Interim Report

An Integrated Approach to III-Nitride Crystal Growth and Wafering

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13. ABSTRACT (MAXIMUM 200 WORDS)

Centimeter size, transparent AlN crystals were grown at NCSU. TEM and XRT examination performed at ASU and SUNYSB revealed that the crystals are of highest quality and do not contain any visible extended defects. GaN crystals grown at Clemson by ammonothermal growth method have been grown to up to 5 mm in size. PL studies at ASU showed sharp excitonic emission, indicative of good quality. XRT showed mosaicity in some crystals. Work at Cornell was focusing on the development of equipment. A sandwich type reactor for vapor growth of GaN and a reactor for flux based growth are near the completion. Reaction modeling efforts have identified equilibrium species in the AlN sublimation growth while the reactor modeling has developed thermal model for the high temperature AlN reactor and flow dynamics for the ammonothermal growth.

14. SUBJECT TERMS

AlN, GaN, ammonothermal growth, bulk crystal growth, flux growth, sublimation growth

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Ab initio Characterization of Gas-Phase Environments for Vapor Deposition Conditions

D.W. Brenner, Co-PI
Yanxin Li, Graduate Student

Objectives

Long Term: Help guide experimental growth studies by predicting optimum growth conditions for AlN and GaN crystals using molecular simulation methods

Steps Toward Long-Term Goal:

- **Characterize gas-phase reactor species, including impurities, and understand their dependence on growth conditions using ab initio methods:**
  -Preliminary results: Equilibrium calculations using ab initio data predict that non-stoichiometric gas-phase Al_3N and Al_4N species are present under vapor deposition conditions
- **Provide data for reactor modeling studies at Stony Brook**
  -Both free energies and kinetic rate constants from quantum chemistry
- **Understand role of growth conditions and species on crystal microstructure, defect density, habit.**
  -Kinetic Monte Carlo simulations for nitrides being developed
  -Rates from ab initio data, simulation timescales to match experimental conditions (e.g. gas-surface collision frequencies)

Model and Strategy

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

Calculating Free Energies

(1) Calculate from first principles:
- ground state electronic energies
- geometries/moments of inertia
- vibrational frequencies
- spin states (for electron degeneracies)

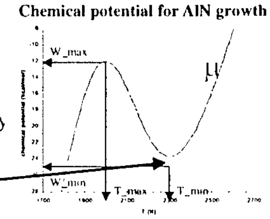
(2) Input to molecular partition functions ➡ entropies +enthalpies = Gibbs Free Energies

(3) Use free energies to predict equilibrium concentrations and chemical potential

Free Energy Growth Model

- Single crystal deposition requires gas-phase flux of fixed composition, suggesting a gas-phase intrinsic stability in the proximity of the growth surface.
- Use chemical potential μ as a measure of stability minimum μ taken as growth T

Chemical potential for AlN growth



Growth temperature
experiment: 2223±150K our model: 2300K

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Gas-Phase Growth Precursors

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

Free energy G(T) for 43 species related to AlN growth initially considered at a relatively low level of *ab initio* theory:

Complete set

16 "Pure" Species:

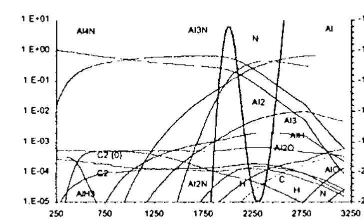
Al, N, Al_2, N_2, AlN , Al_3N, Al_3, N_3, AlN_2, NAlN, AlN_3, Al_2N, Al_4N, Al_2N_2, Al_3N_2, Al_4N_2

27 "Impurity" Species:

H, O, C, H_2, O_2, C_2 (Σ=0), C_2 (Σ=1), AlH, AlH_2, AlH_3, NH, NH_2, NH_3, AlO, AlO_2, Al_2O, AlNO, OH, H_2O, HNO, HONO, NO, NO_2, N_2O, AlHNH, AlH_2NH_2, AlH_3NH_3,

Predicted Concentrations v. temperature

N2 500 tor H2O 500ppm



Predicted Majority Species: Al, N, N_2, Al_3N, Al_4N, AlH, Al_2O

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Appropriate ab initio Theory

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

Experimental and Calculated Formation enthalpies at 298K

(From NIST)

