CVD Deposition of Group-III Nitride Materials

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Outline

1. Why III-Nitrides
2. Material Requirements and Issues
3. Substrate Technology
4. Thick Film Deposition (HVPE)
5. MOCVD Growth
6. MEMOCVD-Digital Epitaxy
7. Ternary and Quaternary Digital Epitaxy
8. Lateral Epitaxial Overgrowth
9. Devices and Conclusions

Work supported by Army, Navy, DARPA and NASA

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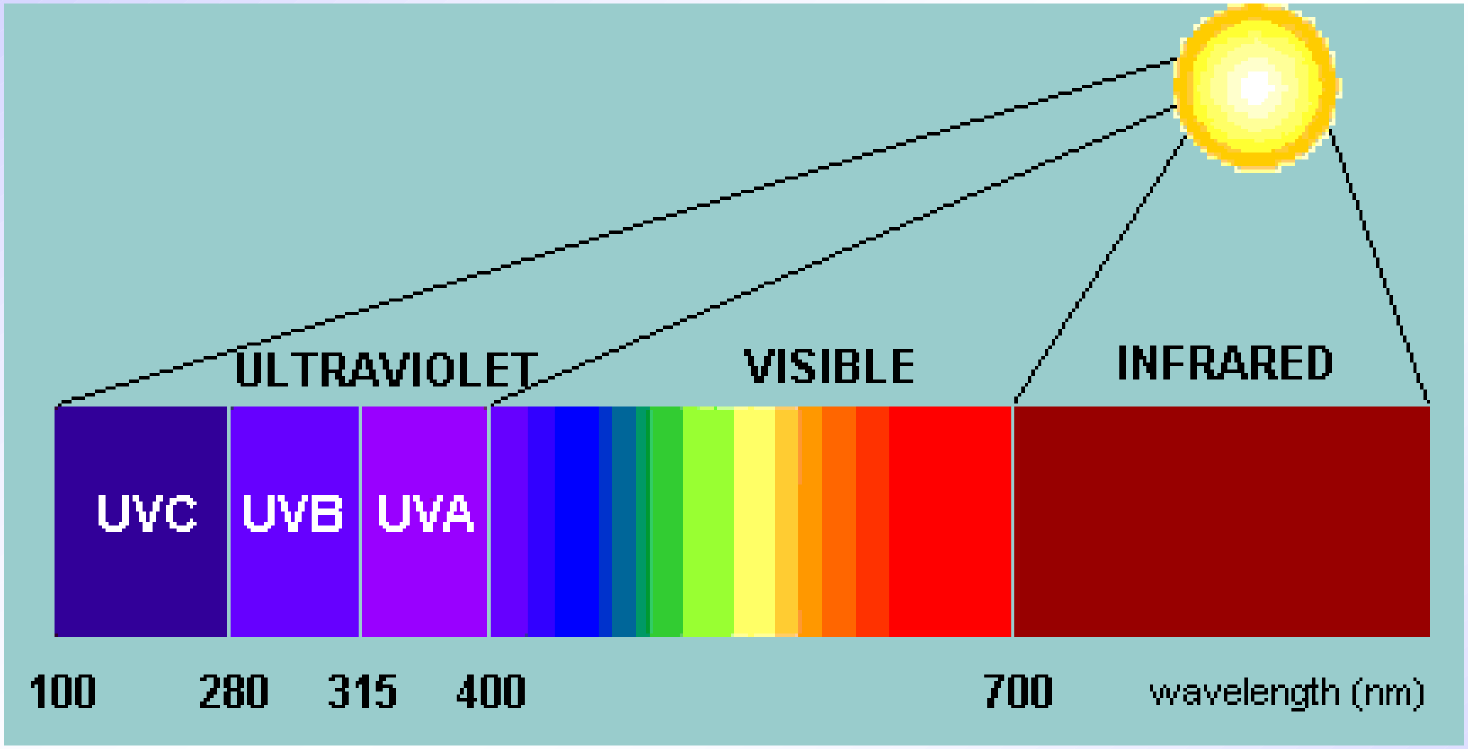
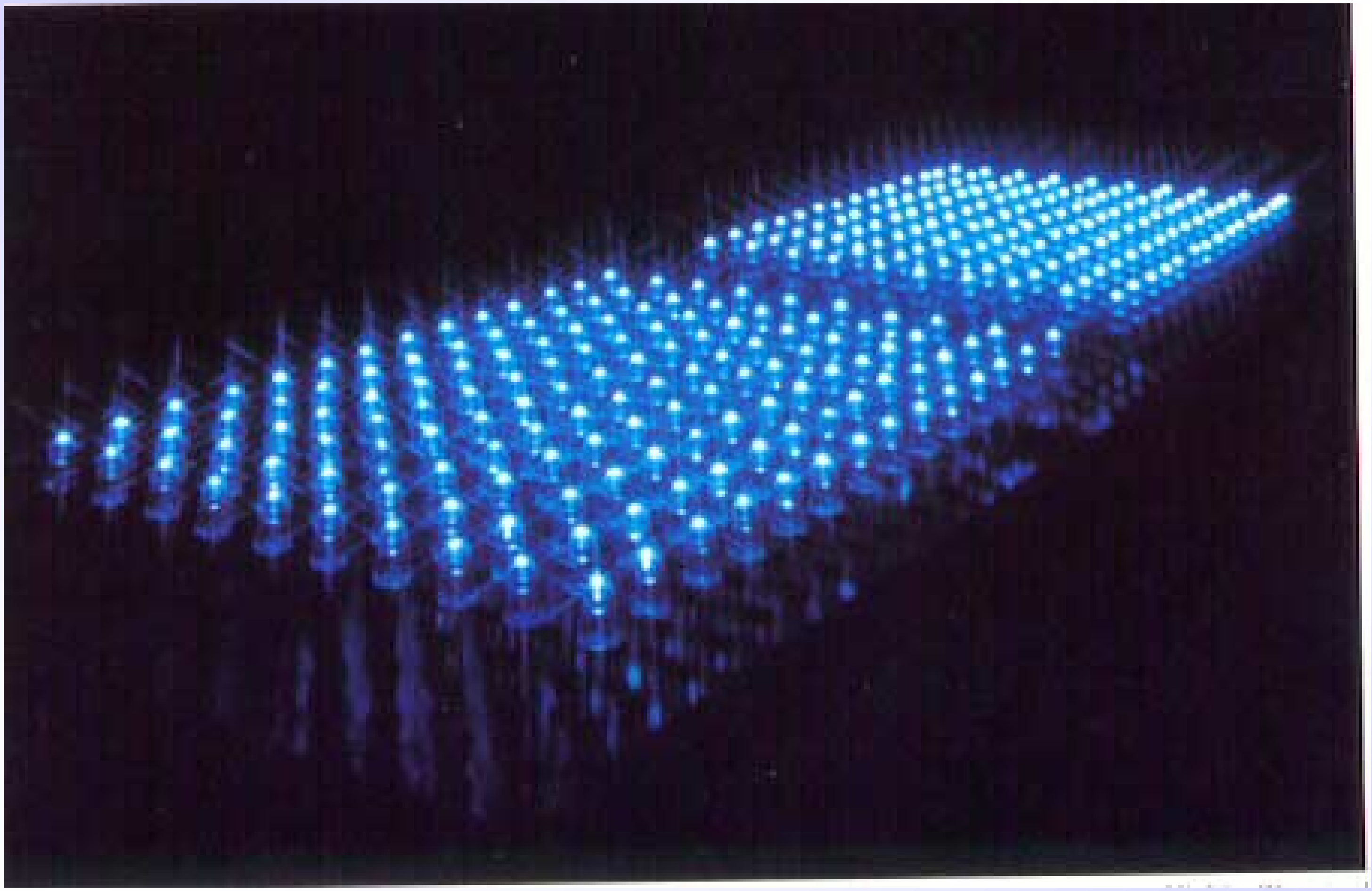
III-N Materials



AlN　**GaN**　**InN** ?

Breakdown Field approximately 5-10 times of GaAs

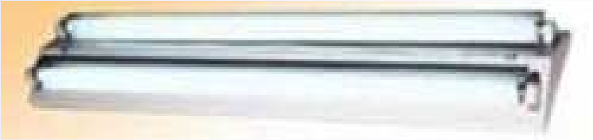
Nichia GaN Blue LEDs

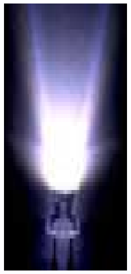


Lighting and Display Technologies

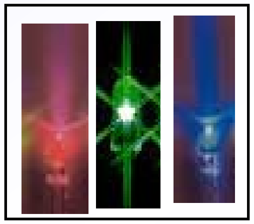
Past and the Present

Lighting



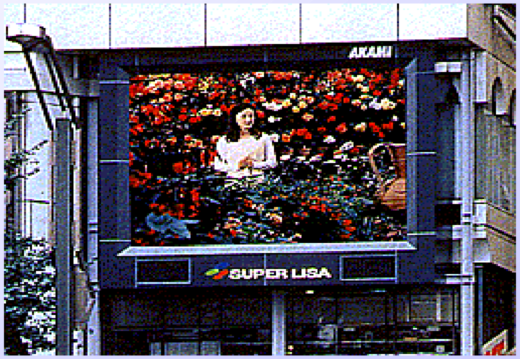


GaAs 1980's



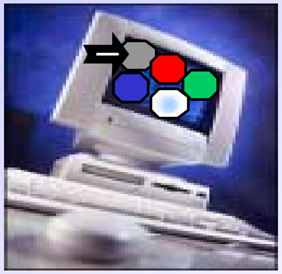
GaN 1990's

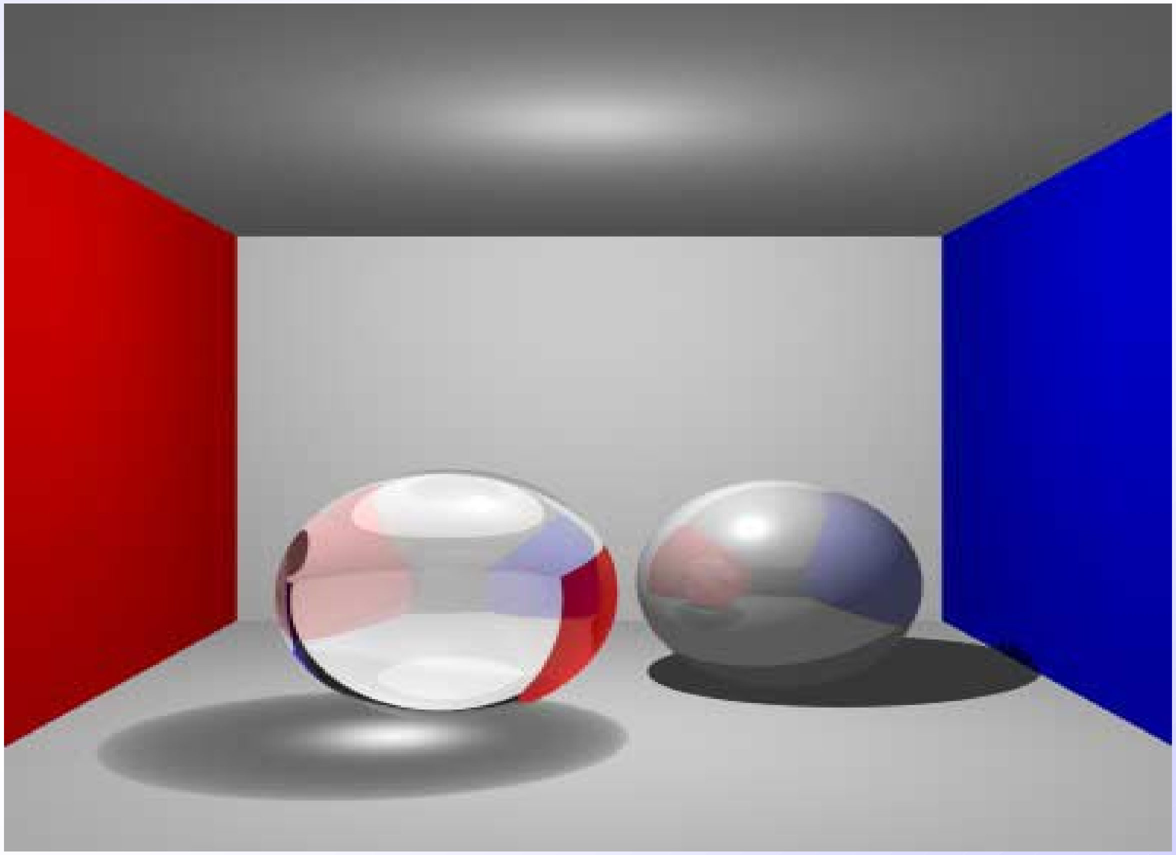
Displays



Next Generation Lighting Systems

- *Low voltage (< 10 V), Digital Controls*
- *High efficiency, Lifetime > 2 years*





Deep Ultraviolet Light Emitting Diodes

Applications

White Lighting

$ 10 billion*

λ ~ 254 nm

Purifiers

$ 20 billion*

λ ~ 265 nm

Bio-Med Sensors

$ 10 billion*

λ ~ 280 nm

**** Strategies unlimited , Compound Semiconductors***

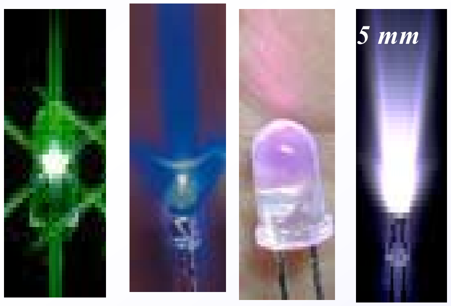
III-N Materials

Technology Applications

	Silicon	GaAs	GaN

Photonics





Electronics





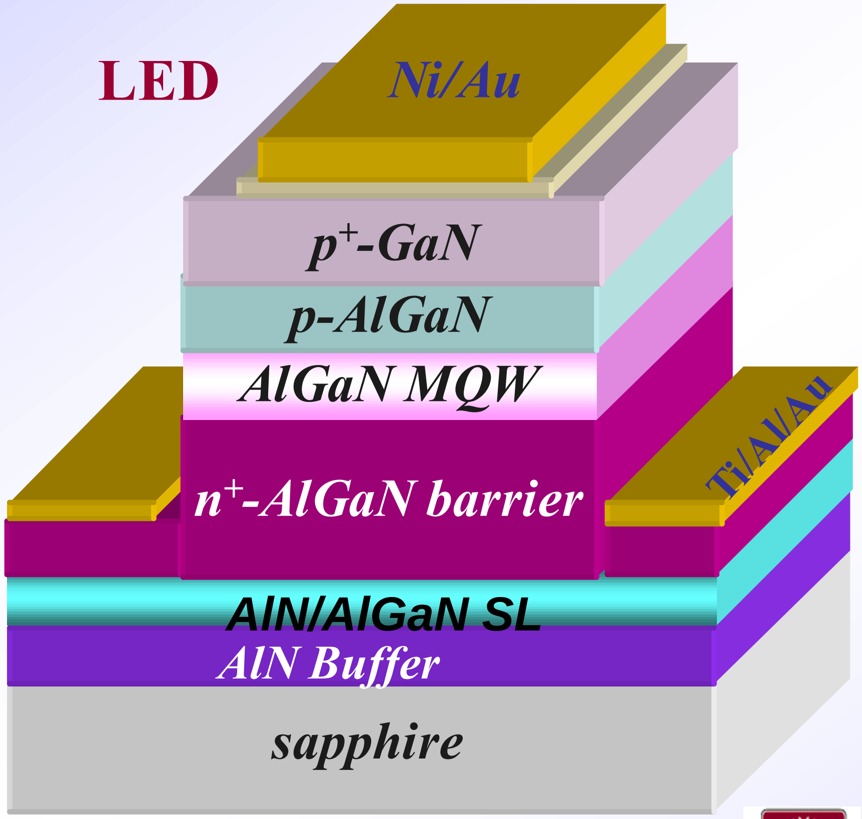
	Silicon	GaAs	GaN
Power:	< 0.1 W/mm	1 W/mm	5-10 W/mm
Operation T:	80 C	125 C	> 300 C

III-N Device Epilayer Needs

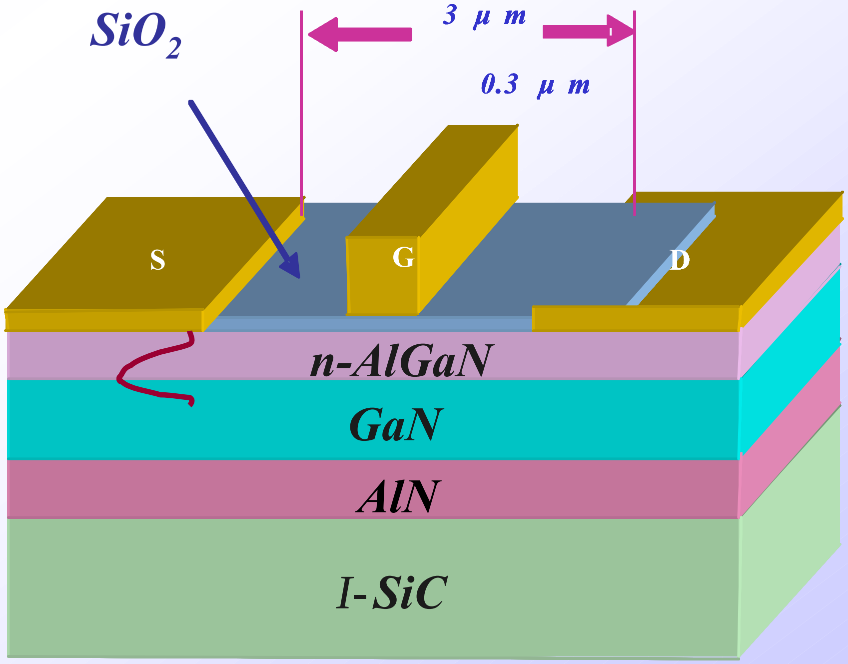
LEDs and Transistors

- *N- and p-doped Layers*
- *Heterojunctions*
- *Quantum Wells and Superlattices*

LED



Microwave Transistors

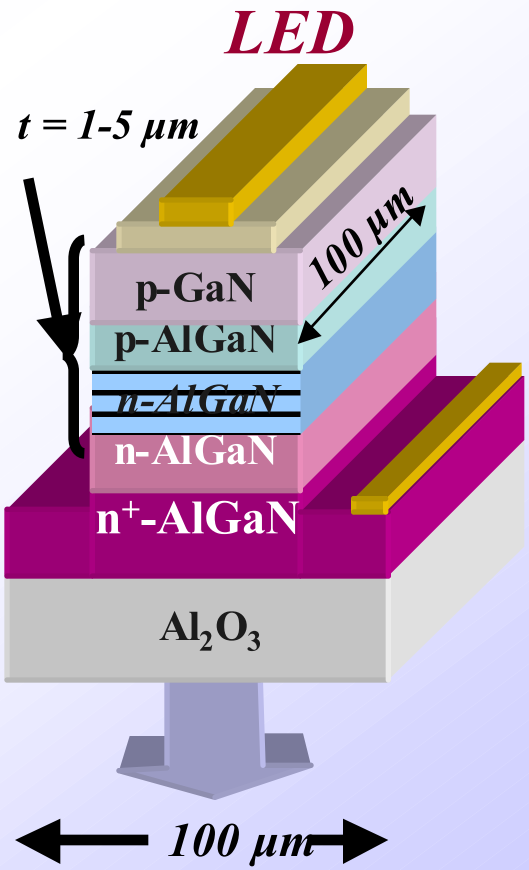


Choice of Substrates

Substrate	Lattice constant (Angstroms) at 300 K	Thermal Conductivity W/cm-K at 300 K	Thermal expansion coefficient $(10^{-6}$ 1/K) at 300 K	Bandgap (eV)
GaN	a = 3.188 c = 5.185	2.0	3.1 (ave. 300 to 3.5 800 K)	3.39
AlN	a = 3.112 c = 4.982	3.2 (c-axis)	2.30 2.69	6.2
6H SiC	a = 3.081 c = 15.117	4.9 (a-axis)	2.9 2.9	3.03
4H-SiC	a = 3.080 c = 10.082	~3.7	~2.8 ~2.8	3.26
Sapphire	a = 4.765 c = 13.001	0.35 (c-axis)	5.9 6.3	9.9
Si	a = 5.4301	1.56	2.57	1.1
GaAs	a = 5.6533	0.54	5.8	1.42

