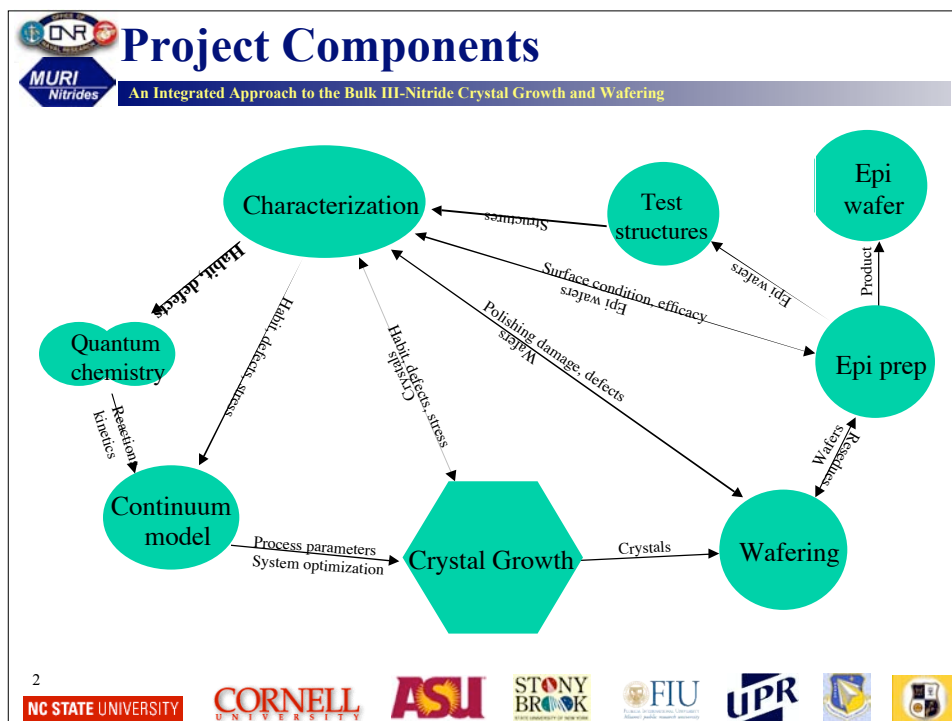
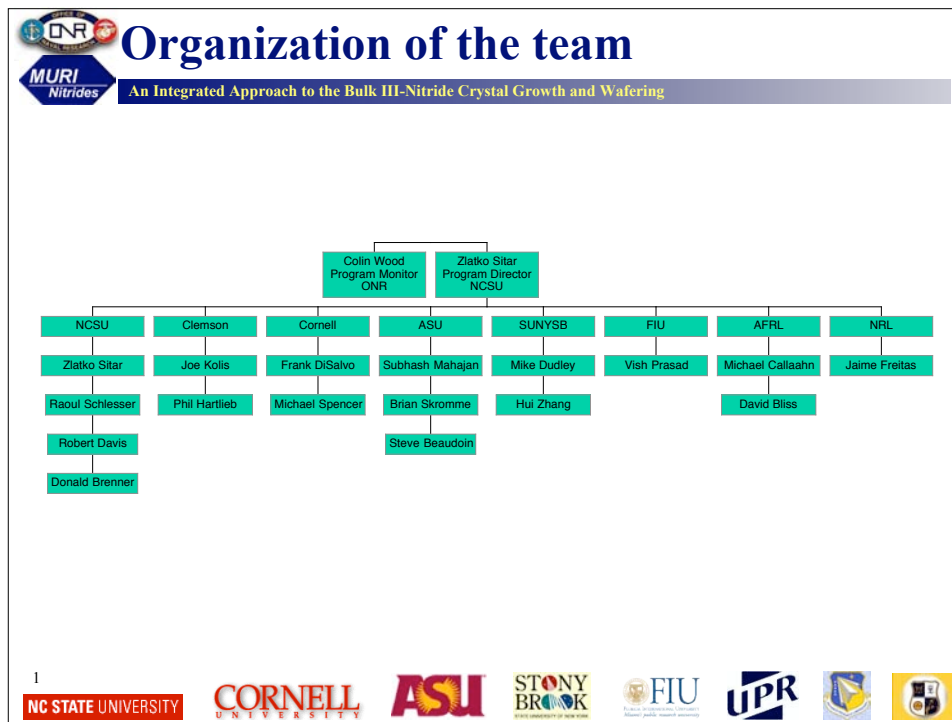


REPORT DOCUMENTATION PAGE				<i>Form Approved</i> <i>OMB No. 0704-0188</i>							
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1. REPORT DATE (DD-MM-YYYY) 12-06-2007		2. REPORT TYPE Final Technical Report		3. DATES COVERED (From - To) May 1, 2001 - December 31, 2006							
4. TITLE AND SUBTITLE An Integrated Approach to the Bulk III-Nitride Crystal Growth and Wafering				5a. CONTRACT NUMBER N00014-01-1-0716							
				5b. GRANT NUMBER							
				5c. PROGRAM ELEMENT NUMBER							
6. AUTHOR(S) Zlatko Sitar, NCSU				5d. PROJECT NUMBER							
				5e. TASK NUMBER							
				5f. WORK UNIT NUMBER							
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) North Carolina State University Materials Science and Engineering Campus Box 7919 Raleigh, NC 27695-7919				8. PERFORMING ORGANIZATION REPORT NUMBER							
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES) Office of Naval Research, Code 312 Ballston Centre Tower One 800 North Quincy Street Arlington, VA 22217-5660				10. SPONSOR/MONITOR'S ACRONYM(S) ONR							
				11. SPONSOR/MONITOR'S REPORT NUMBER(S)							
12. DISTRIBUTION/AVAILABILITY STATEMENT Approved for public release; distribution unlimited.											
13. SUPPLEMENTARY NOTES											
14. ABSTRACT Recognizing that native substrates are crucial for future development of III-nitride-based devices, this MURI investigated several approaches to III-nitride crystal growth: (1) growth of GaN from the vapor phase, (2) growth of GaN from the Na flux, (3) amonothermal growth of GaN and (4) growth of AlN by sublimation. While all approaches generated important findings, the latter two processes have been developed the furthest and are currently being pursued commercially. Following basic studies of solubility and transport in the alkaline supercritical ammonia solutions, seeded growth of GaN has been achieved at rates exceeding 20 µm/day. The process is commercially appealing due to: simple equipment, scalability, high output volume and low growth temperature. Seeded growth of AlN has been achieved on SiC and AlN seeds. While growth on SiC enabled growth over large areas, it produced defective material with dislocation density in the 10 ⁸ cm ⁻² range. In contrast, growth on spontaneously nucleated AlN seeds produced smaller but near perfect crystals with dislocations densities below 10 ³ cm ⁻² . Following these findings, an iterative scheme for gradual crystal expansion was developed, which allowed a diameter expansion of about 5 mm in each step. The quality and properties of grown single crystals were assessed by structural, optical, thermal and electrical characterization techniques.											
15. SUBJECT TERMS crystal growth, aluminum nitride, gallium nitride, sublimation, amonothermal growth, continuum modeling											
16. SECURITY CLASSIFICATION OF: <table style="width: 100%; border-collapse: collapse;"> <tr> <td style="width: 33%; border-bottom: 1px solid black; padding: 2px;">a. REPORT</td> <td style="width: 33%; border-bottom: 1px solid black; padding: 2px;">b. ABSTRACT</td> <td style="width: 33%; border-bottom: 1px solid black; padding: 2px;">c. THIS PAGE</td> </tr> <tr> <td style="border-bottom: 1px solid black; padding: 2px;">Unclassified</td> <td style="border-bottom: 1px solid black; padding: 2px;">Unclassified</td> <td style="border-bottom: 1px solid black; padding: 2px;">Unclassified</td> </tr> </table>			a. REPORT	b. ABSTRACT	c. THIS PAGE	Unclassified	Unclassified	Unclassified	17. LIMITATION OF ABSTRACT Unlimited		18. NUMBER OF PAGES
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An Integrated Approach to the Bulk III-Nitride Crystal Growth and Wafering

Ammonothermal Growth of III-Nitrides

Michael Callahan, Kelly Rakes, Buguo Wang
Air Force Research Laboratory,
Sensors Directorate, Hanscom AFB

1



An Integrated Approach to the Bulk III-Nitride Crystal Growth and Wafering

Current Efforts

- Reduction of Wall Nucleation
- Reduction of oxygen and water in system
 - Use of Getters
 - High purity azides
 - Use of alkali salts (NaBr, KBr)
- Synthesis of InN and AlGaN alloys

2



Wall Nucleation Reduction / Abatement
using temperature gradients and fluid flow
 An Integrated Approach to the Bulk III-Nitride Crystal Growth and Wafering

Wall Nucleation Toolbox

1. Temperature gradient
2. Heating configuration
3. Autoclave furniture/funnel design

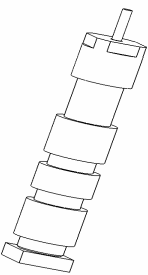
Work Done

- ☐ Model Ideal Heating
- ☐ Model Ideal Furniture
- ☐ Experiment with Both

Conclusions

- Some parasitic wall nucleation will occur even with optimal heating and furniture configurations
- Best way to control parasitic nucleation is modification of temperature profiles
- Modification of temperature profile adversely affects uniform crystallization on seeds by preventing formation of an isothermal zone
- Benefits of heating and furniture have not realized practicable gains

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Wall Nucleation Abatement by use of Sleeves
 An Integrated Approach to the Bulk III-Nitride Crystal Growth and Wafering

Catalytic Properties of Nickel Autoclaves:

- Nickel is a known catalyst for growth of Nitrides and facilitates wall nucleation
- Use of materials that will not react with solvent and also have low affinity for GaN deposition will help reduce wall nucleation
- Molybdenum plates showed reduction in GaN nucleation over nickel plates in test experiment

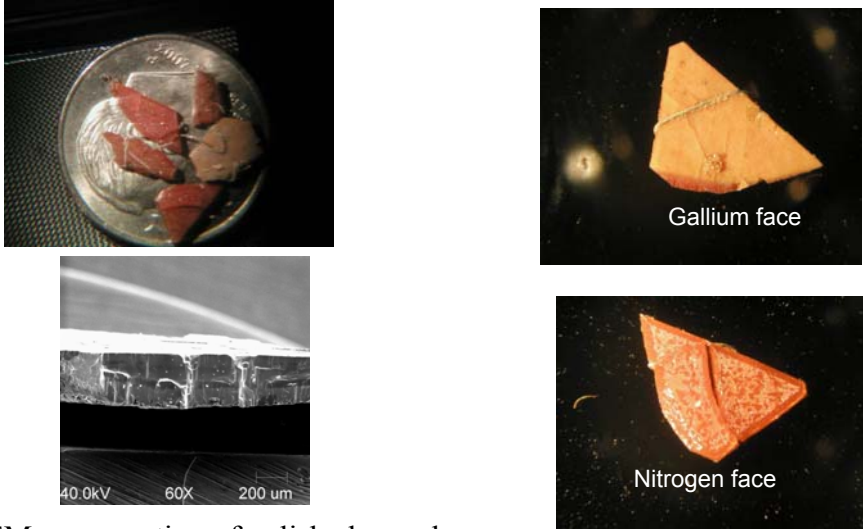
Solution:

- Line crystallization region with Molybdenum liners, seeds racks
- Designed and machined furniture but have not been tested
- Experiment with other materials i.e. Tungsten

4

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Erbium-doped Ammonothermal GaN crystals
 An Integrated Approach to the Bulk III-Nitride Crystal Growth and Wafering



SEM cross section of polished sample

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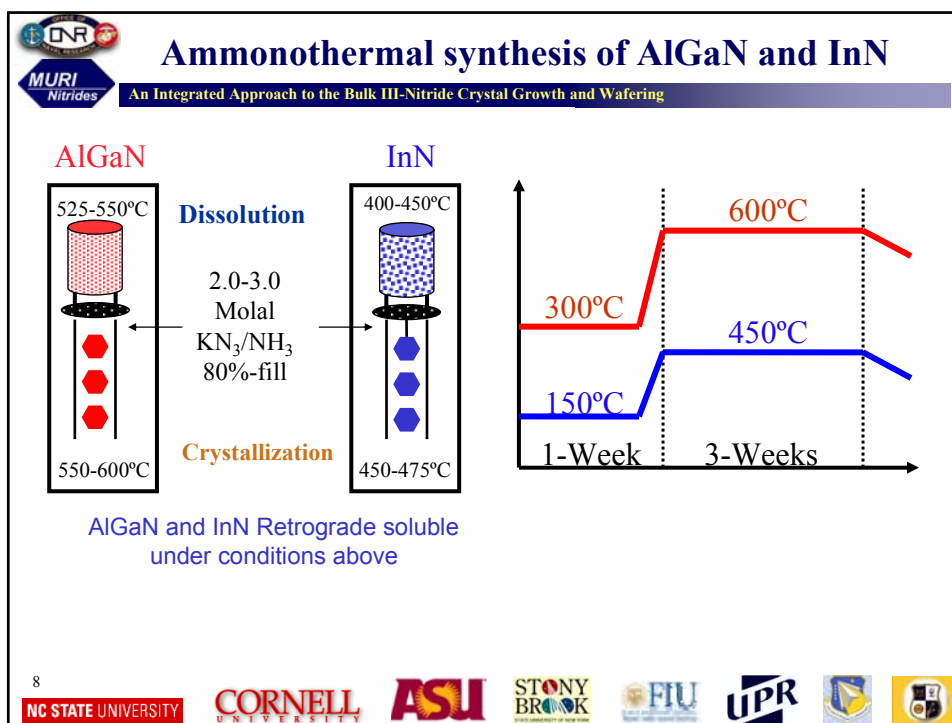
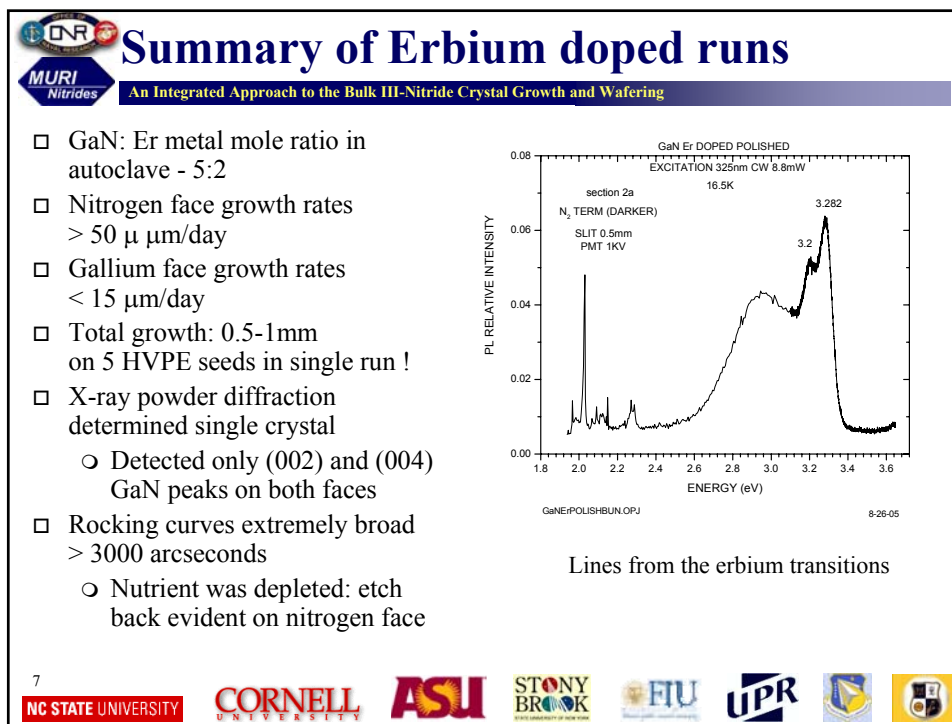
IMPURITY Analysis of Erbium-doped run
 An Integrated Approach to the Bulk III-Nitride Crystal Growth and Wafering

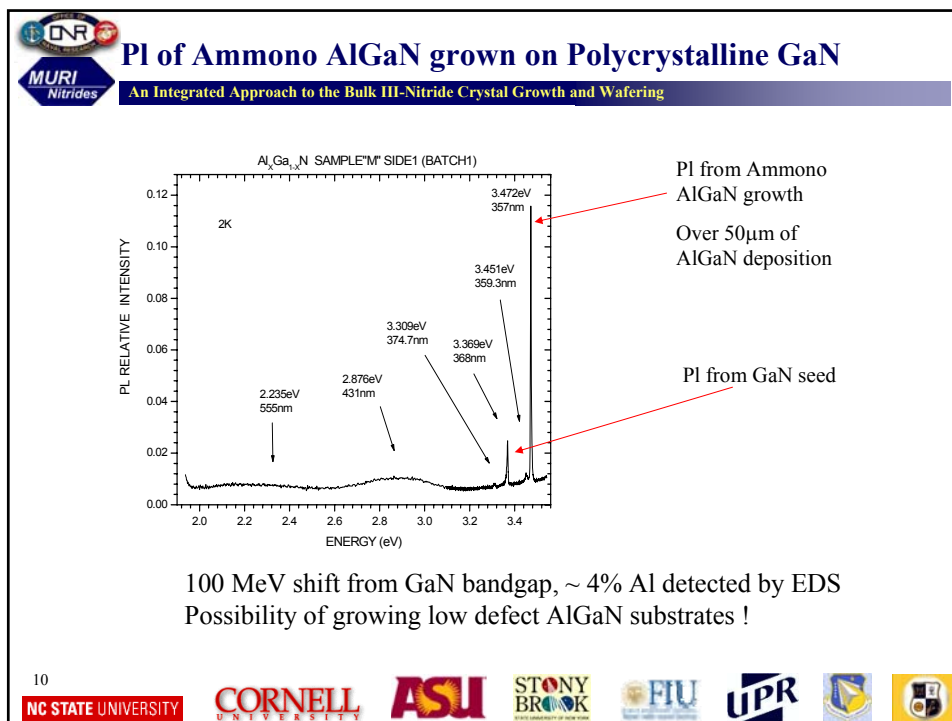
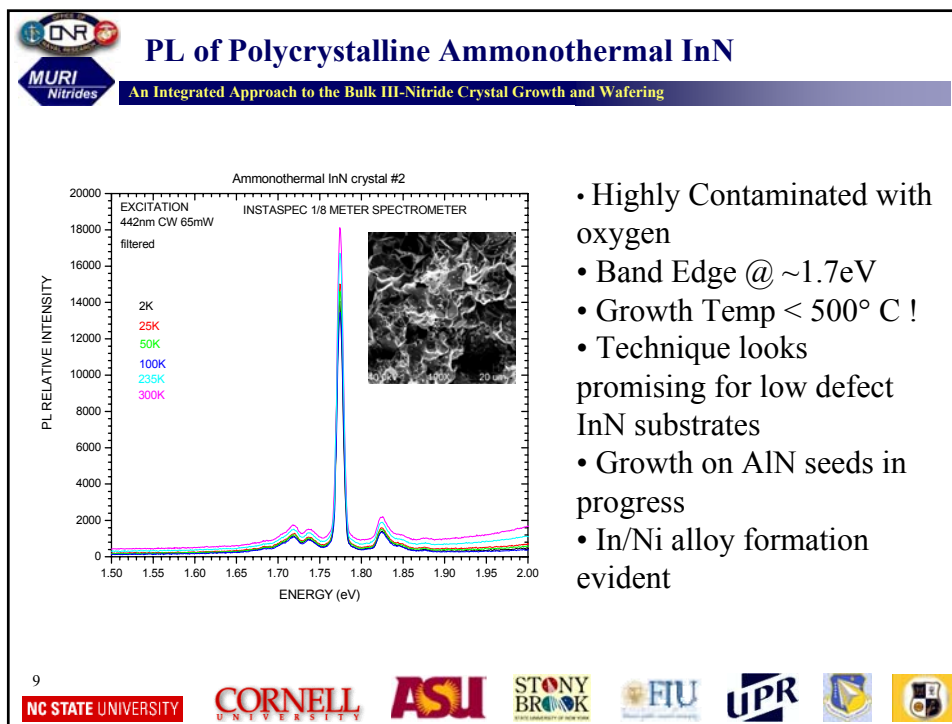
- Erbium incorporation ~ 100 ppma SIMS/GDMS
- Formation of Erbium Oxide at top of autoclave evidence successful of oxygen gettering
- Reduction ~ 5X of oxygen compared to runs not using erbium

Element (atoms/cc)	Ga face	N face
O	1×10^{19}	2×10^{19}
Si	1×10^{19}	5×10^{19}
C	2×10^{19}	2×10^{18}
Fe	2×10^{18}	1×10^{19}
Er	7×10^{17}	5×10^{18}

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Oxygen Contamination

An Integrated Approach to the Bulk III-Nitride Crystal Growth and Wafering

❑ **Oxygen and water impurities now biggest remaining issue**

- **Erbium and Rare Earths doping and gettering**
 - Need to find optimal point of GaN/Er ratio for maximum oxygen gettering without distorting GaN lattice with Er incorporation
 - Investigate other getters
 - Gettering alone will not reduce oxygen to acceptable levels
- **Growth with Salts (NaBr)**
 - GaN can be formed using Ga metal
 - Phase Issues need to be fully investigated
 - Rule out formation of cubic GaN inclusions
 - Can salts dissolve GaN nutrient ?
 - 1 experiment @ 525° C /2M NaBr result in no GaN dissolution

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Future Work

An Integrated Approach to the Bulk III-Nitride Crystal Growth and Wafering

❑ **Greater emphasis on initial growth to reduce defects at seed interface**

- Impurities should low enough level to obtain low defect material
- Prevent nucleation, particulates on seeds during ramp up
 - Etch-back of seeds before growth
- TEM analysis would aid in determination of causes for columnar growth and other defects

❑ **Growth on cm² seeds in 2.2 cm and 3.4 cm autoclaves**

❑ **Further reduction of system impurities particularly water and oxygen**

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Publications

An Integrated Approach to the Bulk III-Nitride Crystal Growth and Wafering

- 1) “Synthesis of dense polycrystalline GaN of high purity by the chemical vapor reaction process”, Buguo Wang, Michael Callahan, and John Bailey, J. Crystal Growth, 286 (2006) 50-54.
- 2) “GaN Single Crystals Grown on HVPE Seeds in Alkaline Supercritical Ammonia”, M. Callahan, K. Rakes, D. Bliss, L. Bouthillette, M. Suscavage, B. Wang, and S-Q. Wang, Journal of Materials Science, 41 (2006) 1399-1407
- 3) “Ammonothermal Synthesis of III-Nitride Crystals”, B. Wang and M. J. Callahan to Cryst. Growth & Design, in press
- 4) “Ammonothermal Synthesis of Aluminum Nitride Crystals”, B. Adekore, K. Rakes, B. Wang, M. Callahan, S. Pendurti, and Z. Sitar, J. Elect. Materials, in press
- 5) “Ammonothermal growth of GaN crystals in alkaline solutions” Buguo Wang, Michael J. Callahan, Kelly Rakes, David F. Bliss, Lionel O. Bouthillette, Sheng-Qi Wang, and Joseph W. Kolis, J. Crystal Growth, 287 (2006)376-380

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Modeling Ammonothermal Growth of GaN