		Density Functional				Composite Hartree Fock				
	exp.	B3LYP/c c-pVTZ	B3PW91 /cc-pVTZ	MP2FC/ cc-pVTZ	B3LYP/ 6-311G*	CBS-Q	G3	G2	G2M2	G1
Al_2	158 7	118 4	138 9	-146.5	113.7	-123	-124	-131	-132.5	-131 4
AlH	288 6	297 8	287 4	280 5	294 1	304 1	304	305	305 6	304 9
NH	332 2	349 6	341 2	303 8	334 5	328 7	338	330	328 6	326 8
OH	427 8	429	423 9	413 3	402 4	429 4	431	429	429 6	423 9
H_2	436	439 6	418 4	411 6	430 9	440 7	438	441	440 5	436 9
AlH_2	489 2	504 9	498 7	481	497 9	504 4	500	501	498 9	498 7
O_2	498 4	511 4	516 7	520 7	502 9	498 1	491	485	486.8	484 4
AlO	512 3	492 3	484 8	441 7	474.6	507 6	511	499	502.9	509 9
NO	631.6	640 3	634 4	620 3	629 5	633 3	630	634	no dala	631 9
NH_2	718 3	712 2	726 7	618 3	710 1	718 4	722	720	719.7	713.4
HNO	832 8	833 7	824.8	818.6	813 9	832 7	828	836	839 3	832.4
AlH_3	855 1	852.3	834 9	817 6	842 4	860 3	854	861	857 6	859.4
H_2O	927	909 3	903 4	911.1	858 3	926 6	924	927	930.3	916 9
NO_2	936 8	958	941	951 6	939 5	945.6	934	938	943 5	935 5
N_2	945 4	947 6	931 1	948.4	931 8	936 9	937	940	940 7	944 3
N_2O	1112.9	1134 9	no dala	1151 8	1209 8	1111	1104	1109	1103 7	1110
NH_3	1172 6	1179 3	1163.5	1128 8	1140 5	1168	1169	1172	1172 3	1162

HF methods inappropriate for Al_2

B3PW91 density functional yields best overall comparison to experiment
(our calculations added diffuse functions to basis set)

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Gas-Phase Growth Precursors

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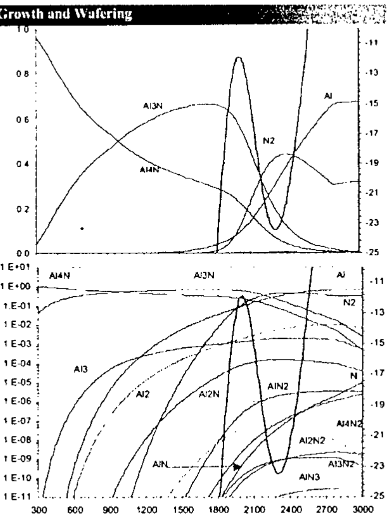
Gas-Phase Concentration Profile
(500 torr N_2, no impurities)



Predicted Dominant Species:
Al, N_2, Al_3N, Al_4N

Al_3N/Al_4N Formation Mechanism:

$Al_2 + N_2 \underset{\longleftarrow}{\overset{T<395K}{\longrightarrow}} AlNNAl + Al \overset{T<1550K}{\longrightarrow} Al_2NNAl$

$Al_2NNAl + Al \overset{T<2150K}{\longrightarrow} Al_4N_2 + Al_2 \overset{All\ T}{\longrightarrow} 2Al_3N$

Feed gas T=298K

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Six Month Plan of Work

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

- Model effect of impurities, especially oxygen, on the composition and chemical potential of gas-phase growth environments
- Explore influence of partial pressures on growth environment
- Implement atomic-scale kinetic Monte Carlo simulations of AlN deposition
- Connect *ab initio* data to reactor modeling

Modeling of Bulk AlN/GaN Vapor Growth

Bei Wu and Hui Zhang
Department of Mechanical Engineering,
SUNY at Stony Brook
Stony Brook, NY
and
V. Prasad
Florida International University
Miami, FL

Milestones and Goals

Goals – To build a thermodynamic, kinetic and reaction-transport model for sublimation, condensation, nucleation, reaction, and crystal growth of III-nitride crystals.