Nitride Materials and Possible Substrates

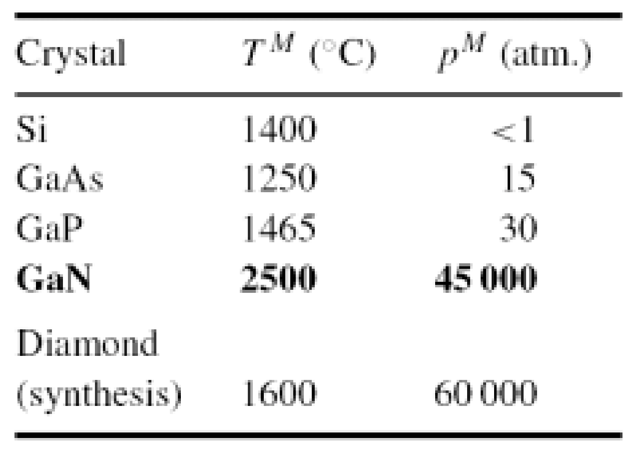
	InN	GaN	AlN	6H-SiC	Al_2O_3	GaAs
a, A	3.54	3.19	3.11	3.08	4.77	5.65
$E_{G,}$ eV	0.89	3.39	6.2	2.86	8.2	1.41
$\mu_{n,}$ cm²/V-s	3200	1000	135	900		8500
e_{14}, C/m²	0.38	0.38	0.92			-0.16



- *No lattice matched substrate*
- *Large polarization effects*

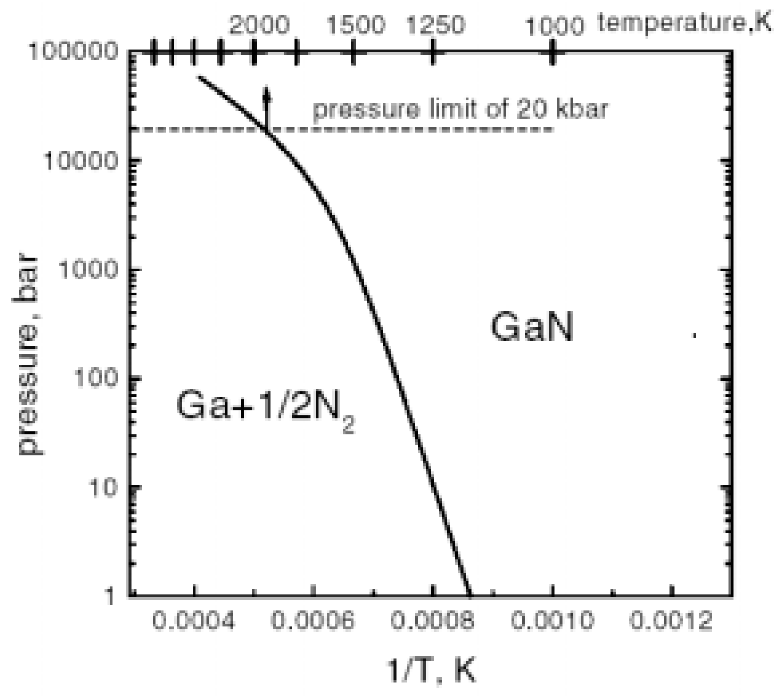
Bulk growth of GaN: direct synthesis

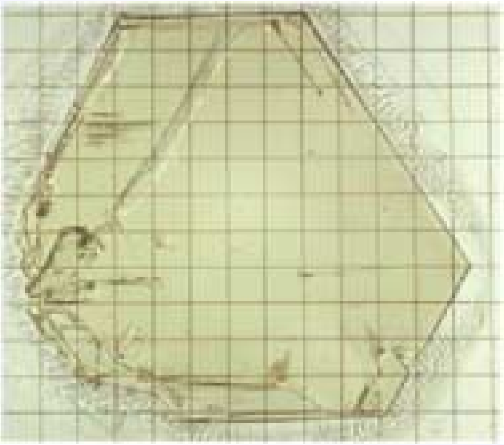
Melting conditions of semiconductors
(without dissociating)



Crystal	T^M (°C)	p^M (atm.)
Si	1400	<1
GaAs	1250	15
GaP	1465	30
GaN	**2500**	**45 000**
Diamond (synthesis)	1600	60 000

Equilibrium curve for GaN





Bulk crystal of GaN, grown at 10 – 20 Kbar, and 1400 – 1600 °C without seed, along the 10-10 direction). Squares grids have 1 mm sides

$$2Ga\ (melt) + N_2 = 2GaN$$

Sublimation Growth of AlN

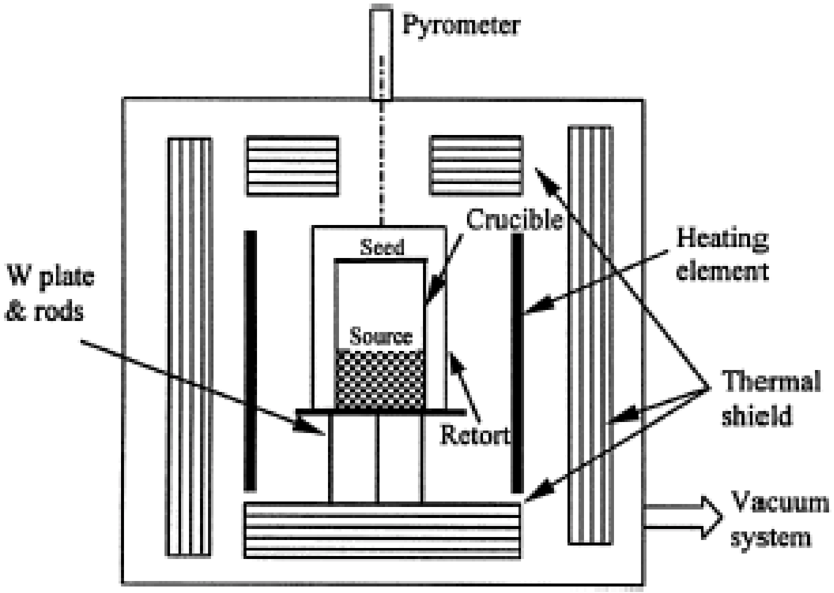


Fig. 1. Schematic view of AlN sublimation growth system.

AlN sublimes dissociatively at the hotter source and condenses reversibly at the colder seed

Lianghong Liu, James H. Edgar*

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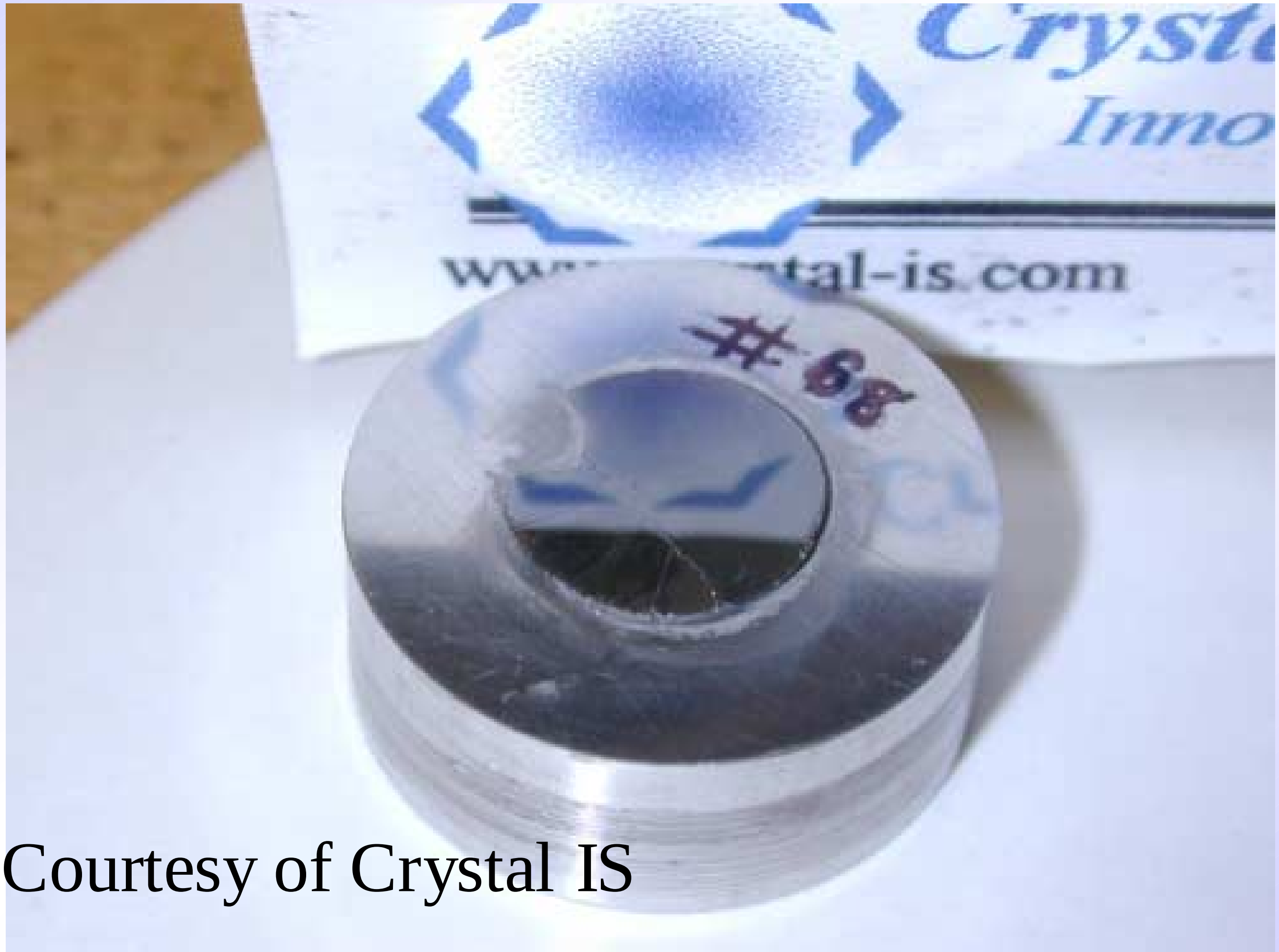
15 mm Diameter AlN Boule



Courtesy of Crystal IS

Bulk AlN PVT

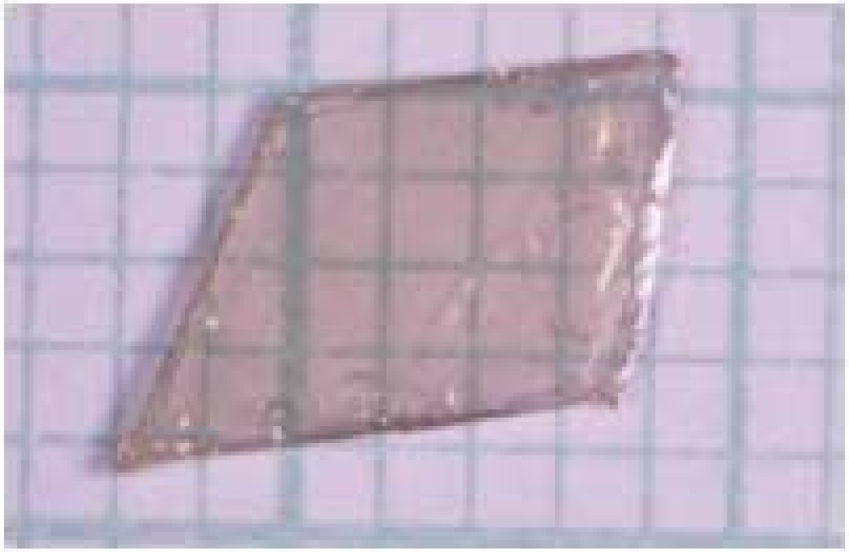


Figure 2. Photograph of pure AlN grown for 100 hours, one grid represents 1mm.

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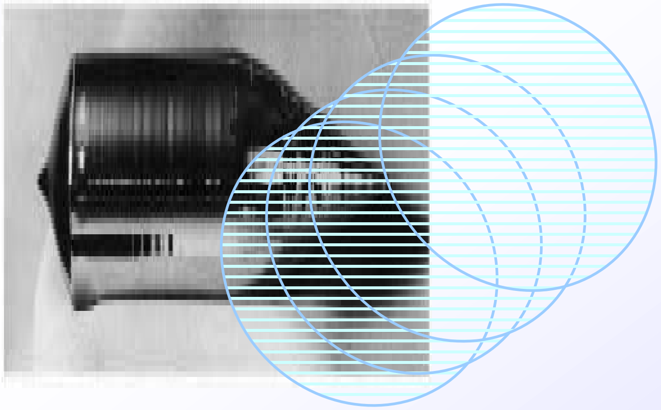
Bulk Crystal Growth Facilities

Crystal Growth

CUTTING



GRINDING

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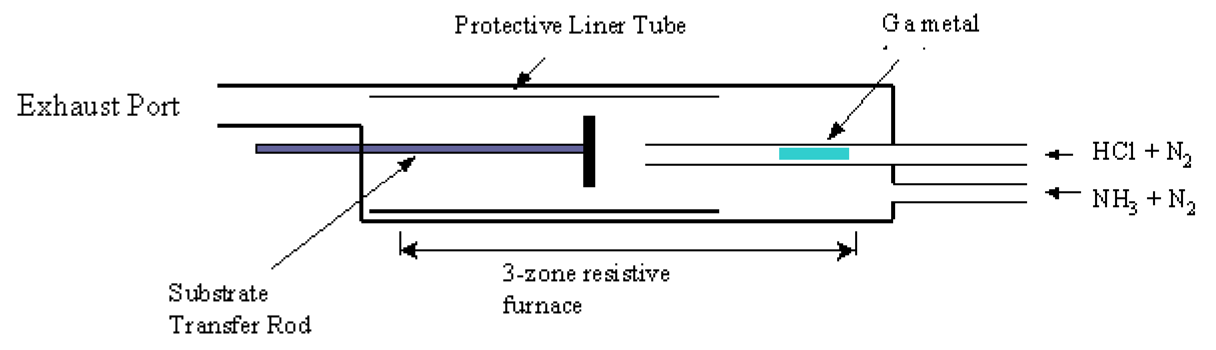
SiC CRYSTALS

(2" dia. ingot)

(0001)

(1120)

Halide Vapor Phase Epitaxy (HVPE)



Epitaxial Nitride Films by HVPE

- *Gallium transport by halide (chloride) formation*

$2HCl(g) + 2Ga(l) \rightarrow 2GaCl(g) + H_2(g) \quad T = 800\,^{o}C$

- *Reaction with chloride to form the nitride*

$GaCl(g) + NH_3(g) \rightarrow GaN(s) + HCl(g) + H_2(g); \quad T = 1030\,^{o}C$

- **Growth rate is determined by HCl flux**
- **High growth rates are possible due to low probability of gas phase nucleation**
- **Growth rates can exceed 100 mm/min**

HVPE GaN

Defect Reduction with Thickness

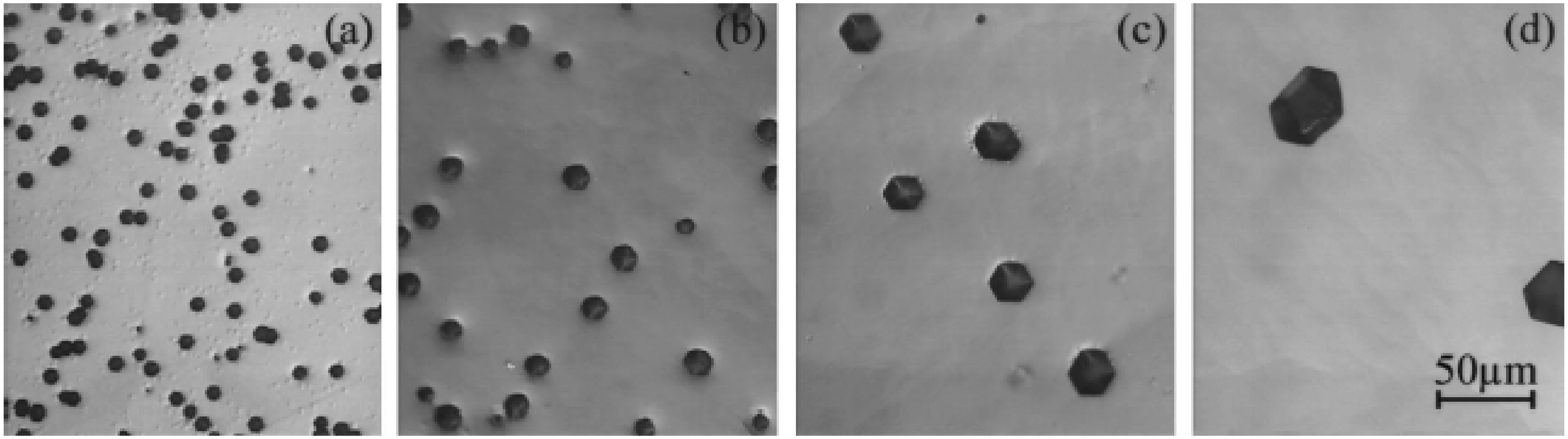
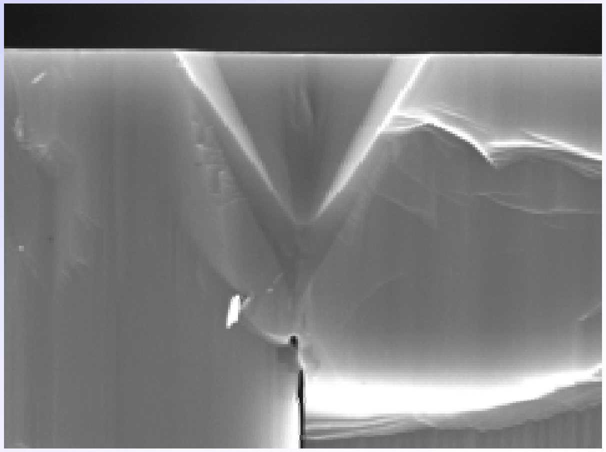
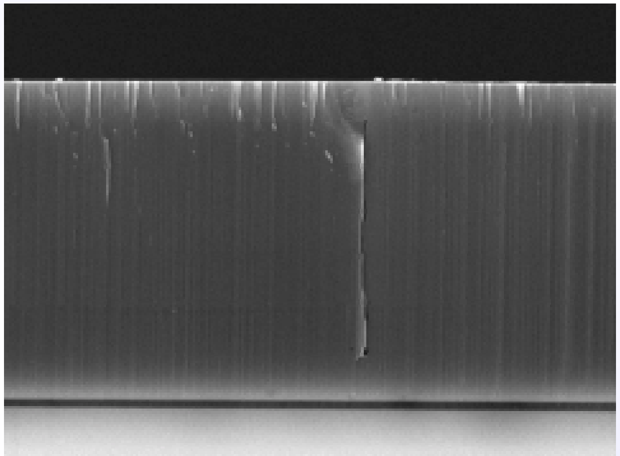


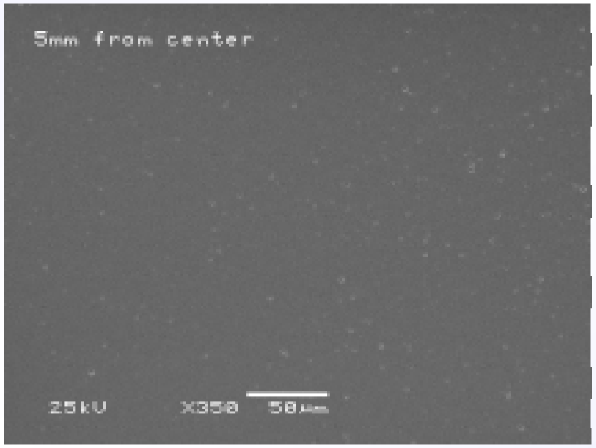
Fig. 1. The surface morphology of GaN layers with different thicknesses of 15 µm (a); 26 µm (b); 42 µm (c); 96 µm (d), grown at the same growth conditions.