An Integrated Approach to the Bulk III-Nitride Crystal Growth and Wafering



S. Pendurti and V. Prasad



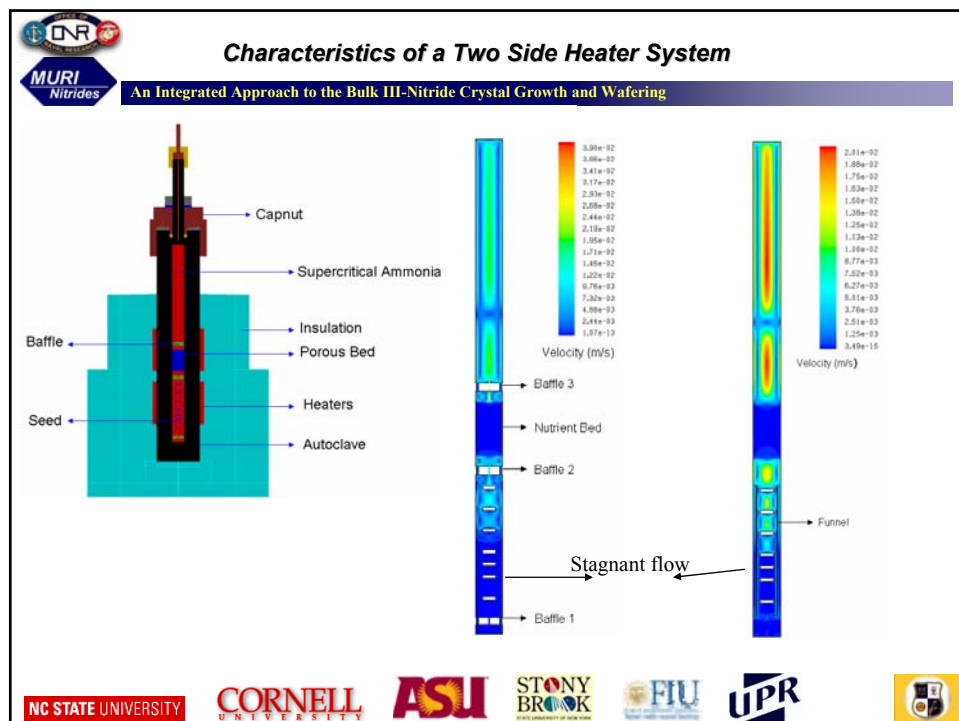
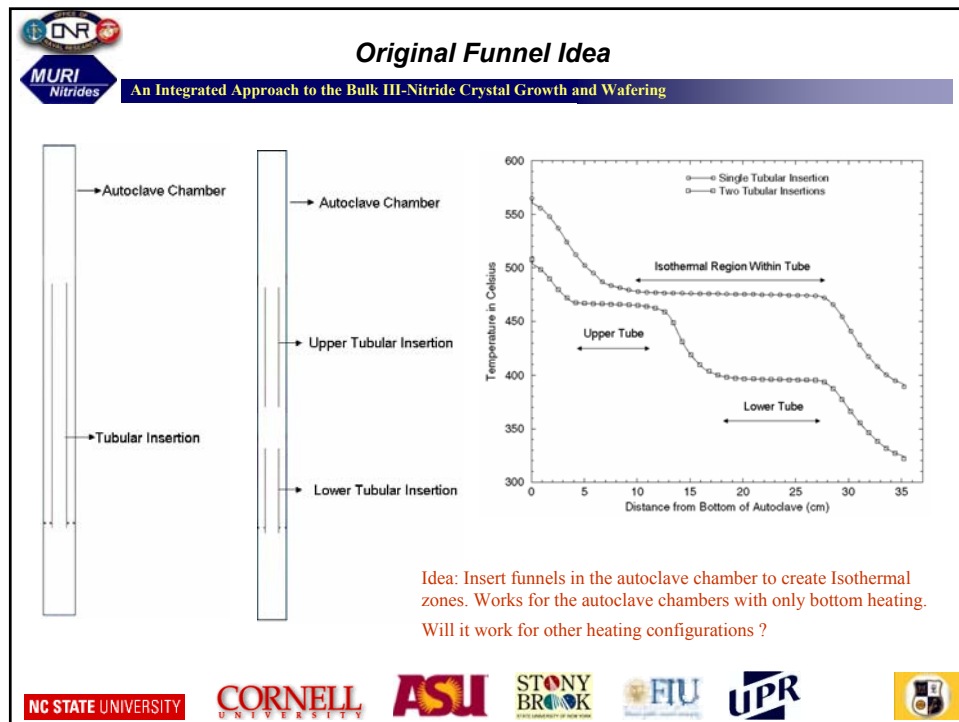


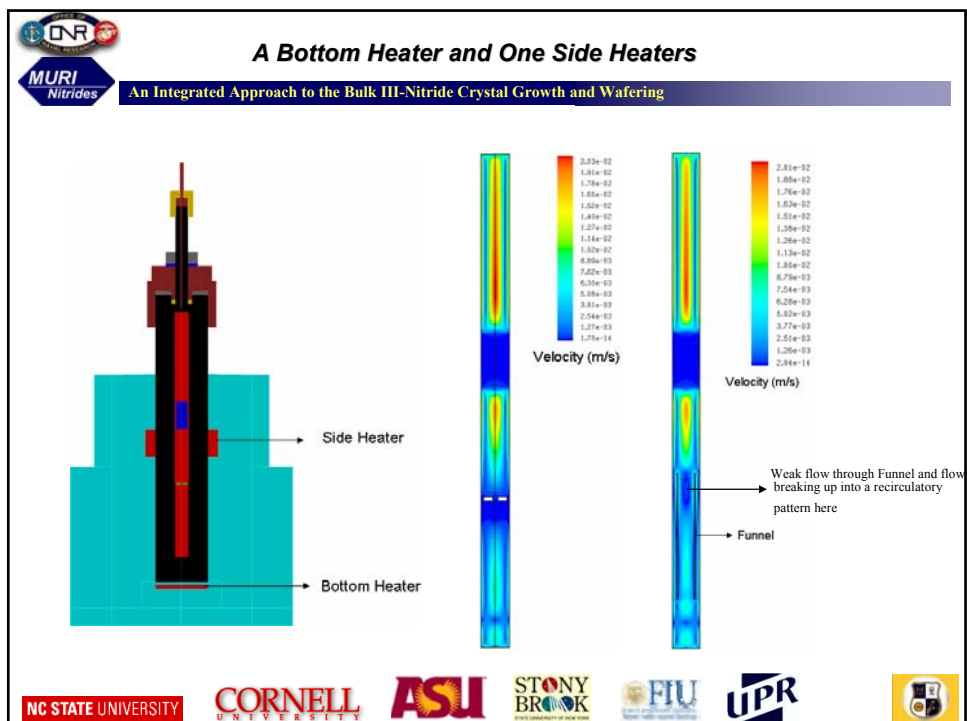
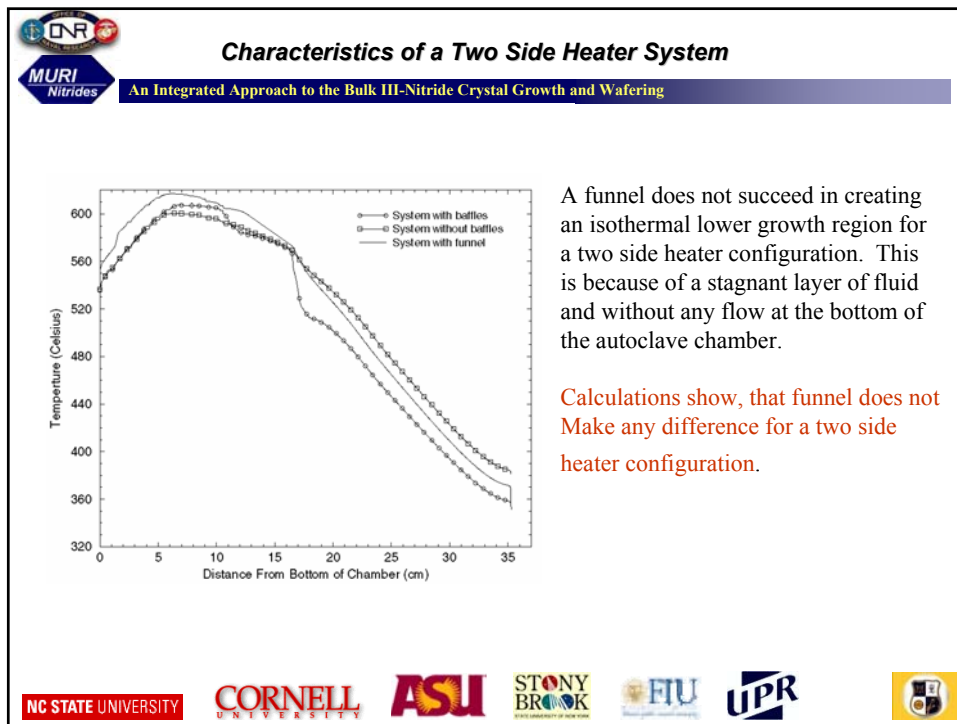
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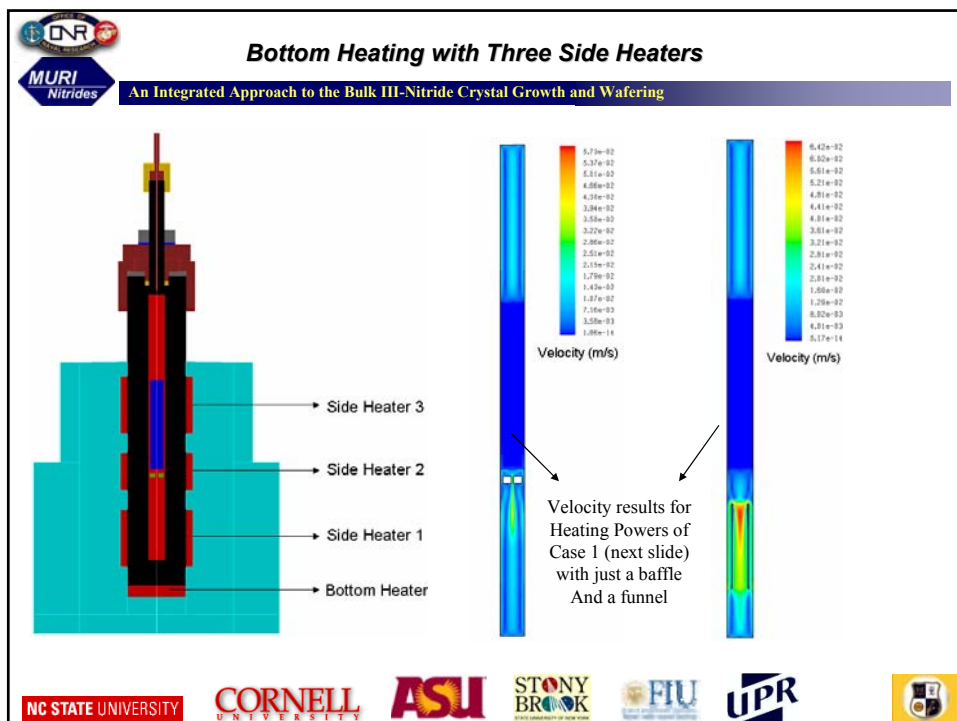
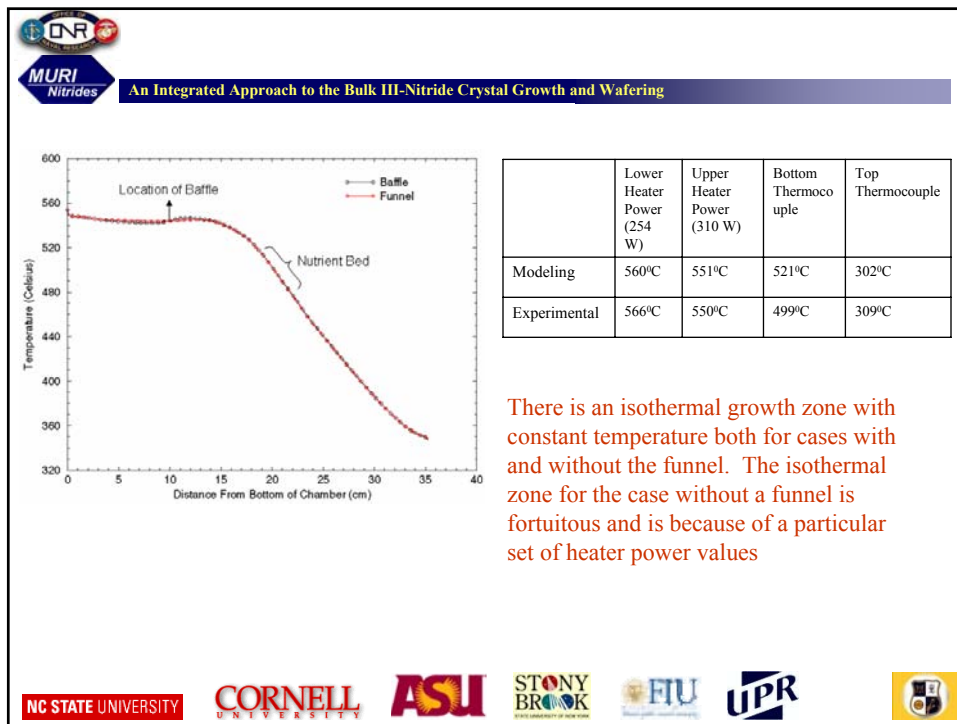
An Integrated Approach to the Bulk III-Nitride Crystal Growth and Wafering

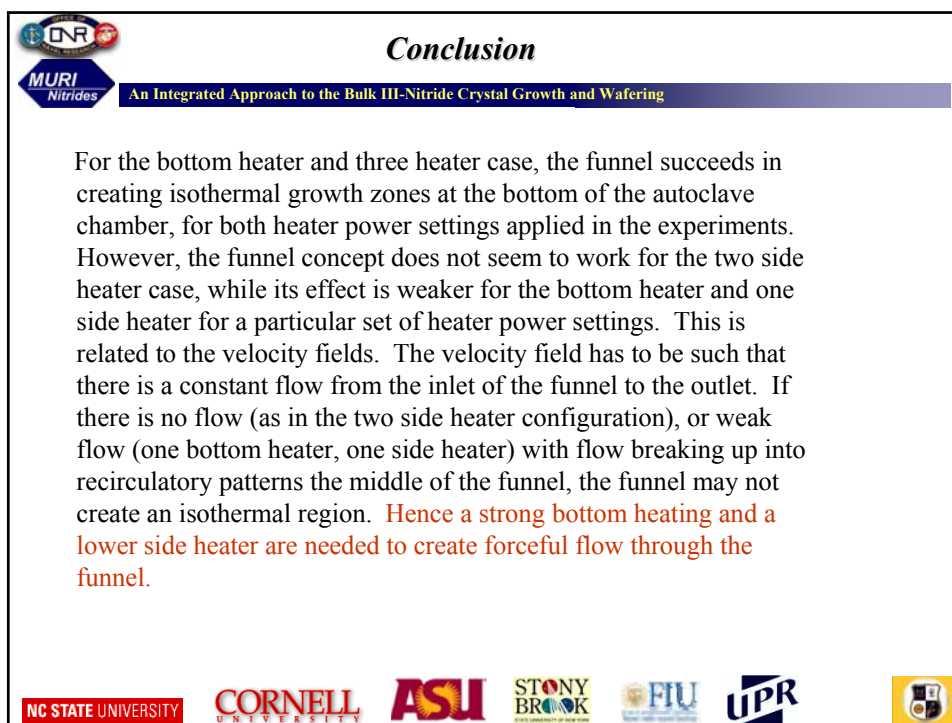
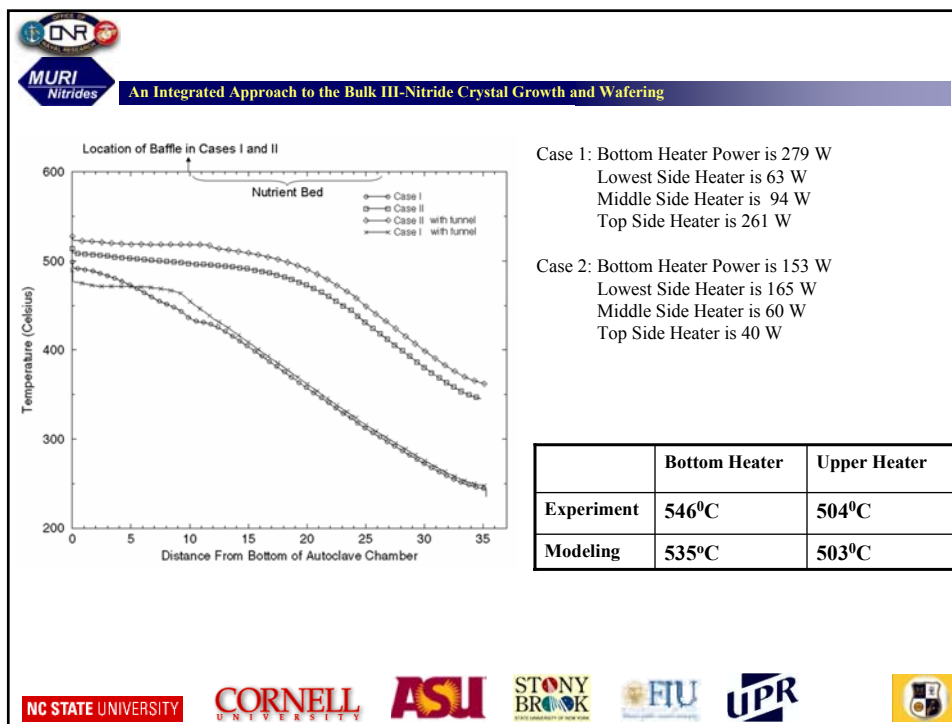
- *Funnel Idea*
- *Two Side Heater System*
- *Bottom Heater and One Side Heater*
- *Bottom Heater and Three Side Heaters*
- *Conclusion*
- *Summary*













Summary

An Integrated Approach to the Bulk III-Nitride Crystal Growth and Wafering

- *All heating configuration used in Hanscom have been explored, and a funnel tried out in them .*
- *Bottom heating, and lower side heater are necessary for the funnel to work*
- *Calculations on, with porous bed as exactly used in Hanscom.*

Acknowledgements

Kelly Rakes, Bumni Adekore, Michael Callahan.





An Integrated Approach to the Bulk III-Nitride Crystal Growth and Wafering

Raman Spectroscopy of Ammonothermal Growth Environment

James Perkins
Dr. Robert Nemanich
Dr. Zlatko Sitar
North Carolina State University

1

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Outline and Motivation

An Integrated Approach to the Bulk III-Nitride Crystal Growth and Wafering

- ❑ Raman Spectra of Neat Ammonia
 - Function of Temperature, Pressure, Density, and Time
 - Dissociation $2\text{NH}_3 \rightarrow \text{N}_2 + 3\text{H}_2$
 - Extent of Dimerization and H-Bonding
- ❑ NH_3 as a Solvent
 - Band Dependence on Association Strength with Ions
 - Perturbed Spectra of Solutes
- ❑ Determination of Intermediate Species

2

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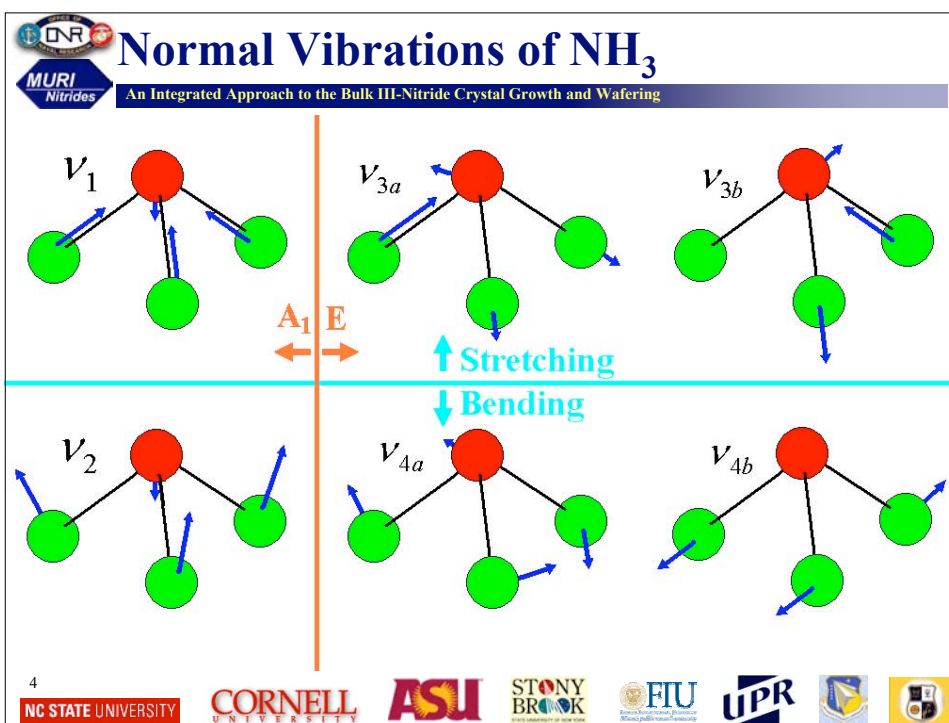
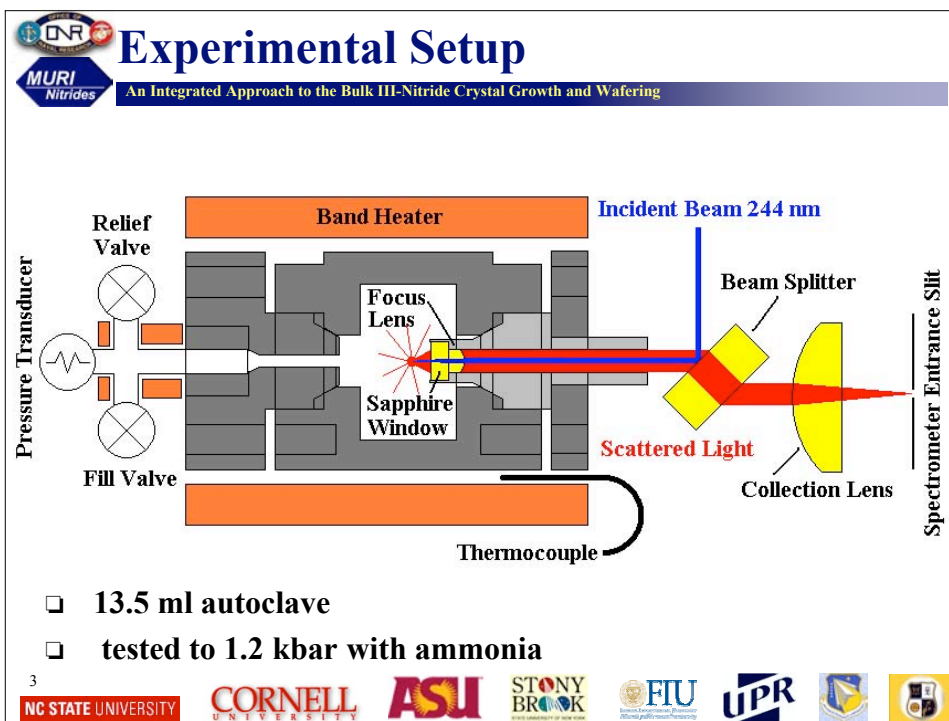
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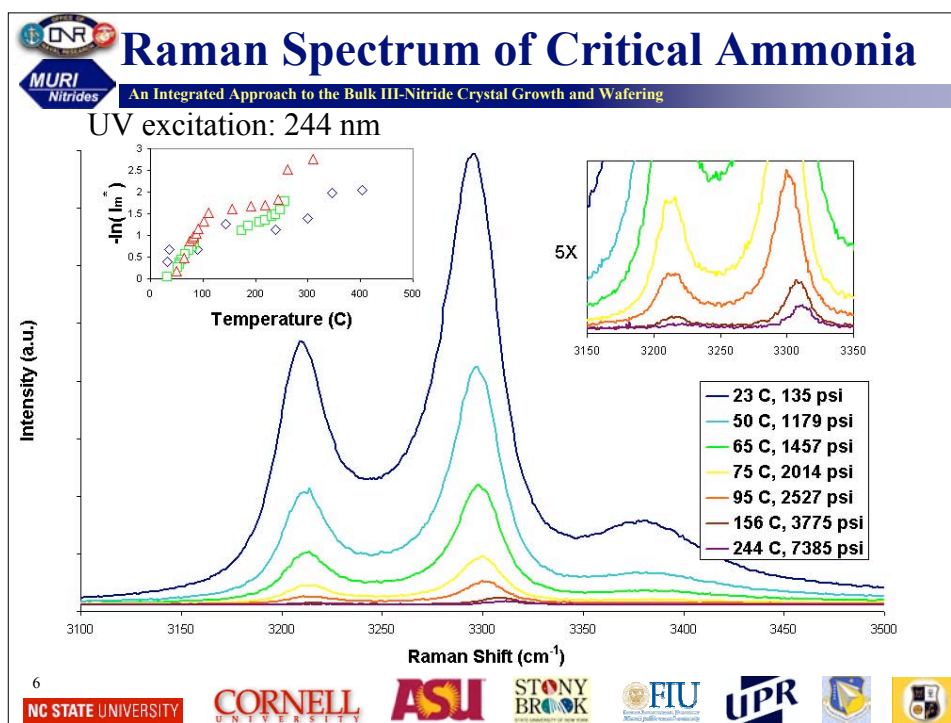
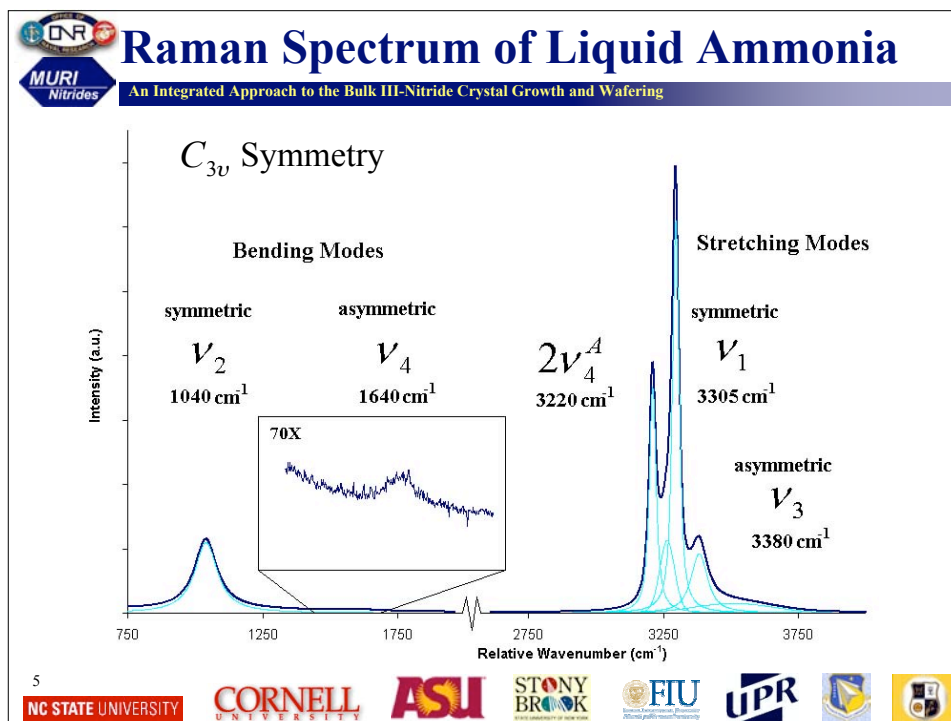
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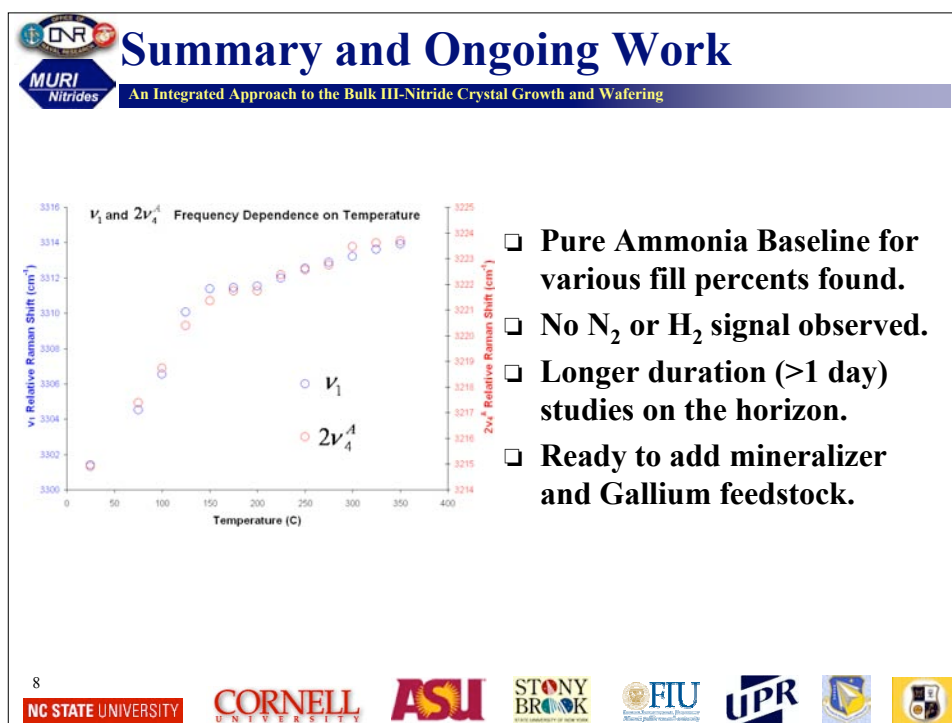
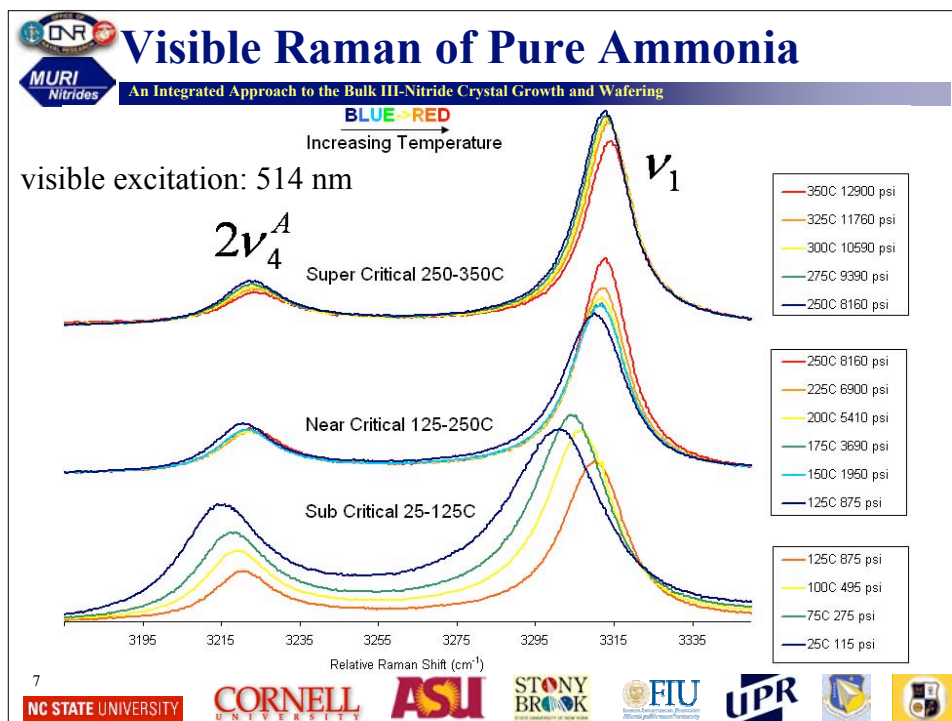
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An Integrated Approach to the Bulk III-Nitride Crystal Growth and Wafering