Short Team (one-year)

- Develop a macroscopic model for furnace design
- Develop a microscopic model at growth interface
- Simulations of AlN/GaN growth
- Model validation

Long Team (five-year)

- Integrated with an atomistic model (second year)
- Understand growth habit and defect formation
- Improve throughput and yield
- System optimization and control

Strongly-Coupled, Transport and Reaction Model for GaN / AlN Bulk Growth

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

Electromagnetic / Radiation calculations ⇓		
Heat generation in the heater ⇓	⇒ ⇐	Power generation Heating system design/up-scale Optimization
Thermodynamic calculations ⇓	⇒	GaN and AlN growth kinetics ⇐
Temp. in system / Op. conditions ⇓	⇔	vapor species and pressure ⇑
III-nitride / graphite elements ⇓	⇔	Heat/mass transfer and gas reaction ⇑
Sublimation/decomposition ⇓	⇔	Phase change / chemical reaction ⇑
Species transport ⇓		Vapor transport and reaction ⇑
Crystallization/Deposition	⇔	Habit, Defects, Stress, Reaction Kinetics

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Research Challenges

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

- Heat generation by induction or resistant,
- Heat and mass transfer in the growth furnace,
- Sublimation/decomposition, and chemical reaction in the source materials,
- Vapor transport and chemical reaction,
- Interplay between surface kinetics and vapor transport
- Morphological stability at the growth interface,
- Deposition, habit, faceted, stresses and defects,
- Stoichiometric, segregation and uniformity,
- High-fidelity representation of system geometry, and
- System integration, optimization, and control.

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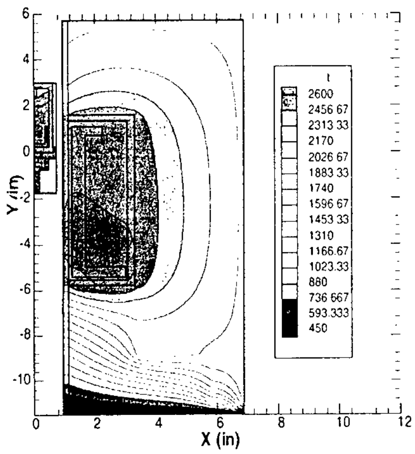
Global Heat Transfer in an AlN Growth System

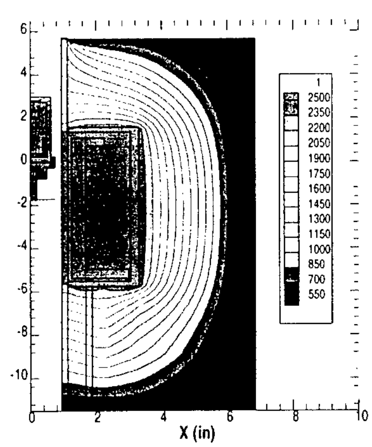
An Integrated Approach to the Bulk III-Nitride Crystal Growth and Wafering



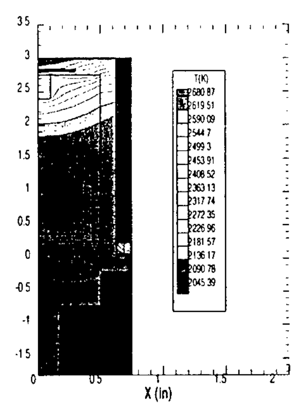
- Continuity Equation
- Conservation of Momentum
- Conservation of Energy
  - Convection
  - Radiation
  - Resistant heating system
- Species Transport
  - Transport and Kinetic
  - Reaction
- Growth Rate Model
  - Deposition
  - Sticking

Global Heat Transfer for AlN Growth System

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



Temperature distribution in the entire system



Temperature distribution in the furnace

Interrelationship between Furnace and Heater

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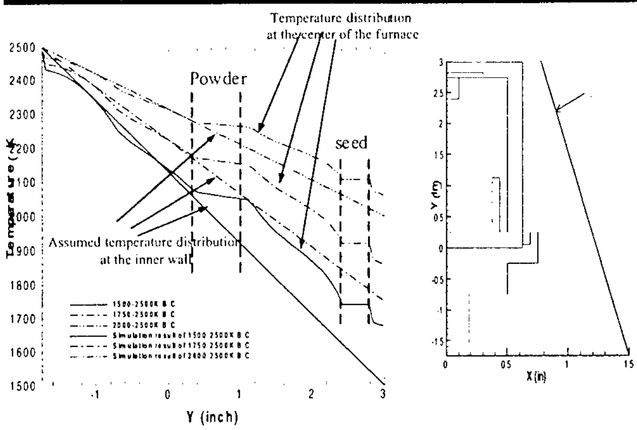

Conclusion: Temperature gradient in the furnace is strongly function of the temperature profile at the inner wall of the heater. Re-design of the heating zone is needed to improve the temperature gradient in the furnace.

