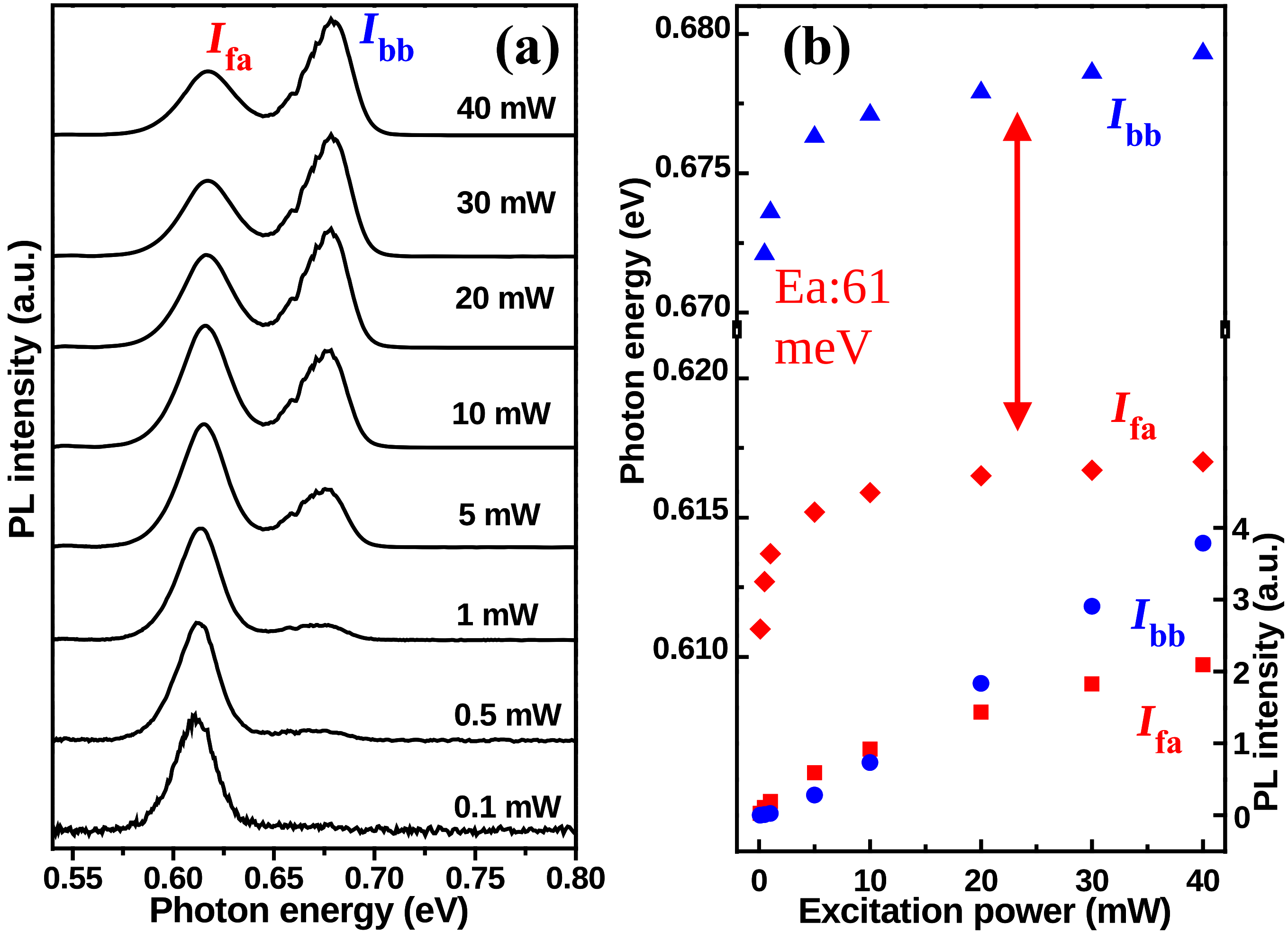
X Wang, S Che, Y Ishitani, A Yoshikawa, *Appl. Phys. Lett. 92 (2008) 132108.*

Photoluminescence study of Mg-doped InN



PL intensity was greatly reduced with Mg doping.