Optical Characterization of III-Nitrides

B. J. Skromme and S. Sivasubramanian

*Department of Electrical Engineering and
Center for Solid State Electronics Research
Arizona State University, Tempe, AZ 85287-5706*

1





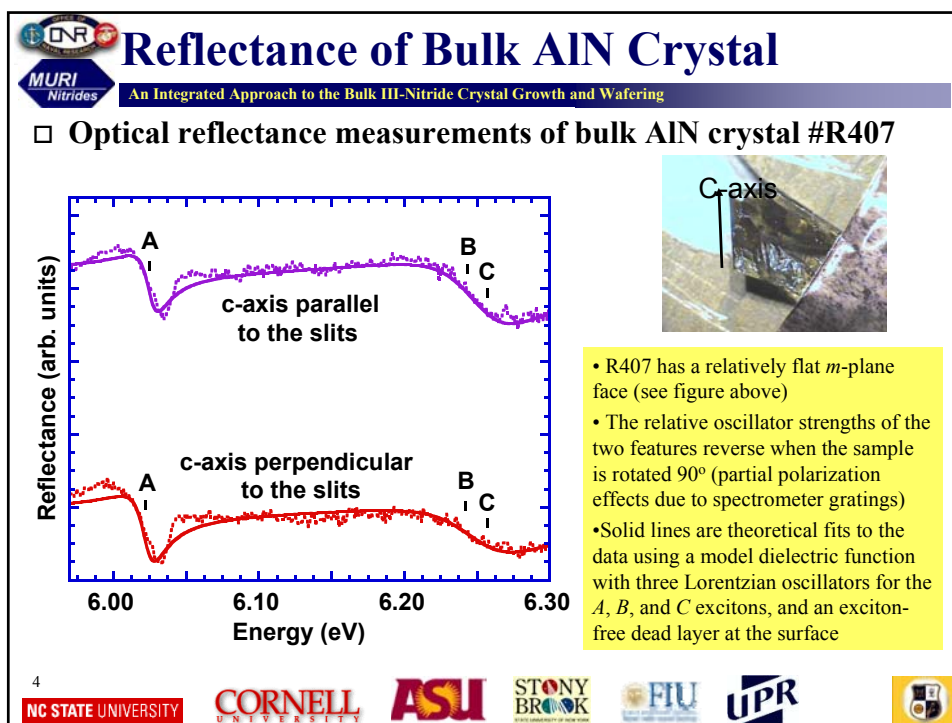
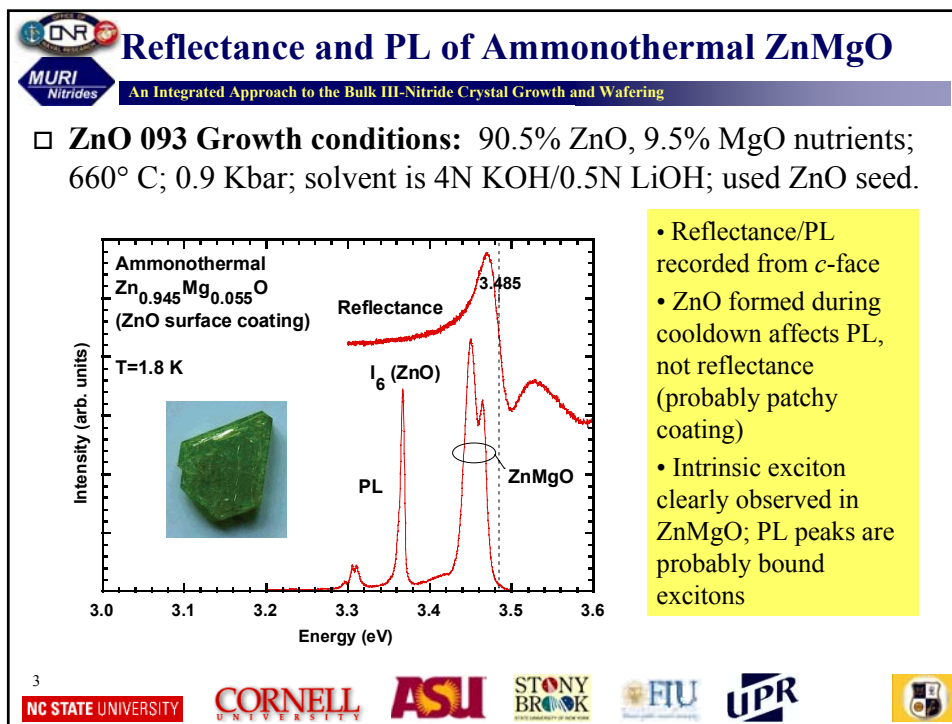
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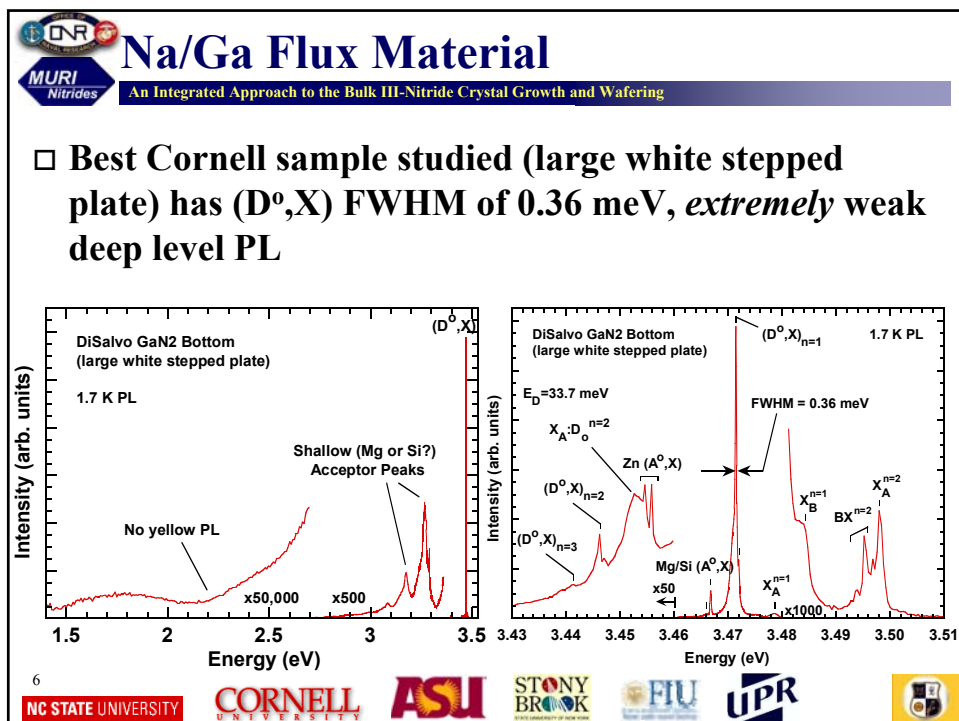
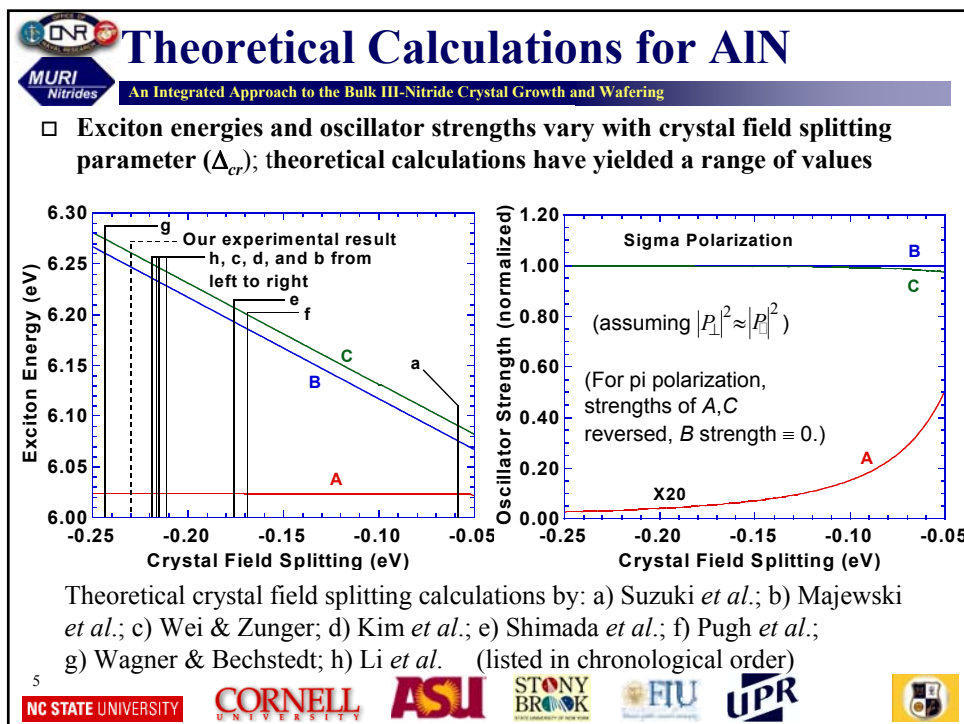
Overview of Progress

- Reflectance & PL on ammonothermal ZnMgO (recent work)
- Reflectance of bulk AlN: Determination of the crystal-field splitting and valence band structure
- Optical characterization of bulk GaN grown by Na/Ga flux
- Structural-defect related PL in GaN: Folded prismatic faults in GaN/SiC
- Ion implantations to identify spectral fingerprints of various impurities in GaN (e.g., Cu, As, P, etc.) and study the origins of yellow PL in GaN

2







Folded Prismatic Faults in GaN/SiC
 An Integrated Approach to the Bulk III-Nitride Crystal Growth and Wafering

- We previously identified basal plane stacking faults as origins of ~3.4 eV PL peak in bulk ammonothermal GaN, and observed new ~3.2 eV peak in heteroepitaxial MOCVD GaN on SiC misoriented from [0001] towards the [11-20] direction (provided by R.F. Davis and collaborators)
- Prior TEM work by Dudley's group suggested the latter peak may be associated with folded I_1 basal plane/prismatic fault configurations and the associated stair-rod dislocations
- We have extended this study to use AFM, conductive AFM, and CL spectral imaging to study the intersections of these faults with the surface
- The results prove the electrically active nature of the faults and support the association of the 3.2 eV peak with these fault configurations (possibly with the lattice disconnections)

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Folded Prismatic Faults in GaN/SiC
 An Integrated Approach to the Bulk III-Nitride Crystal Growth and Wafering

- 1 μm GaN / 0.1 μm AlN / 6H-SiC tilted 3.5° from [0001] to [11-20]
- GaN grown by MOCVD at 1020 °C, AlN grown at 1100 °C
- 4 K CL spectrum on area showing folded faults intersecting surface

4 K CL

Intensity (arb. units)

3.205 eV

Mg/Si (e-A°)

BSF

(D°,X)

3.15 3.25 3.35 3.45

Energy (eV)

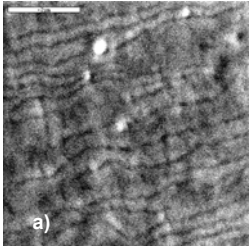
• 3.205 eV peak (and higher energy shoulder at ~3.225 eV, observed at higher temperature) believed uniquely related to folded fault configurations

8

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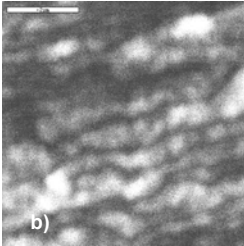
Folded Prismatic Faults in GaN/SiC
An Integrated Approach to the Bulk III-Nitride Crystal Growth and Wafering

SEI



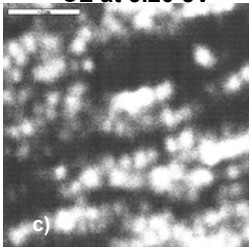
a)

CL at 3.456 eV



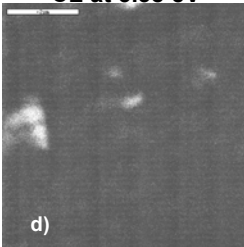
b)

CL at 3.20 eV



c)

CL at 3.38 eV



d)

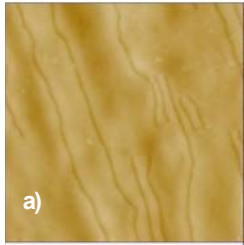
- Secondary electron image reveals zigzagged lines where prismatic faults (PSFs) intersect surface
- Monochromatic CL image at 3.456 eV [(D⁰,X) peak] is dark at positions of PSFs (competing processes)
- CL image at 3.20 eV is spotty, shows high intensity near the fault lines at specific locations believed to correspond to locations of stair-rod dislocations and lattice disconnections
- CL image at 3.38 eV shows a few bright spots possibly related to BSFs

9

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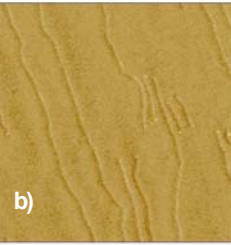
Folded Prismatic Faults in GaN/SiC
An Integrated Approach to the Bulk III-Nitride Crystal Growth and Wafering

AFM



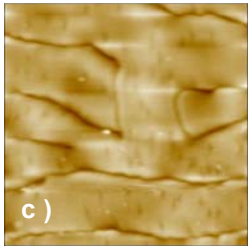
a)

CAFM



b)

AFM



c)

• Magnified AFM image at left shows evidence of shallowly inclined BSFs intersecting the surface (faint ~vertical lines)

- Atomic force microscopy (AFM) image (left) shows clear evidence of shallow (~3 nm deep) trenches corresponding to surface fault terminations
- Conductive AFM image (right) shows enhanced or reduced conductivity along the edges of the trenches, and enhanced conductivity (white spots) at the ends of each fault, where dislocations should be present
- First direct evidence for electrically active nature of these faults and associated dislocations; should impact device performance

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Ion implanted HVPE GaN

An Integrated Approach to the Bulk III-Nitride Crystal Growth and Wafering

- Implantations performed to identify spectral fingerprints and behavior of various impurities in GaN
- Implanted species included Cu, to determine if it is electrically or optically active in GaN; As and P, to study the related isoelectronic centers; and various impurities including C, O, and N to study their effect on the yellow PL band in GaN

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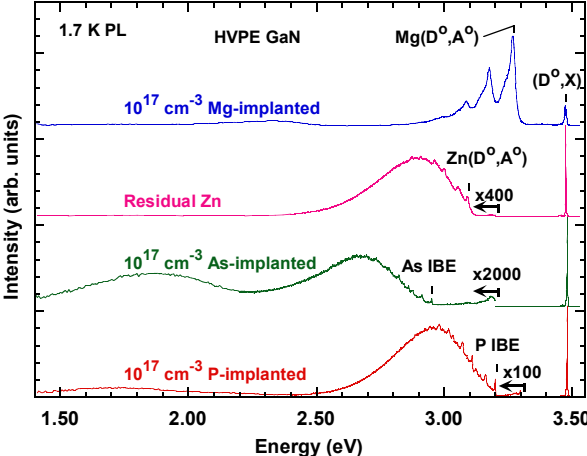




Ion Implantation Study Using HVPE GaN

An Integrated Approach to the Bulk III-Nitride Crystal Growth and Wafering

- Low temperature PL measurements of Mg, As, and P-implanted and residual Zn-doped HVPE GaN samples



As and P implants yield highly resolved spectra of isoelectronic-bound excitons with phonon replicas

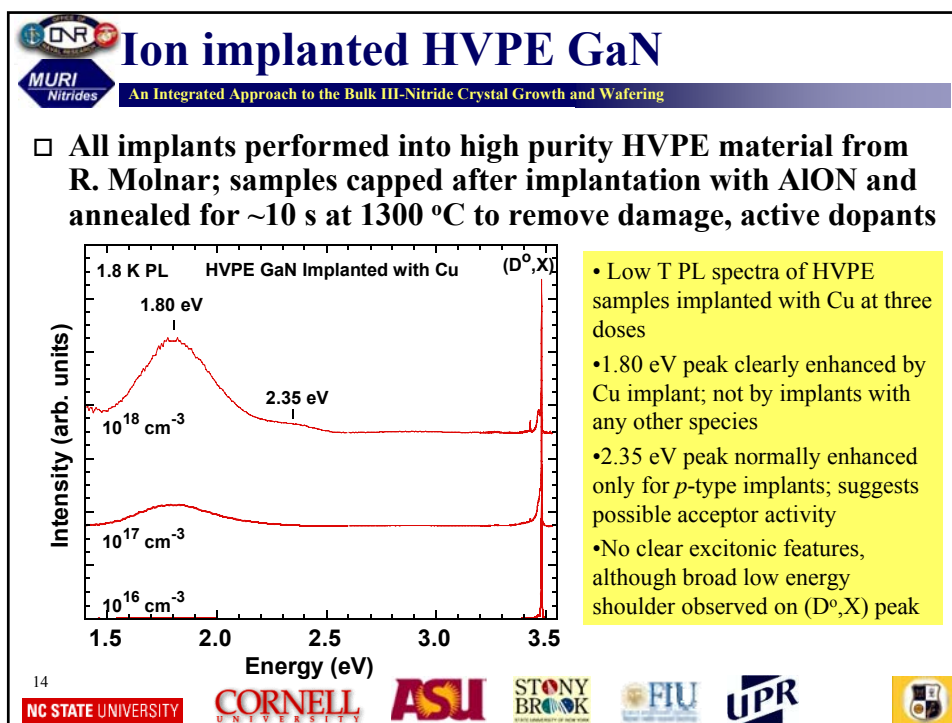
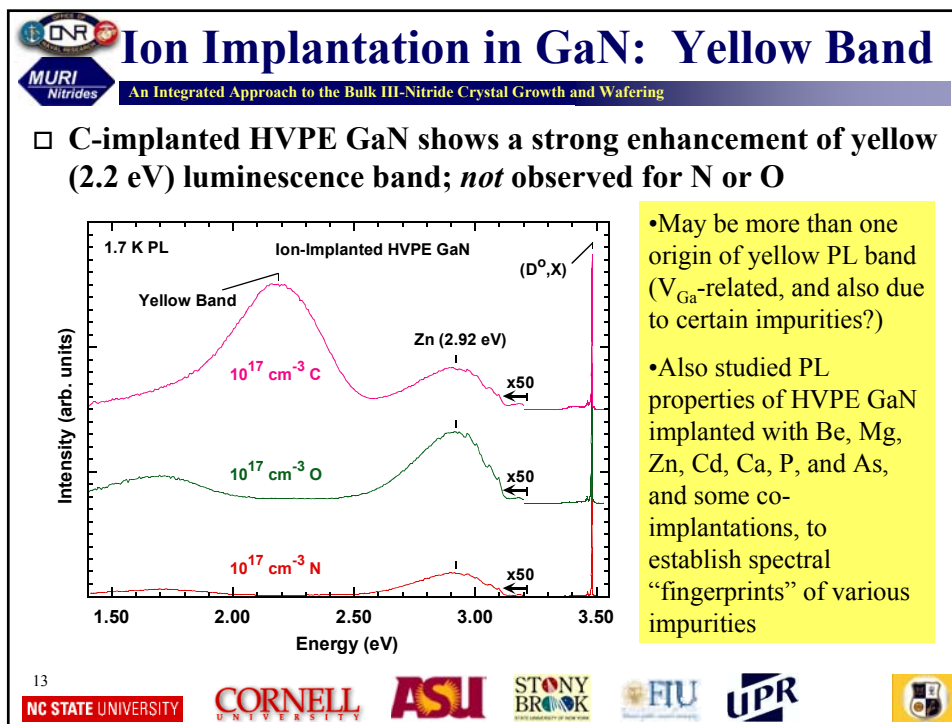
12













MURI
Nitrides

Accomplishments

An Integrated Approach to the Bulk III-Nitride Crystal Growth and Wafering

- ❑ **First reflectance studies of ZnMgO, gave clear evidence of excitonic transitions in this system**
- ❑ **Determined crystal field splitting parameter of $\Delta_{cr} = -230$ meV in unstrained bulk AlN, and characterized valence band splittings accurately for the first time in this material; selection rules have important implications for light-emitting devices in Al-rich AlGaN**
- ❑ **Characterized folded prismatic fault configurations in GaN using monochromatic CL imaging, AFM, and CAFM**
- ❑ **Found clear evidence associating 3.2 eV PL peak with specific locations along faults; 3.4 eV peak more generally associated with basal-plane faults**
- ❑ **Found first evidence for optical activity of Cu in GaN, in a 1.8 eV PL peak in Cu-implanted material. Identified clear isoelectronic behavior of As and P substituting for N, including site-switching behavior of P. Found that both C and Be enhance intensity of yellow PL, but not N, O, or other implants**