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SWBXT of AlN Sample and Thermal Stress Distribution

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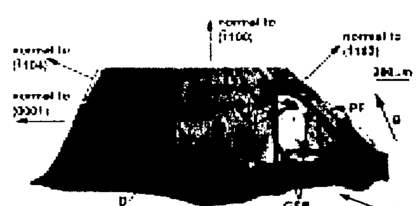
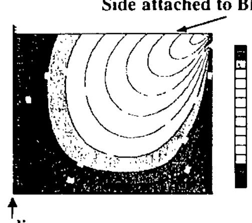
X-ray topograph is obtained from M. Dudley



An anisotropic thermal elastic model has been developed to link the dislocation density with stress distribution. High stress appears near the wall, and stress density is function of the sample thickness and temperature gradient in the furnace.



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Modeling for a vertical HVPE GaN Growth

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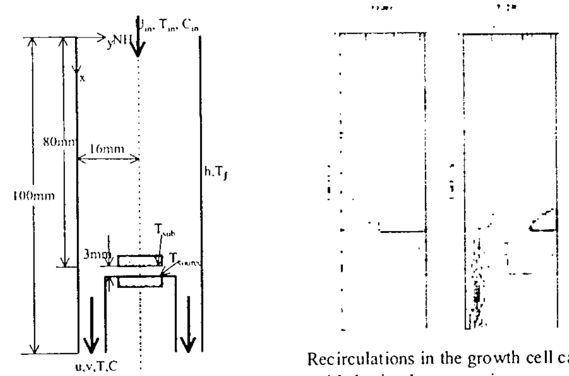

New GaN growth furnace at NCSU will be a horizontal one.

Recirculations in the growth cell can be avoided using low operating pressure and susceptor rotation

Wu, B., and Zhang, H., 2001, "Intensity and Uniformity of Gallium Nitride Deposition in Sublimation Sandwich Growth," Proceedings of 2001 ASME International Mechanical Engineer Congress and Exposition, November, New York.

Research Roadmap for an Integrated Model

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

GaN Crystal Growth

	Transport Mechanism	Physical Mathematical Description	Crystal Inhomogeneties
Crystal	Diffusion, radiation	Diffusion laws for solid	Polycrystalline, stress, defect
Vapor Transport	Stefan flow, species transport	Conservation laws	Growth rate and morphology
Charge	Sublimation, decomposition	Reaction heat, pressure balance	Polycrystalline, stoichiometry
Global Assembly	Heater, crucible, flow control	Radiation, magnetic potential, heat generation	Stress, defect, impurity

Kinetic Model + Reaction-Transport Model

Kinetic and Reaction Models will interface with Atomic Model developed at NCSU.
Transport Model will be validated with experiments at NCSU.
Prediction will be compared with characterization at USB and ASU.

Research Plan on Vapor Growth (Next 6 Months)

Mrs Bei Wu has worked on this project (full time). She is currently focusing on AlN growth. One more student at Stony Brook will be working on GaN growth (half time).

Numerical simulations of AlN bulk growth. The growth model of AlN bulk growth has been developed and used to determine the growth rates at different pressure, temperature and temperature gradient. Temperature distribution in the growth furnace has been predicted which will be compared with experimental measurements. Dr. Schlesser at NCSU will provide temperature profiles at the inner wall of the heater for three power levels and two gas flow rates. Temperature variation on the top surface of the furnace and temperatures at two locations inside the furnace will be measured and compared with simulation results. The agreement between modeling and experiment will give us the confidence on the model of the heating system. Simulations will help in redesign of the heating zone.

Numerical simulations of GaN bulk growth. The GaN growth furnace is developing at UCSB. New furnace is similar to the HVPE process. Preliminary simulation for a vertical HVPE system has been performed. The model can be used to simulate the GaN bulk growth at NCSU.

Stick coefficient is the key to link the macroscopic model developed at Stony Brook and atomistic model developed at Dr. Donald Brenner's research group. The future work will be focused on relating the growth morphology to the operating conditions.