Activation Energy

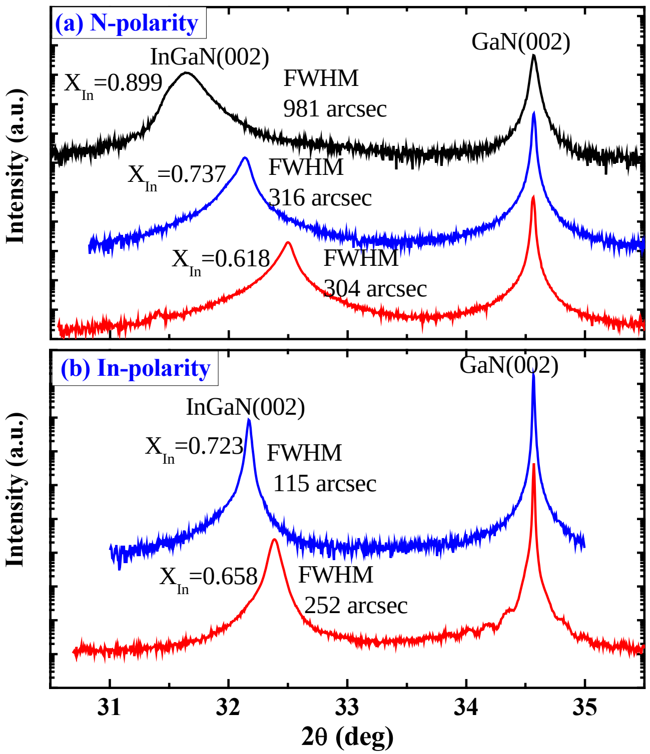


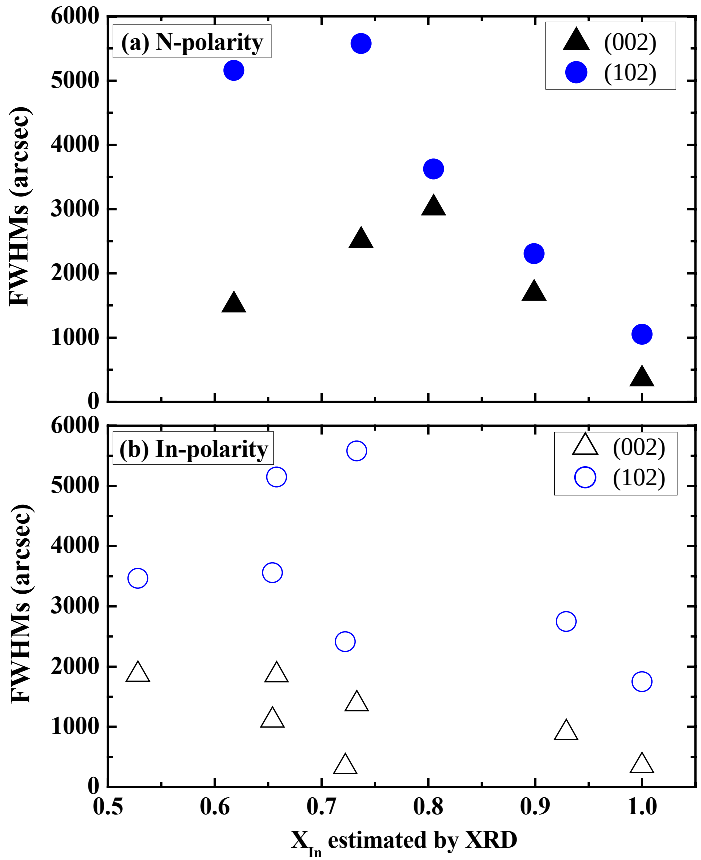
A Mg-related acceptor level of about 61 meV above the valence band

This value was confirm by Jiang Group, APL 91(2007) 012101.