15















**MURI**
Nitrides

An Integrated Approach to the Bulk III-Nitride Crystal Growth and Wafering

Seeded Growth of AlN Single Crystals

**Ziad G. Herro, Dejin Zhuang, Raoul Schlessler, Ramon Collazo,
Rafael Dalmau and Zlatko Sitar**

North Carolina State University

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**MURI**
Nitrides

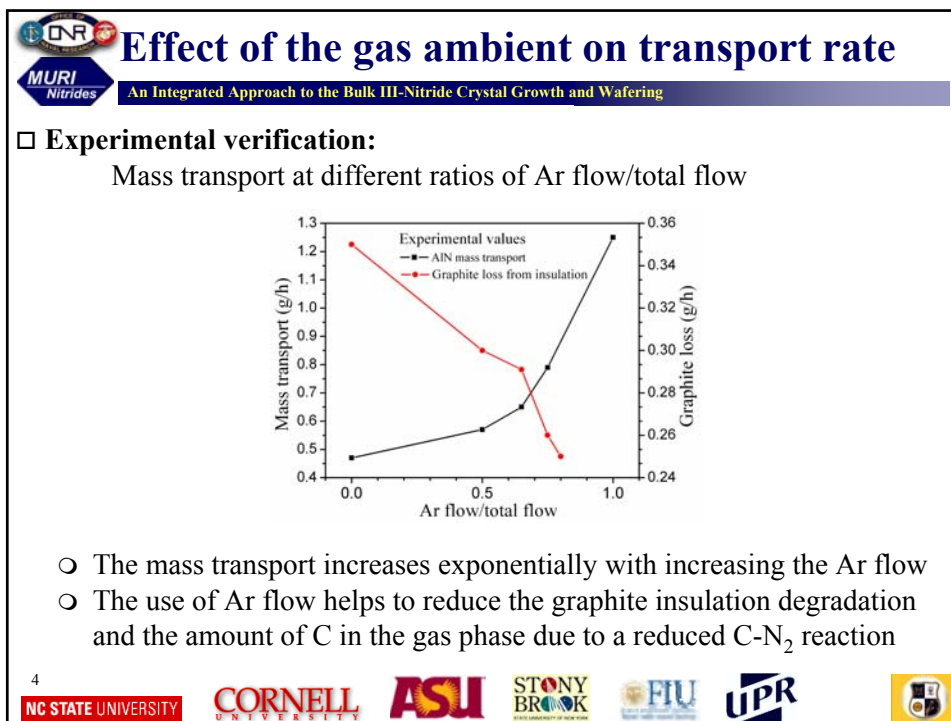
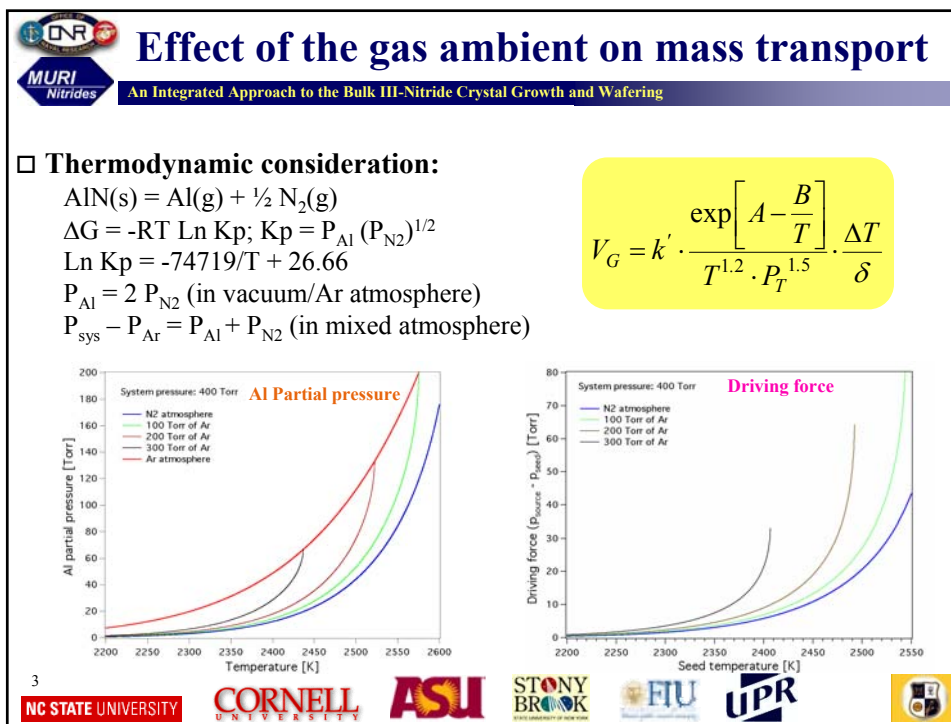
An Integrated Approach to the Bulk III-Nitride Crystal Growth and Wafering

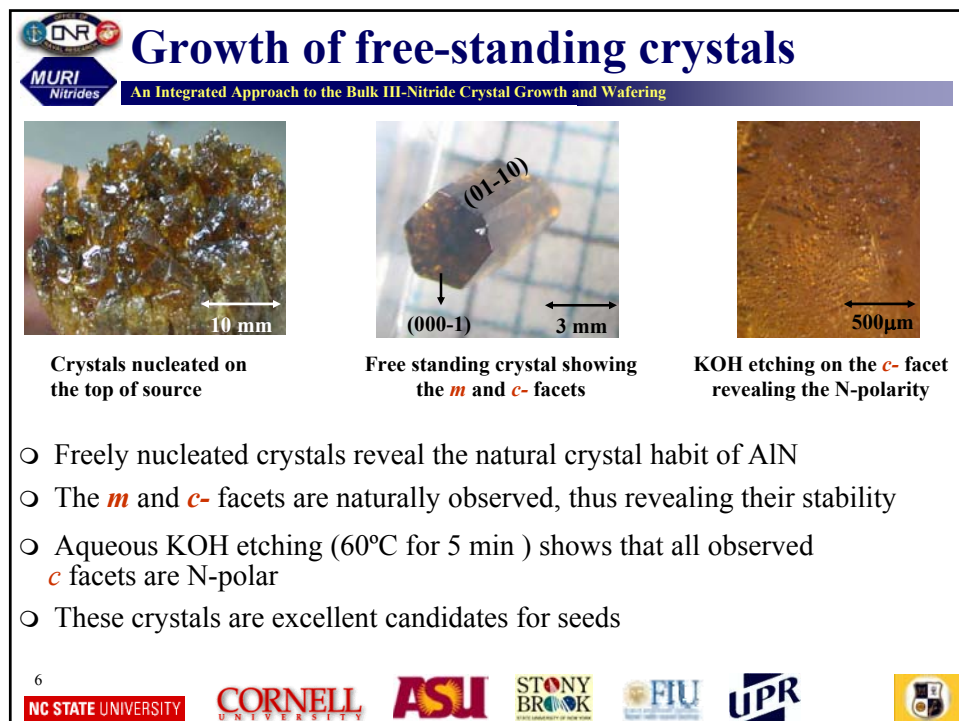
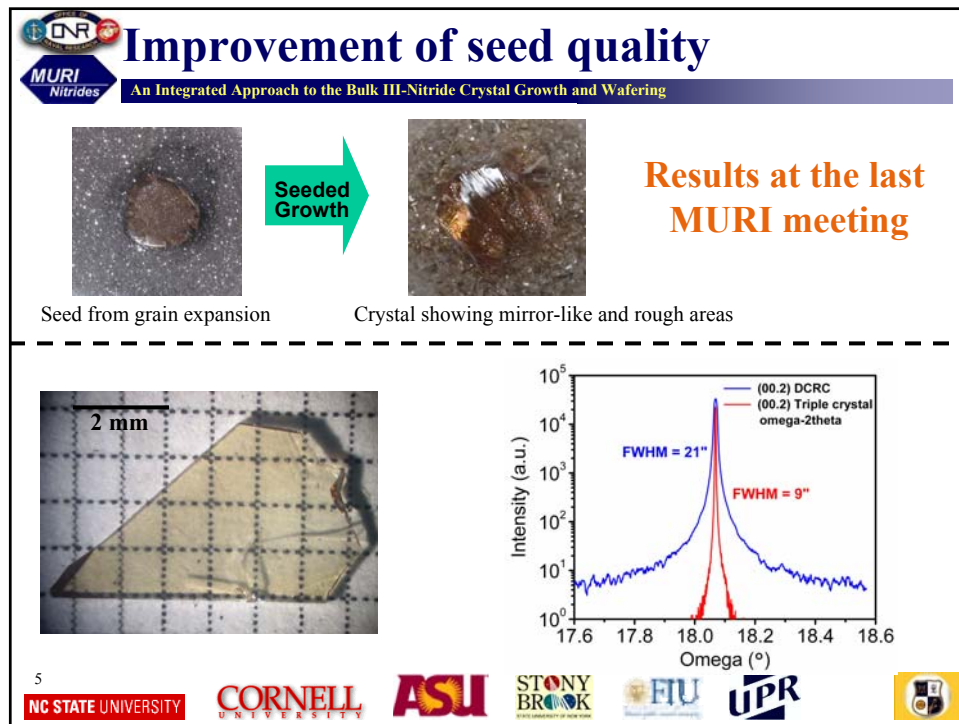
Outline

- **Thermodynamics of crystal growth**
 - Effect of the ambient gas on mass transport (N_2 versus Ar)
- **Progress in seed and crystal quality**
 - seed preparation
 - growth process optimization
 - crystal expansion
- **Growth results and morphology**
 - Growth along the c-direction (Al and N-face)
 - Effect of surface energy on growth morphology
- **Conclusion**

2



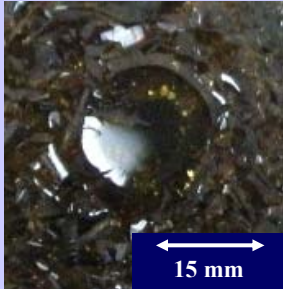






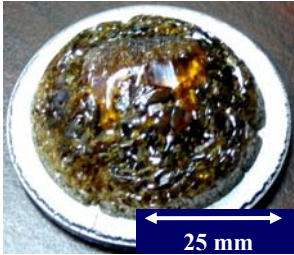
Improvement of crystal quality

An Integrated Approach to the Bulk III-Nitride Crystal Growth and Wafering



15 mm

Results at the last MURI meeting



25 mm

- Photograph of a crystal, 15 mm in diameter and 12 mm in height, grown along the [002] direction from a 5 mm N-polar seed
 - A single, mirror-like facet is observed in the middle that covers nearly the whole monocrystalline area
 - Parasitic polycrystalline nucleation is confined around the central monocrystalline area

7











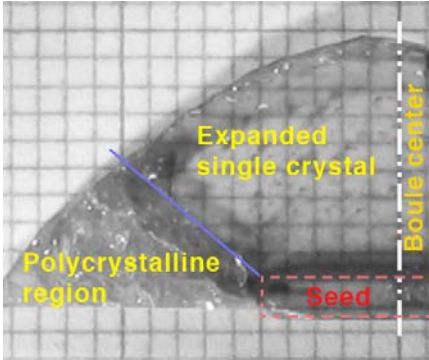


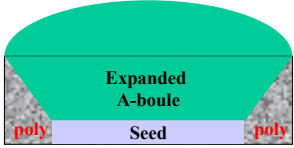




Crystal expansion angle

An Integrated Approach to the Bulk III-Nitride Crystal Growth and Wafering

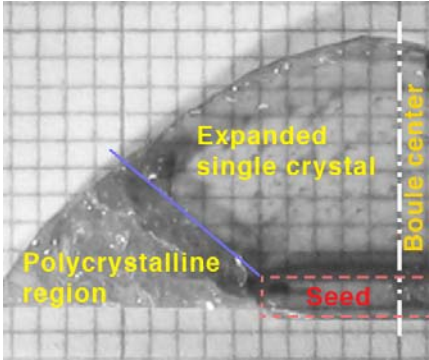


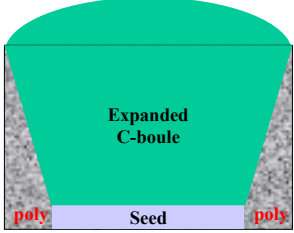


Expanded A-boule

poly Seed poly

■ Expansion angle $\sim 45^\circ$





Expanded C-boule

poly Seed poly

■ Expansion angle $\sim 18-20^\circ$

■ Good facet control

8

















25 mm



Effect of seed temperature

An Integrated Approach to the Bulk III-Nitride Crystal Growth and Wafering

$T_{\text{seed}} < 2150^{\circ}\text{C}$

$T_{\text{seed}} > 2150^{\circ}\text{C}$

- Besides the seed quality, seed temperature is an important parameter to control to avoid surface roughness
 - Al_2O_3 and Al_4C_3 nucleate at low temperatures

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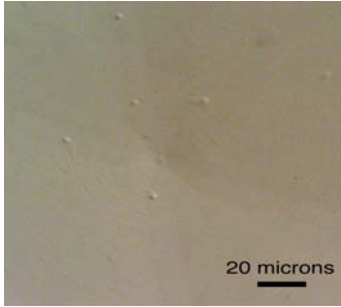
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STONY BROOK

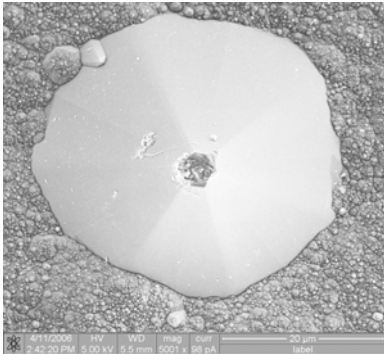
FIU

UPR





20 microns



Wet etching

An Integrated Approach to the Bulk III-Nitride Crystal Growth and Wafering

- N-polar facet etched in 6M KOH solution at 60°C for 10 minutes
- Well defined hexagonal hillocks

- Al-polar facet etched in KOH/NaOH eutectic at 430°C for 2 minutes
- Well defined hexagonal pits - defect etching
- EPD is about $2.5 \times 10^4 \text{ cm}^{-2}$

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FIU

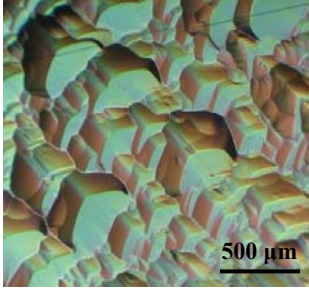
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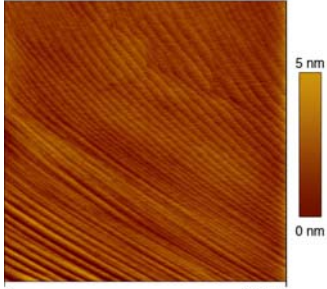
Growth on (002)-oriented seeds (Al-face)

An Integrated Approach to the Bulk III-Nitride Crystal Growth and Wafering

- Many growth centers are observed on as-grown crystal surfaces reflecting a rather high supersaturation
- Step height of about 1 lattice parameter unit (0.5 nm)
- Terrace width varies between 50 nm and 70 nm



Optical microscopy



AFM measurement

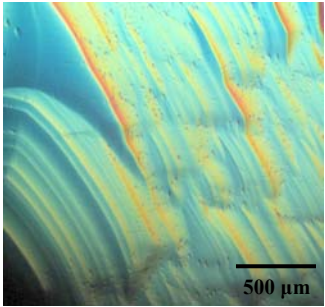
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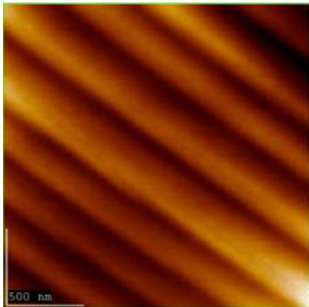
Growth on (002)-oriented seeds (N-face)

An Integrated Approach to the Bulk III-Nitride Crystal Growth and Wafering

- One growth center controls the whole growth surface; step flow growth mechanism.
- Step height of about 1 lattice parameter unit (0.5 nm).
- Terrace width L varies between 200 nm and 250 nm.



Optical microscopy



AFM measurement

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Model for surface morphology difference

An Integrated Approach to the Bulk III-Nitride Crystal Growth and Wafering

- According to the BCF theory:
$$L = 4\pi \frac{\gamma a}{kT \ln(1 + \sigma)}$$

a is the lattice parameter, γ is the surface energy,

σ is the vapor supersaturation; $\sigma = \frac{P}{P_{eq}} - 1$ estimated to be around 2%
- As seen by the arriving Al species, N-polar (0001) surfaces have three dangling bonds while Al-polar surfaces have only one.
- $\gamma_N = 3 \gamma_{Al}$, therefore $L_N = 3 L_{Al}$, experimental results from AFM measurements agree with the theory.
- To have the same L in the case of Al-polarity as in N-polarity σ should be reduced to 0.6 %, leading to very low growth rates.

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Conclusion

An Integrated Approach to the Bulk III-Nitride Crystal Growth and Wafering

- **The use of Ar as ambient gas**
 - **Implementation of an additional growth parameter**
 - **Increase the transport rate while keeping the same temperature, pressure and temperature gradient**
- **AlN boule growth**
 - **Very high quality (002)-seeds and (002)-crystals were obtained**
 - **Very uniform crystals having one single facet covering the whole area were obtained**
 - **Due to its high surface energy the N-polar face is very suitable for growth**

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An Integrated Approach to the Bulk III-Nitride Crystal Growth and Wafering

On the nature of the AlN surface oxide

Rafael Dalmau, Ramon Collazo, Seiji Mita, Zlatko Sitar
Department of Materials Science and Engineering
North Carolina State University

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Outline

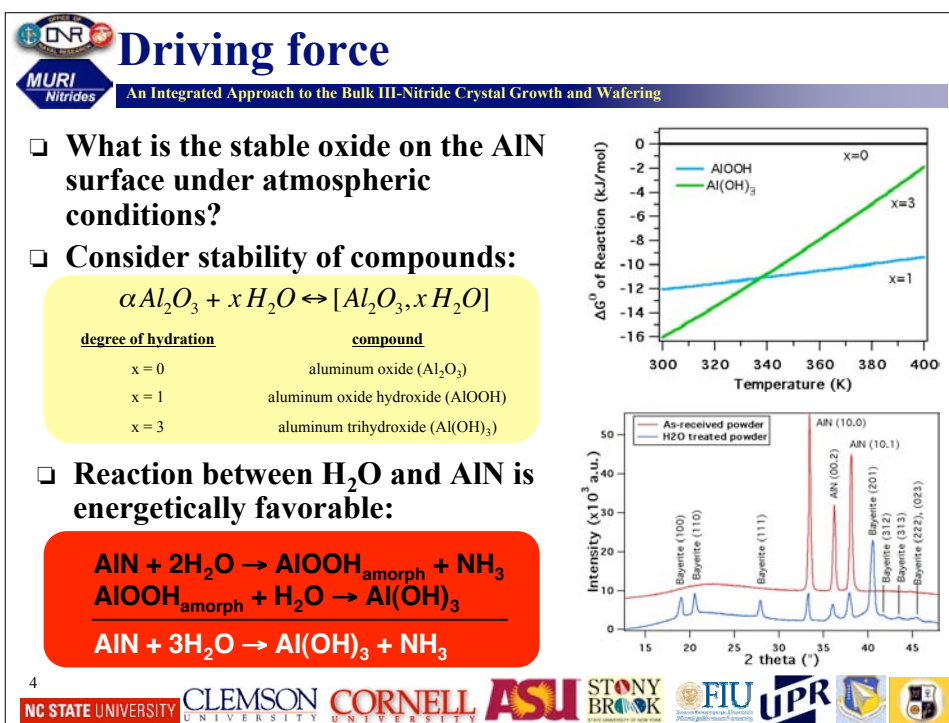
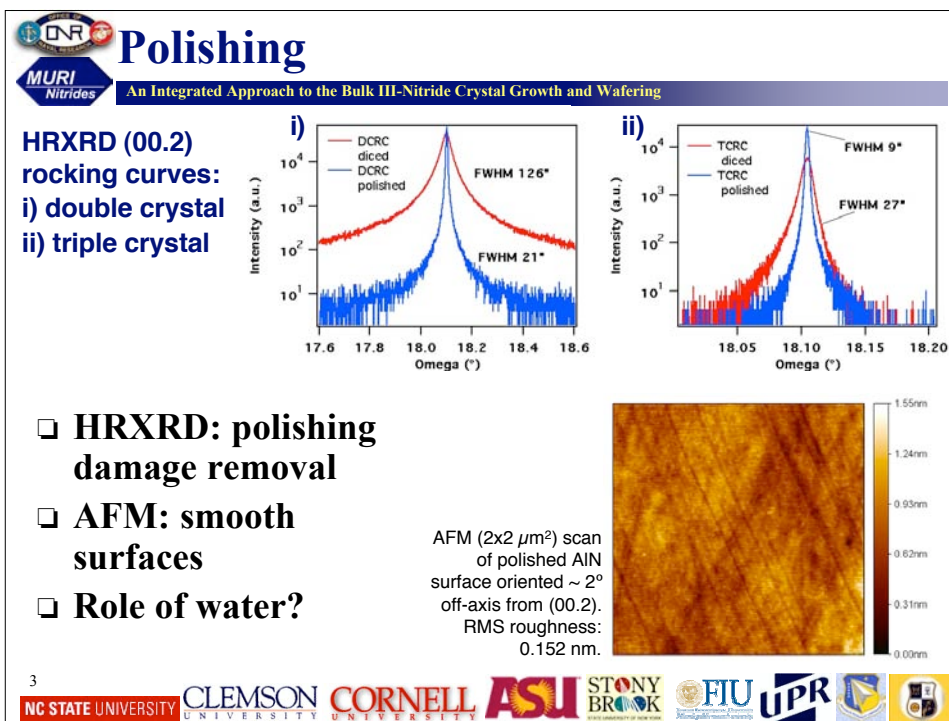
An Integrated Approach to the Bulk III-Nitride Crystal Growth and Wafering

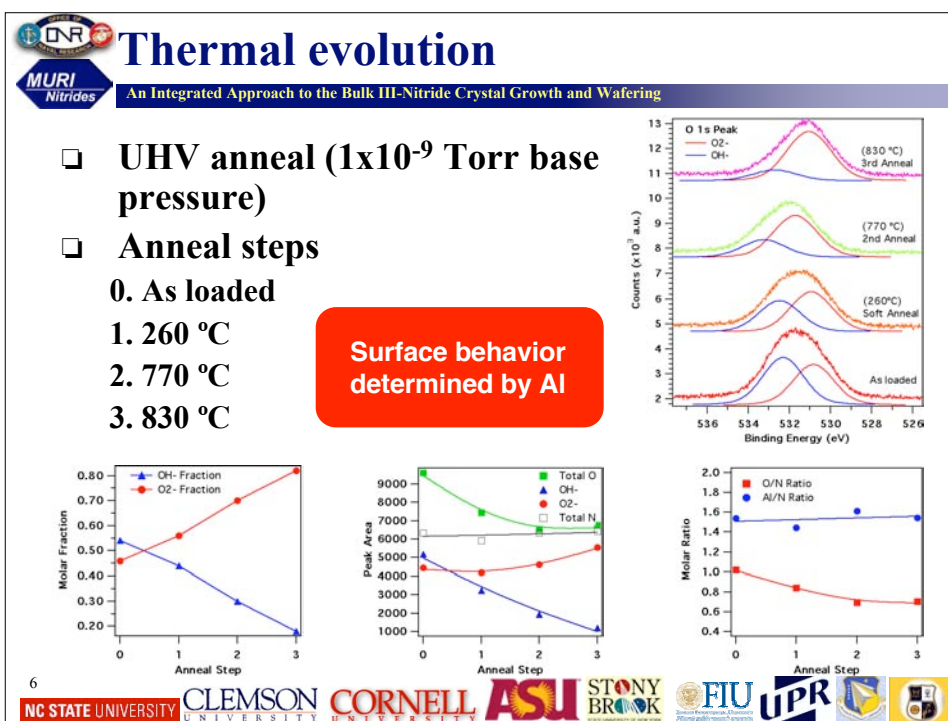
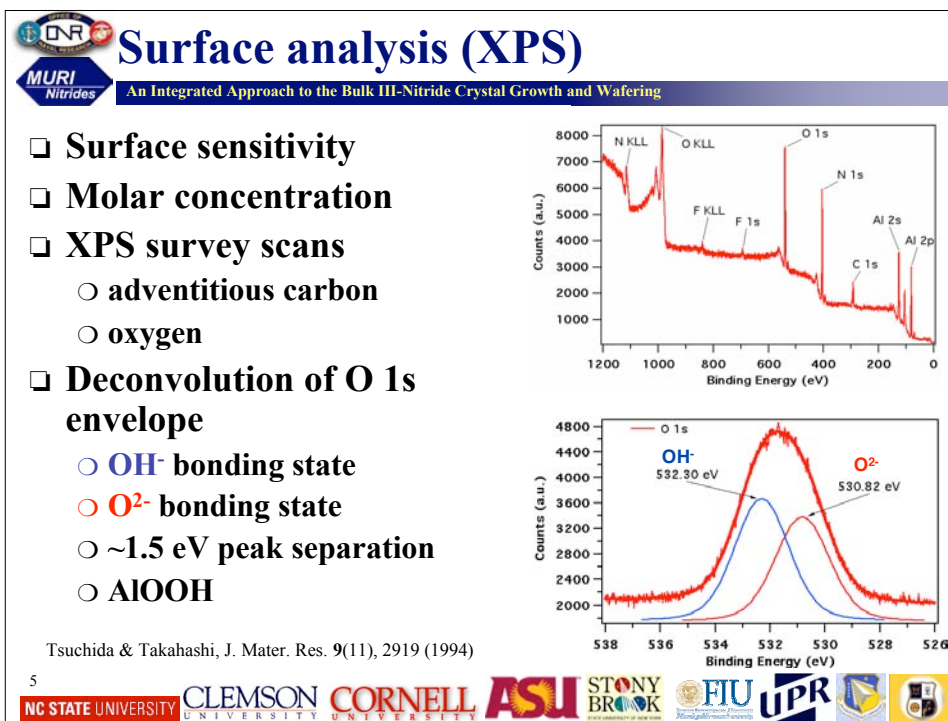
- ❑ Polishing
- ❑ Oxide stability
- ❑ Surface analysis
 - Thermal evolution
 - Stoichiometry
 - Thickness
- ❑ Wet chemistry
- ❑ Summary