B. Monemar, J Crystal Growth, Vol. 208, p. 18, 2000

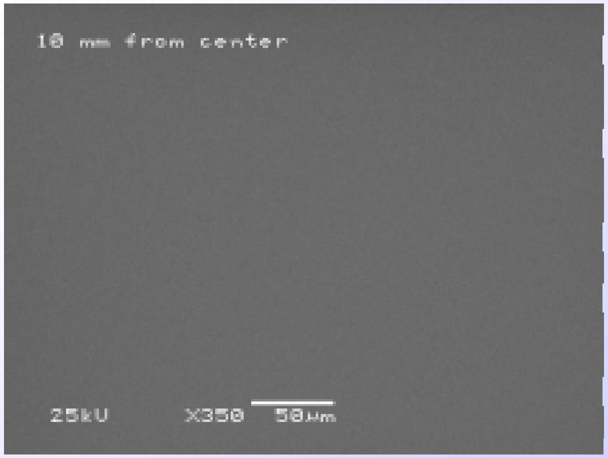
Defects in HVPE GaN Films


Cross section of pit with crack


Cross section of crack



Surface with small pits



Featureless surface

PML

Free Standing GaN Wafer by HVPE

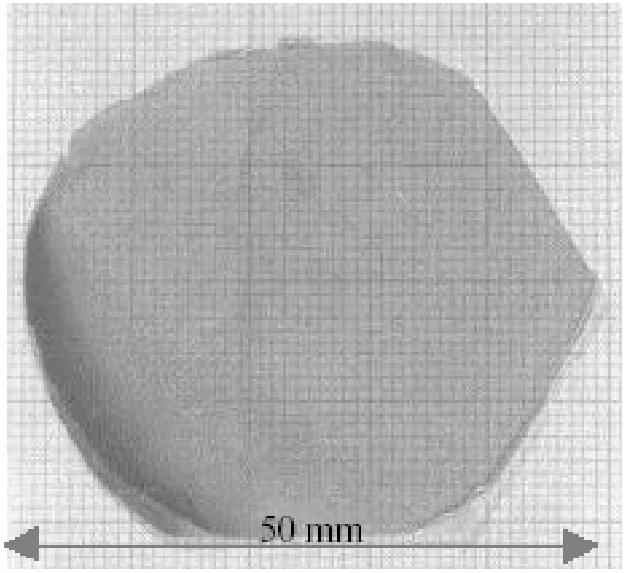


Figure 1. Low magnification optical photograph of freestanding GaN. The GaN is 250 µm thick and the crack-free right hand piece measures ~970 mm^2 in area. Note small grid elements are 1 mm^2.

R. Vaudo, ATMI

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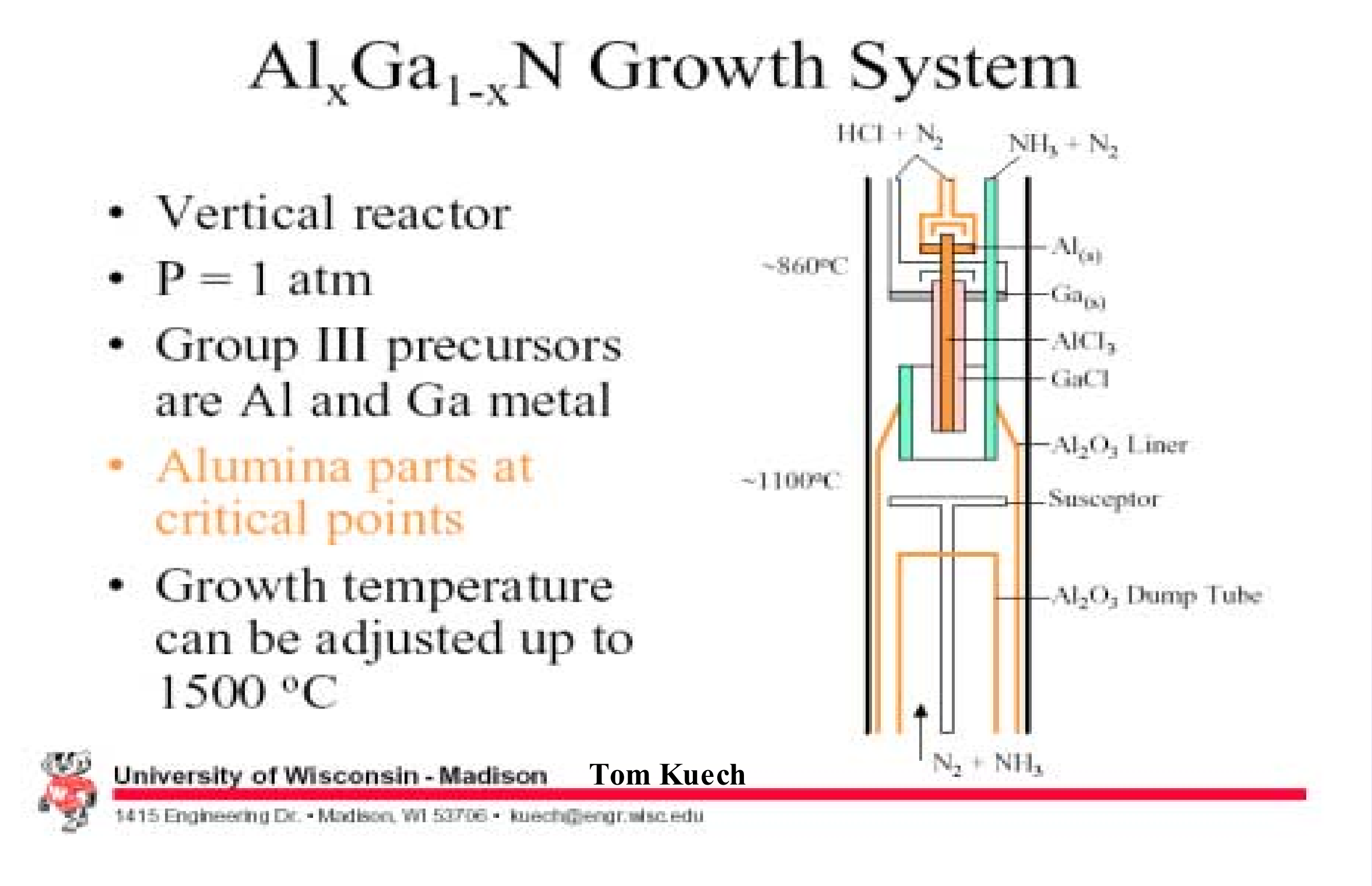
Growth of AlN & AlGaN by HVPE

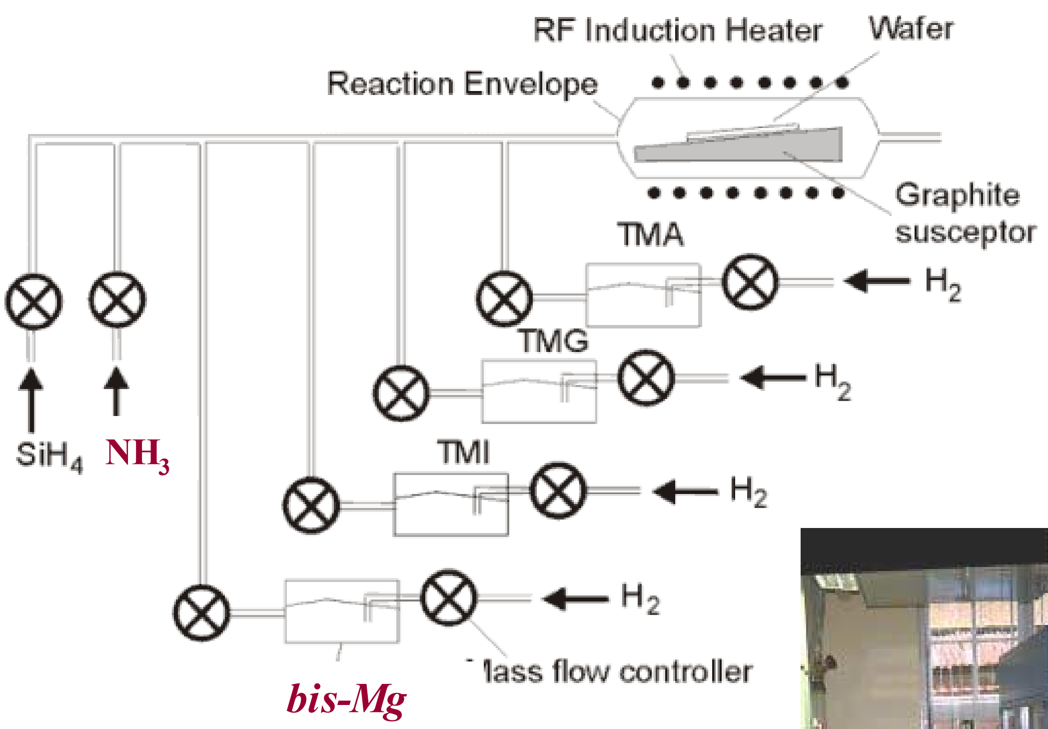


$Al_xGa_{1-x}N$ Growth System

- Vertical reactor
- P = 1 atm
- Group III precursors are Al and Ga metal
- Alumina parts at critical points
- Growth temperature can be adjusted up to 1500 °C

University of Wisconsin - Madison **Tom Kuech**
1415 Engineering Dr. • Madison, WI 53706 • kuech@engr.wisc.edu

MOCVD growth system

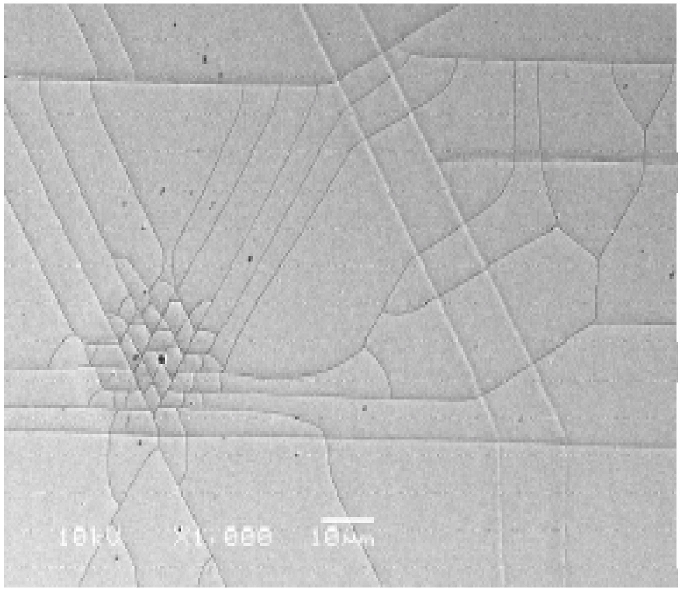


Various problems associated with mismatches

Substrate Property	Consequence
1. Lattice (a-lattice constant) mismatch	1. All problems typically associated with high dislocation density
2. Vertical (c-lattice constant mismatch)	2. Anti-phase boundaries, inversion domain boundaries
3. Coefficient of thermal expansion mismatch	3. Thermally induced stress, cracks in epitaxial films
4. Low thermal conductivity	4. Poor heat conduction; unsuitability for high power devices
5. Different chemical composition of the epitaxial film	5. Contamination, interface states, poor wetting of surface during growth
6. Polar surface	6. Mixed polarity; inversion domains

MOCVD III-N growth issues

Strain/thermal mismatch

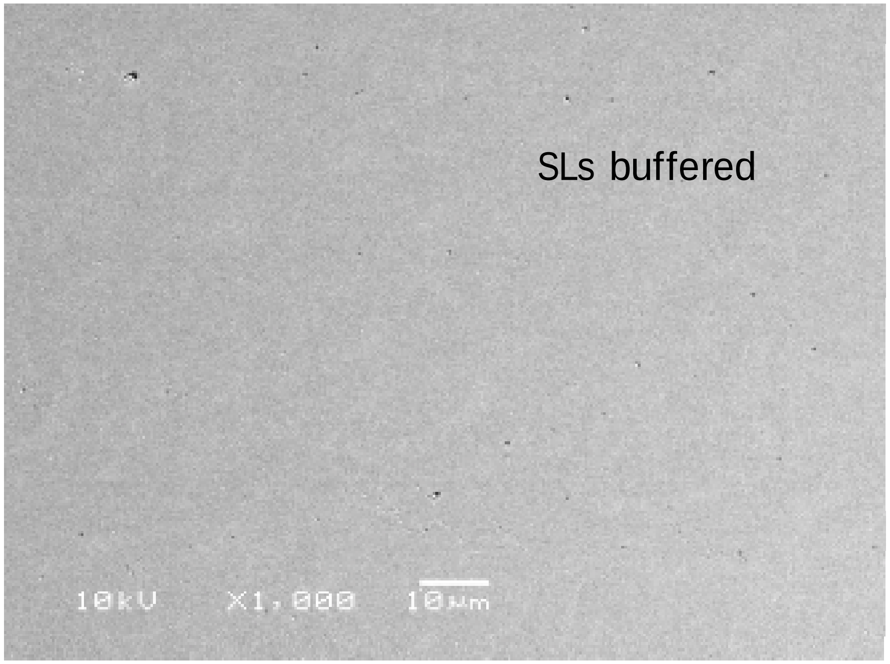


Lattice mismatched Substrates

Growth Temperature compatibility

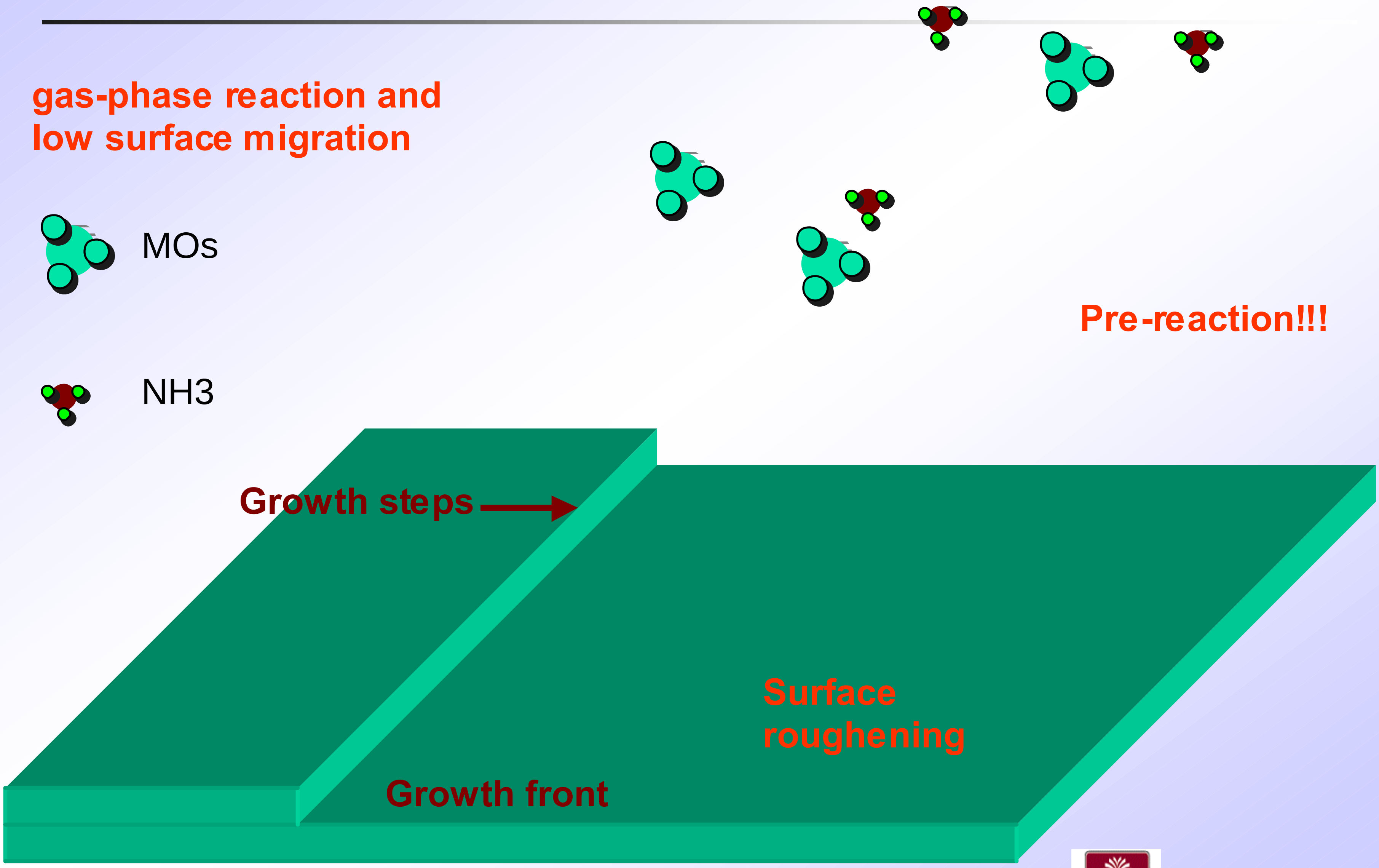
- InN 600 C
- GaN 1000 C
- AlN 1150 C

SLs Strain-management for crack-free AlGaN growth



Conventional-MOCVD

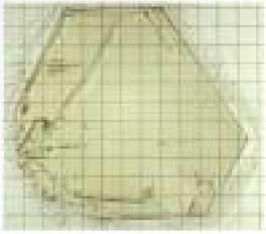
gas-phase reaction and
low surface migration



III-N Conventional MOCVD growth

Problem

Native substrates availablity → Technology in infancy



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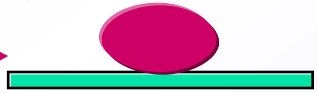
Heteroepitaxy

↓

Thermal mismatch resulted cracking

Lattice mismatch induced huge surface energy difference results in random island growth → Analogy to mercury on glass