X Wang, S Che, Y Ishitani, A Yoshikawa, *Appl. Phys. Lett. 90 (2007) 201903*

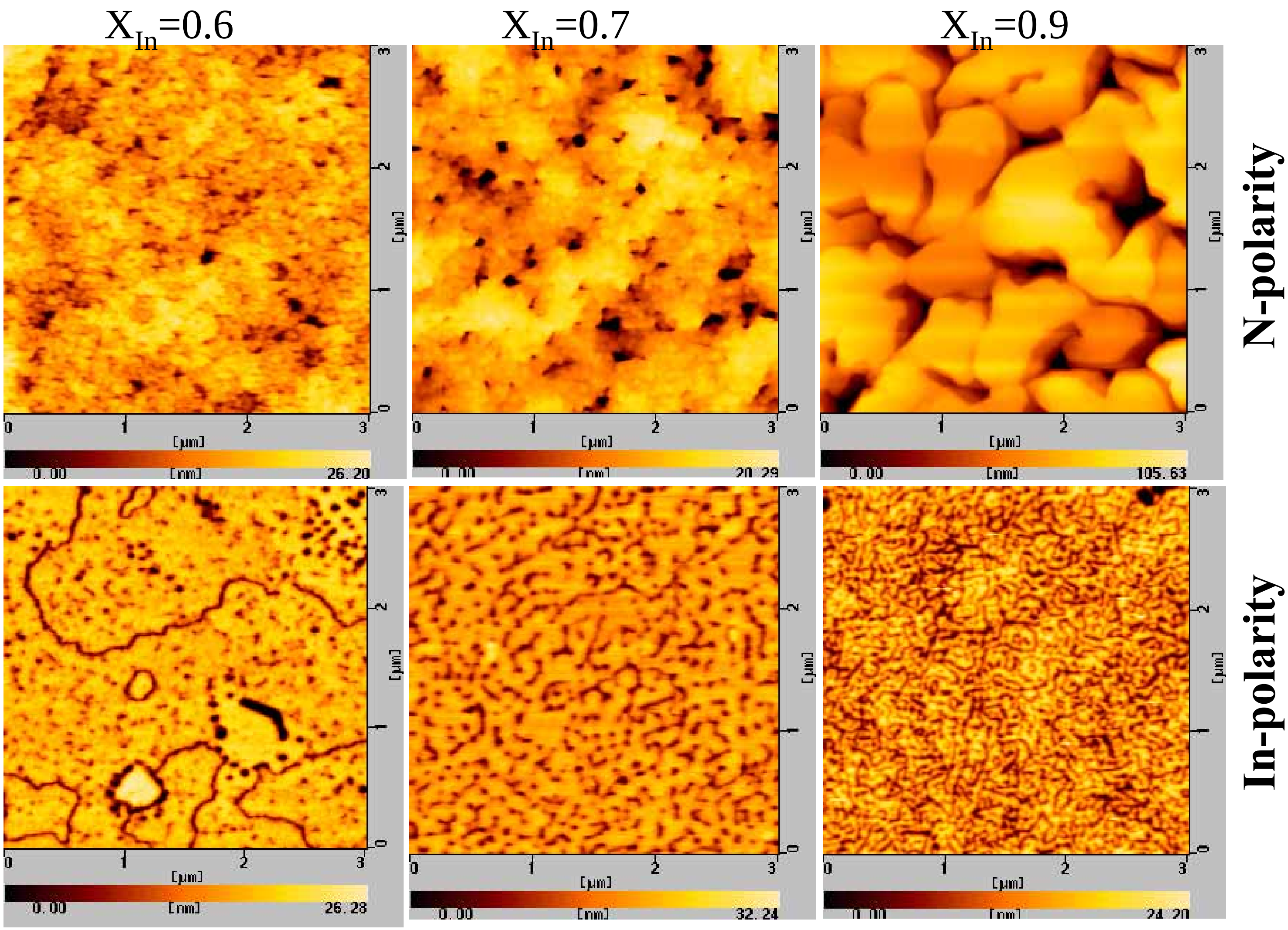
High In-content InGaN





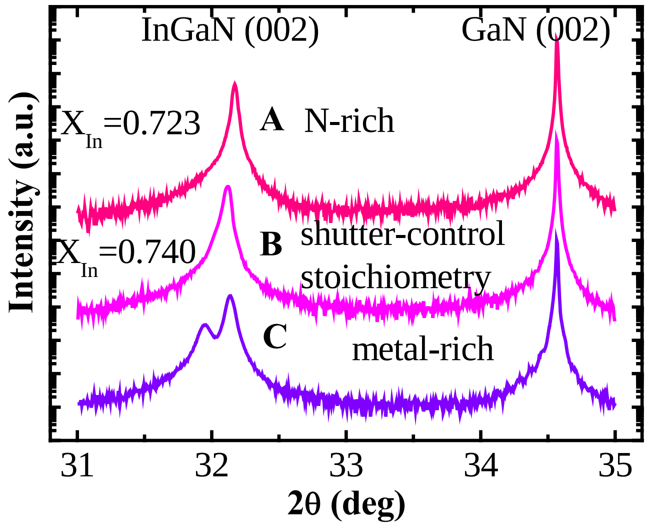
High In composition InGaN usually shows bad quality