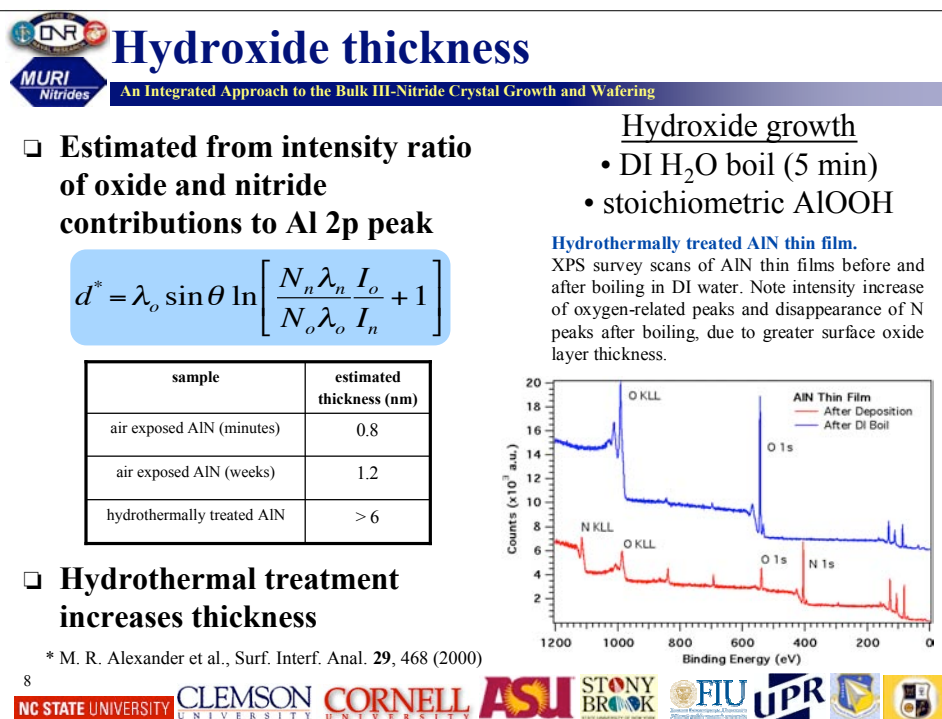
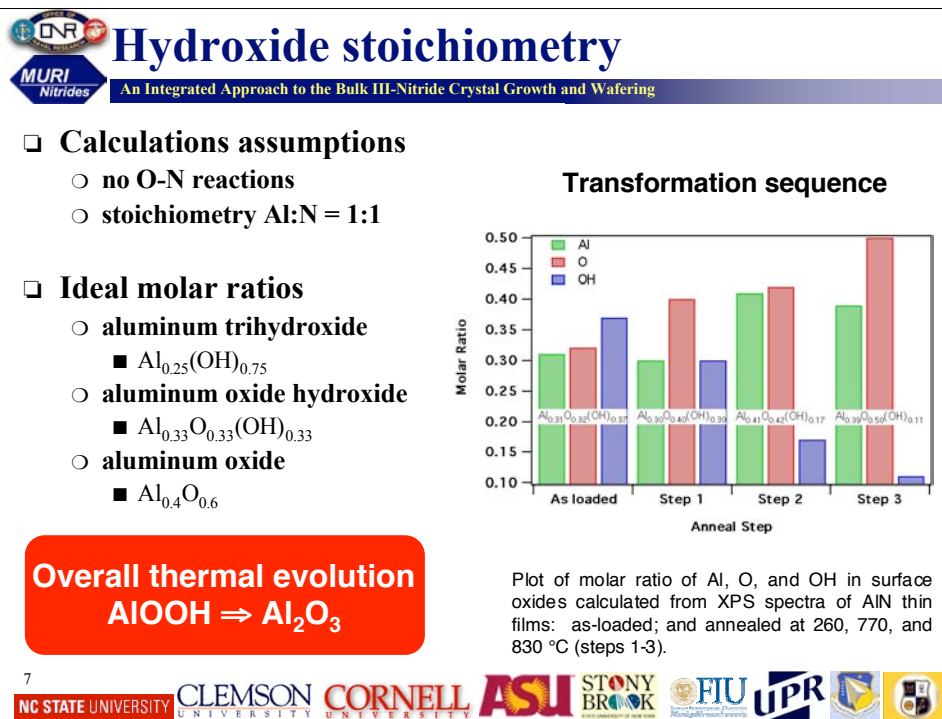
Motivation: Demands of conventional AlN homoepitaxy place stringent requirements on bulk crystal surface preparation

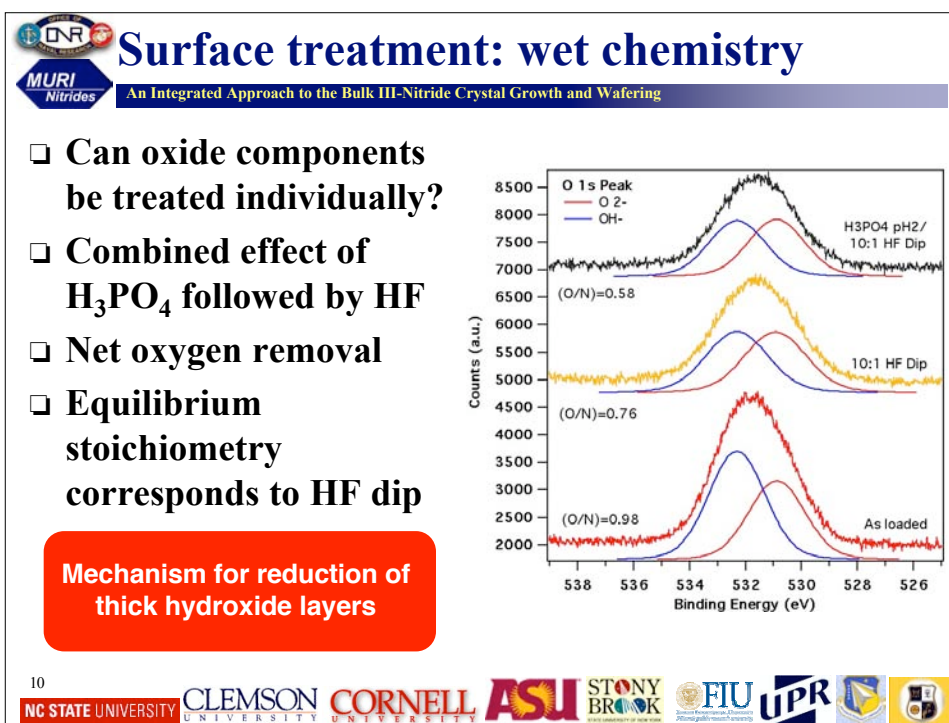
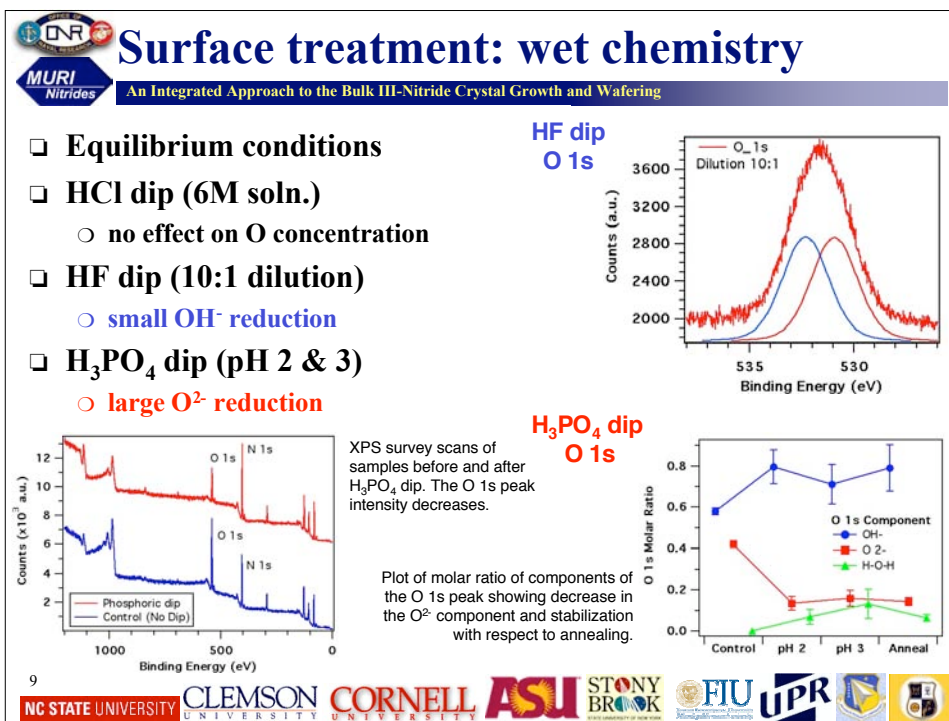
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Summary

An Integrated Approach to the Bulk III-Nitride Crystal Growth and Wafering

- ❑ Reproducibly attained smooth high-quality polished surfaces
- ❑ Identified the oxide on RT air-exposed AlN surfaces: aluminum oxide hydroxide (AlOOH)
- ❑ Analyzed the thermal, hydrothermal evolution of the surface oxide; surface behavior determined by Al
- ❑ Estimated the thickness of hydroxide layers
- ❑ Studied the effectiveness of wet chemical treatments for hydroxide removal
- ❑ Identified a mechanism for reduction of thick hydroxide layers

11



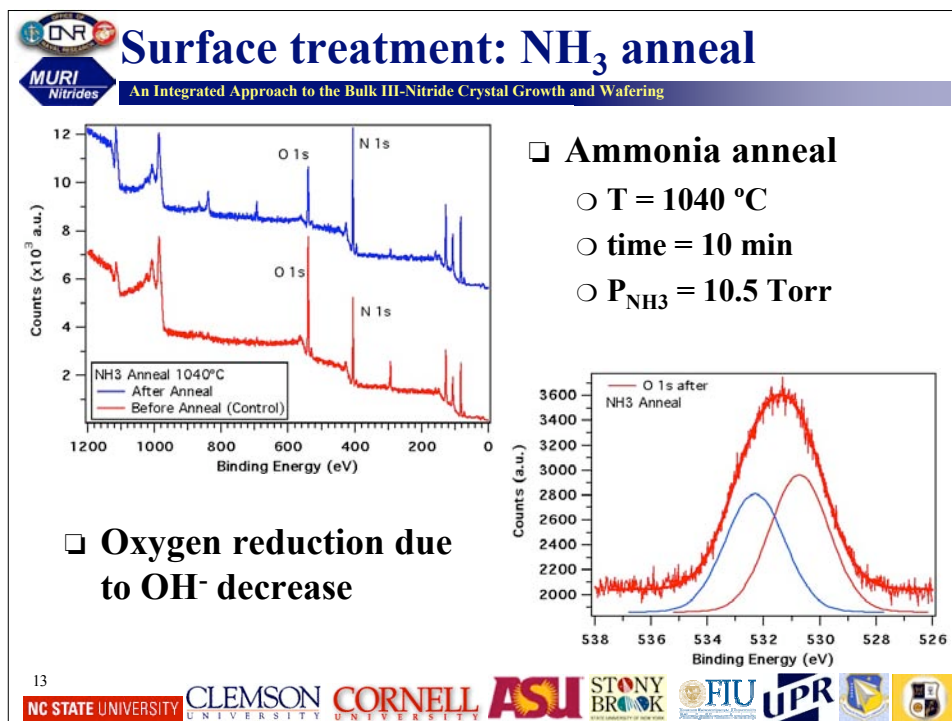

Additional research

An Integrated Approach to the Bulk III-Nitride Crystal Growth and Wafering

- ❑ X-ray reflectivity & TEM studies of polished samples for near-surface evaluation
- ❑ Investigate *in situ* oxide removal processes compatible with MOCVD
- ❑ Homoepitaxial growth of AlN on bulk crystals by MOCVD

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An Integrated Approach to the Bulk III-Nitride Crystal Growth and Wafering

Is HVPE Fundamentally Inferior to PVT of AlN

Ramon Collazo, Rafael Dalmau, Ziad Herro, Deijin Zhuang,
Zlatko Sitar

North Carolina State University

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Motivation

An Integrated Approach to the Bulk III-Nitride Crystal Growth and Wafering

HVPE

- ❑ Low temperature, <1400°C
- ❑ Growth rate: 100-200 $\mu\text{m/hr}$

❑ Properties

- Opaque
- DCRC: 1200 arcsec

PVT

- ❑ High temperature, >2200°C
 - material compatibility
 - thermal stress
 - growth control
- ❑ Growth rate: 100-500 $\mu\text{m/hr}$

❑ Properties

- Transparent
- DCRC: 20 arcsec

2



Evolution of Surface Morphology
An Integrated Approach to the Bulk III-Nitride Crystal Growth and Wafering

Development of surface morphology determined by

- local surface curvature, K
- velocity of species on the surface, v_s

3

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Model of Surface Evolution
An Integrated Approach to the Bulk III-Nitride Crystal Growth and Wafering

$$\frac{\partial h(x,t)}{\partial t} = F(x,t) - v_{\perp}(x,t)$$

Deposition, $F(x,t)$

- Constant incoming flux, J
- Finite atomic size, δ
- Surface curvature, $K(x,t)$

$$F(x,t) = J + \delta JK(x,t)$$

Surface diffusion

- Perpendicular surface velocity due to surface diffusion, $v_{\perp}$

$$v_{\perp}(x,t) = -D_e \nabla_s^2 K(x,t)$$

$D_e = \frac{D_s \sigma_s \Omega^2 \varepsilon}{k_B T}$; effective diffusivity
 D_s = surface diffusivity
 σ_s = isotropic surface energy density
 Ω = atomic volume
 ε = number of atoms per unit area

4

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Perturbation Analysis
An Integrated Approach to the Bulk III-Nitride Crystal Growth and Wafering

In the small slope limit: $\frac{\partial h}{\partial x} \approx 0$

Initial sinusoidal perturbation: $\sin(kx)$ and subtracting J

$$\frac{\partial h}{\partial t} = J - \delta J \frac{\partial^2 h}{\partial x^2} - D_e \frac{\partial^4 h}{\partial x^4} \quad \leftarrow \quad h(x,t) = A(t)h(x,0)$$

Surface morphology given by:

$$h(x,t) = e^{(\delta J k^2 - D_e k^4)t} \sin(kx)$$

- Non-linear terms in overall equation saturate instability into a relatively small amplitude surface profile.

Unstable mode:

$$\delta J k^2 - D_e k^4 > 0 \quad \lambda = \frac{2\pi}{k} \quad \lambda > \lambda_0$$

λ is the wavelength of the initial perturbation

where $\lambda_0 = \sqrt{\frac{4\pi^2 D_e}{\delta J}}$

“effective” diffusion length

$\lambda_m = \sqrt{2}\lambda_0$ is the most unstable mode

Substrate

- Supersaturation
- Initial surface preparation

Growth Process (J)

Surface/ Surface Diffusion

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Process Conditions (λ_0)
An Integrated Approach to the Bulk III-Nitride Crystal Growth and Wafering

“Effective” diffusion length

$$\lambda_0 = \sqrt{\frac{4\pi^2 D_e}{\delta J}}$$

Limiting reactant specie flux (J)

$$J \propto \Delta p = p_i \quad \text{input partial pressure of the limiting reactant. } (p_i \gg p_{eq})$$

At a given temperature

$$\frac{\lambda_0}{\lambda_0'} = \sqrt{\frac{p_i'}{p_i}}$$

Temperature (Surface diffusion)

D_S is the surface diffusion, with a given activation energy E_A . $D_S = D_0 e^{-E_A/k_B T}$

$$\lambda_0 = \sqrt{\frac{Ae^{-E_A/k_B T}}{T}} \quad \rightarrow \quad \frac{\Delta \lambda_0}{\lambda_0} = \frac{(E_A - k_B T) \Delta T}{2k_B T^2}$$

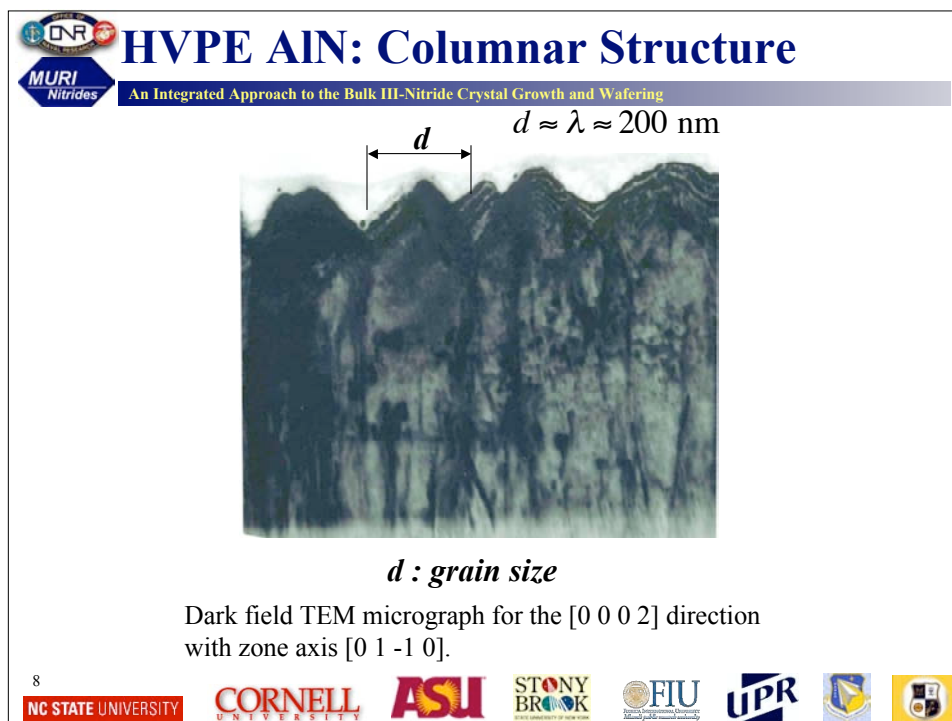
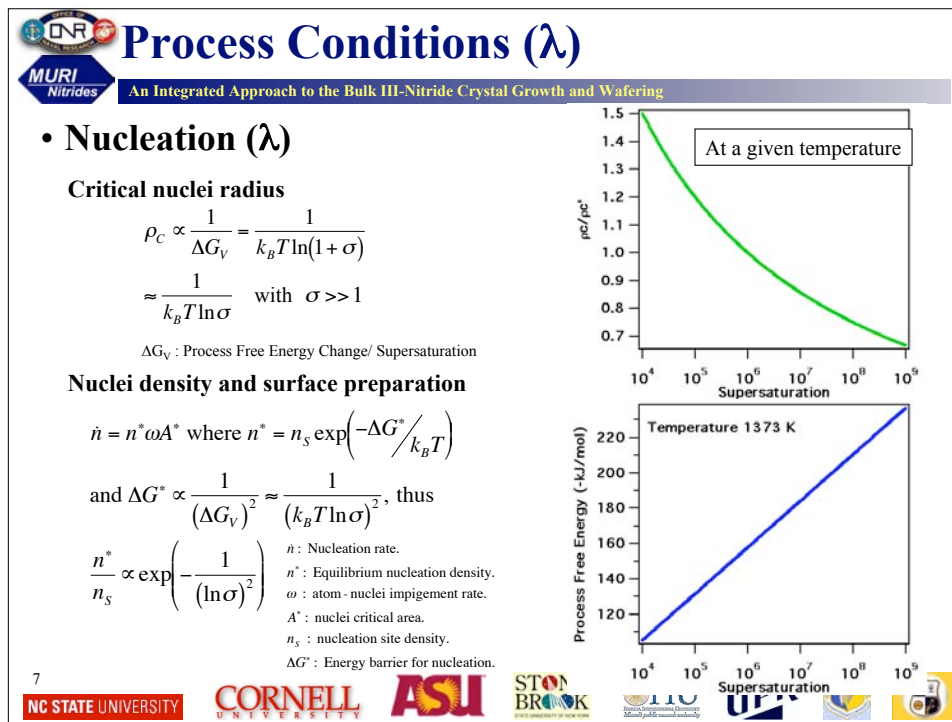
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Graphs:

Top graph: $\lambda_0 / \Delta p$ vs p_i / p_i' . The curve shows a decreasing trend as p_i / p_i' increases from 0.1 to 10.

Bottom graph: $\Delta \lambda_0 / E_A$ (1/eV) vs Temperature (K). The curve shows a decreasing trend as temperature increases from 800 to 2000 K. The graph is labeled $\Delta T = 100$ K and $\text{For } E_A \gg k_B T \text{ and a given } p_i$.





Conclusions

An Integrated Approach to the Bulk III-Nitride Crystal Growth and Wafering

- ❑ **HVPE of AlN has fundamental limitations that are manifested in the mosaicity of deposited films and stability of the growth surface**
 - due to a low growth temperature, the growth surface can be controlled only through the nucleation process and columnar growth
 - coalescence of columns into structures wider than the critical surface diffusion distance results in surface roughening and deterioration of crystalline quality
- ❑ **seeded PVT growth of AlN does not suffer from above limitations**

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An Integrated Approach to the Bulk III-Nitride Crystal Growth and Wafering

Physical Modeling of AlN/GaN Vapor Growth

Dang Cai, Xiaolin Wang, Hui Zhang
Department of Mechanical Engineering
State University of New York at Stony Brook

May 08, 2006









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An Integrated Approach to the Bulk III-Nitride Crystal Growth and Wafering

Summary of AlN/GaN Growth Simulations

- ❑ **AlN Sublimation Growth**
 - Heat and mass transport in AlN sublimation growth;
 - Source powder size/porosity, Stefan flow and diffusion controlled flow;
 - Isotropic/anisotropic models for vapor deposition process;
 - Seed, axial and radial temperature and poly-crystal effects on growth, stresses and defects.
- ❑ **GaN IVPE Growth**
 - Optimization of geometrical parameters and operating conditions for fast and uniform GaN IVPE deposition;
 - Thermodynamic and kinetic analysis of gas phase/surface reactions in source bubbler and reactor chamber to identify critical reaction steps;
 - Quasi-equilibrium and kinetic models developed to predict GaN growth rate.

Publications: 1 book chapter, 7 journal papers and 14 conference papers









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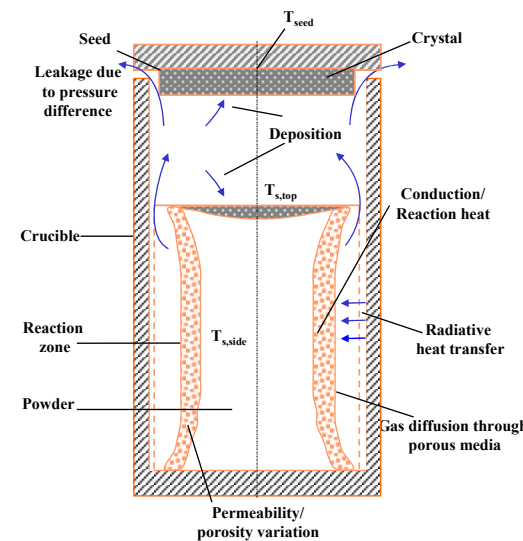
Powder Sublimation & Vapor Deposition
An Integrated Approach to the Bulk III-Nitride Crystal Growth and Wafering

■ Reaction zone size & movement are controlled by driving force, porosity and permeability.

■ Driving force is due to the following temperature difference at different locations:

- From source to seed
- From leakage to cold surfaces
- From side to top surfaces

■ Temperature variation is due to powder decomposition, coupling between source and heater.