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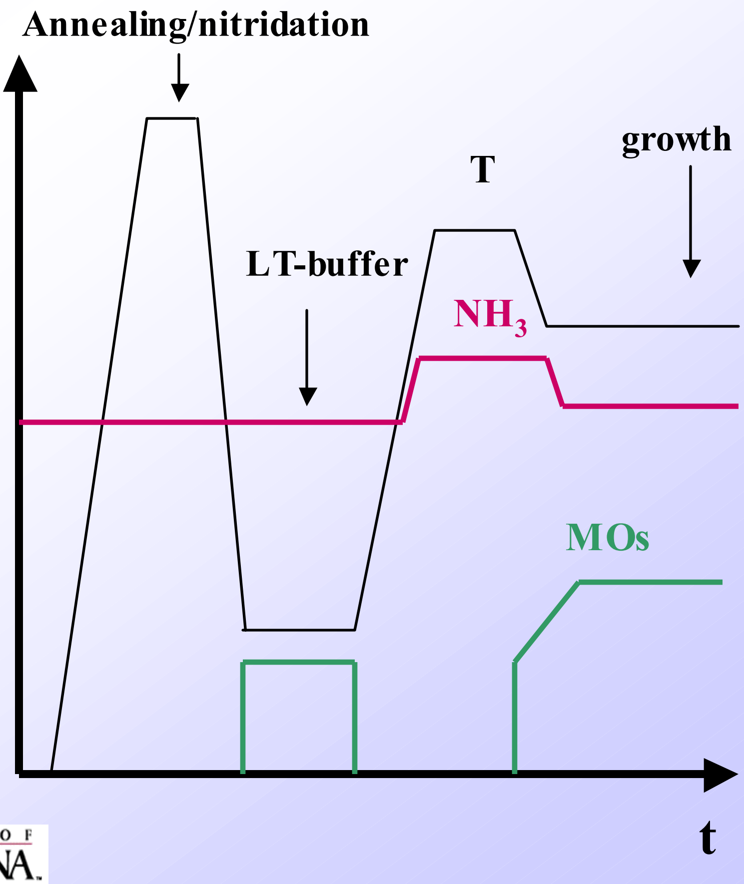
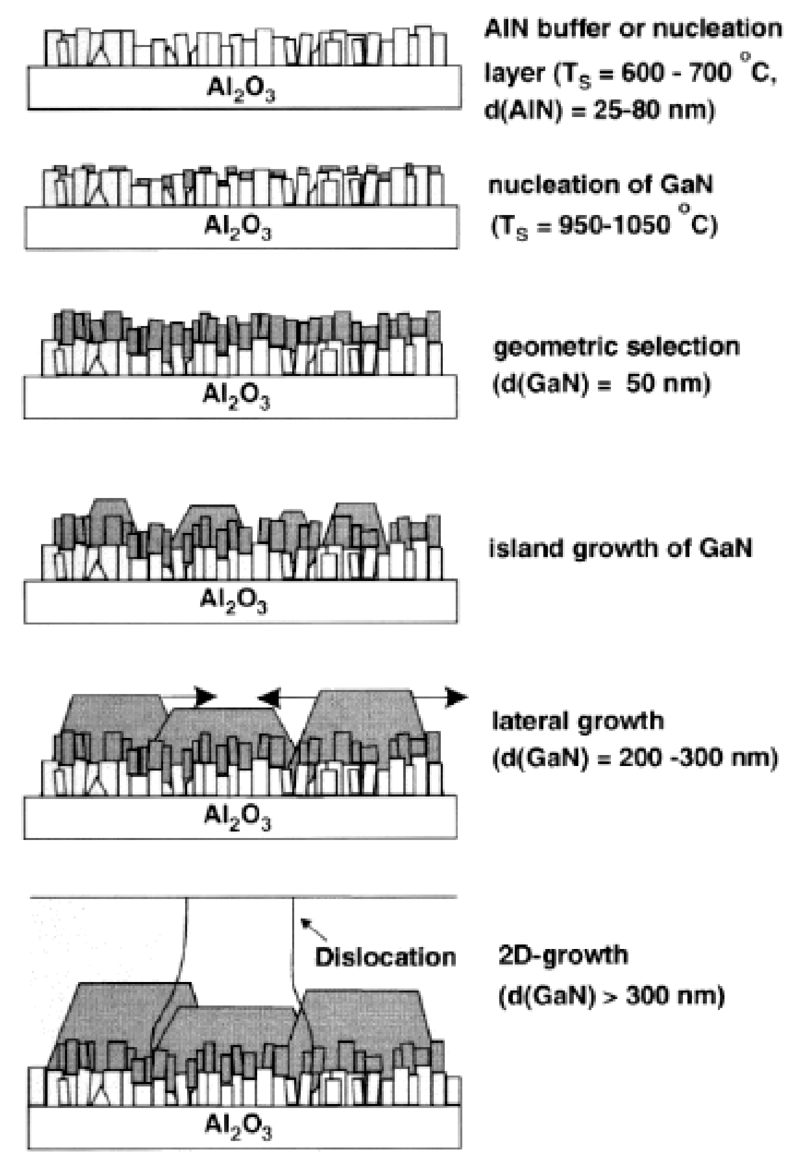
Low T amorphous AlN/GaN/InN buffer developed → Well-established procedure for III-nitrides on sapphire



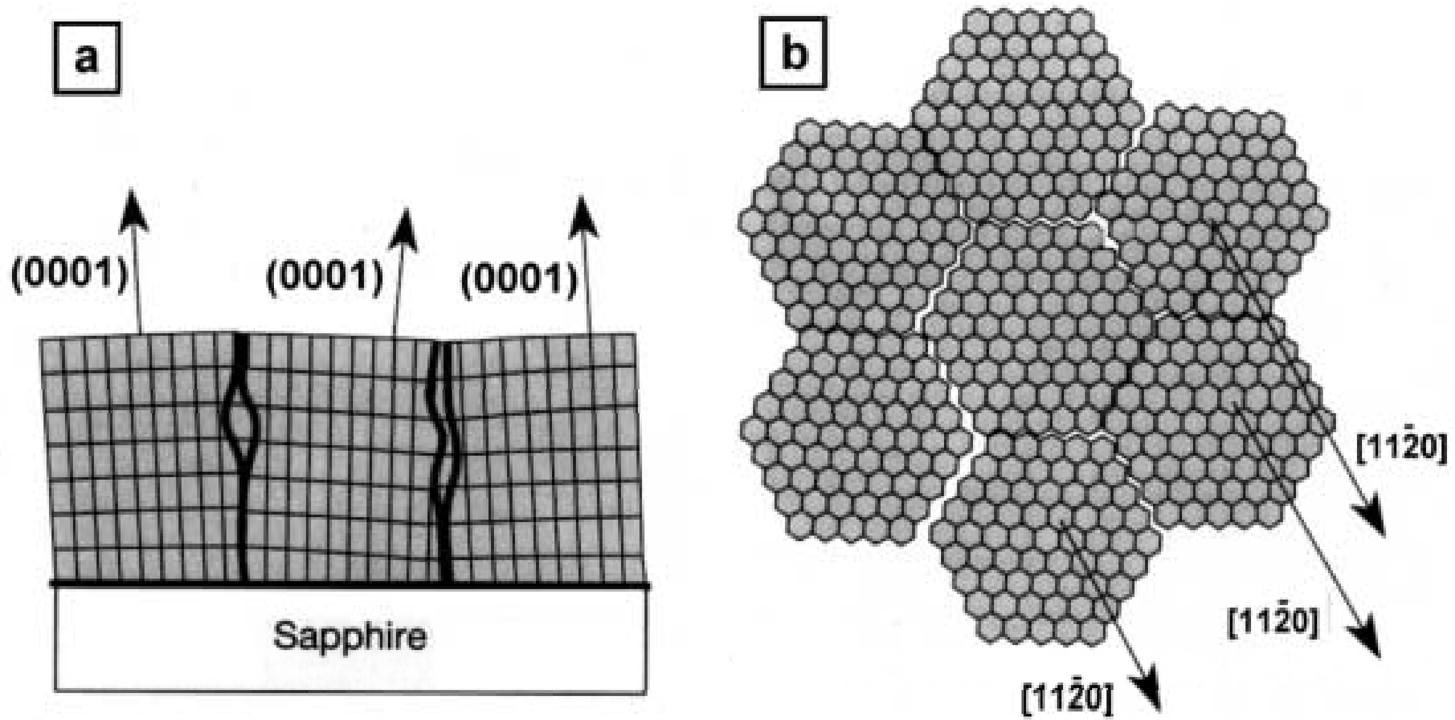
GaN on Sapphire substrate

Growth steps of GaN on sapphire

- The lattice mismatch with GaN is 13.9%
- The steps for GaN growth includes: (a) Nitridation and (b) low temperature buffer layer (usually AlN) growth
- Growth on c-plane of sapphire gives c-plane GaN, while growth on r-plane gives a-plane GaN
- Energy gap of sapphire is > 8eV so light extraction possible from substrate side for LEDs



Microstructure of GaN on Sapphire



Ordered polycrystalline microstructure of GaN on sapphire. (a) Side view showing relative tilt of (0001) directions between grains; (b) Plan view showing relative twists of polycrystal $(11\bar{2}0)$ directions.

Standard MOCVD vs MEMOCVD

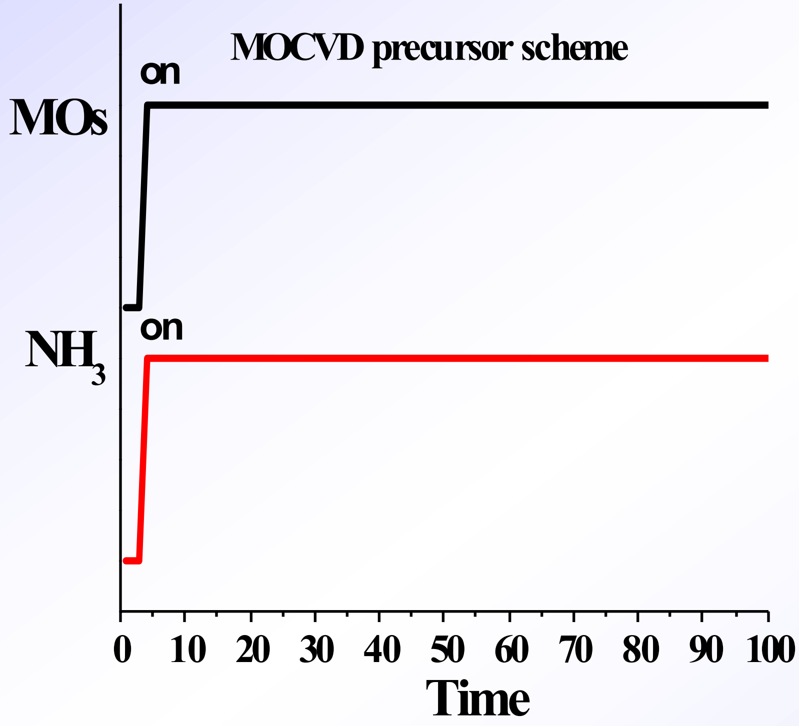
* Gas-phase prereaction

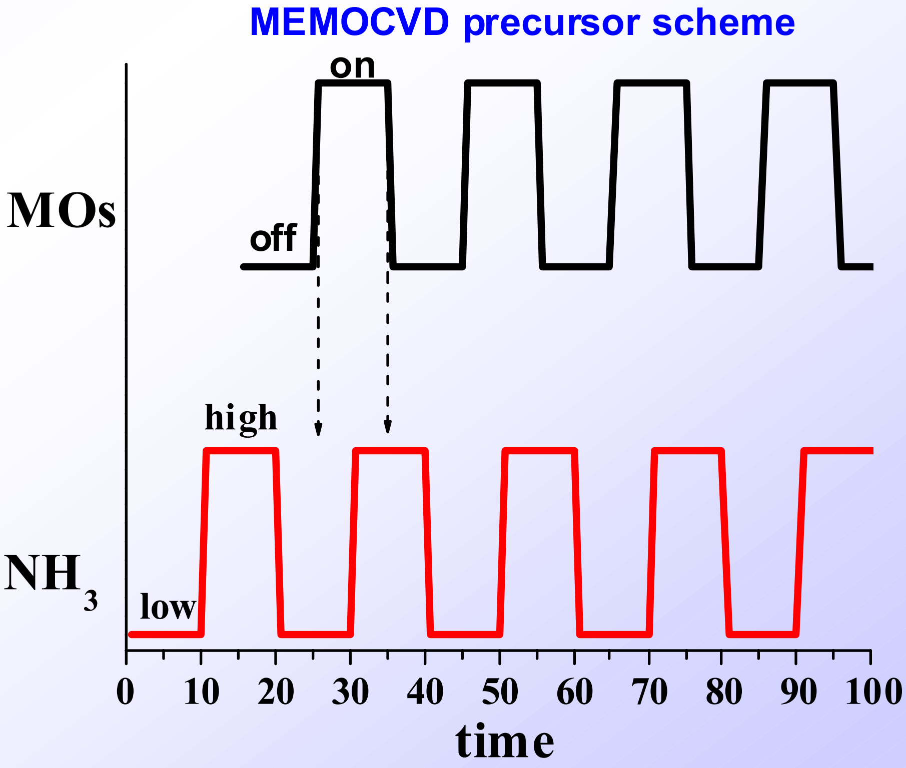
* Low surface mobility

* Precursors' overlap adjustable

* Minimize prereaction and enhance migration

* AlInGaN digital alloys and SLS





Custom MEMOCVD system for III-Nitrides

MOCVD system contains:

Vacuum system

Gas delivery system

Heating system

Control system

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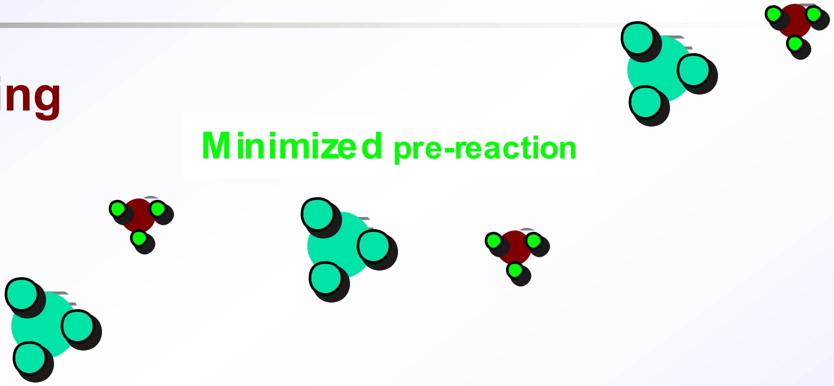
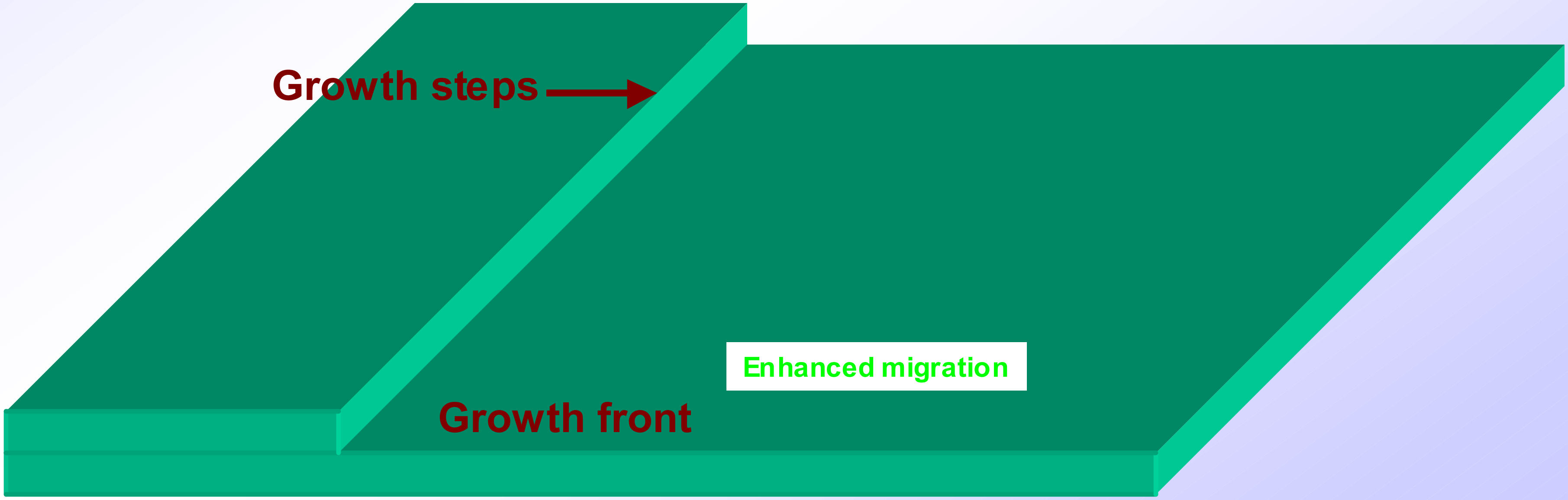
MEMOCVD of III-N Materials

allowing V/III separation hence reducing gas-phase reaction & enhancing surface migration