InN-based Alloys-InGaN

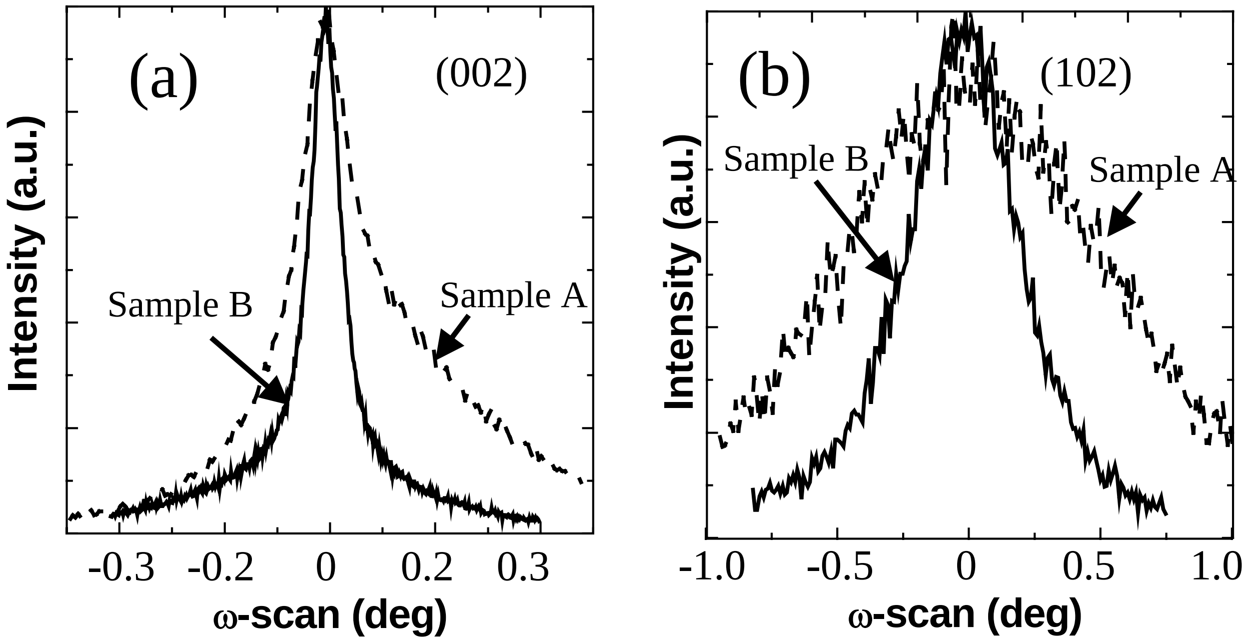


Surface morphologies of InGaN in both polarities

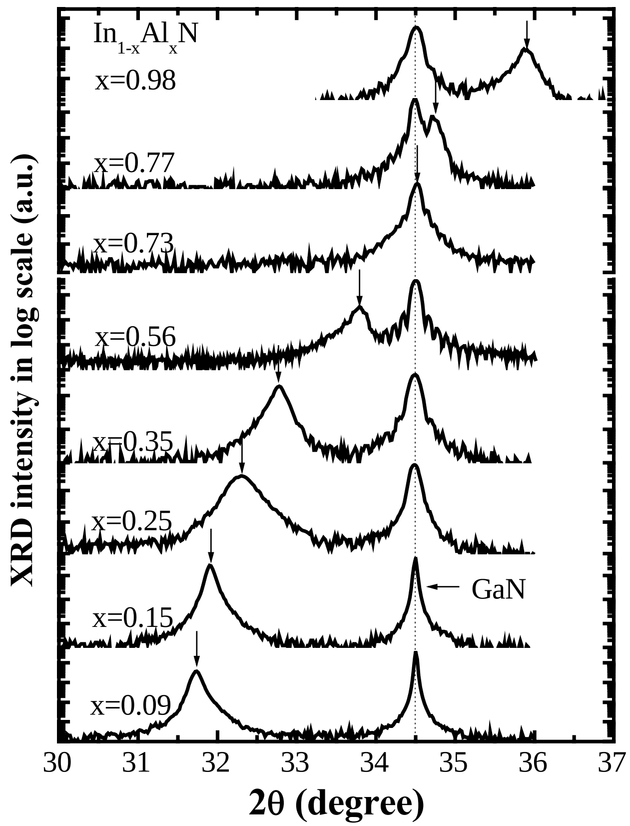
InN-based Alloys-InGaN

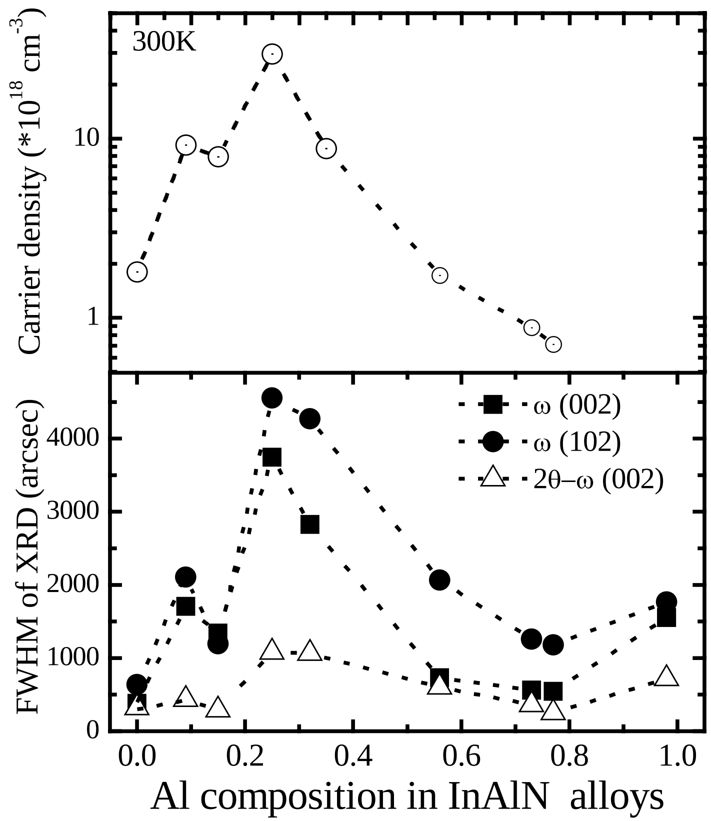


A shutter control method was used to improve quality of InGaN. XRD results showed that the quality was improved as expected.