3





Powder Sublimation and Porosity Evolution
An Integrated Approach to the Bulk III-Nitride Crystal Growth and Wafering

Assumptions:

- Neglecting temperature change
- Considering uniform particle size for initial source material
- Diffusion only due to low Grashof number & low Stefan flow velocity

Continuity equation: $\frac{\partial}{\partial t} [\rho_s (1-\phi) + \rho_g \phi] + \frac{1}{r} \frac{\partial}{\partial r} (r \phi \rho_g u_r) = 0$

Reaction equation: $\frac{\partial \rho_s (1-\phi)}{\partial t} = -R_p$

→ $\frac{\partial \phi}{\partial t} = \frac{R_p}{\rho_s}$

→ $\frac{1}{r} \frac{\partial}{\partial r} (r \phi u_r) = \frac{R_p}{\rho_g}$

$R_p = Z \exp(A - \frac{B}{T})$

$u = \frac{K}{\mu} \nabla p$

↓

$p = \int \frac{\mu}{K} u_r dr$

Energy Conservation: $(1-\phi) \rho_s C_s \frac{\partial T}{\partial t} + \phi \rho_g u_z C_g \frac{\partial T}{\partial z} = \frac{\partial}{\partial x} \left(k \frac{\partial T}{\partial x} \right) + \frac{1}{r} \frac{\partial}{\partial r} \left(r k \frac{\partial T}{\partial r} \right) - (1-\phi) Q_p R_p$

$k = \phi (k_{gas} + \frac{32}{3} \epsilon \sigma T^3 d_p) + (1-\phi) k_{solid}$

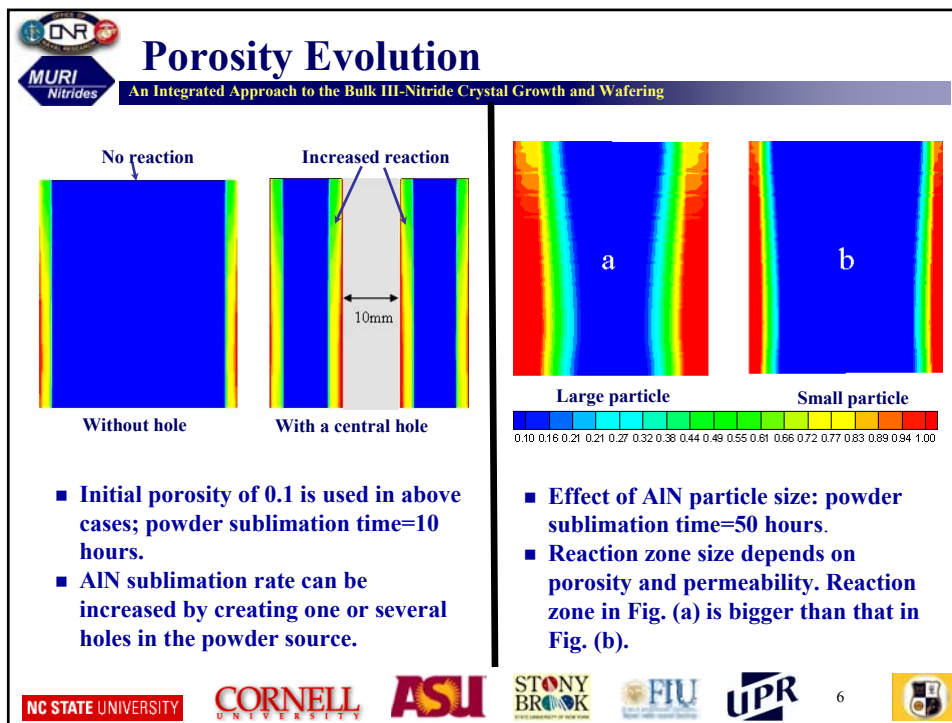
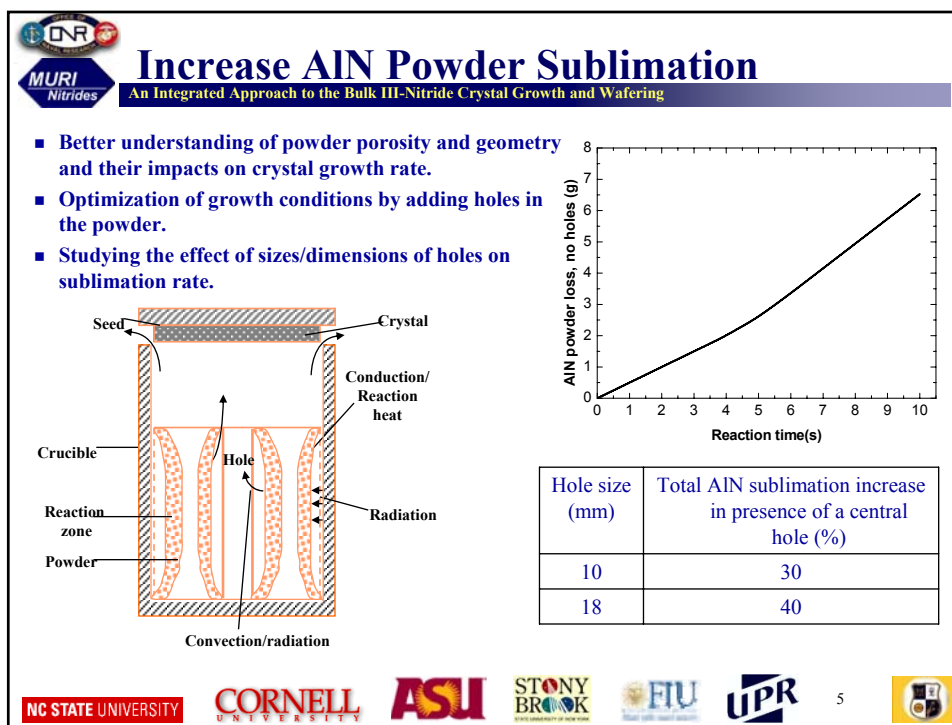


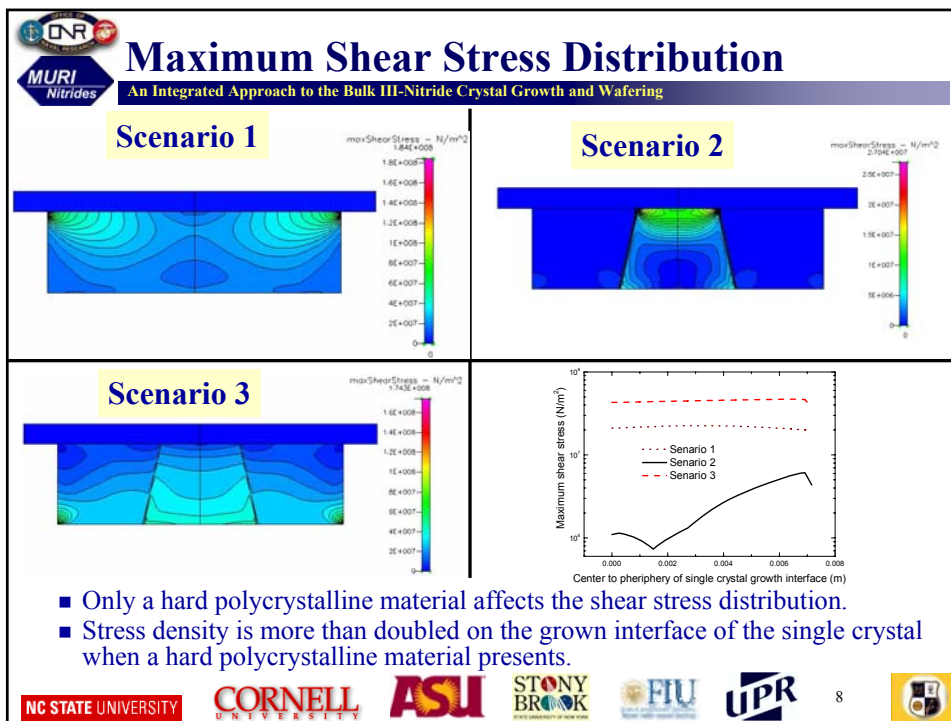
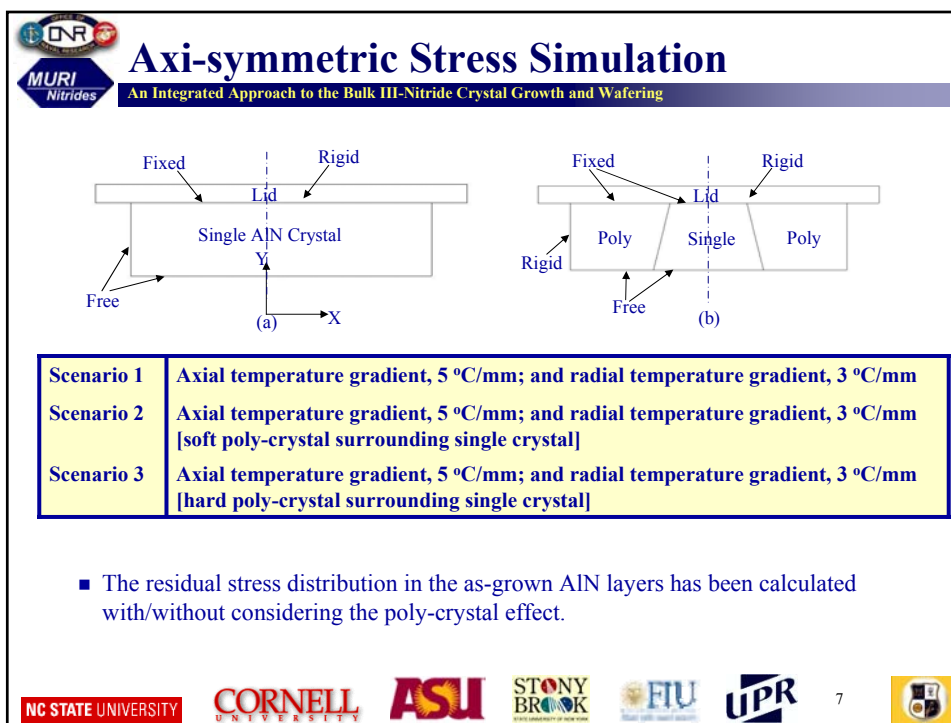


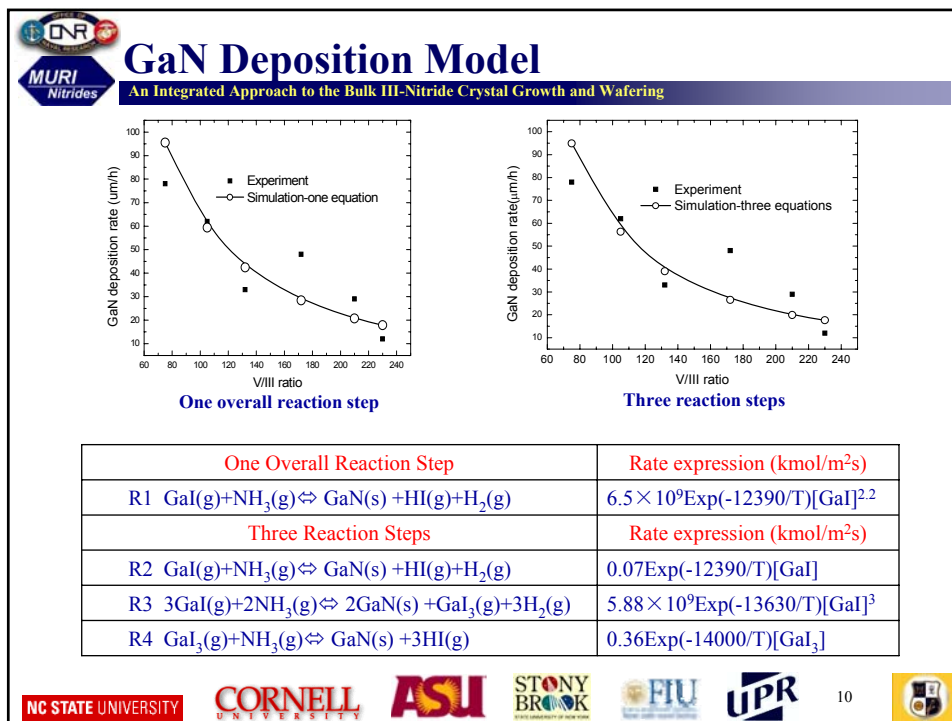
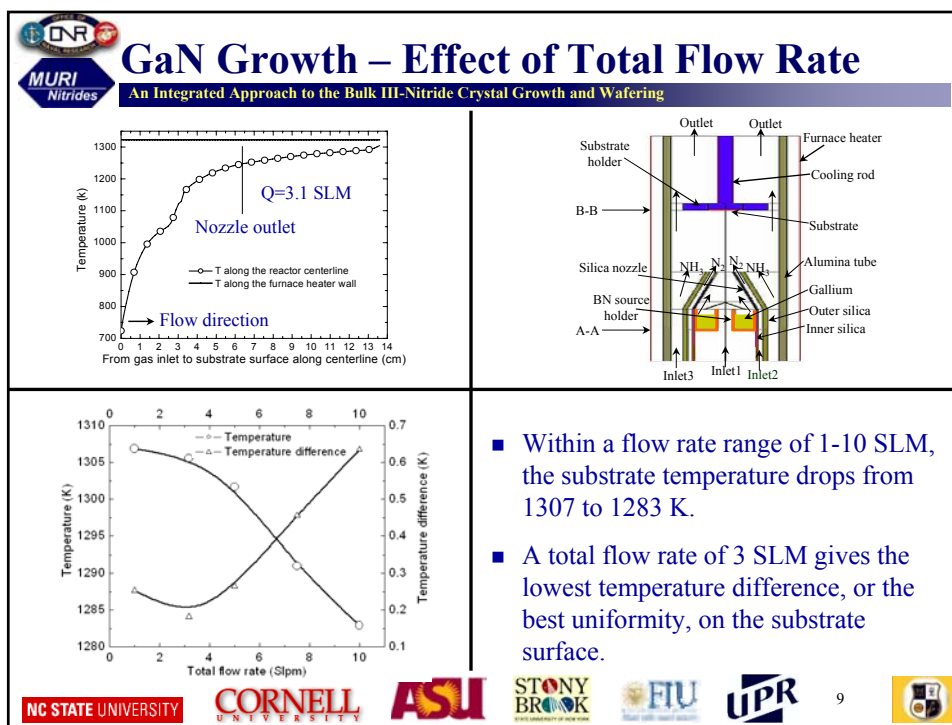


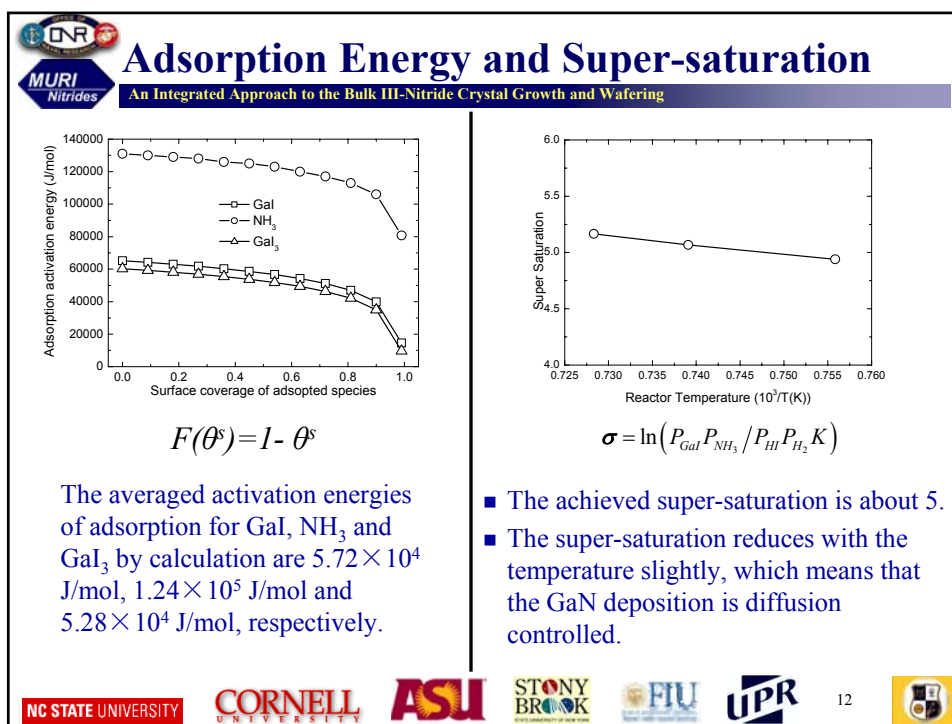
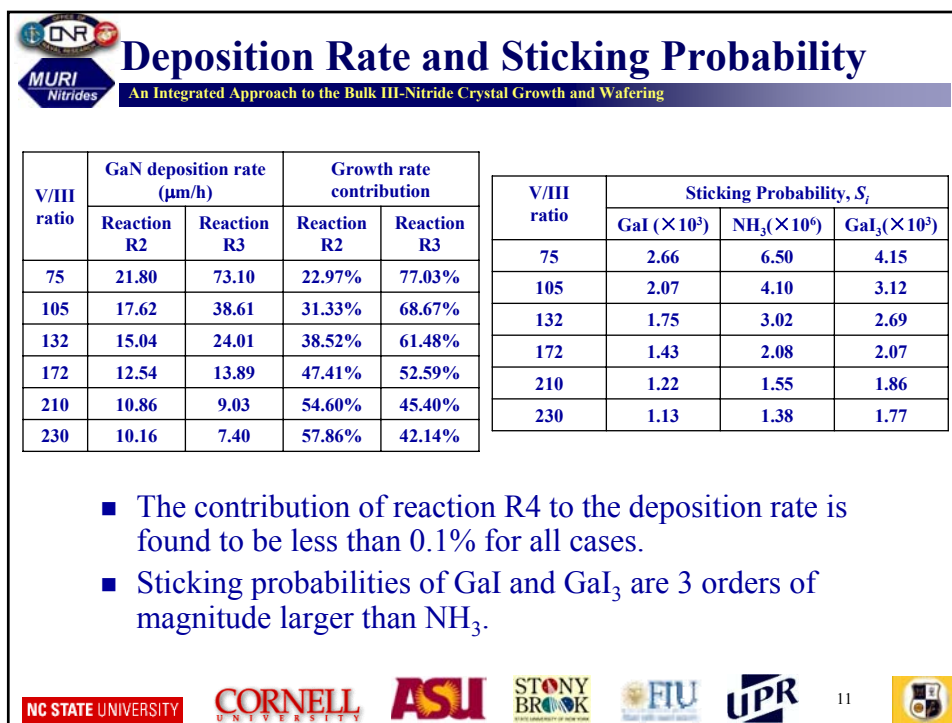

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Conclusions

An Integrated Approach to the Bulk III-Nitride Crystal Growth and Wafering

- AlN powder sublimation model was built, and effect of holes on the powder sublimation was investigated;
- Residual stress distribution in the as-grown AlN layers was studied;
- Temperature and its distribution on the substrate for GaN growth was studied;
- Surface reactions and their rates were determined;
- Sticking probability, species adsorption energy and super-saturation were calculated.

13

**MURI**
Nitrides

An Integrated Approach to the Bulk III-Nitride Crystal Growth and Wafering

Bulk GaN crystal growth through Ga vapor transport technique

**Huaqiang Wu, Phani Konkapaka, Barry Butterfield
Yuri Makarov*, and Michael Spencer
Cornell University
* STR**

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**MURI**
Nitrides

An Integrated Approach to the Bulk III-Nitride Crystal Growth and Wafering

Outline

- ☐ GaN powder decomposition;
- ☐ The efficient Ga transport through Ga_2O_3 ;
- ☐ Improved design to prevent gas phase particles formation;
- ☐ Growth rate versus different growth parameter;
- ☐ Surface morphology of the grown GaN layer;
- ☐ Cracks in the sapphire substrate due to thick GaN layer;
- ☐ XRD Characterization of GaN layer;
- ☐ Summary

2





GaN powder decomposition - I

An Integrated Approach to the Bulk III-Nitride Crystal Growth and Wafering

- Lab made GaN powder has very high purity. Oxygen concentration is less than 400ppm;
- The commercial GaN powder is converted from Ga_2O_3 . The powder purity is less than 91% with more than 3% oxygen concentration.
- The very low equilibrium Ga vapor pressure over liquid Ga (several Pascal at 1000°C) limited the total amount transferred out from the GaN powder;
- From thermo dynamical calculations, Ga_2O has much higher vapor pressure and could serve as efficient Ga carrier.
- Ga_2O is unstable and can react with NH_3 to form GaN easily;

	Lab-made powder	Commercial powder
Gas species	$\text{N}_2, \text{Ga(g)}$	$\text{N}_2, \text{Ga(g)}, \text{GaO(g)}, \text{Ga}_2\text{O(g)}$
Condensed phases	$\text{GaN(s)}, \text{Ga(l)}$	$\text{GaN(s)}, \text{Ga}_2\text{O}_3, \text{Ga(l)}$
Heterogeneous chemistry	$2\text{GaN(s)} = 2\text{Ga(s)} + \text{N}_2\text{(g)}$ $\text{Ga(l)} = \text{Ga(g)}$	$2\text{GaN(s)} = 2\text{Ga(s)} + \text{N}_2\text{(g)}$ $\text{Ga}_2\text{O}_3\text{(s)} + \text{Ga} = 3\text{GaO(g)}$ $\text{GaO(g)} + \text{Ga(g)} = \text{Ga}_2\text{O(g)}$ $\text{Ga(l)} = \text{Ga(g)}$

3





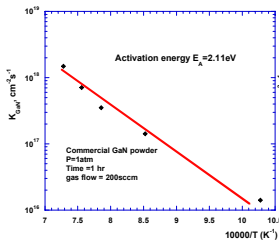




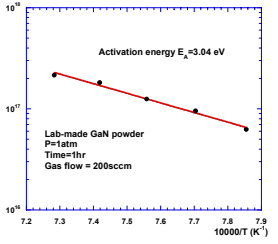


GaN powder decomposition - II

An Integrated Approach to the Bulk III-Nitride Crystal Growth and Wafering

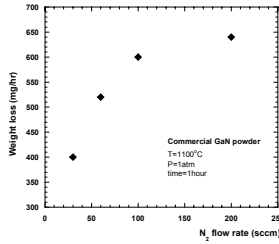


Commercial GaN powder
P=1atm
Time=1 hr
gas flow = 200sccm

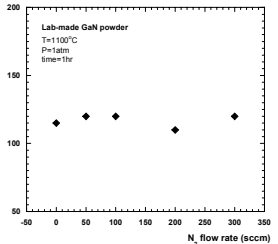


Lab-made GaN powder
P=1atm
Time=1hr
Gas flow = 200sccm

➤ Based on the experimental results, the equivalent activation energy of lab-made GaN powder is much higher than the commercial GaN powder. This may be due to the lower Ga_2O formation and desorption barrier.



Commercial GaN powder
T=1100°C
P=1atm
Time=1hour



Lab-made GaN powder
T=1100°C
P=1atm
Time=1hr

➤ The weight loss of commercial GaN powder increases with the carrier gas N_2 flow rate. This provides additional freedom to control the growth. The lab-made powder weight loss is relatively independent on the N_2 flow rate.