Growth of Bulk GaN by Sublimation Technology

First Six Months

M.G. Spencer
Dept. of Electrical Engineering
Cornell University

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

Goals

- Understanding the general trends in GaN sublimation growth from a GaN powder source (and later liquid source) and gaseous $N_2/NH_3/H_2$ mixture;

- Analysis of the growth rate in a wide range of pressures and temperatures;

- Detection of key parameters governing the growth rate;

- Optimization of operating conditions and growth system design and experimental verification of predicted growth and sublimation rates

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Work Plan

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- Based on adaptor flange prepare detailed drawing for growth fixtures. (These growth fixtures will be SiC coated graphite)-finish date Nov 15, 2001
- Submit drawings for fixture manufacture-est. delivery date of fixtures Jan 15, 2001
- Thermal modeling of growth fixtures (Yuri Makov)-est. finish date Jan 15, 2001
- Initial startup and break in of growth furnace by vendors-est. finish date Dec 15, 2001
- Continued optimization and characterization of GaN powder growth process
- Start of characterization of sublimation rate of GaN powder under various growth conditions as modeled by Yuri Makrov-est. start date Jan 20, 2001
- Depending on VI start of growth experiments-est. start March 15, 2001

Personnel

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

- **Two P.I.'s-M. G. Spencer &Yuri Markov**
- **Two Graduate students-Phanikumar Konkapaka and Huaqiang Wu**
- **Part time technician support**

Equipment and Facilities Status

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

- New laboratory-construction completed May1
- GaN Powder furnace-construction (home built) completed July 30
- GaN Bulk furnace-delivery September 1
- GaN Bulk furnace-physical installation September 15
- GaN Bulk furnace-electrical installation expected Nov
- GaN Bulk furnace-gas panel construction, gas lines and vacuum expected finish in Nov
- GaN Bulk furnace-process adaptor flange delivery Sept 30
- GaN Bulk furnace-puller rod expected January

Powder furnace process tube

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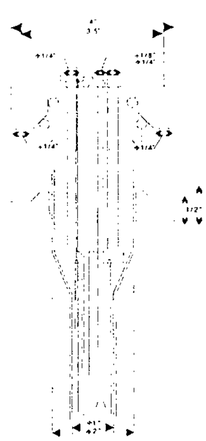

- Utilize bubbling through Ga liquid
- Two successful powder runs
- One major design revision implemented another design revision in progress

Powder Characterization

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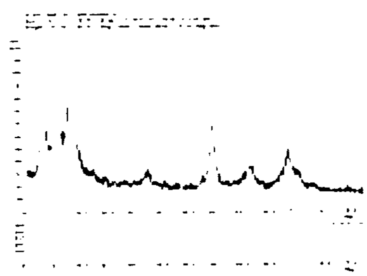
- X-ray diffractometry confirms that powder is GaN
- Cathodalumenescense is observed from the powder
- Crystal size is estimated at 200-250 angstroms
- Measurements of particle size are underway



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Model used for growth rate prediction

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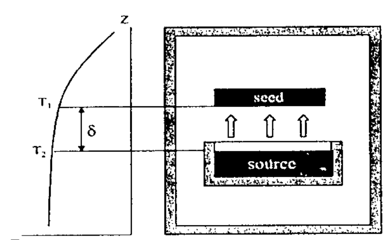
Geometry parameters: δ, R_s, R_c ;
Operating parameters: P_{tot} , T_1 , $\Delta T=T_2-T_1$, gas composition in the ambient;
Species involved in mass transport computations: Ga, N_2, NH_3, H_2, GaH, GaH_2, and GaH_3 .