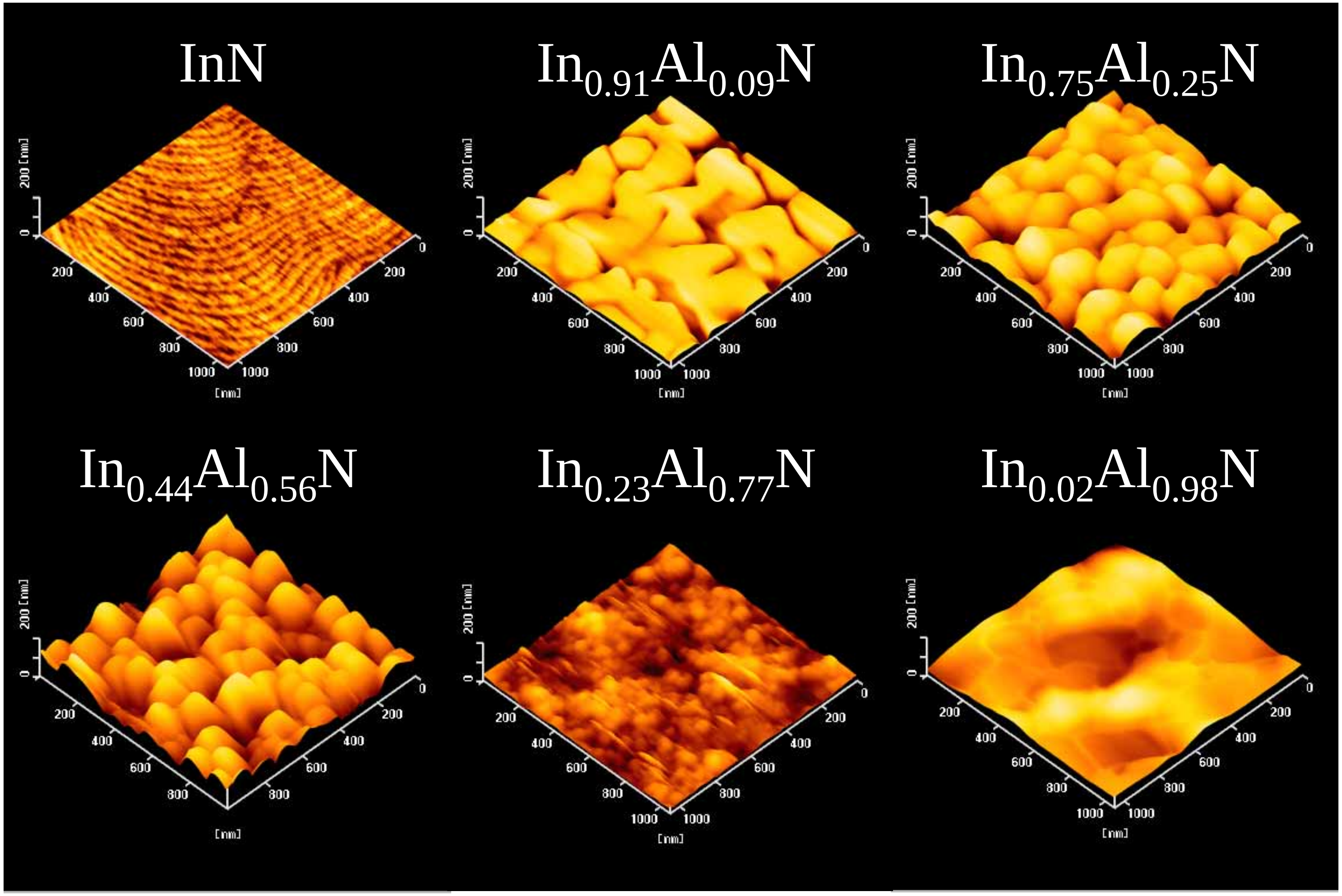
InN-based Alloys-InAlN





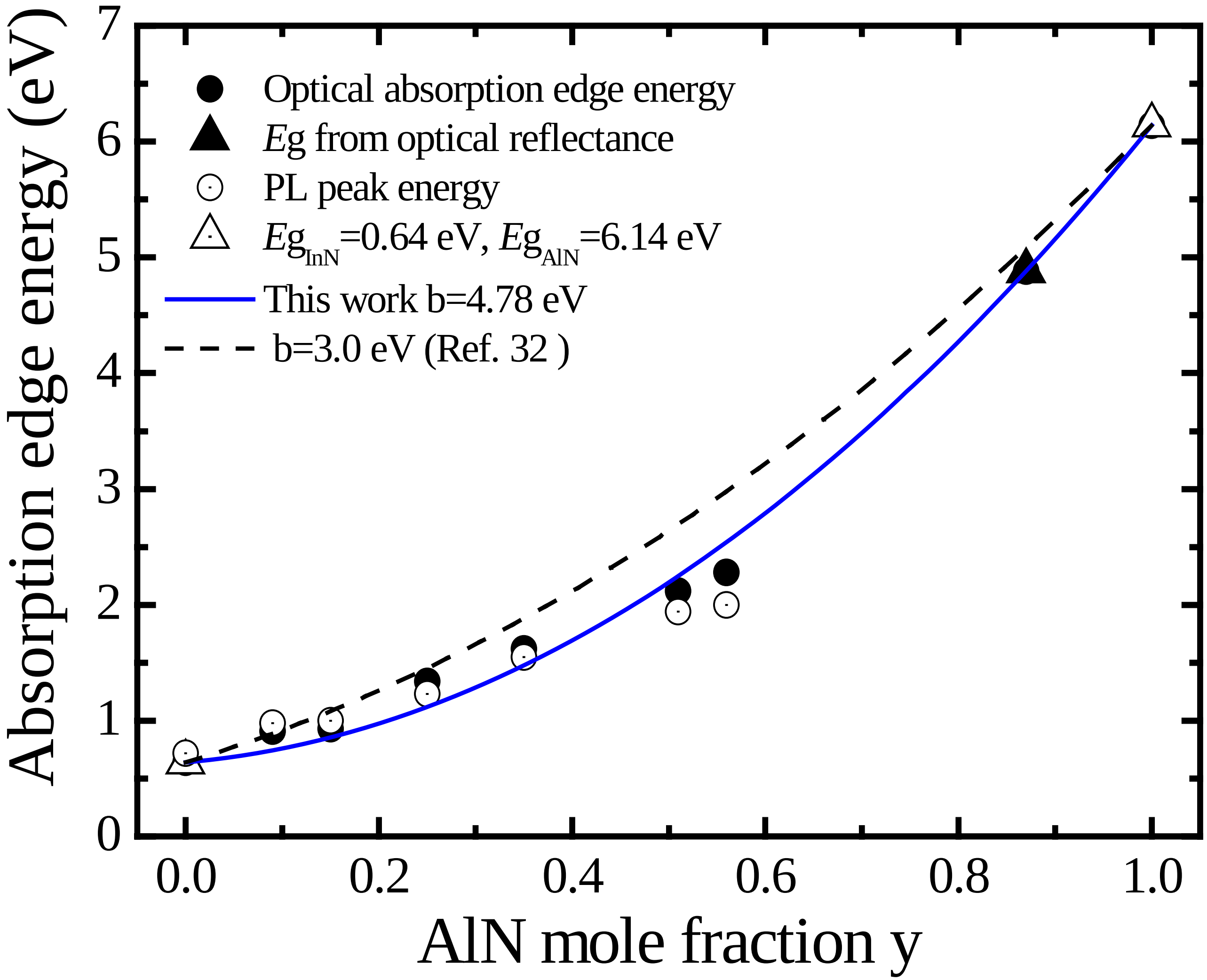
Full In composition InAlN with N-polarity were grown. Single phase alloys were observed in the whole composition. Basically, crystal quality of InAlN is poor in comparison to InN.