Commercial GaN powder

Lab-made GaN powder

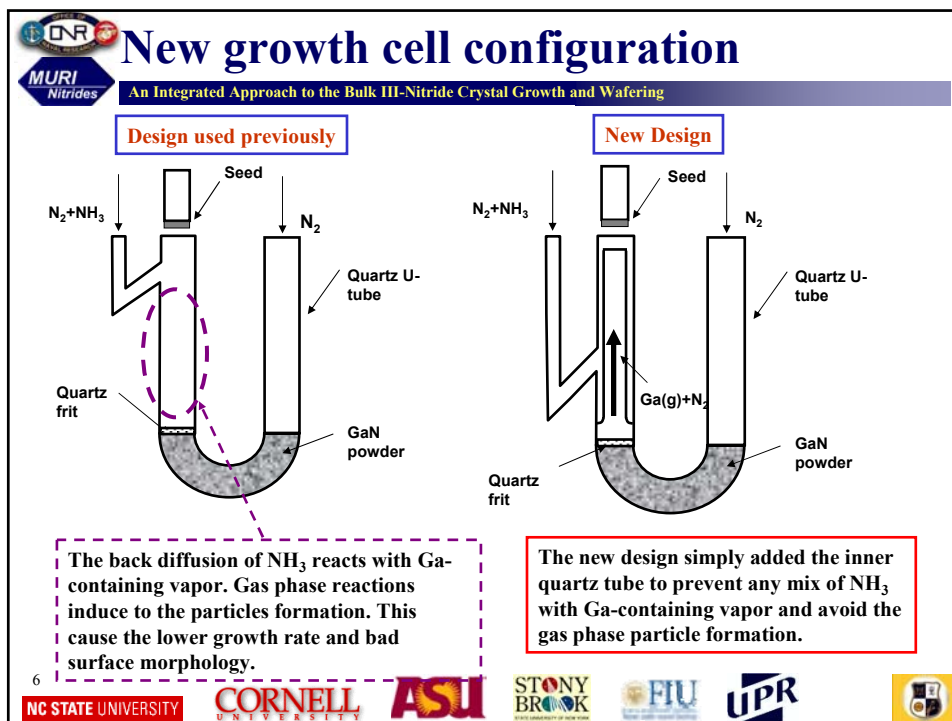
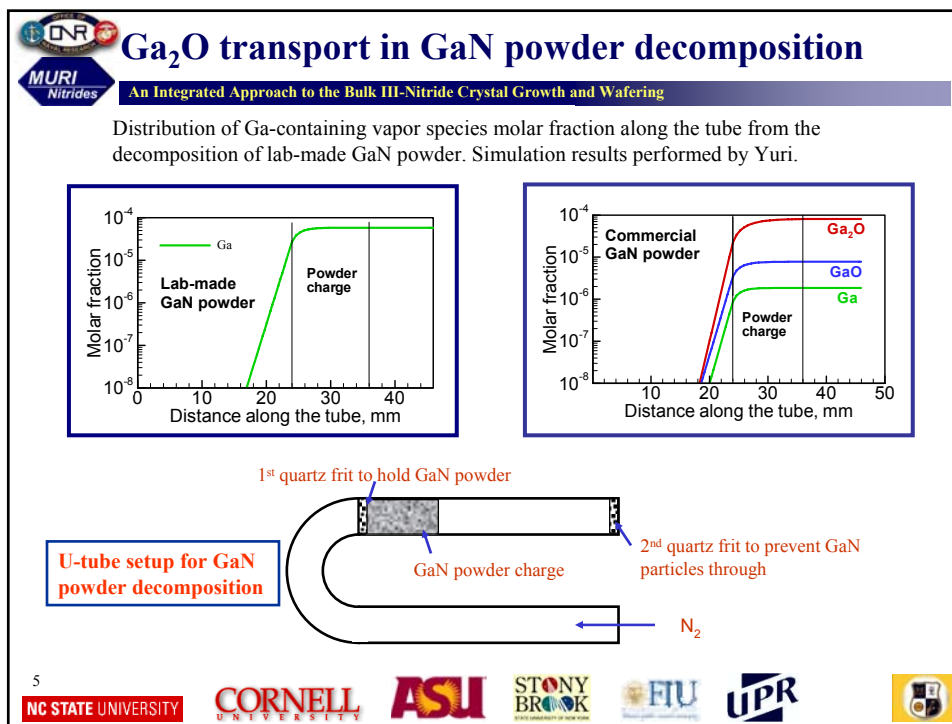
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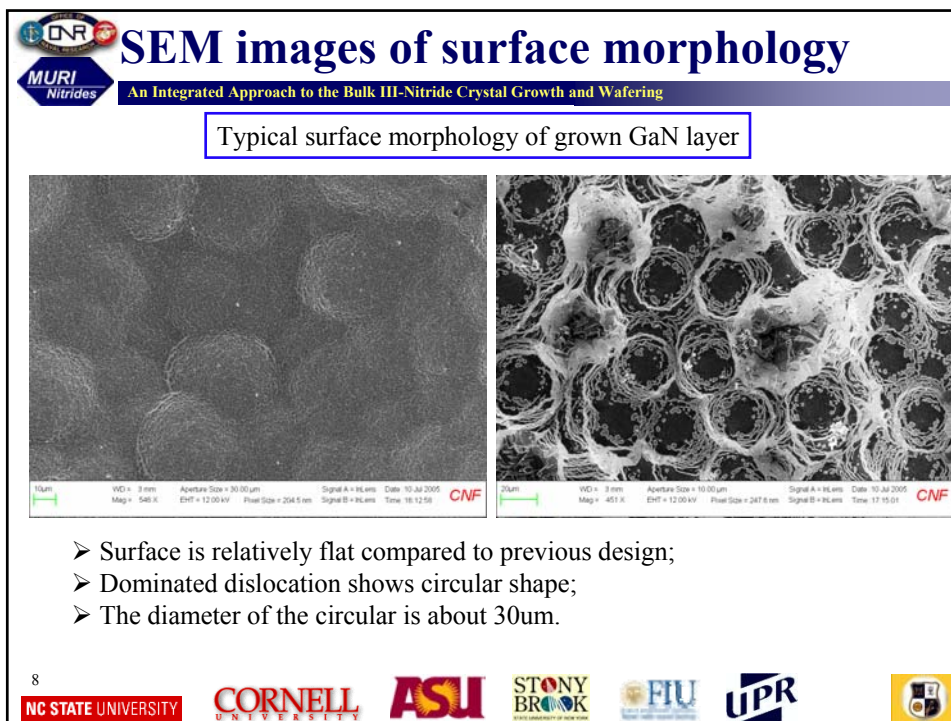
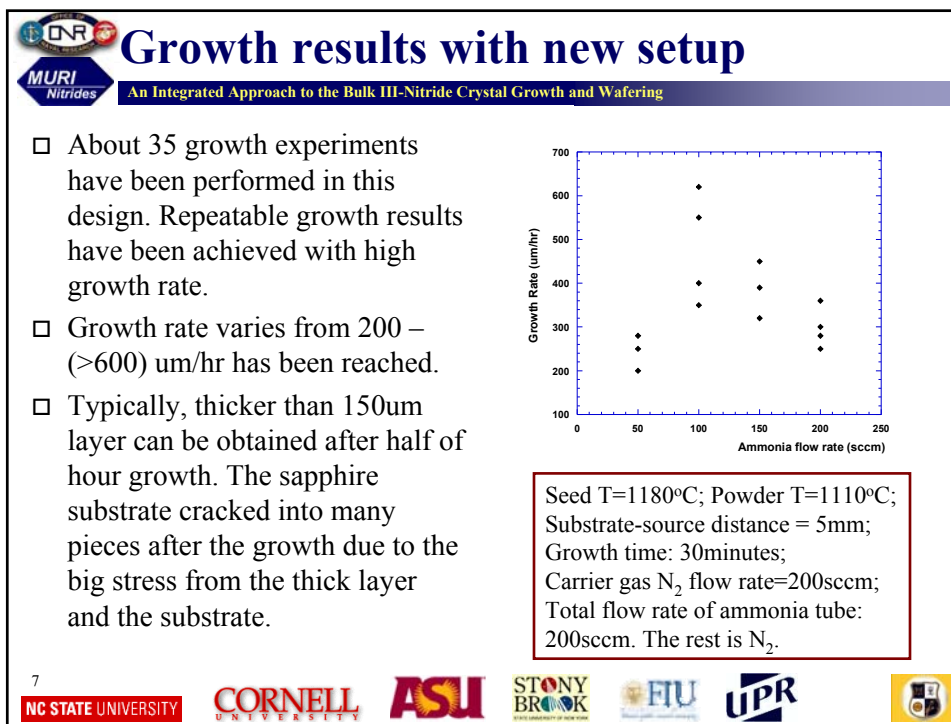












SEM image of cross section
 An Integrated Approach to the Bulk III-Nitride Crystal Growth and Wafering

Cross section view of grown GaN layer

25µm VED = 6 mm Aperture Size = 30.00 µm Signal A = SE2 Date: 21 Jul 2005
 Mag = 200 X EHT = 1.00 kV Pixel Size = 417.3 nm Signal B = InLens Time: 13:16:57 CNF

100µm VED = 6 mm Aperture Size = 30.00 µm Signal A = InLens Date: 19 Jul 2005
 Mag = 400 X EHT = 10.00 kV Pixel Size = 766.4 nm Signal B = InLens Time: 23:48:19 CNF

- Cross section SEMs indicate uniform layer on substrate;
- The layer thickness varies from 150µm to more than 300µm;
- Surface is not flat which might due to particles formation in the cooling down period .

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Cracking of seed substrate
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Picture of backside of the sample

Many small cracks originate from the lattice mismatch and thermal mismatch.

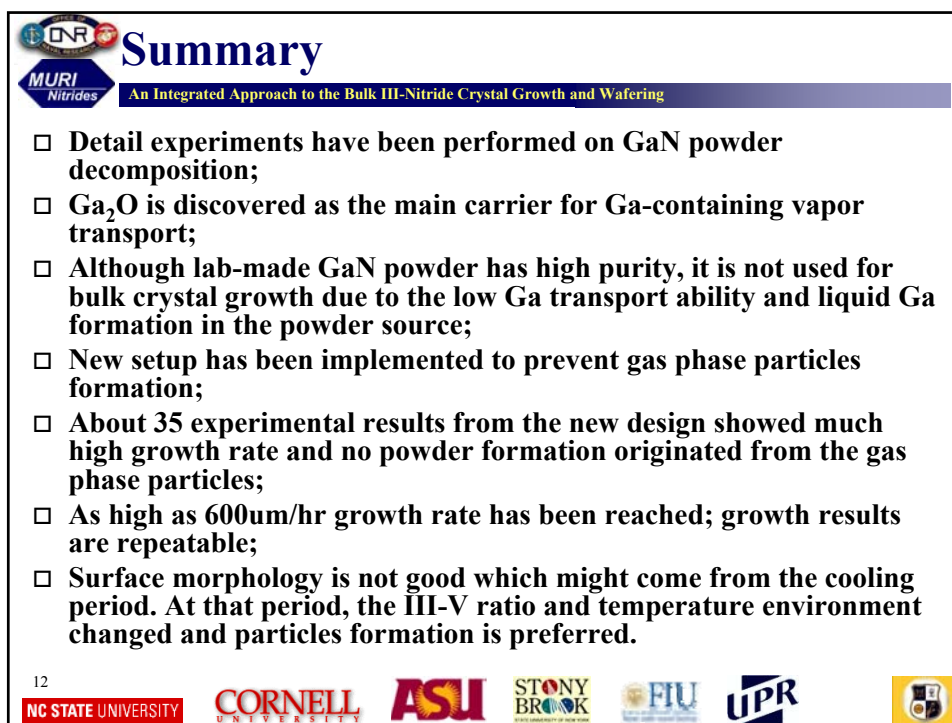
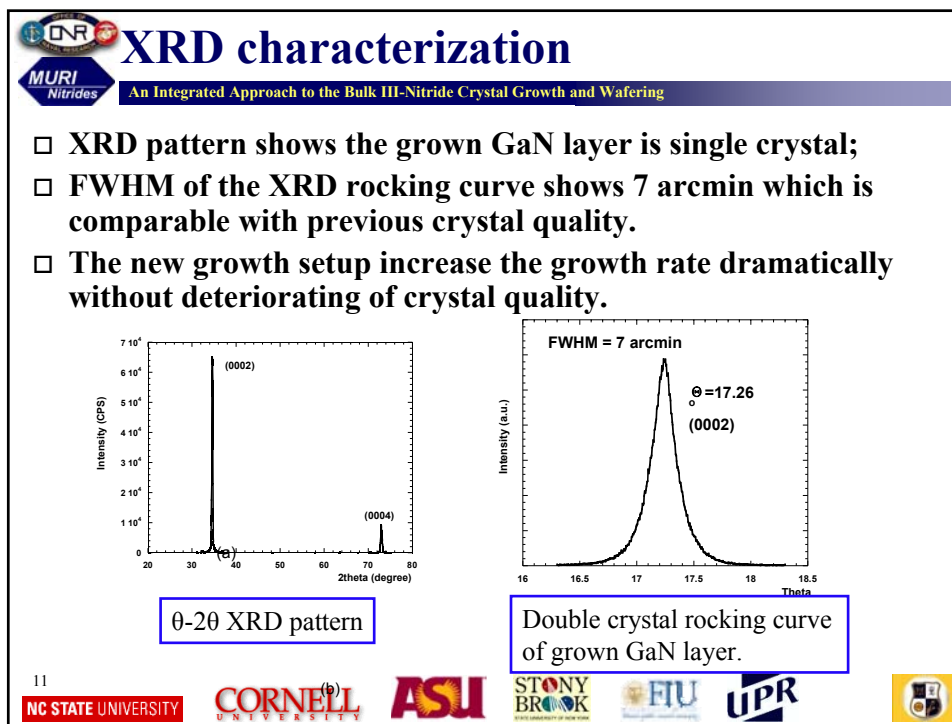
Big stress cause the break of the sample. 120o angle crack has been observed.

SEM image of the crack

The crack break both substrate and the grown GaN layer.

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 **An Integrated Approach to the Bulk III-Nitride Crystal Growth and Wafering**

Characterization of AlN and GaN crystals by Synchrotron White Beam X-ray Topography (SWBXT) and High Resolution X-ray Diffraction (HRXRD)

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Dept. of Materials Science & Engineering, North Carolina State University, Raleigh NC

B. Wang and M. Callahan
Air Force Research Laboratory, Hanscom AFB MA

P. Konkapaka, H. Wu and M. Spencer
Dept. of Electrical and Computer Engineering, Cornell University, Ithaca NY

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 **An Integrated Approach to the Bulk III-Nitride Crystal Growth and Wafering**

Ammonothermal growth of GaN (AFRL)

Defect Characterization of HVPE GaN seeds prior to ammonothermal growth

- HVPE GaN substrates (from MIT Lincoln Lab (Rich Molnar)) to be used as seeds.
- Defects in seed are usually replicated in the overgrown crystal. Mapping the defect distribution in seeds prior to growth facilitates separation of defects generated during growth from those propagating from the seed in the grown crystal.
- X-ray topographs:
 - Uniform distribution of high density of dislocations ($> 10^6/\text{cm}^2$). Typically, no individual dislocations are resolved.
 - Considerably distorted w.r.t original sample shapes indicating significant lattice plane bending due to residual strains.
- HRXRD measurements:
 - Considerable broadening of rocking curves due to due to a combination of tilt and lattice plane bending is observed.
 - Multiple peaks indicate presence of several subgrains.
 - Triple axis ω - 2θ widths vary from 20-40" indicating good quality GaN with low impurities (perfect crystal rocking curve is 10").

Summary of results from HVPE GaN seeds

Sample	Ga (growth) face		N (detached) face	
	DCRC (sec)	TCRC (sec)	DCRC (sec)	TCRC (sec)
2045a	1056	32	1282	34
2045b	1060	31	1068	20
2046G	1387	29	1421	20
2046H	1536	25	1477	20
2060a	1121	29	1070	18
2060b	1640	26	1413	23
2060c	1787	29	1447	20
2060d	1798	27	1823	20
2060e	1692	25	1941	18
2109H	497	30	1511	22
2109I	690	31	1404	25
2113G	1423	27	1007	18
2116E	1097	35	1626	35
2116F	780	33	1609	27
2116a	916	34	1036	38
2116b	814	38	1256	25

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Ammonothermal growth of GaN (AFRL)
 An Integrated Approach to the Bulk III-Nitride Crystal Growth and Wafering

Typical features of HVPE GaN seeds

- Comparison of optical pictures and corresponding transmission x-ray topographs ($g = 11-20$) reveals elongation or contraction of topographs depending on direction of bending.
- Inclusion-like contrast observed on x-ray topographs is actually from hexagonal pits on the Ga growth surface (see: T. Paskova, E. M. Goldys, R. Yakimova, E. B. Svedberg, A. Henry and B. Monemar, JCG, 208 (2000), pp.18-26).
- Double axis rocking curves recorded from the Ga and N faces exhibit different FWHM widths due to bending in opposite directions.
- Reciprocal space maps recorded from the N face exhibit somewhat lower triple axis ω -2 θ widths than those from Ga face.

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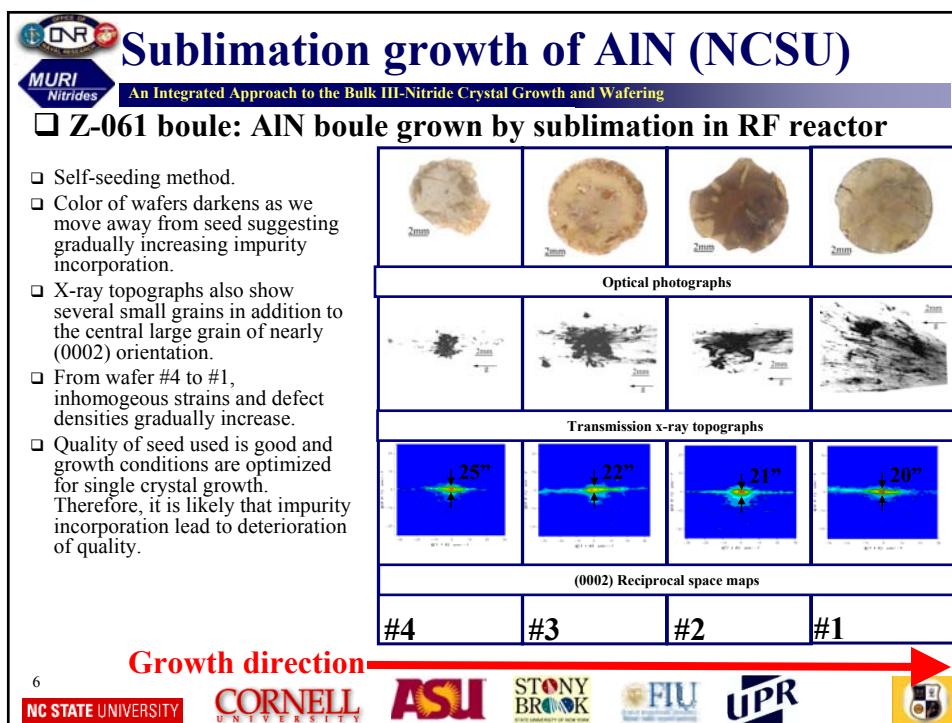
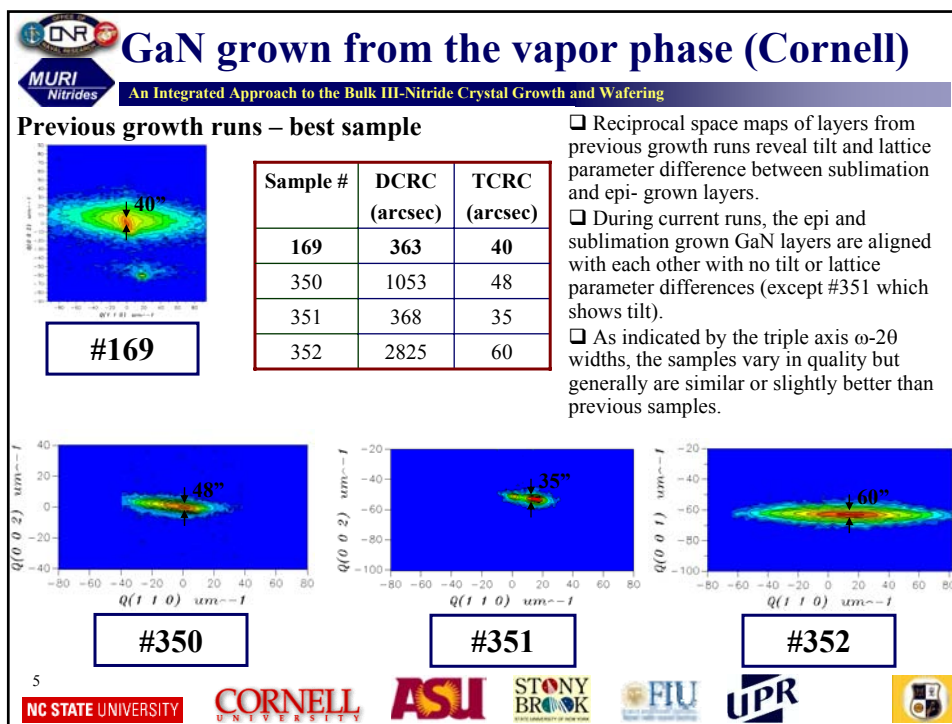
GaN grown from the vapor phase (Cornell)
 An Integrated Approach to the Bulk III-Nitride Crystal Growth and Wafering

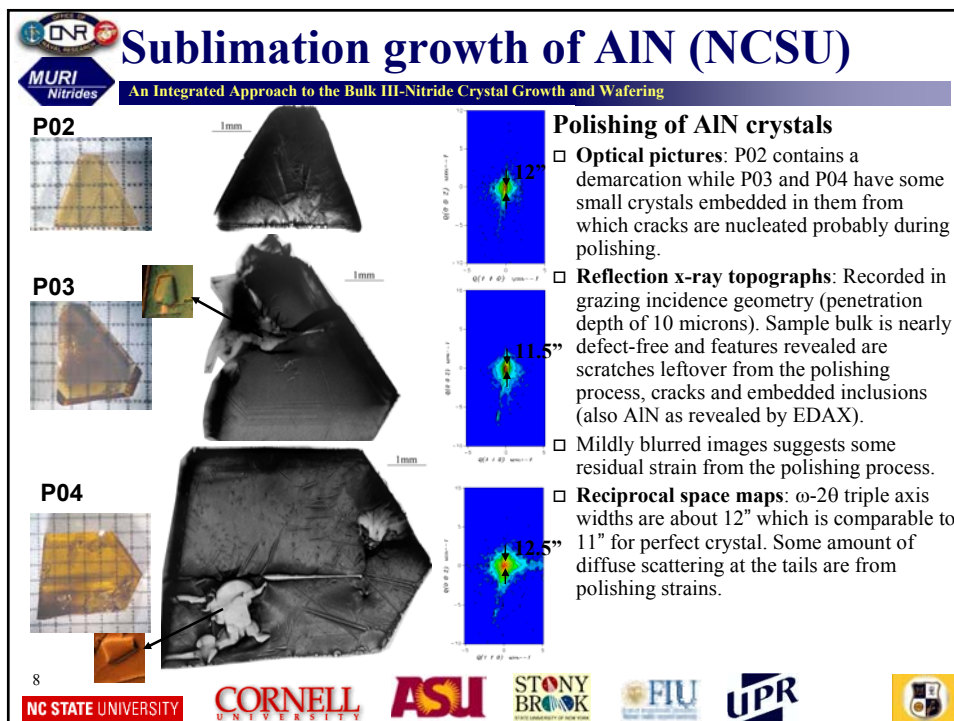
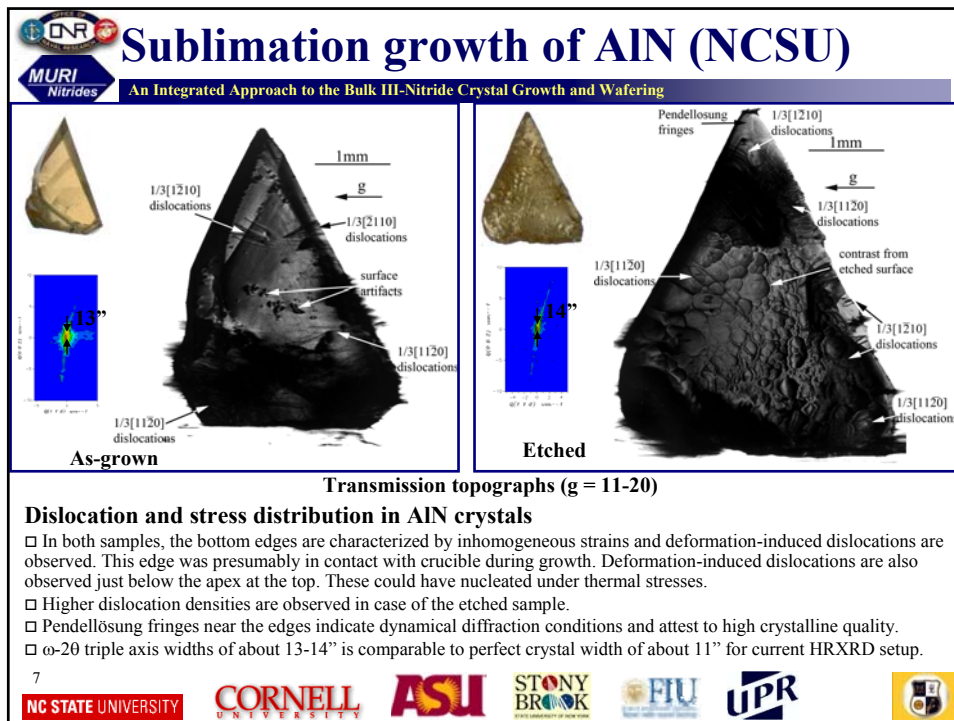
Sublimation growth using Ga_2O_3 powders

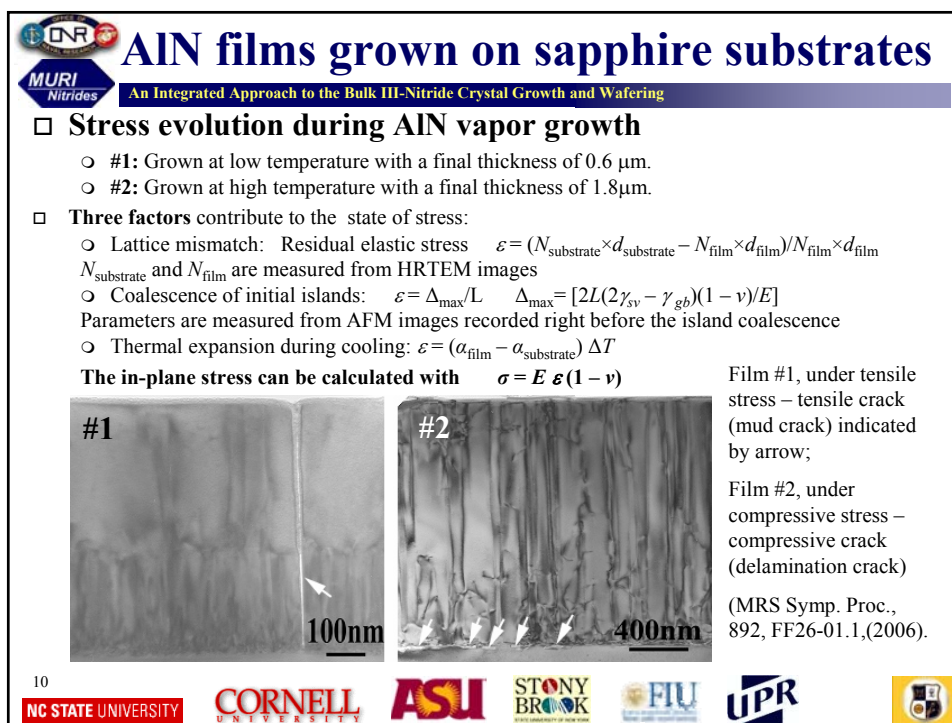
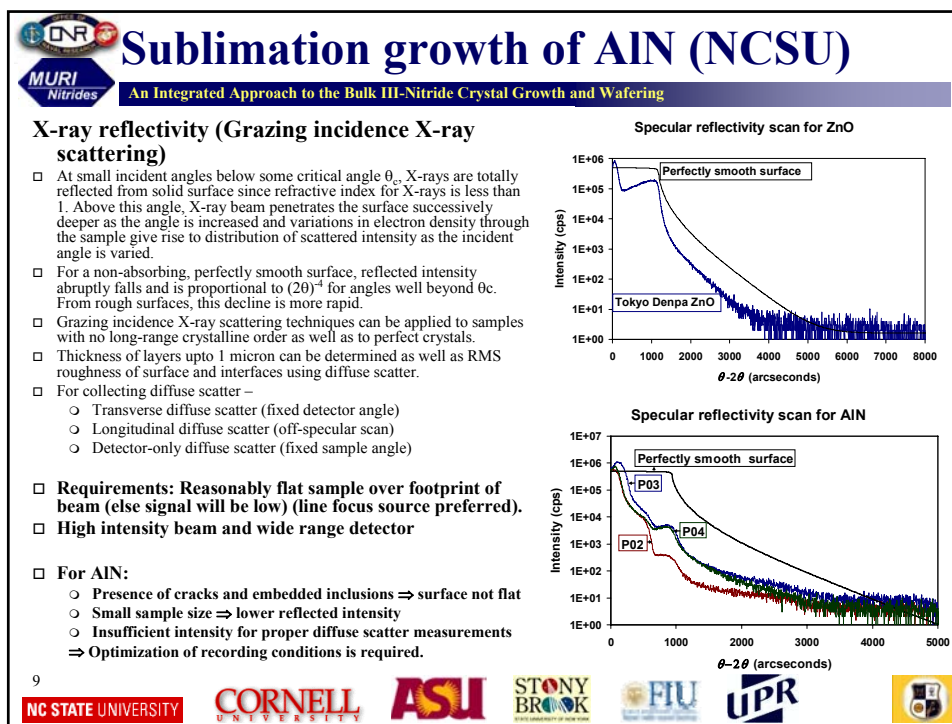
- Sublimation growth from GaN powders is hindered by formation of liquid Ga in the source, leading to rapidly decreasing growth rates. Further, it is surmised that GaN growth actually occurs by Ga transport in the form of Ga_2O (oxygen present in the source powder).
- Therefore, a new experimental setup to conduct growth using a mixture of Ga_2O_3 and graphite (carbon) powders as the source was designed. At the growth temperature, Ga_2O_3 reacts with carbon to produce Ga_2O which reacts with the ammonia gas to produce GaN.
- Typical growth conditions:
 - Seed temperature – 1100-1200°C; Source temperature - 1050-1130°C
 - Pressure - 600 torr; Carrier gas: Nitrogen (450 sccm);
 - Central tube: 10sccm ammonia + 90sccm nitrogen

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AIN films grown on sapphire substrates
 An Integrated Approach to the Bulk III-Nitride Crystal Growth and Wafering

Bending of threading dislocations driven by growth mode modification

- The V/III ratio was changed to ~11500 and the TMA and NH_3 flow rates were changed to ~9.6 and ~111500 $\mu\text{mol/min}$, respectively at the sub-interface.
- Large kinks or dipole half loops formed at the sub-interface.
- Threading dislocation density dropped by a factor of three at the sub-interface.
- The dislocations which experience bending are predominantly of pure screw or mostly screw character.