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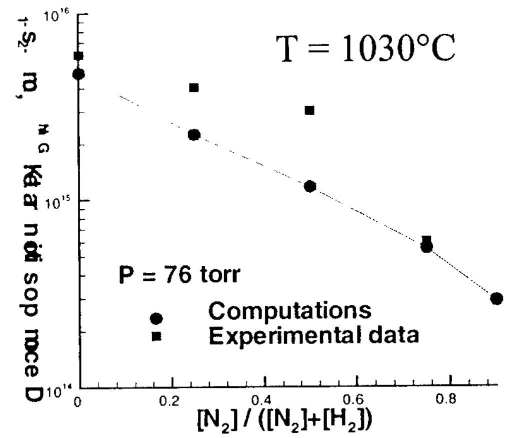
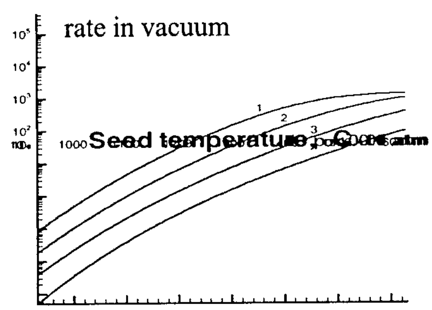
GaN annealing (Koleske, 1999)

GaN decomposition rate K_{GaN} as a function of vapor composition



The value K_{GaN} = 1.23_10^{15}cm^{-2}s^{-1} corresponds to the sublimation rate of ~1_m/h.



Operating conditions:
ΔT = 0 K, δ = 3 mm.

Sublimation rate in a nitrogen atmosphere

Temperature dependencies of sublimation and growth rates

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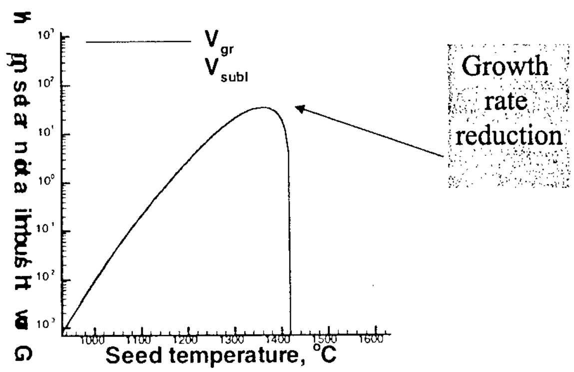

Operating conditions: $\Delta T = 10K$, $\delta = 3$ mm, $P_{tot} = 0.1$ atm, ambient composition is $80\% N_2$, $20\% NH_3$

Effect of pressure and gas composition

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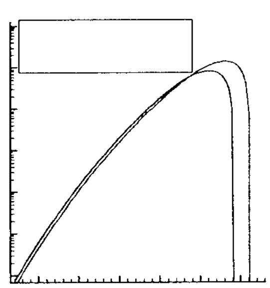
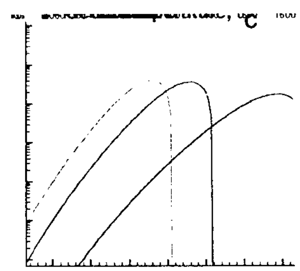
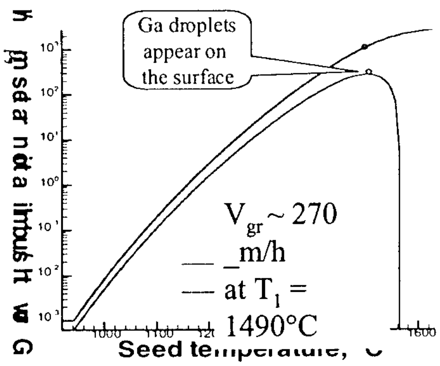
GaN growth rate as a function of pressure





GaN growth rate as a function of gas composition in the ambient

Growth rate at the "optimized" operating conditions



Operating conditions:
ΔT = 20 K, δ = 5 mm,
P_{tot} = 0.1 atm, NH_3 ambient gas

Further pressure lowering results in droplet disappearance and growth rate increase.

Growth of AlN from the vapor phase

Raoul Schlesser, Rafael Dalmau, and Zlatko Sitar

Dept. of Mat. Sci. & Engr., NCSU

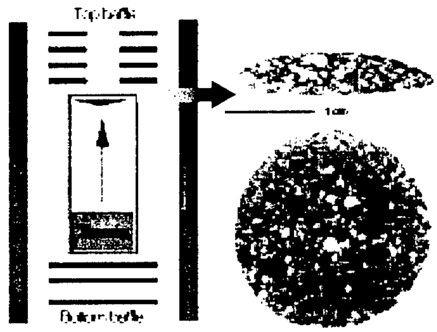
Outline

- **Current status of experimental work**
  - **Optimization of reactor temperature profile**
    - Control over temp. gradients using BN baffle structures
    - Introduction of radial gradient to prevent wall nucleation
  - **Growth results for varying temp. gradients**
    - Crystal morphology for small and large gradients
    - AlN recondensation data
  - **Cathodoluminescence results**
  - **Crystal polishing**
    - Initial results
- **MURI team interactions**
- **Research plan**