InN-based Alloys-InAlN



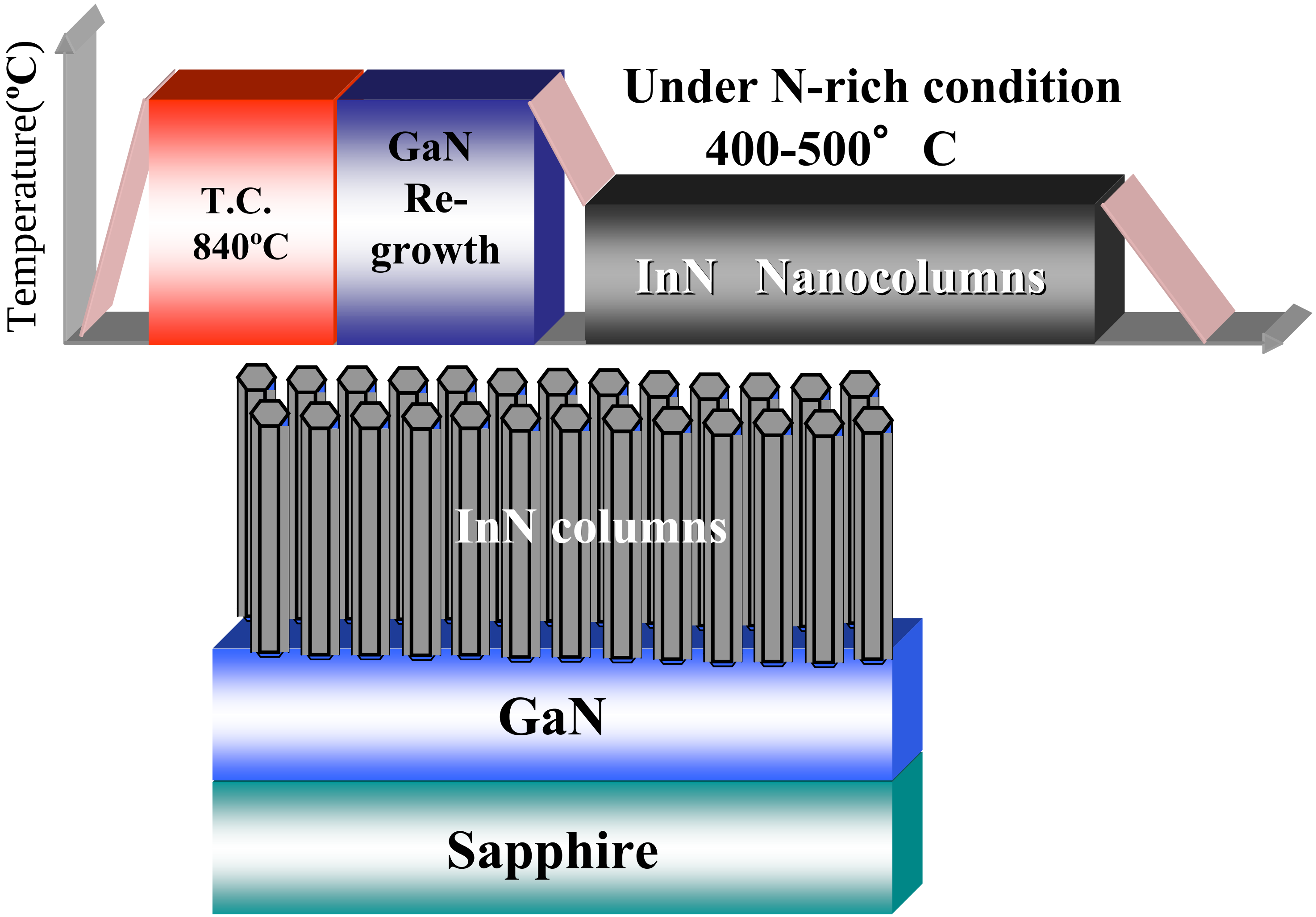
Surface morphology of InAlN, grain structure was observed .