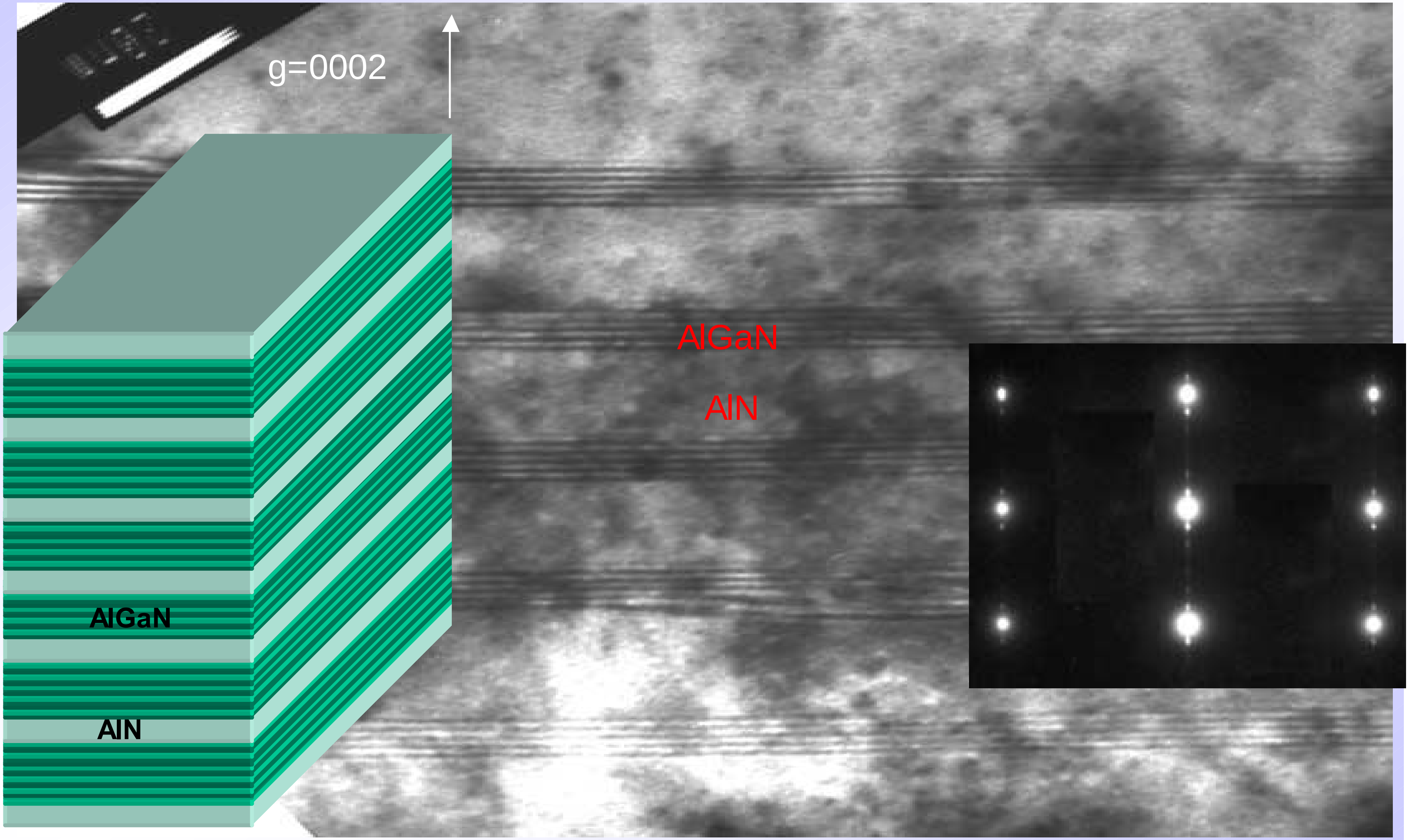


MOs

NH3

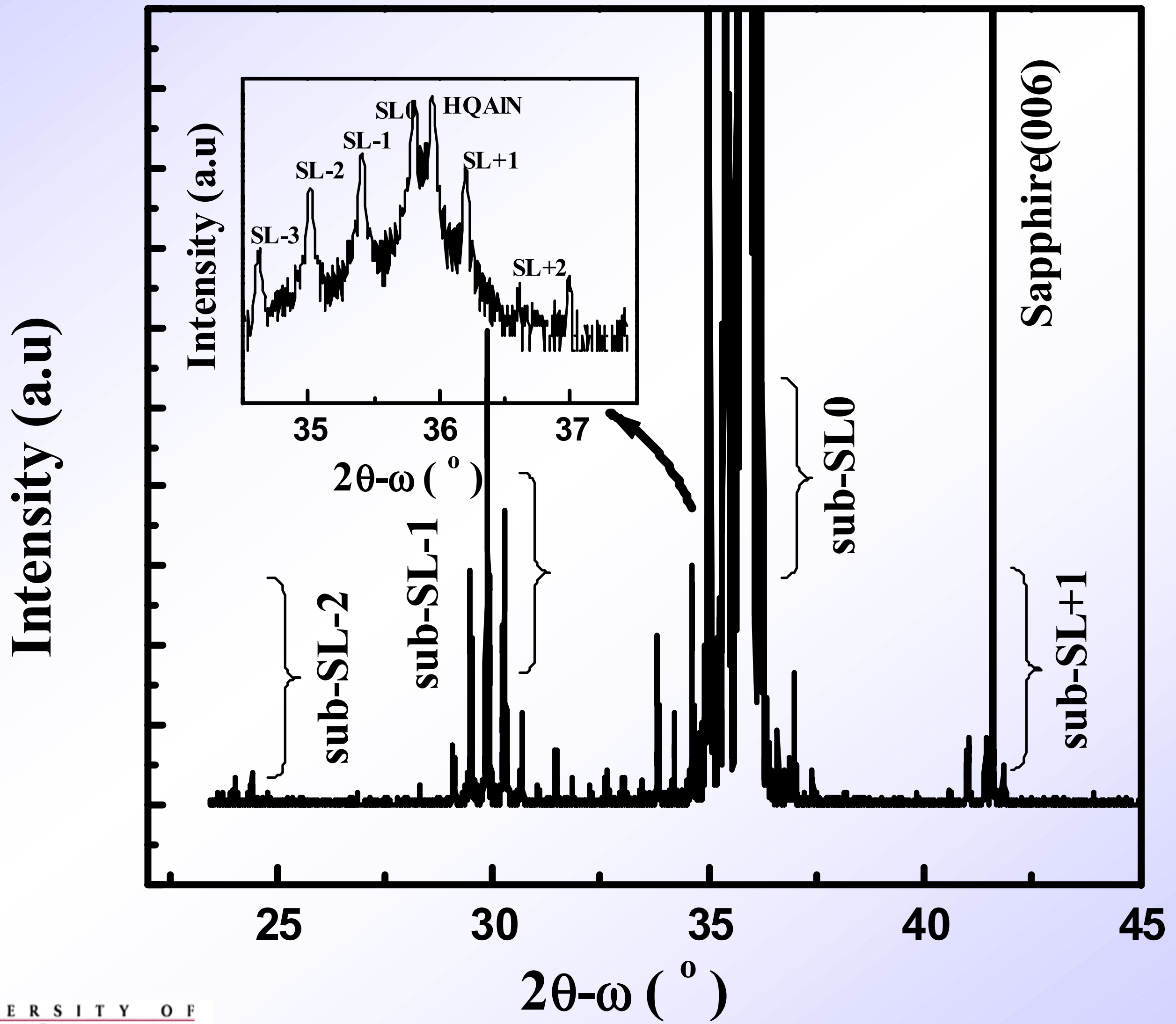


MEMOCVD AlN/ALGaN SLs-complex



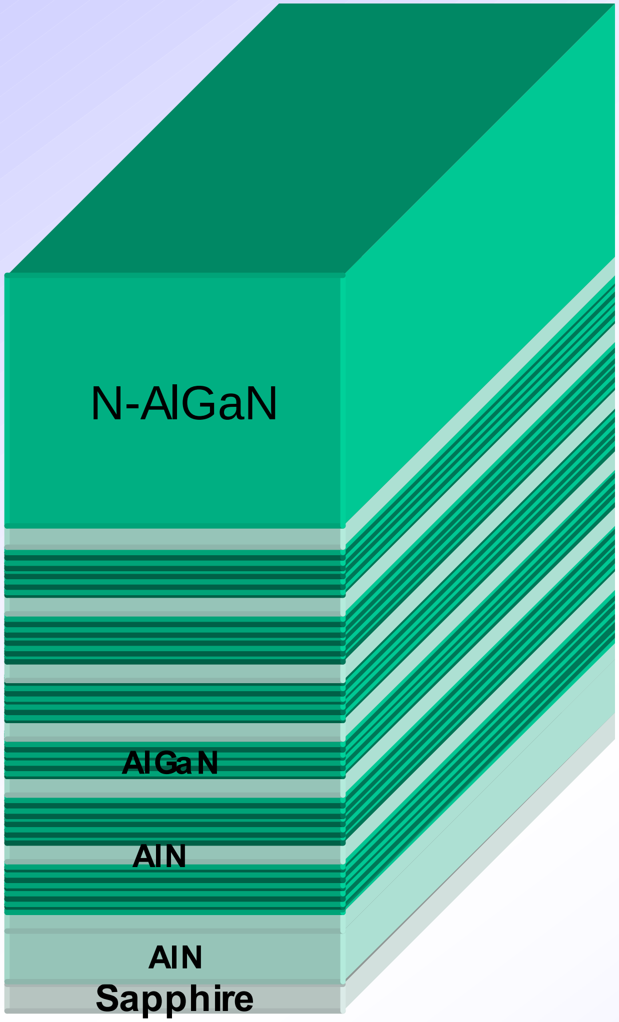
Deep UV LEDs (250-280 nm)

X-ray spectra of MEMOCVD AlN/AlGaN SL buffer

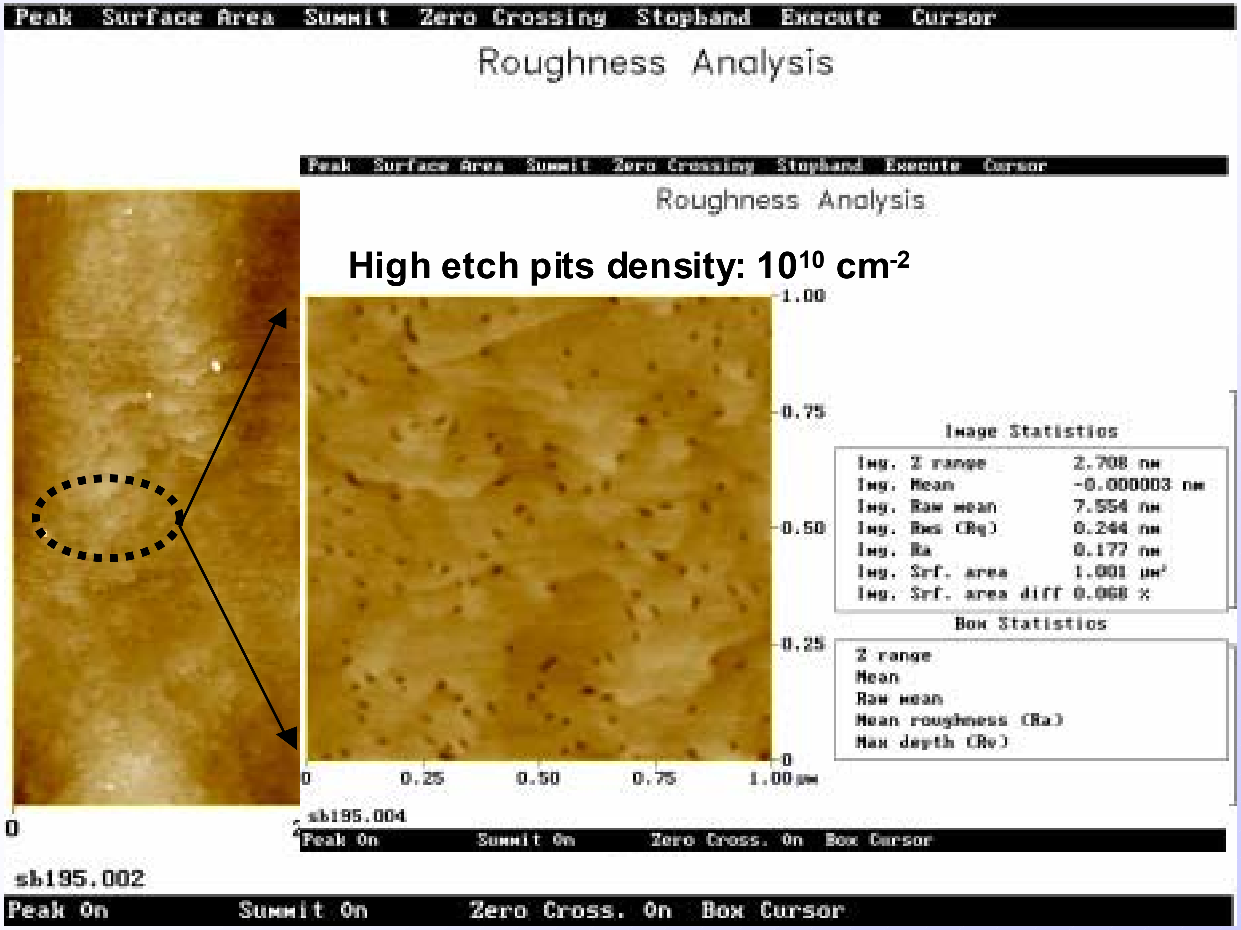


N-AlGaN on MEMOCVD AlN+SLs buffer:

$Al_{0.66}Ga_{0.34}N$ for sub-260nm LEDs



RMS=7A with atomic steps



High etch pits density: 10^{10} cm^{-2}

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            Image Statistics
Img. Z range            2.708 nm
Img. Mean               -0.000003 nm
Img. Raw mean           7.554 nm
Img. Rms (Rq)           0.244 nm
Img. Ra                 0.177 nm
Img. Srf. area          1.001 µm²
Img. Srf. area diff 0.068 %
             Box Statistics
Z range
Mean
Raw mean
Mean roughness (Ra)
Max depth (Rv)
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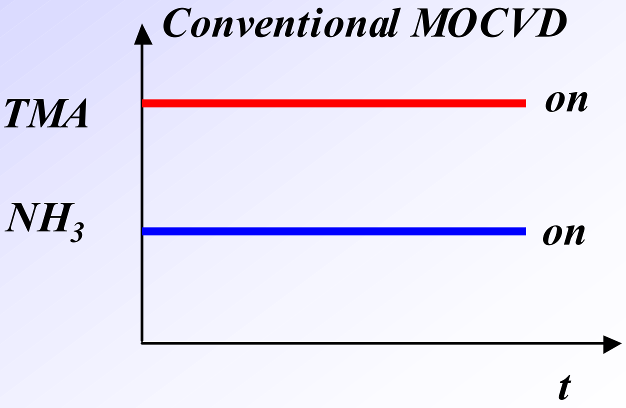
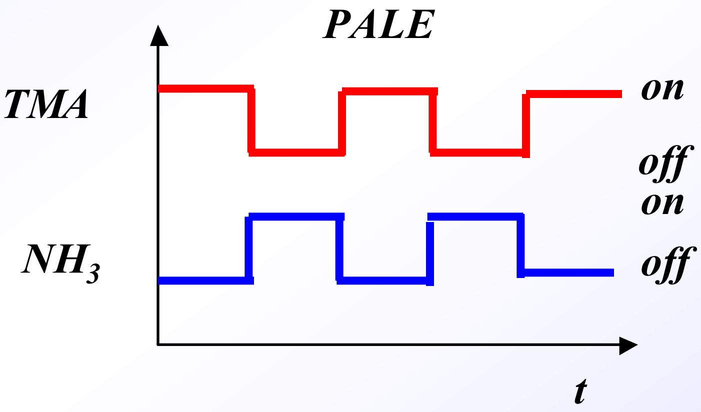
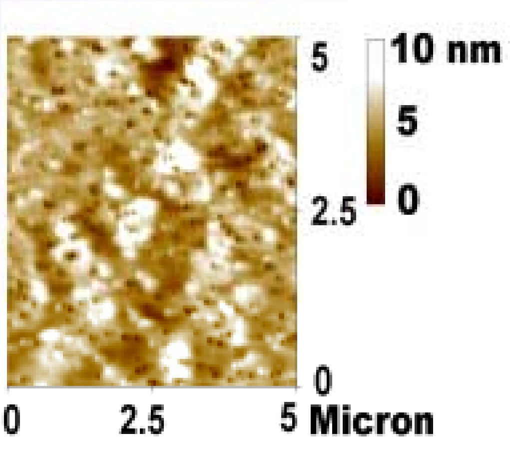
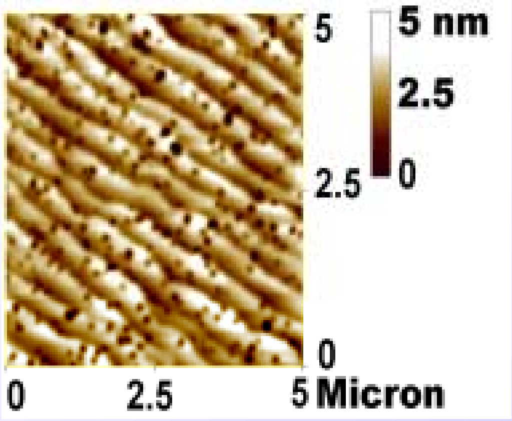
MOCVD vs MEMOCVD AlN







MOCVD AlN

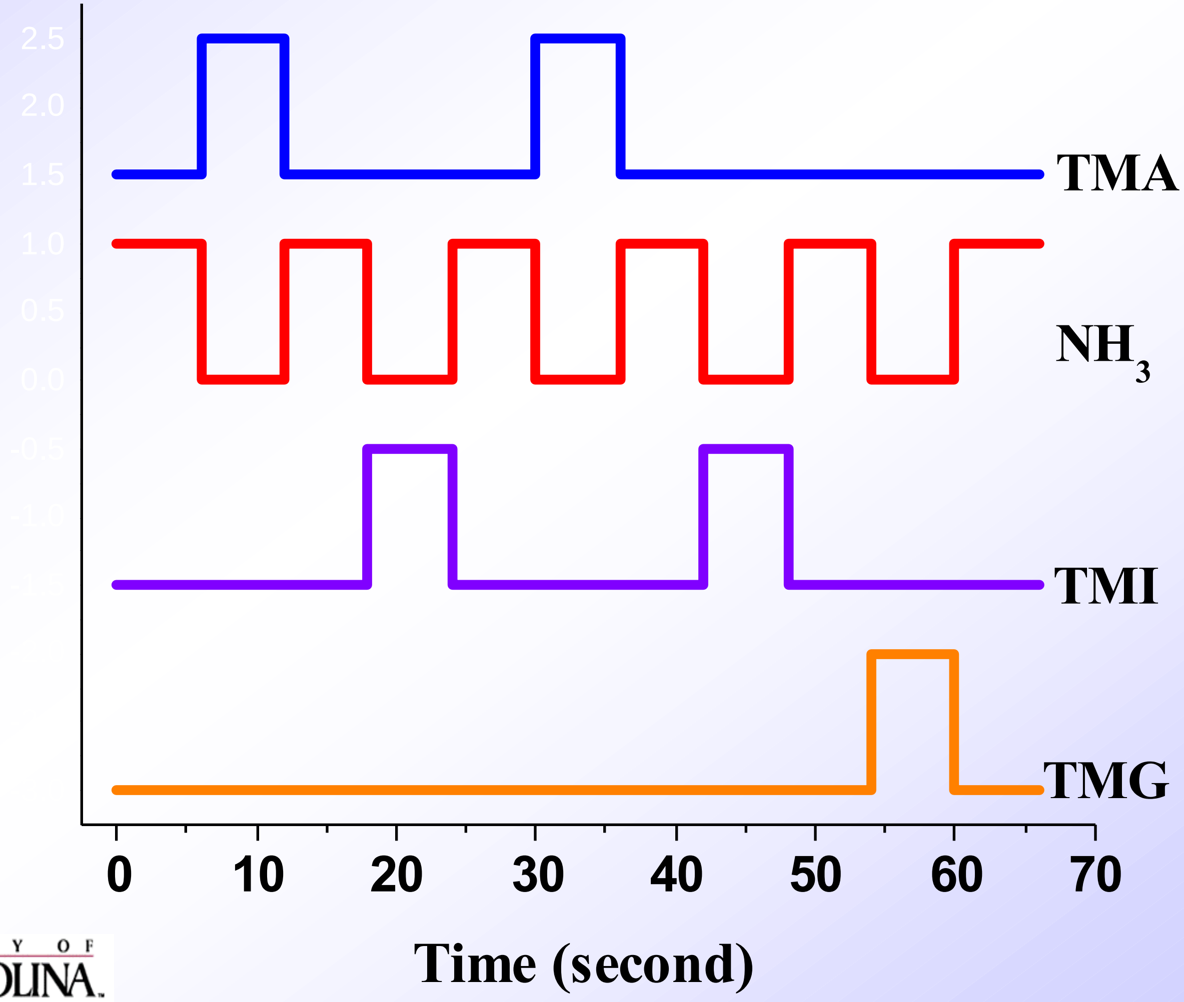


PALE AlN

MEMOCVD AlInGaN digital alloys

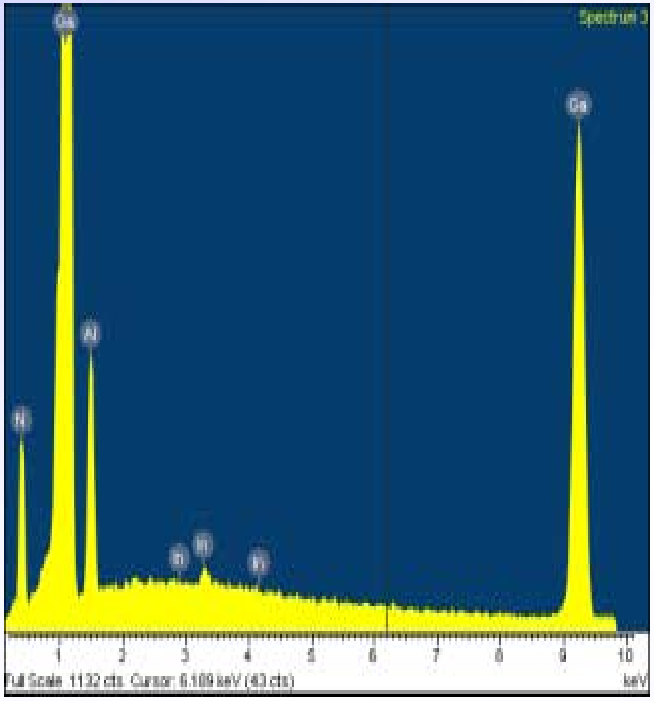
A representative MEMOCVD growth unit cell, AlInGaN (2,2,1)

The number of repeats of Al, In, and Ga pulses in the unit cell are 2, 2, and 1, respectively. Pulse length is kept as 6 seconds.