Reorientation of a screw type TD (J. Bai *et al* APL, 88,051903,2006)

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GaN films grown on on-axis and vicinal SiC substrates with AIN buffer
 An Integrated Approach to the Bulk III-Nitride Crystal Growth and Wafering

- **Sample #1:** on-axis (misct $< 0.1^\circ$)
- **Sample #2:** offcut by 3.5°
- FWHM of #2 is only half of that in #1: Vicinal GaN has much higher crystalline quality.
- **Strain relaxation (lower figure):**
 - **Vicinal sample #2:** GaN fully relaxed with a uniform lattice constant. Slight compression in AIN
 - **On-axis sample #1:** GaN with compressive strains and graded lattice constants. The compressive strain of AIN is three times that of #2.
- **Advantage of VSE: Higher crystalline quality, facilitating rapid and smooth strain relaxation at the interface (X. Huang *et al* PRL, 95, 086101-1 (2005); APL, 86, 211916, (2005)).**

Double-axis rocking curves of on-axis sample (#1) and vicinal sample (#2) - quite different!

Triple-axis rocking curves (d-spacing scans)

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GPMD-driven Strain Relaxation Mechanisms in the vicinal system
 An Integrated Approach to the Bulk III-Nitride Crystal Growth and Wafering

High resolution TEM and reconstructed FFT images of the AlN/6H-SiC interface

- **GPMD: Geometrical partial misfit dislocation**
 GPMDs accommodate the lattice mismatch and stacking sequence mismatch simultaneously! More energetically favorable.
- **Practical importance:** Offcut angle determines step density, the latter determines GPMD density. So by optimizing the offcut angle one can let the GPMDs alone fully relax mismatch without the formation of other defects.
- **Theoretical optimal offcut angles:**
 - AlN/6H-SiC: 2.8° ($\Delta a/a = 1\%$)
 - GaN/6H-SiC: 9.7° ($\Delta a/a = 3.5\%$)

(a) Formation of GPMDs at 2H/6H interface steps. (b) Gradual transition of the stacking sequence of a 60° GPMD connecting the A and C stacking layers on a B layer. Dashed circles represent the original stacking positions without deformation. (c) "Symbol change" above a GPMD with no vertical boundary.

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Overview of Results
 An Integrated Approach to the Bulk III-Nitride Crystal Growth and Wafering

- **Ammonothermal grown GaN single crystals:**
 - A series of HVPE GaN substrates to be used as seeds for ammonothermal growth have been systematically studied to map their defect distributions in order to facilitate separation of defects due to growth from defects due to propagation from seed.
- **GaN layers grown from the vapor phase:**
 - Several samples grown using the new experimental setup with Ga_2O_3 source have been characterized.
 - Growth optimization has eliminated the tilt and lattice parameter differences between sublimation and epi layers.
- **AlN boule grown from seed in RF reactor:**
 - Gradual increase in defect densities and inhomogeneous strains during growth suggest an increasing impurity incorporation.
- **Polishing of AlN crystals**
 - A combination of SWBXT, HRXRD, AFM and x-ray reflectivity has been used to analyze the polished surface of AlN crystals. Surfaces are characterized by some scratches and mild residual strains.
- **AlN films grown on sapphire substrates**
 - Bending of screw dislocations driven by growth mode modification leads to mutual annihilation and reduction in threading dislocation density.
- **GaN films grown on on-axis and vicinal SiC substrates with AlN buffer**
 - GPMDs accommodate the lattice mismatch and stacking sequence mismatch simultaneously. By optimizing the offcut angle, GPMDs alone fully relax mismatch without the formation of other defects. Optimal offcut angles have been theoretically determined for AlN and GaN on 6H-SiC.

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MURI
Nitrides

Work plan for next 6 months

An Integrated Approach to the Bulk III-Nitride Crystal Growth and Wafering

Ammonothermal grown GaN single crystals (Hanscom):

- ☐ Structural defect characterization of ammonothermal layers grown on HVPE GaN crystals (already characterized by SWBXT and HRXRD).
- ☐ SEM and TEM studies of cross-sectional samples to investigate the nature of the interface (impurities, voids, presence of oxide layer, etc.) and defect generation and propagation.

GaN layers grown from the vapor phase (Cornell):

- ☐ Continued structural characterization of GaN layers grown from Ga₂O₃ source under different growth conditions to further optimize conditions for growing high quality layers.

AlN grown from the vapor phase (NCSU):

- ☐ Detailed characterization of wafers sliced from AlN boules and correlation with growth conditions as well as modeling predictions.
- ☐ Evaluation of polished AlN samples using a combination of SWBXT, AFM and grazing incidence x-ray scattering.

☐ **Systematic study of the relationship between the quality of GaN epilayers and the off-cut conditions of the substrate (both SiC and sapphire) using HRTEM, HRXRD and strain modeling.**

☐ **For GaN samples: Correlation of X-ray and TEM observations with PL measurements (from Prof. Skromme).**

☐ **For AlN samples: Correlation of HRXRD results with reflectance measurements (from Prof. Skromme).**

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An Integrated Approach to the Bulk III-Nitride Crystal Growth and Wafering

Identification of Inversion Domain Boundaries in AlN Layers and their Influence on Optical Properties

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Outline

An Integrated Approach to the Bulk III-Nitride Crystal Growth and Wafering

- ☐ Introduction
- ☐ Properties and microstructures of AlN layers
- ☐ Identification inversion domain boundaries (IDBs)
- ☐ Optical properties
- ☐ Summary

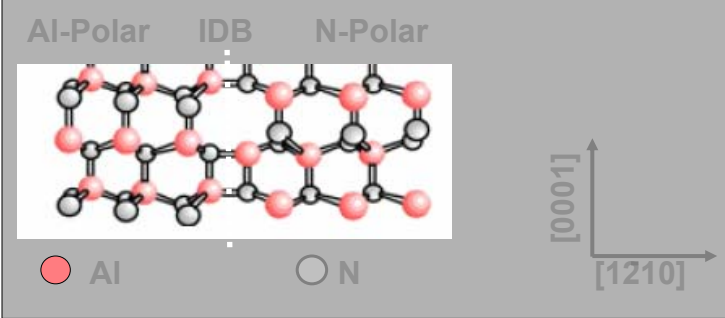
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Introduction
An Integrated Approach to the Bulk III-Nitride Crystal Growth and Wafering

□ Structure of an IDB



Atomic Structure of an inversion domain boundary

□ Schottky barrier height on group III-polar surface is higher and leakage current is lower

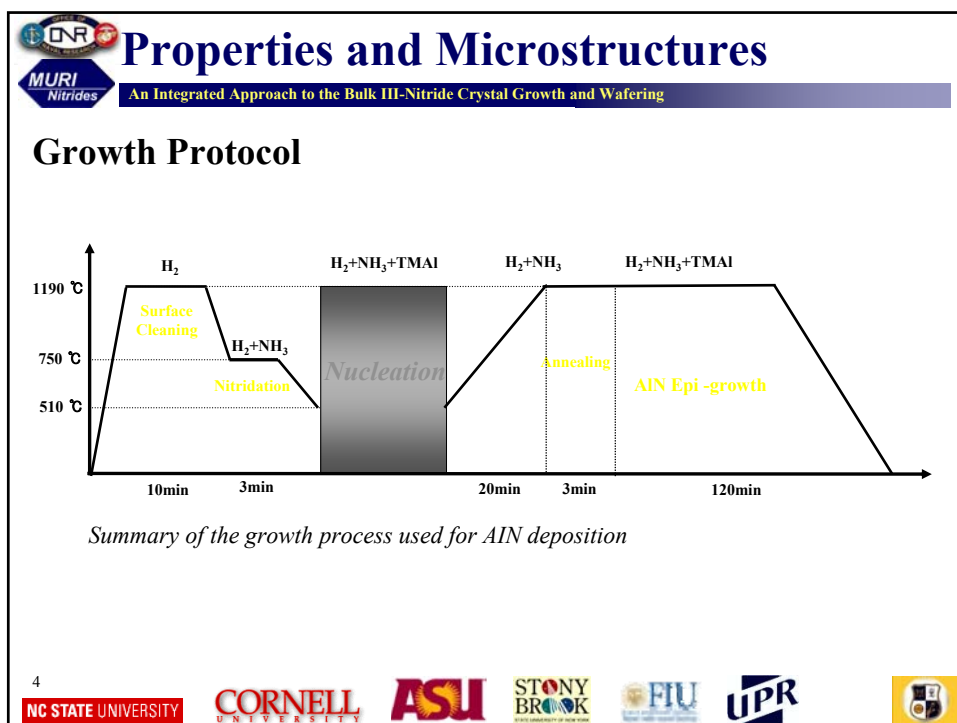
□ Photoluminescence properties of group V-polar films grown by MOCVD are better than group III-polar films











Properties and Microstructures (Cont'd)
 An Integrated Approach to the Bulk III-Nitride Crystal Growth and Wafering

□ Growth Conditions

Set I		Set II	
Sample ID	Condition	Sample ID	Condition
031114B	460°C 1min	040123A	510°C 15sec
031108B	510°C 1min	040127A	510°C 30sec
031105A	560°C 1min	031108B	510°C 60sec
031022B	670°C 3min	040113A	510°C 90sec
031029A	890°C 7min	031214B	510°C 120sec

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Properties and Microstructures (Cont'd)
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□ XRD FWHM

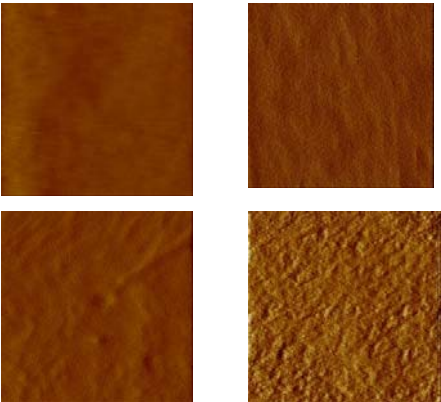
XRD FWHM of AlN films as a function of NL growth temperature and time

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Properties and Microstructures (Cont'd)
 An Integrated Approach to the Bulk III-Nitride Crystal Growth and Wafering

□ Surface Morphology of Nucleation Layers



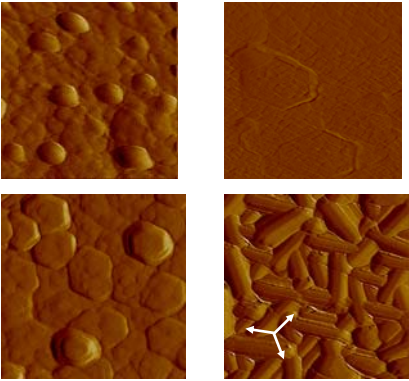
AFM images (1x1 μm) of as-deposited NLs as a function of nucleation temperatures (a) 460 °C (b) 510 °C (c) 560 °C (d) 670 °C

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Properties and Microstructures (Cont'd)
 An Integrated Approach to the Bulk III-Nitride Crystal Growth and Wafering

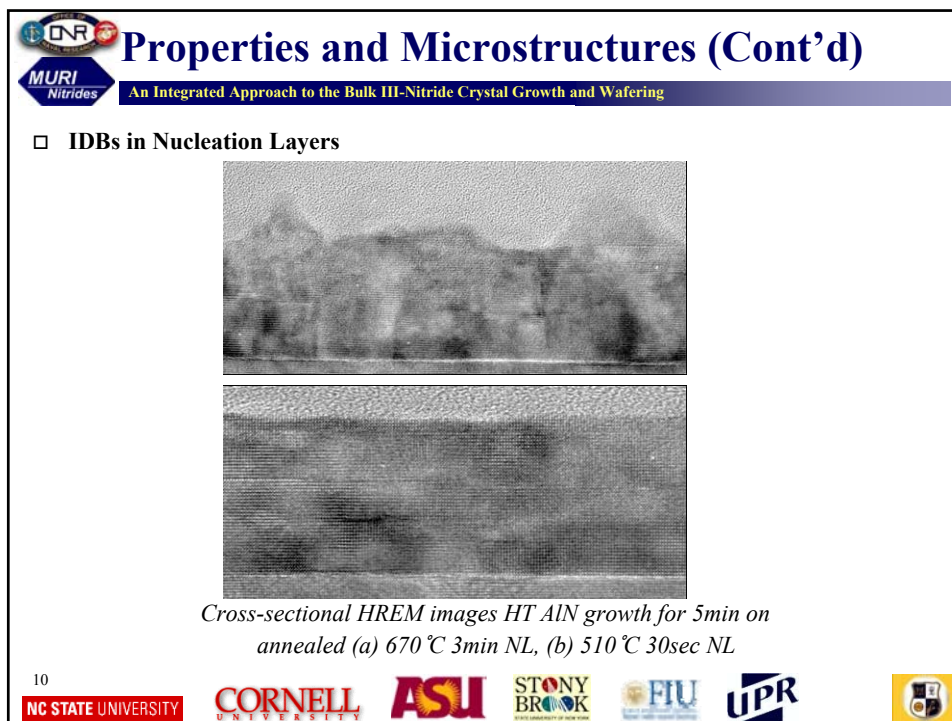
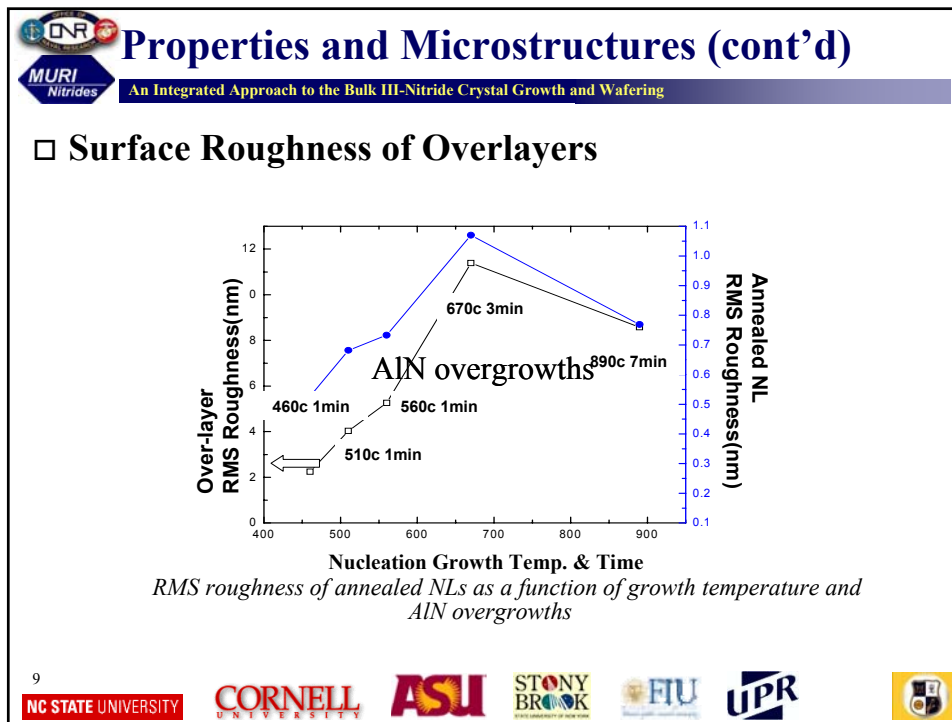
□ Surface Morphologies of Overlays



AFM images (1x1 μm) of AlN overlayer as a function of nucleation temperatures (a) 460 °C (b) 510 °C (c) 560 °C (d) 670 °C

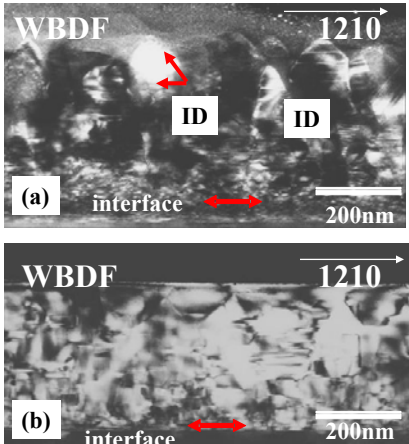
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Properties and Microstructures (Cont'd)
 An Integrated Approach to the Bulk III-Nitride Crystal Growth and Wafering

□ IDBs in Overlayers



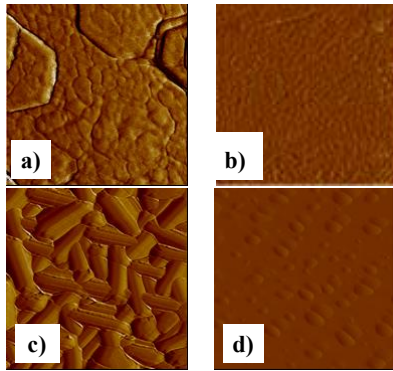
WBDF images HT AlN growth for 2 hours on annealed
 (a) 670 °C 3min NL, (b) 510 °C 30sec NL

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Properties and Microstructures (Cont'd)
 An Integrated Approach to the Bulk III-Nitride Crystal Growth and Wafering

□ KOH Etching Response of Overlayers

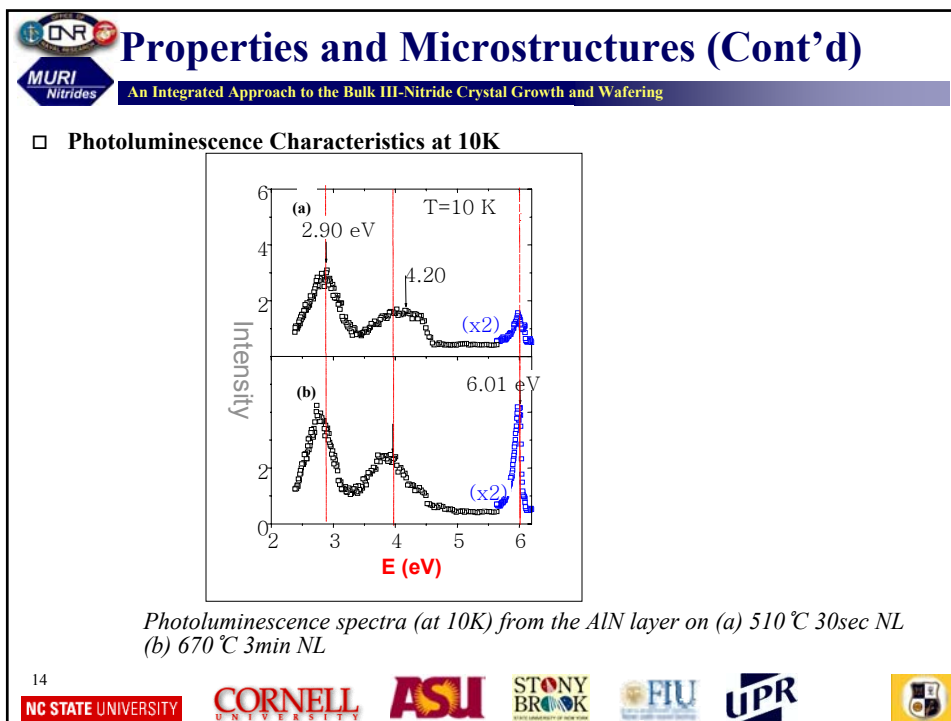
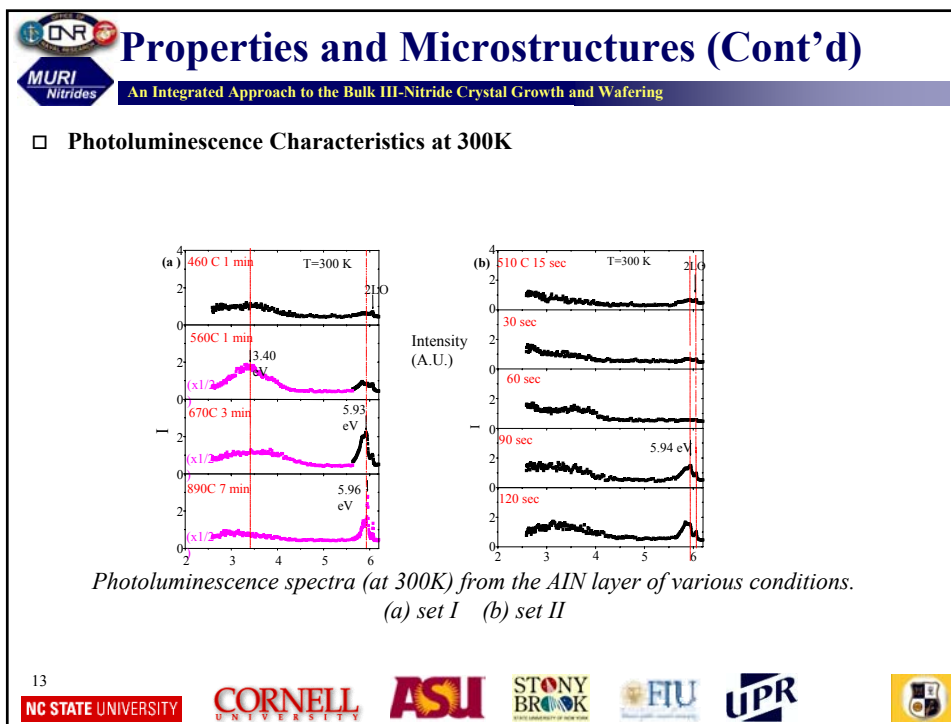


AFM images (a) as grown and (b) etched AlN on 510 °C 30sec NL
 (c) as grown and (d) etched AlN on 670 °C 3min NL

- RMS roughness changes from 1.69 in (a) to 0.98 nm in (b)
- RMS roughness changes from 11 nm in (c) to 5 nm in (d)

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Summary

An Integrated Approach to the Bulk III-Nitride Crystal Growth and Wafering

- Nucleation layer growth conditions influence the formation of IDBs in AlN
- IDBs can be identified by chemical etching
- Presence of IDBs enhances band-edge emission in AlN layers.

15



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