InN-based Alloys-InAlN

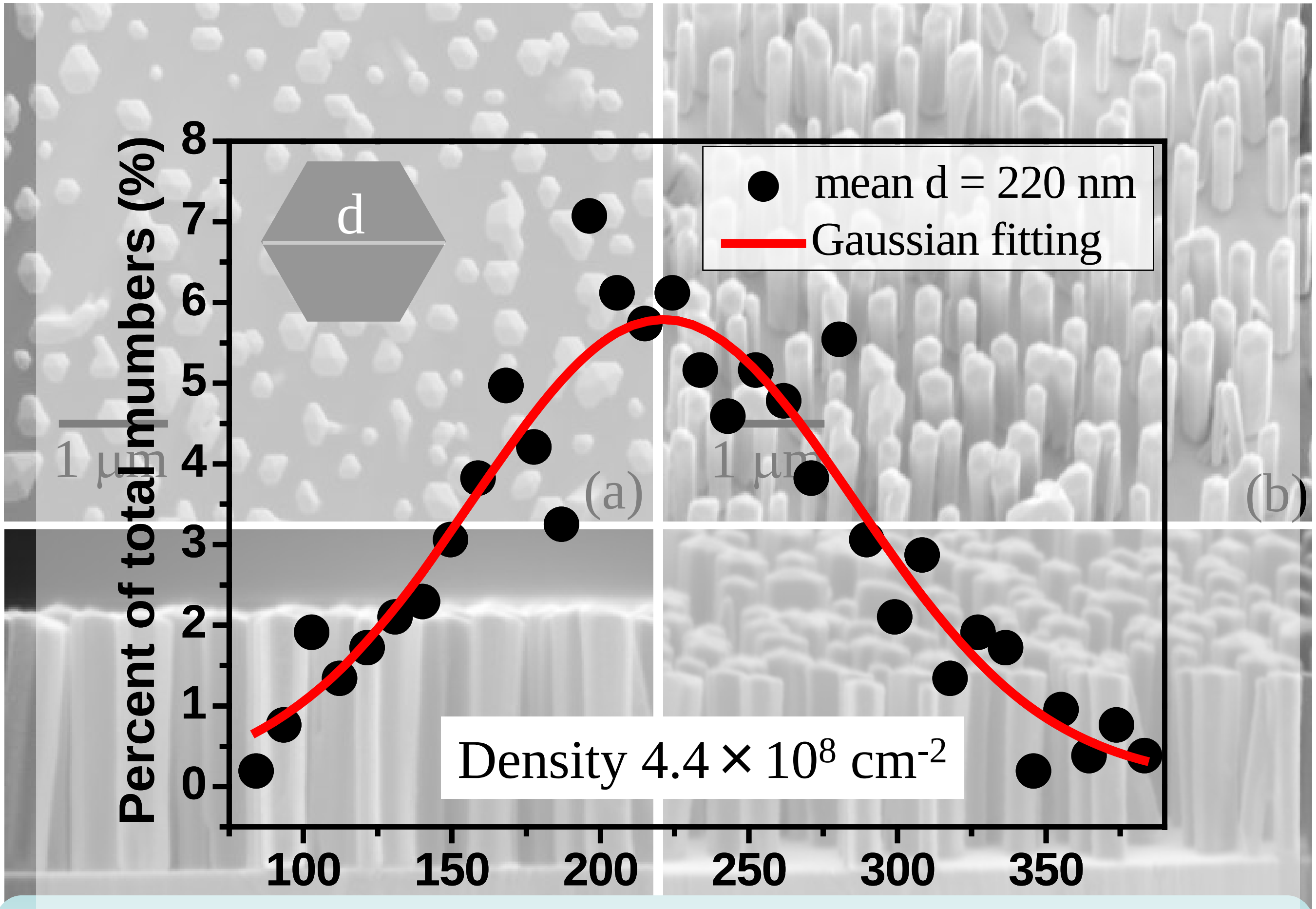


A bowing parameter b=4.78±0.30 eV was observed for InAlN

InN nanocolumns-growth process



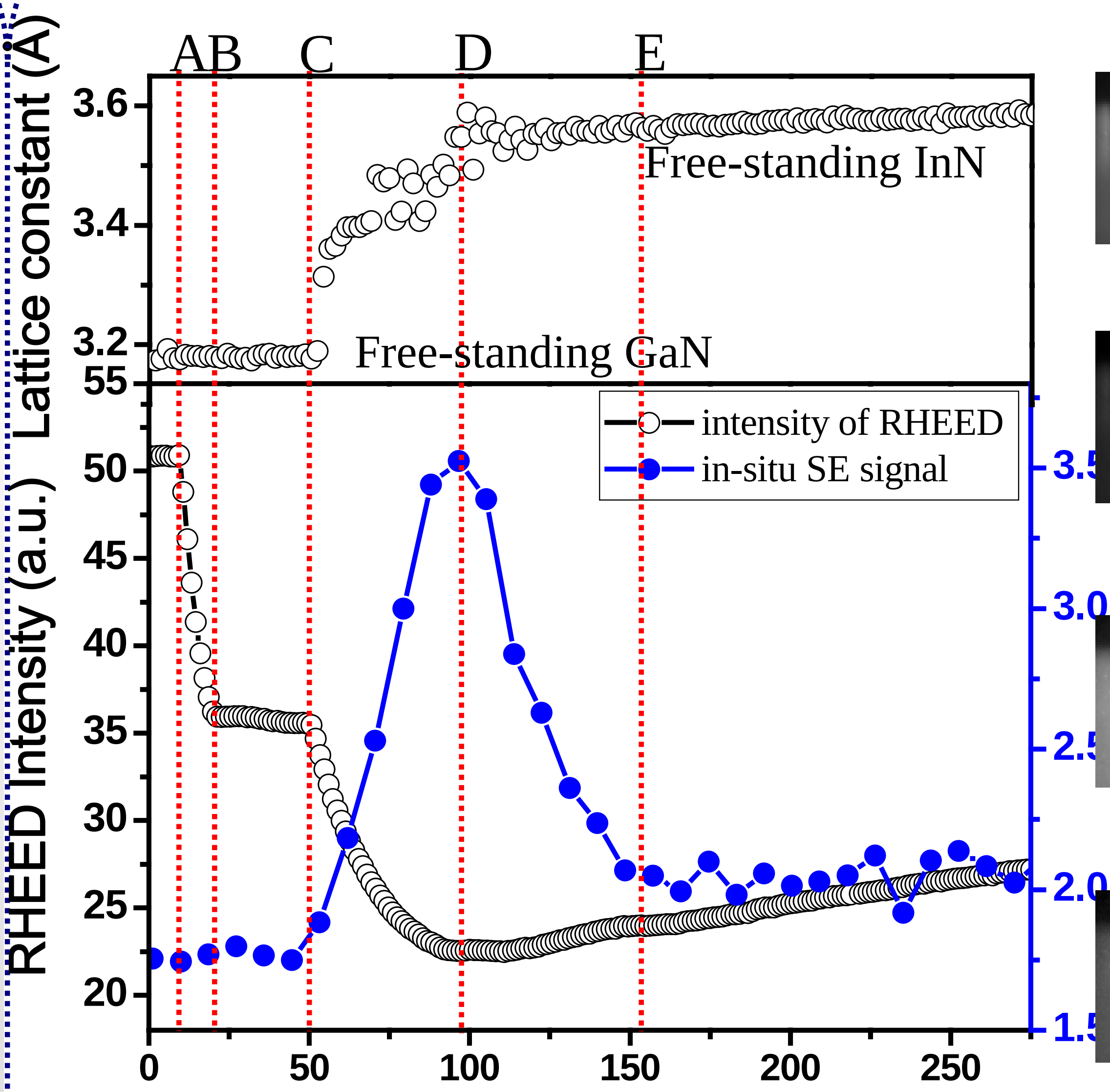
InN NCs-typical morphology

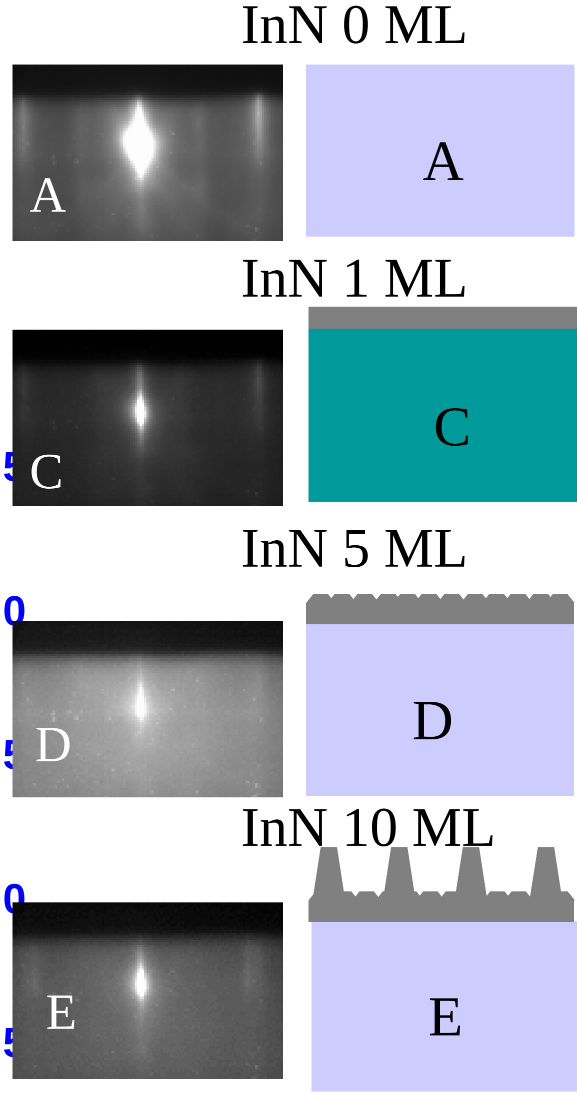


Growth rate 2.5-3 times to InN film, hexagonal shape, uniform height of 1.2 um, smooth side walls