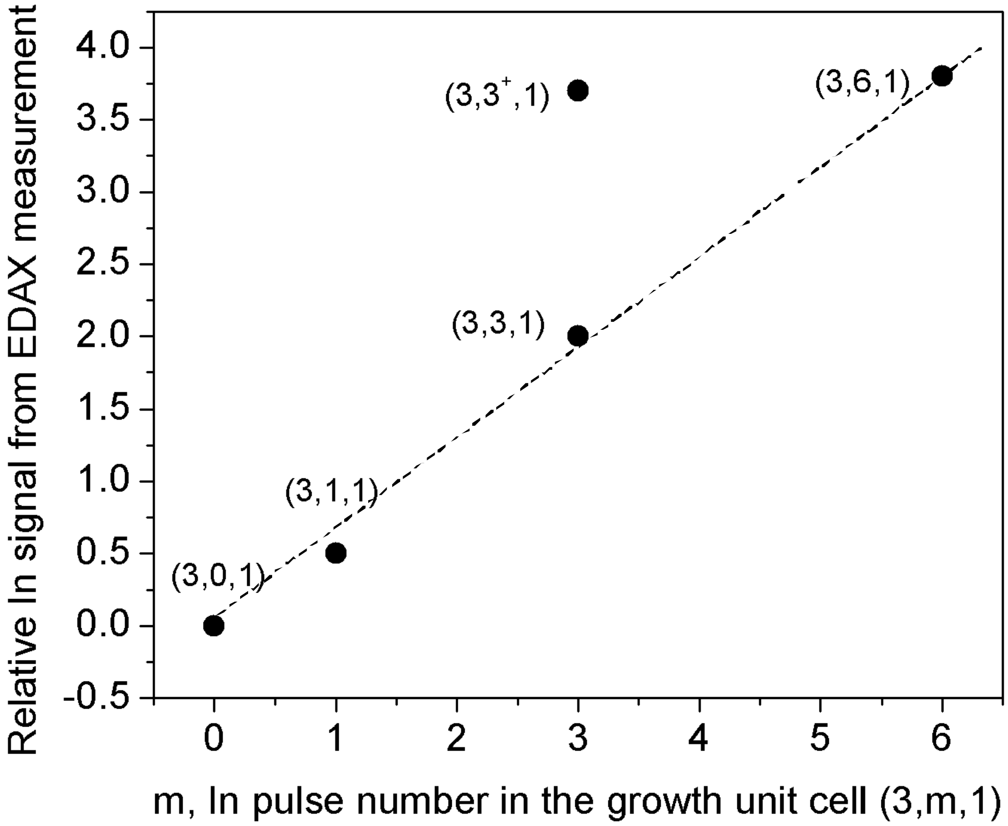


MEMOCVD AlInGaN digital alloys

Composition control

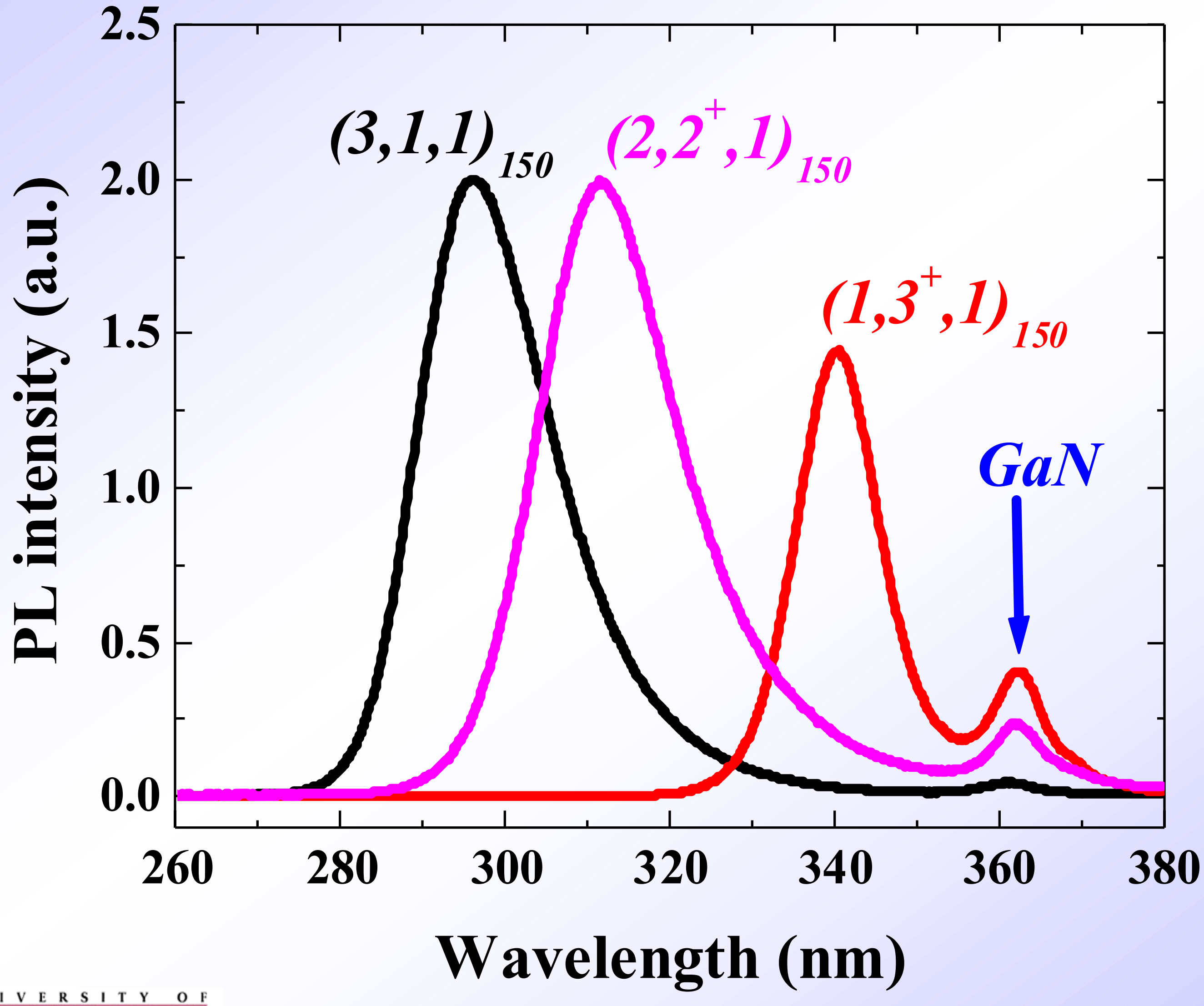


A typical EDAX spectrum for our AlInGaN samples



EDAX In fraction as a function of m, In pulses within one growth unit cell for (3,m,1)

MEMOCVD AlInGaN Digital Alloy PL



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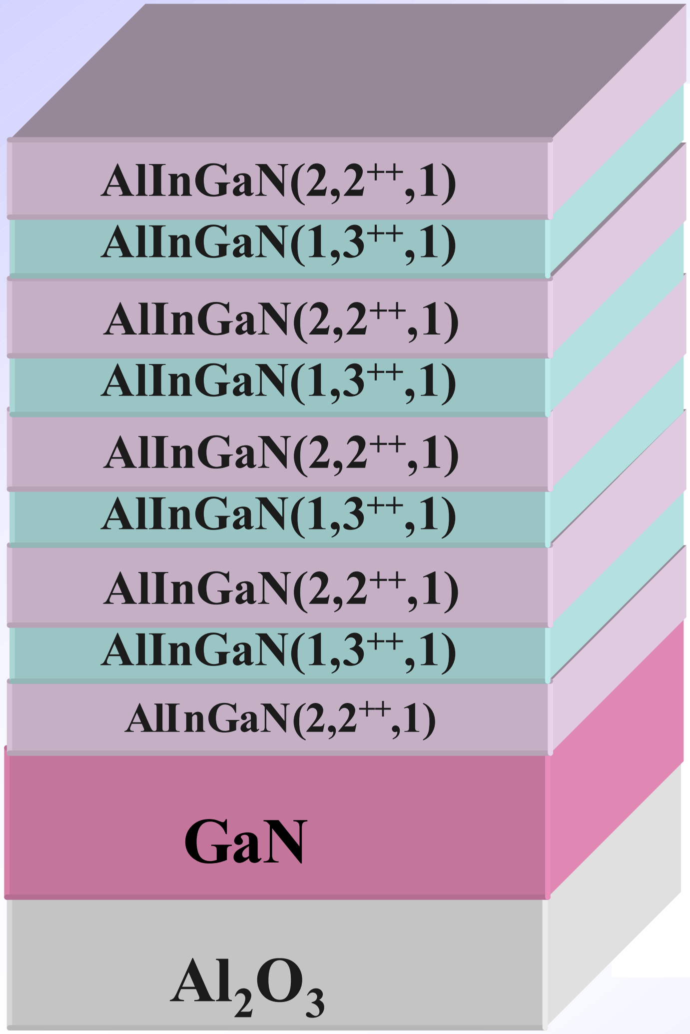
Quaternary Digital Superlattices

XRD Spectra



AlInGaN$(2,2^{++},1)$

AlInGaN$(1,3^{++},1)$

AlInGaN$(2,2^{++},1)$

AlInGaN$(1,3^{++},1)$

AlInGaN$(2,2^{++},1)$

AlInGaN$(1,3^{++},1)$

AlInGaN$(2,2^{++},1)$

AlInGaN$(1,3^{++},1)$

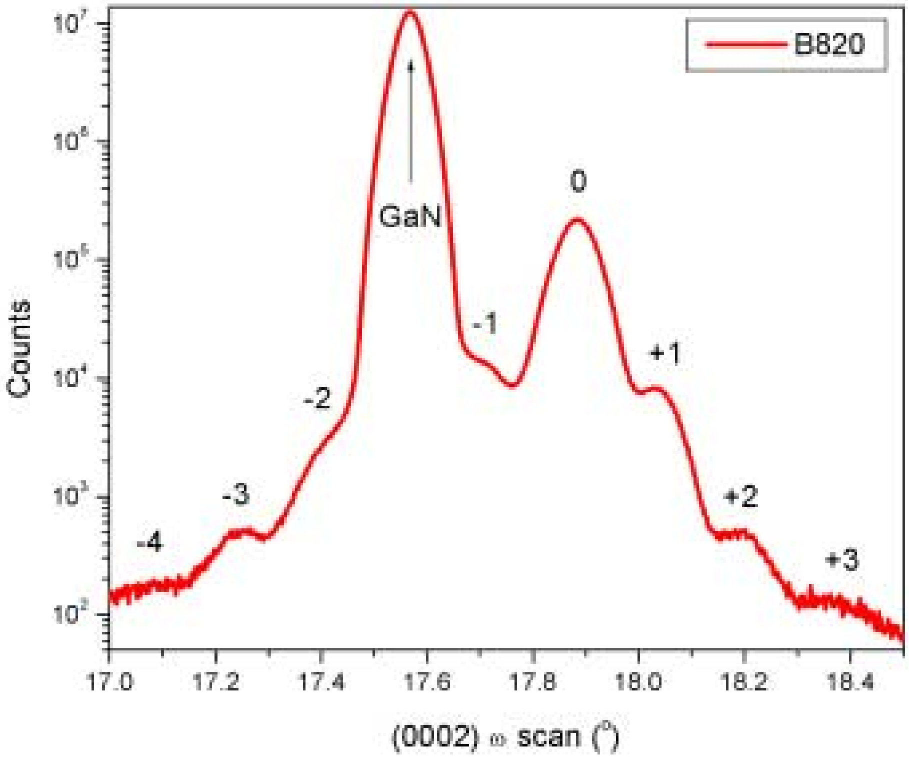
AlInGaN$(2,2^{++},1)$

GaN

Al_2O_3

MEMOCVD AlInGaN MQWs

$4x\{(2,2^{++},1)_{30}/(1,3^{++},1)_{10}\}$



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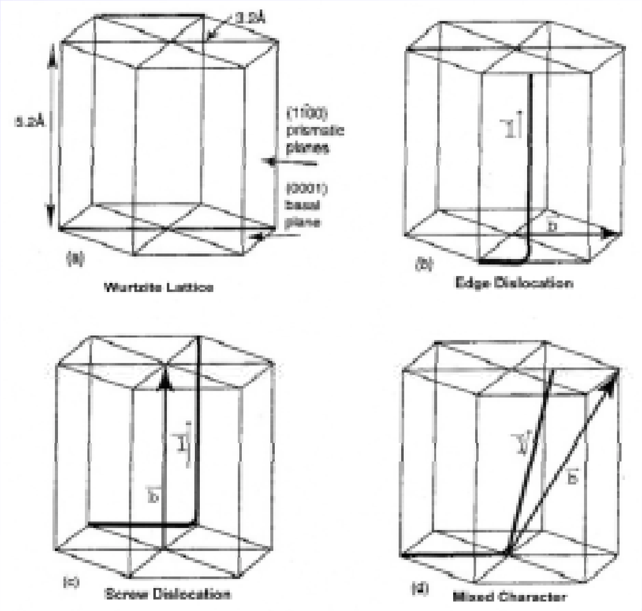
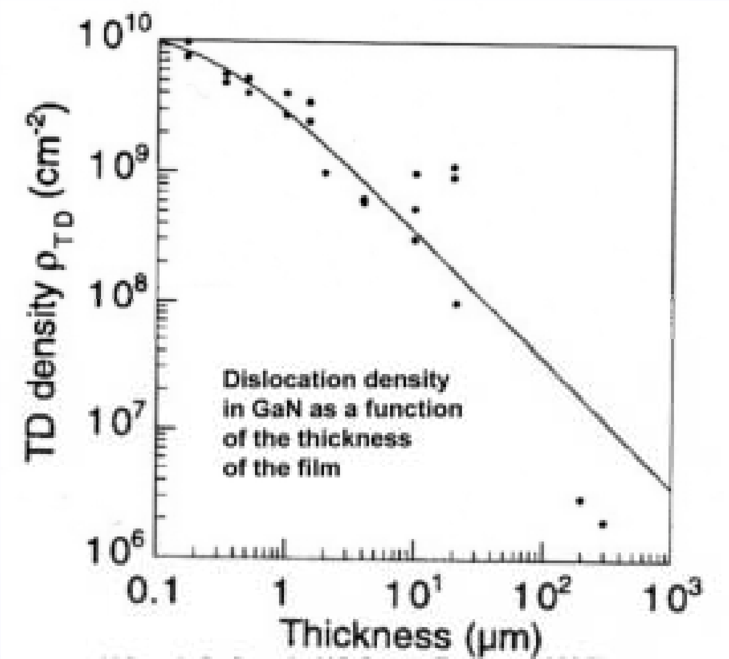
Dislocations and Dislocation Reduction

The majority of dislocations in GaN result from the coalescence of misoriented islands





(After J. S. Speck, UC Santa Barbara, 1996)

- Dislocations can interact and be annihilated

Stimulated Emission at 258 nm in AlN/AlGaN Quantum Wells Grown on Bulk AlN Substrates

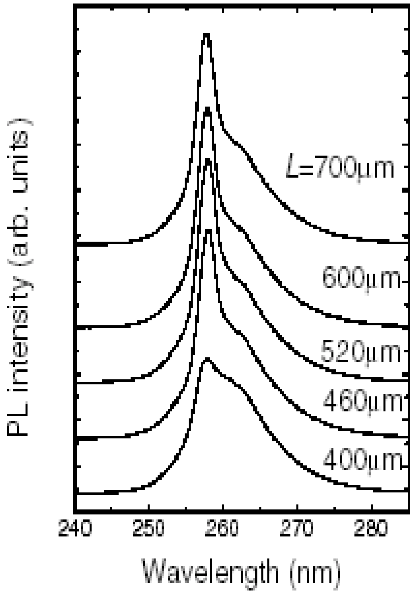
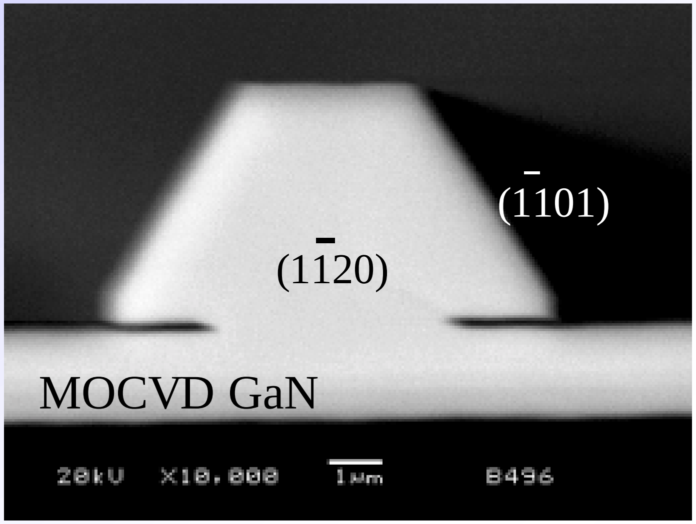
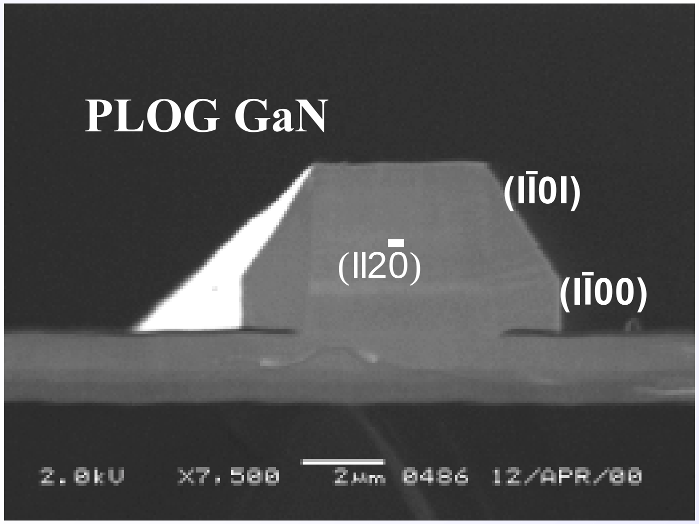


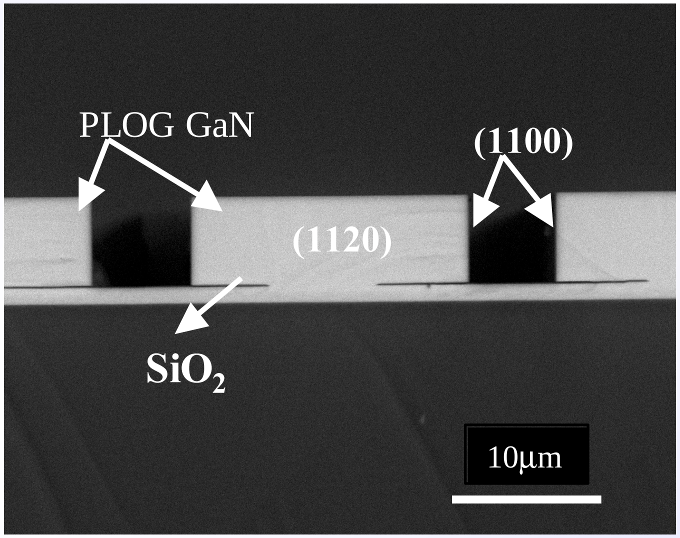
Figure 4. Sample-edge emission spectra of $Al_{0.5}Ga_{0.5}N/AlN$ quantum wells on bulk AlN under excitation power density of 7.5 MW/cm^2 at different stripe lengths *L* (indicated). The base lines of the spectra are vertically shifted.

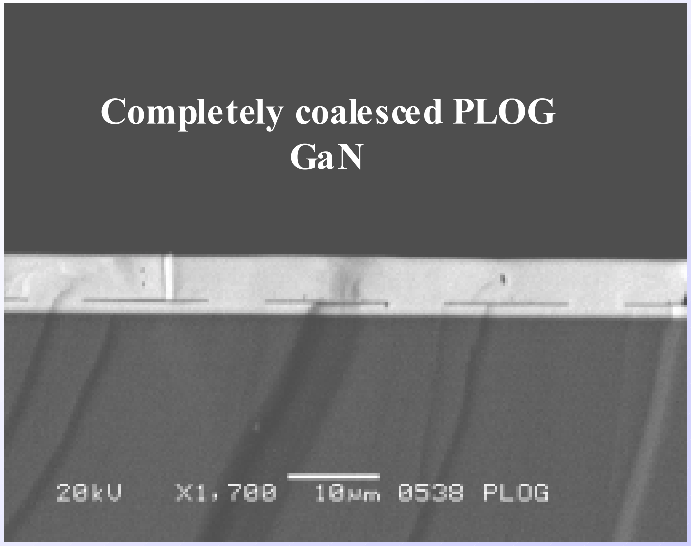
Pulsed Lateral Overgrowth (PLOG)

Different Pulse time for NH_3 ‘on’ and ‘Off’