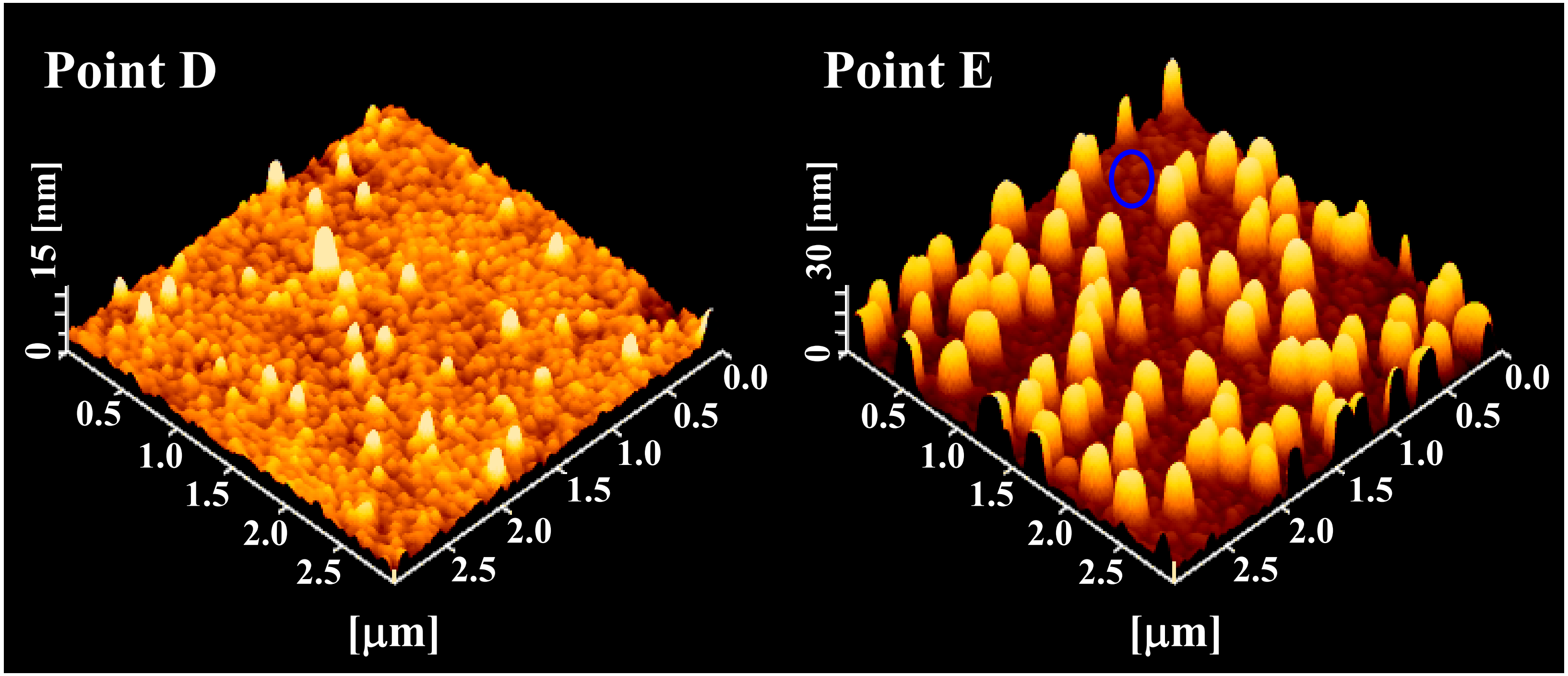
X Wang, S Che, Y Ishitani, A Yoshikawa, *J. Cryst. Growth 301 (2007) 496*

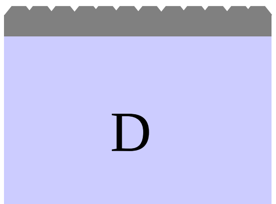
InN NCs-Nucleation Mechanism



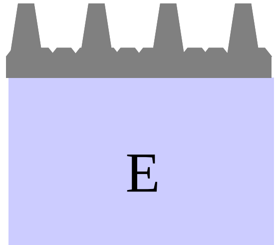


InN NCs-Nucleation Mechanism





5 ML, QDs



10 ML, embryonic, columns

InN NCs growth was initiated from InN QDs growth in S-K mode

Summary

- Atomically flat InN in step-flow-growth mode was obtained. The surface was quite smooth with rms roughness of less than 1 nm (the best one 0.3 nm) in 10μm×10μm area .
- InN films were dominated by edge-type TDs while the density of screw-type TDs NCs were about two orders lower. InN film with edge-type TDs density in low 10^9 cm^{-3} was obtained.
- Electron accumulation layer exist in the surface of InN or interface between InN/GaN with sheet electron concentration of about $3\text{-}5\times10^{13}$ cm^{-2}. InN film with ne=2×10^{17} cm^{-2} and mobility of about 2150 cm^2/Vs at RT was obtained.
- SIMS results showed that Mg concentration was linearly proportional to Mg-beam flux, indicating Mg-sticking coefficient is almost unity.
- Polarity inversion was found when [Mg] is over 10^{19} cm-3.
- Buried p-type InN was confirmed by ECV measurment in Mg:InN films at [Mg] of $1\text{-}30\times10^{18}$ cm^{-3}. An acceptor activation energy of about 61 meV for Mg acceptor was obtained. Mobility of holes in p-type InN was estimated to be about 17 to 36 cm^2/Vs for hole concentration of 3.0×10^{18} to 1.4×10^{18} cm^{-3}.

THANK YOU FOR YOUR ATTENTION