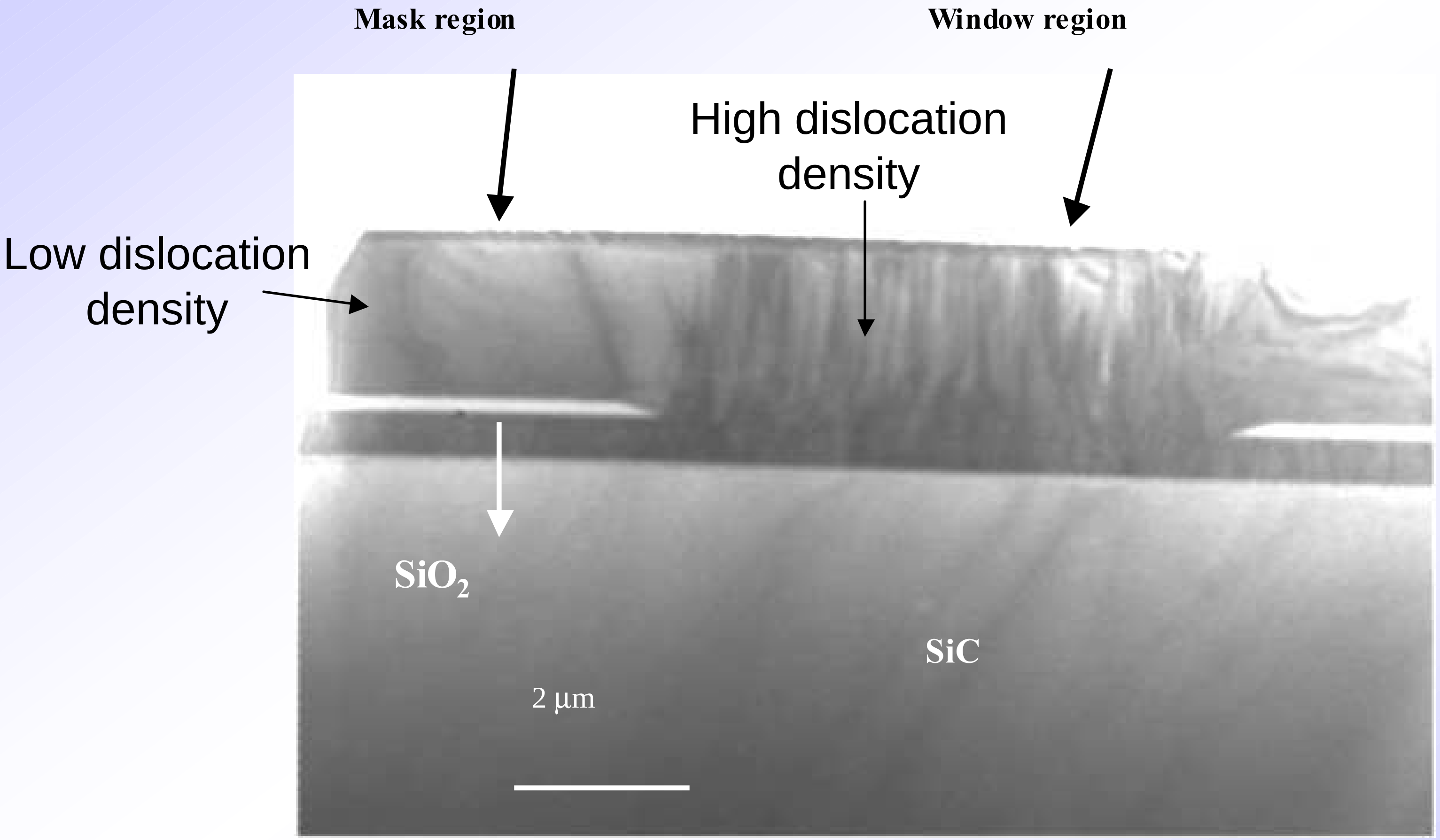




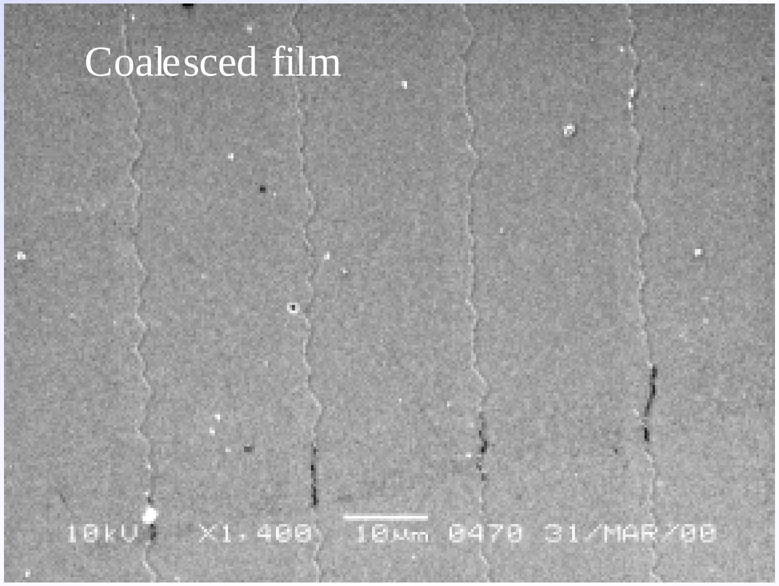


Pulsed Lateral Overgrowth (PLOG)

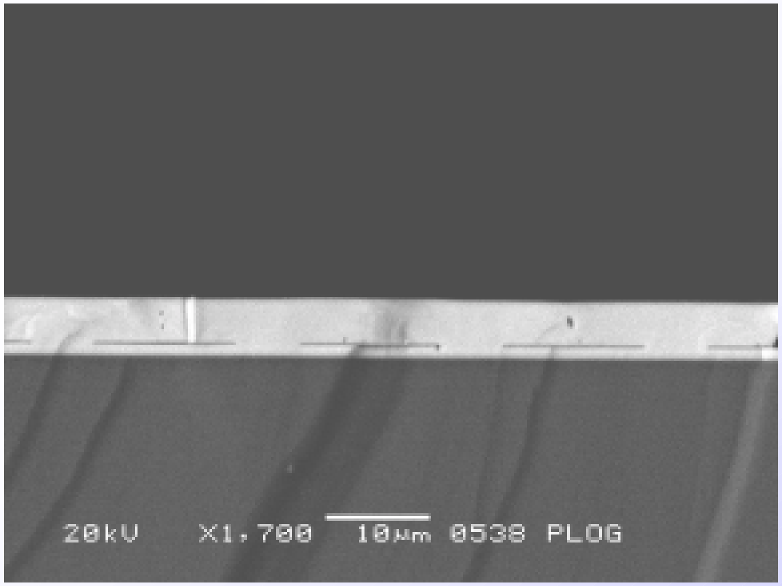
TEM X-section Image



Complete coalescence of GaN by lateral overgrowth method

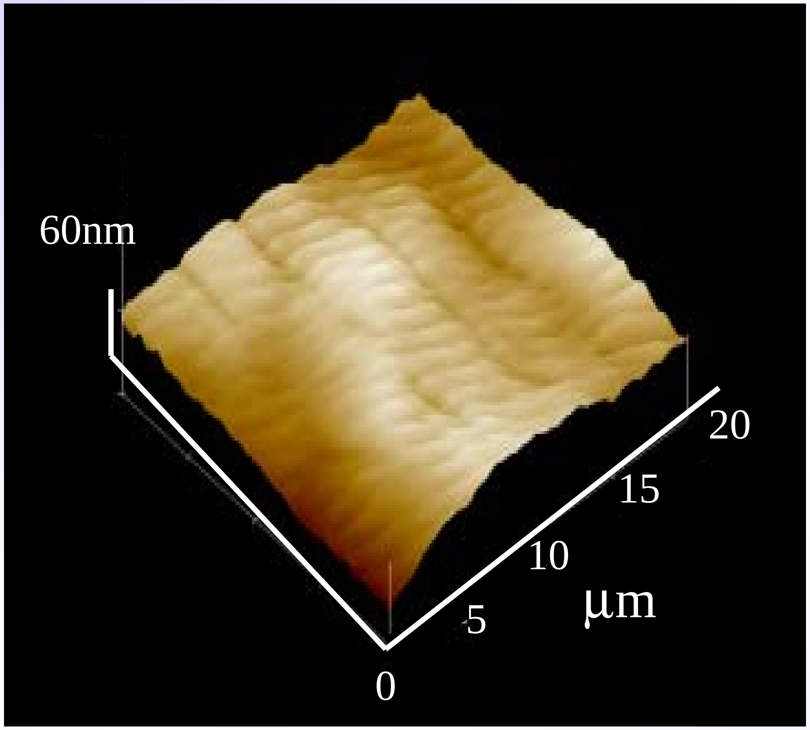


Plane view



Cross sectional view

Surface roughness of PLOG GaN



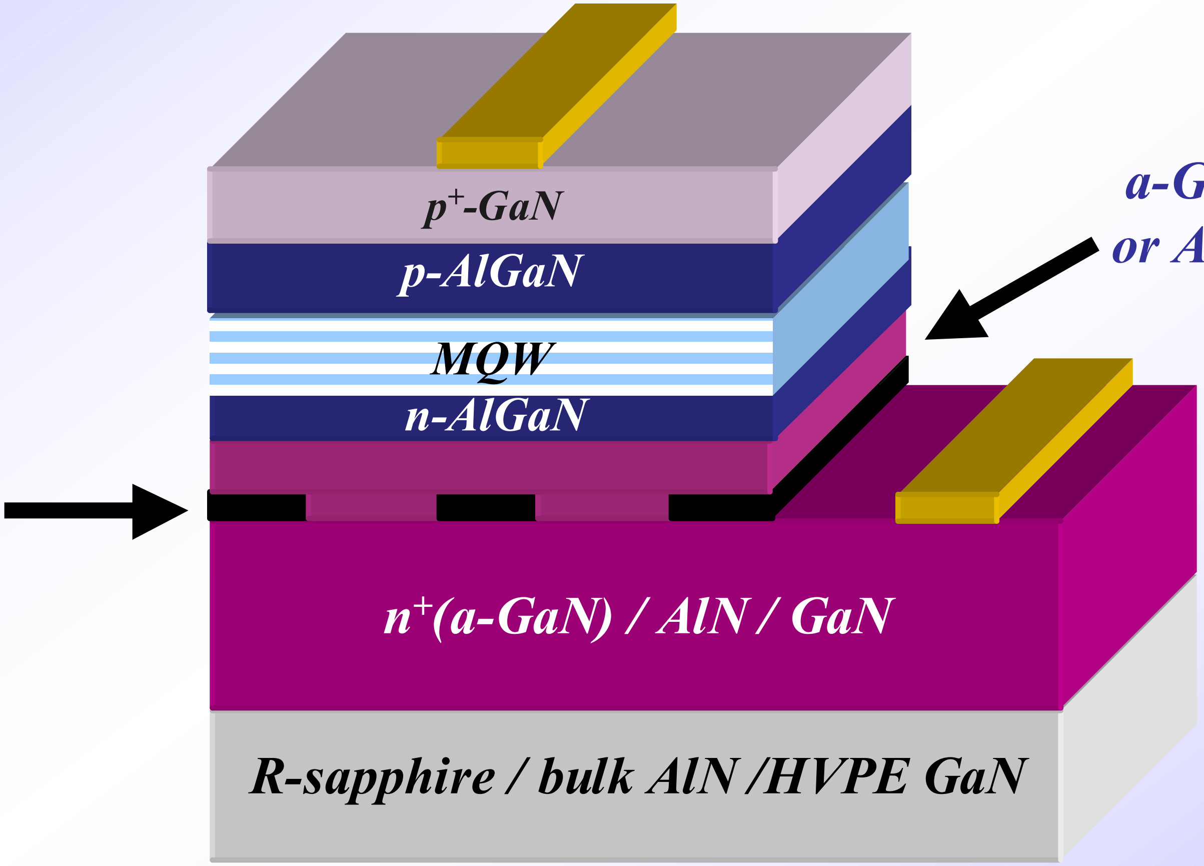
RMS roughness

PLOG GaN = 7-10 Å

- **No step termination observed**
- **Reduction of screw component threading dislocation**

Edge Emitting UV LEDs

Device Design



p^+-GaN

p-AlGaN

MQW

n-AlGaN

n^+(a-GaN) / AlN / GaN

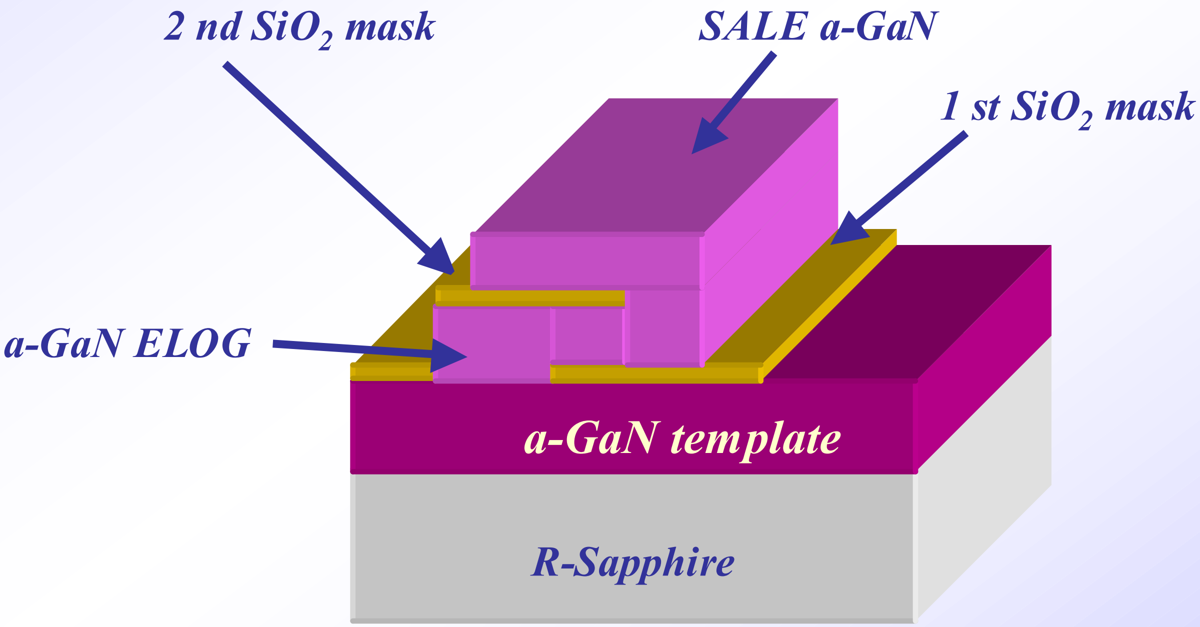
R-sapphire / bulk AlN /HVPE GaN

a-GaN (ELOG)
or AlN or c-GaN

SiO_2 mask

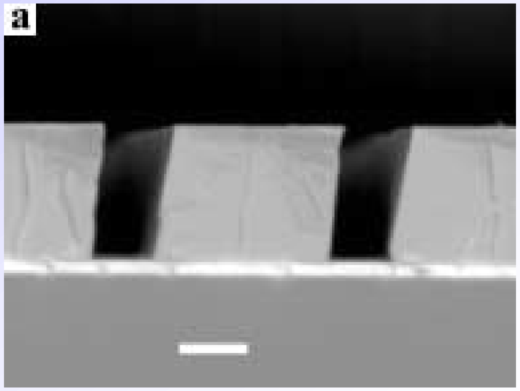
Non Polar III-N Device Development

Approach 2: Selective Area Lateral Epitaxy (SALE)

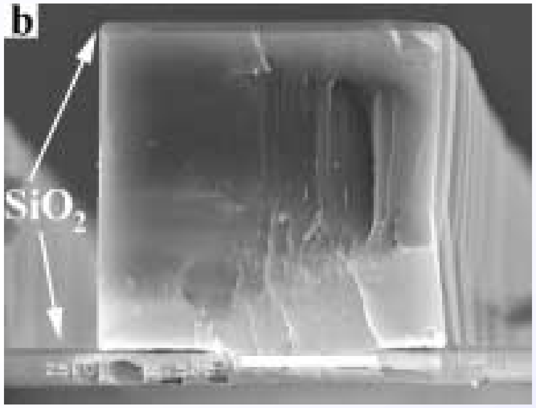


Non Polar III-N Device Development

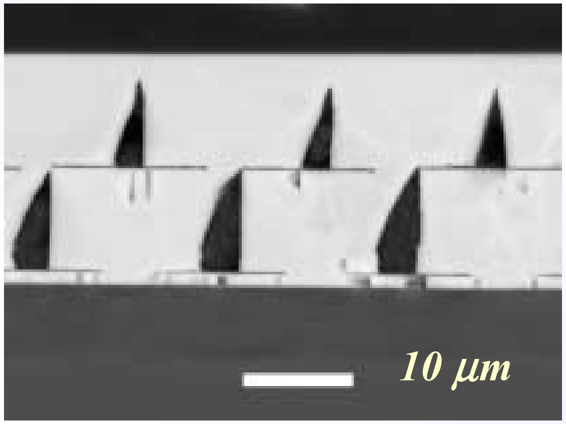
Selective Area Lateral Epitaxy (SALE)



Step 1. a-plane GaN pillar on R-plane Sapphire



Step 2. a-plane GaN pillar after SiO_2 deposition

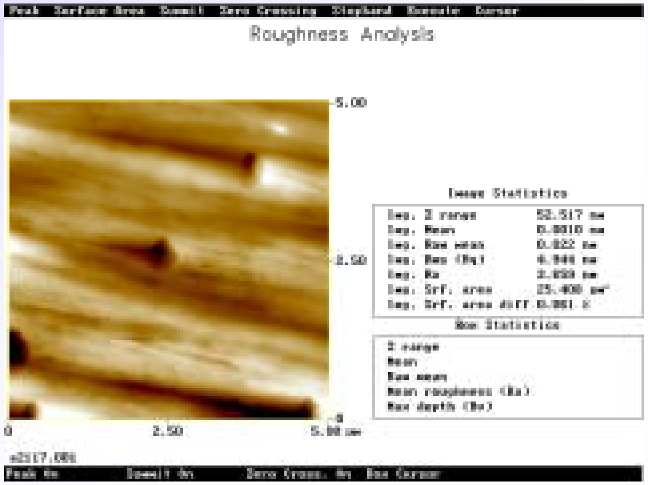


SEM image of fully coalesced

SALE a-plane GaN layer

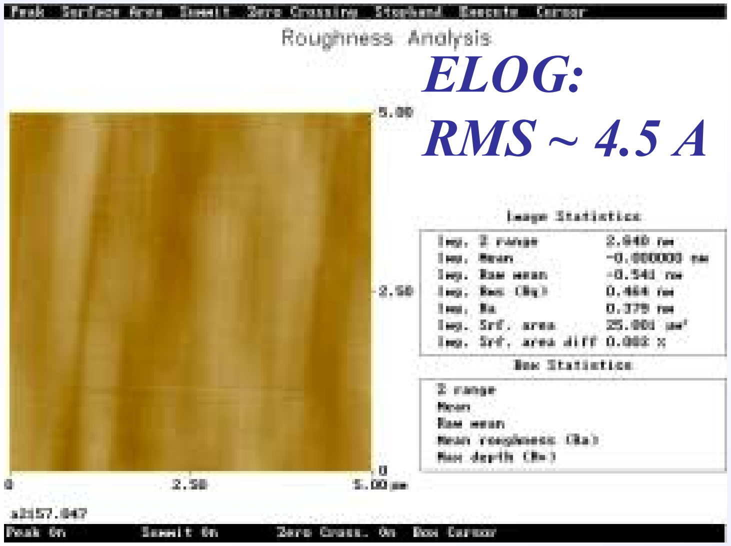
a-plane GaN Template, ELOG, SALE

RMS surface Roughness



```
Image Statistics
Img. Z range          52.517 nm
Img. Mean             0.0010 nm
Img. Raw mean         0.022 nm
Img. Rms (Rq)         4.946 nm
Img. Ra               3.893 nm
Img. Srf. area        25.400 µm²
Img. Srf. area diff 0.001 %
Box Statistics
Z range
Mean
Raw mean
Mean roughness (Ra)
Max depth (Rm)
```

Template:
RMS ~ 50 A



```
Image Statistics
Img. Z range          2.840 nm
Img. Mean             -0.000000 nm
Img. Raw mean         -0.540 nm
Img. Rms (Rq)         0.464 nm
Img. Ra               0.379 nm
Img. Srf. area        25.001 µm²
Img. Srf. area diff 0.003 %
Box Statistics
Z range
Mean
Raw mean
Mean roughness (Ra)
Max depth (Rm)
```

ELOG:
RMS ~ 4.5 A

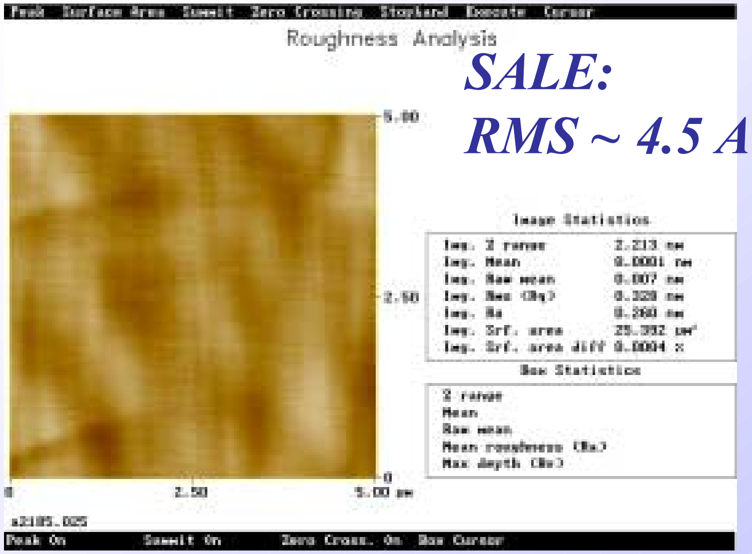


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Image Statistics
Img. Z range          2.213 nm
Img. Mean             0.0001 nm
Img. Raw mean         0.007 nm
Img. Rms (Rq)         0.328 nm
Img. Ra               0.260 nm
Img. Srf. area        25.392 µm²
Img. Srf. area diff 0.0004 %
Box Statistics
Z range
Mean
Raw mean
Mean roughness (Ra)
Max depth (Rm)
```

SALE:
RMS ~ 4.5 A

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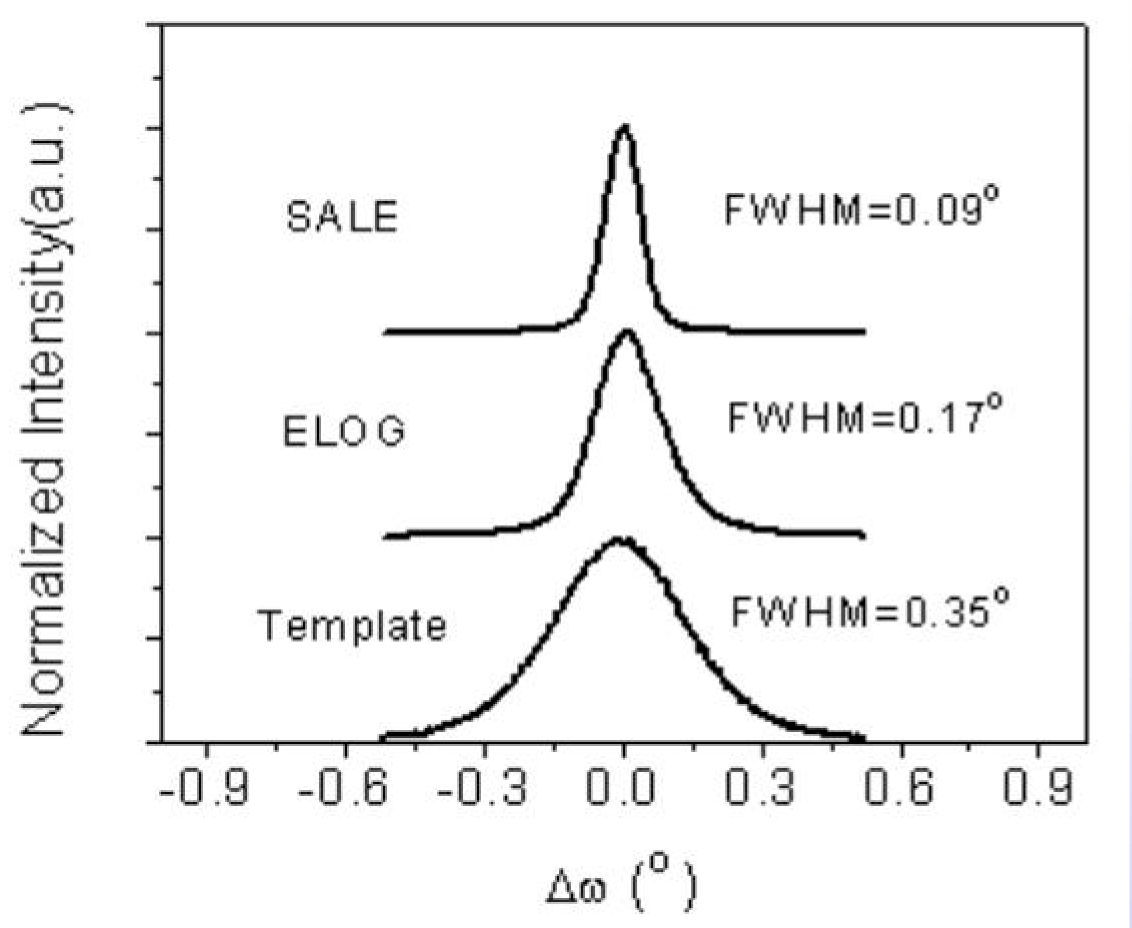
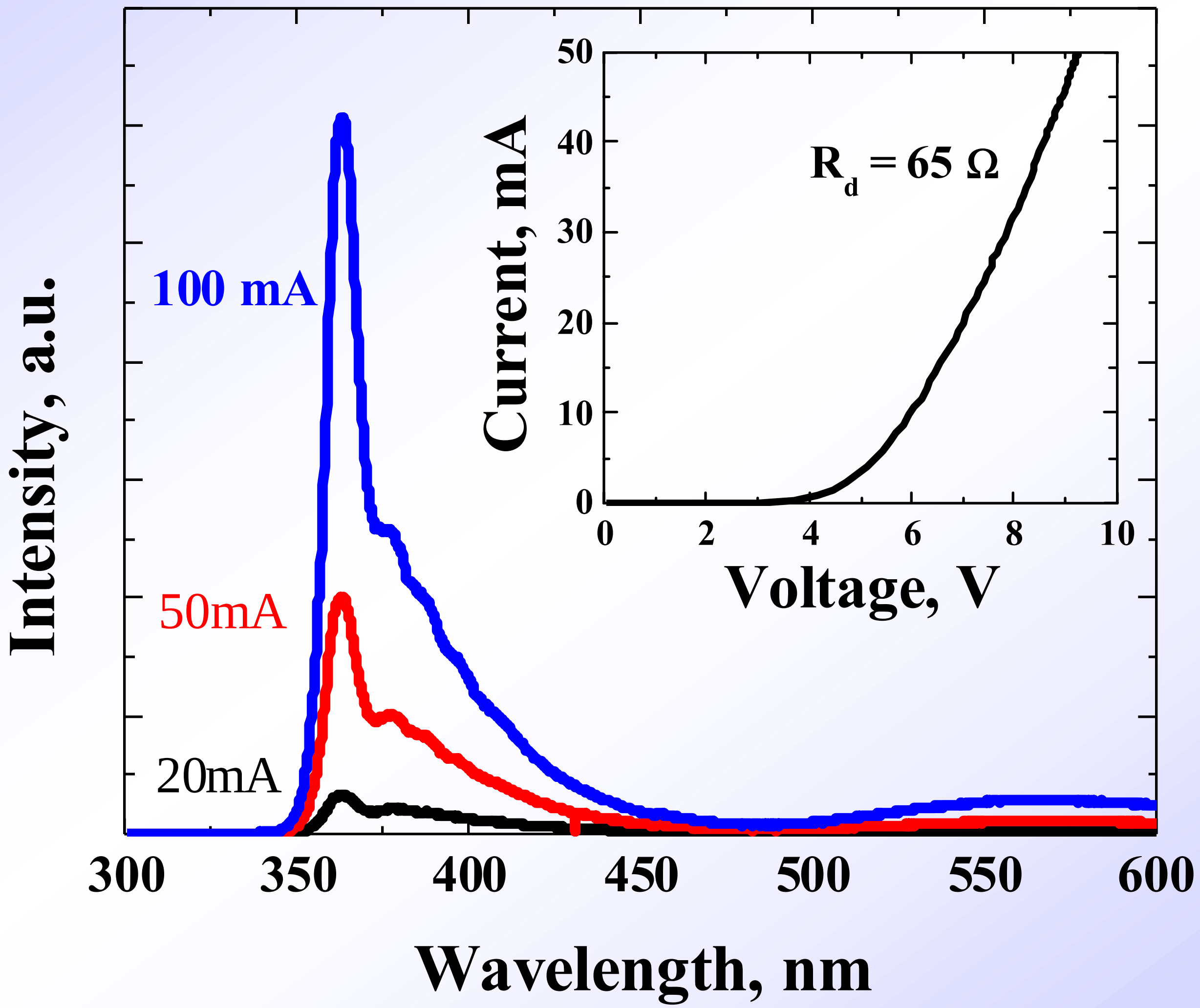
a-plane GaN Template, ELOG, SALE

X-Ray Rocking Curve Comparison a-plane GaN



Edge Emitting Non Polar UV LEDs

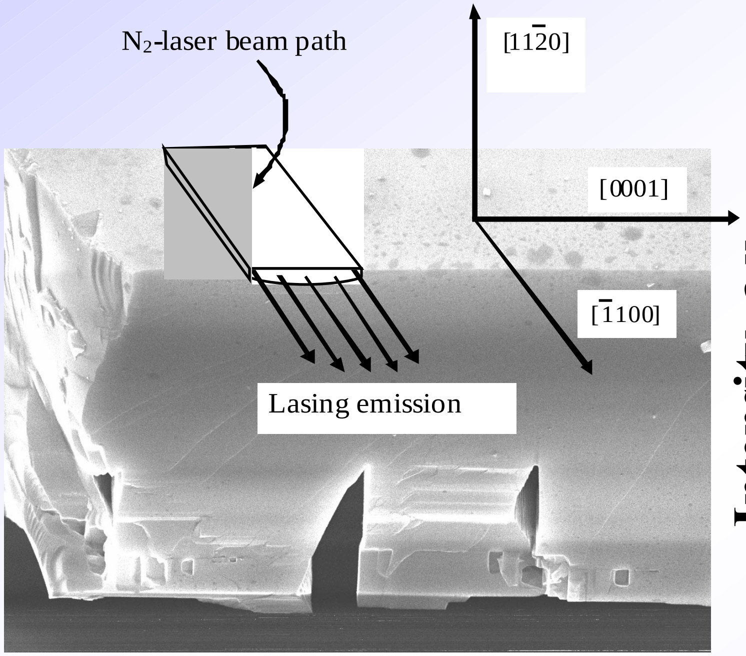
362 nm Peak Emission LED over r-sapphire

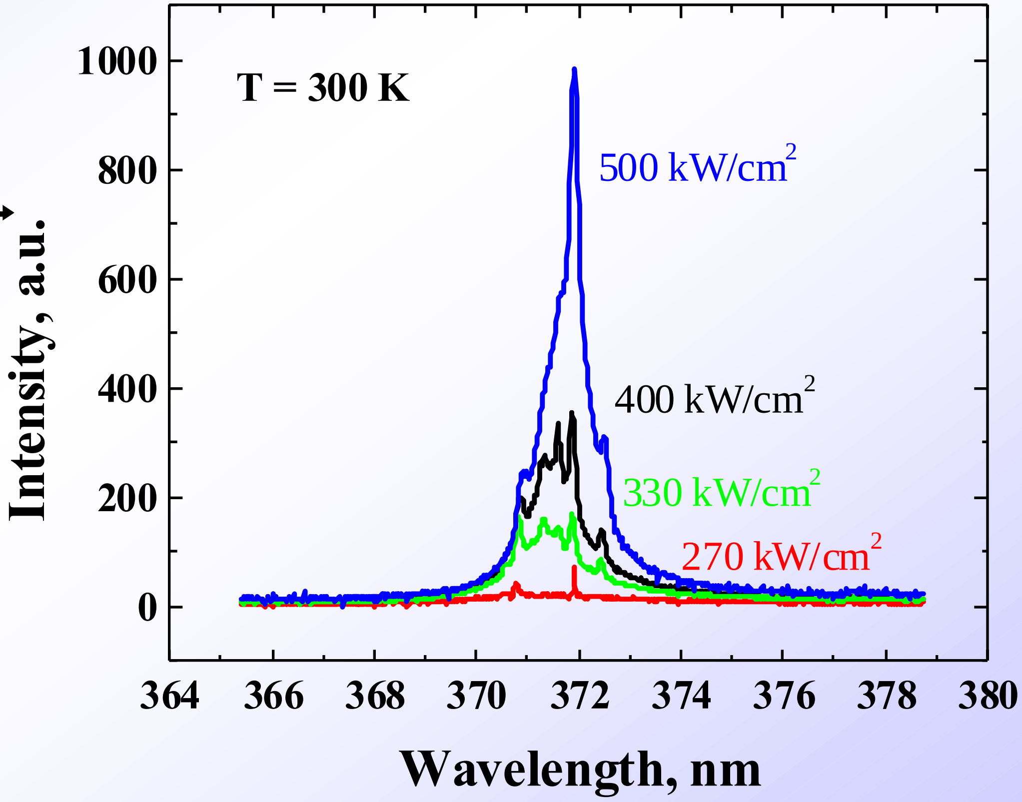


C. Chen et. al. Jpn. J. Appl. Phys., 42, Part 2, No. 9A/B, pp. L1039-L1040 (2003).

Edge Emitting Non Polar UV Laser

SALE a-plane GaN cavity





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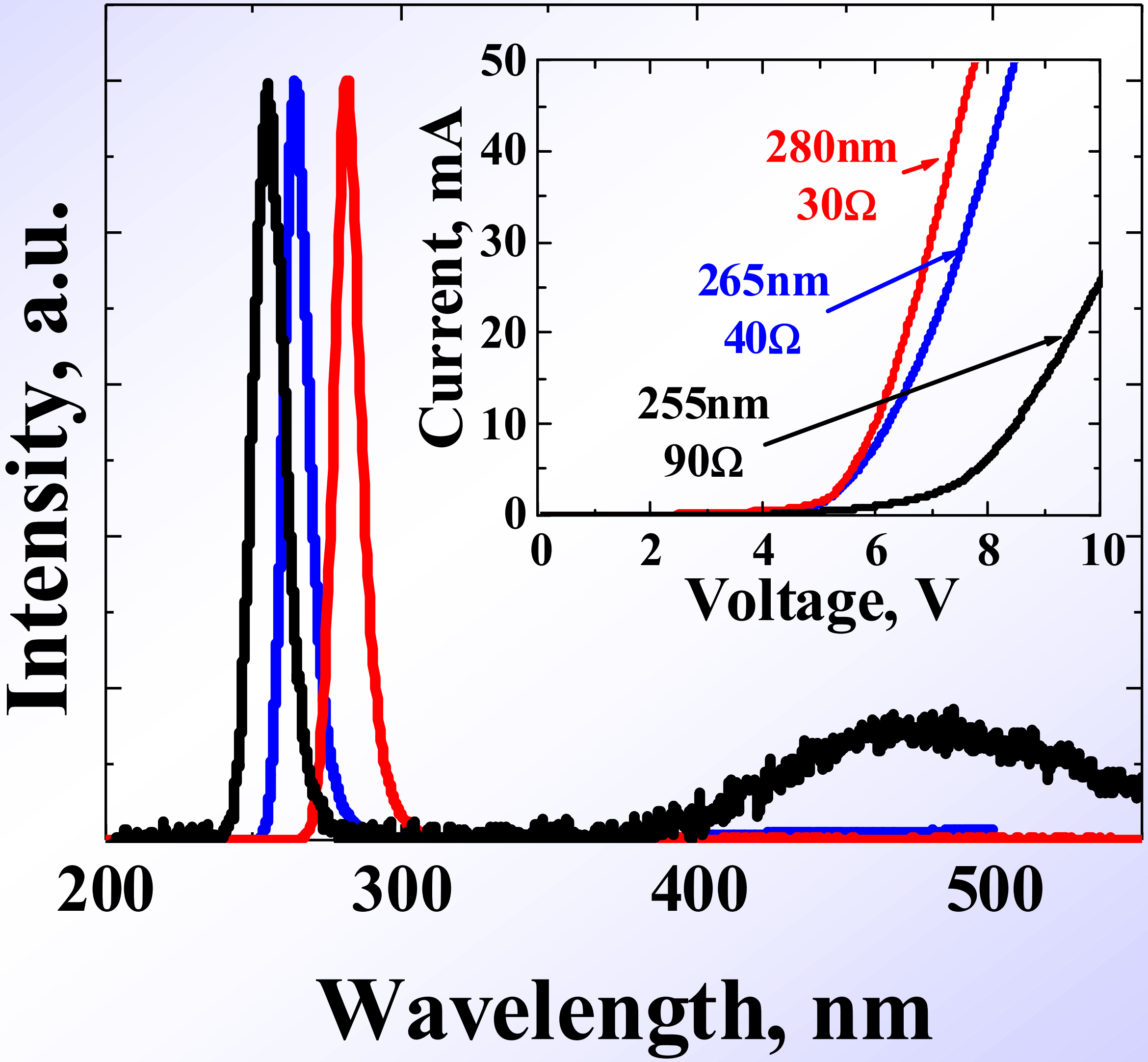
Deep UV LEDs (250-280 nm)

I-V and Spectral Emission

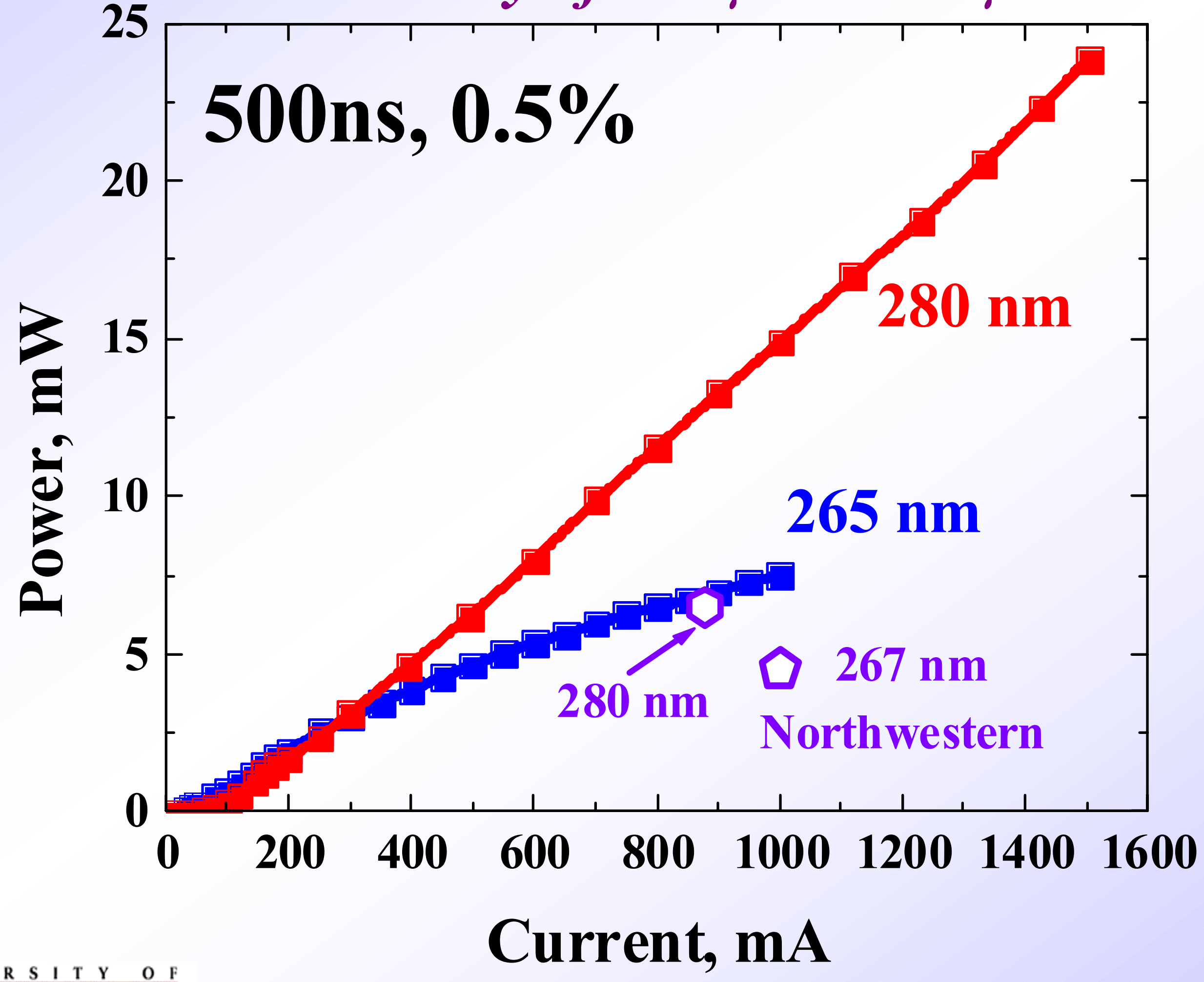
100 μm x 100 μm



Deep UV LEDs (250-280 nm)

Pulsed powers

2 x 2 array of 100 µm x 100 µm



280 nm
EQE 0.355%
WPE 0.122%

265 nm
EQE 0.217%
WPE 0.107%

PML Integrated AlGaN Research Team

Professor Asif Khan

RESEARCH TEAM

Matl. Growth

Matl. Test

Device Process

Device Test

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Mr. N. Tiperneni

Support

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Mr. Bin Zhang
Mr. D. Johnson
Ms. Quinhua Zhang
Ms. T. Osborne
Ms. Pat Dedman

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Photonics Microelectronics Lab

20,000 sq. ft. class 100 clean rooms

Materials

Matl. Testing

Lithography

Device Process

Device Package

Optical Test

Electrical Test

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