Hot zone temperature distribution

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

- Reactor hot zone temperature gradients have been accurately determined by pyrometer measurements.
- Baffle structures have been designed and manufactured to allow variation of longitudinal temperature gradient in a wider range (0.5°C/mm .. 5 °C/mm).
- Introduction of a radial gradient in the growth plane inhibits spontaneous nucleation on crucible walls and enables seeded growth of free-standing, stress-free crystals.

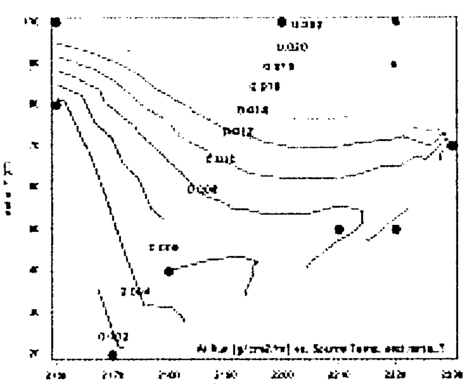


Longitudinal and radial temperature gradients in reactor hot zone (left) and AlN (right) deposited by spontaneous nucleation in a radial gradient enhancing growth in the center of the crucible and suppressing wall nucleation. Growth rate in center: 270 μm/hr.

AlN recondensation vs. ΔT

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

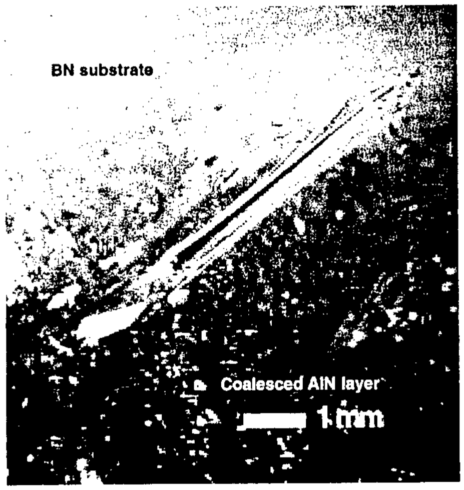
- AlN recondensation has been measured as a function of source temp. and temp. difference between source and seed.
  - recondensation increases with source temp.
  - recondensation increases with temp. gradient.
  - Colder deposition area reduces Al losses into reactor when using open crucibles.
  - Tightly closed crucibles improve growth rate in experiments with small temp. gradients.



Crystal morphology: small gradients

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

- In small temp. gradients (< 1°C/mm) deposition of coalesced AlN layers can be achieved.
- Needle growth, primarily in c-direction, occurs by spontaneous nucleation.
- Needle growth can be reduced by increasing Al vapor pressure (e.g. by using tightly closed crucibles).



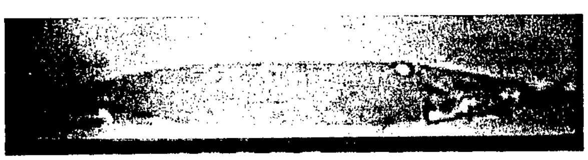
Example of a coalesced AlN layer deposited on BN in a gradient of 0.5 °C/mm, with needle grown on top of coalesced AlN layer.

Crystal morphology : large gradients

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

- Growth in larger temp. gradients (2-5 °C/mm) yields increased growth rates normal to the c-axis.

Growth around a threading dislocation (left) and a screw dislocation (right).

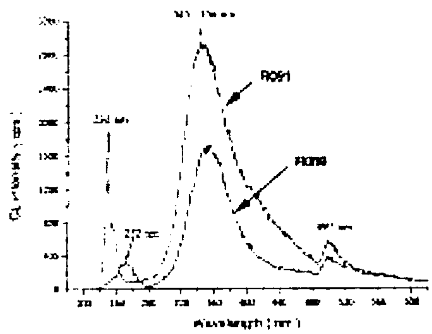


15 mm long c-platelet grown in 4 hours; source temp. = 2200°C, gradient = 3 °C/mm.

Cathodoluminescence

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

- o Cathodoluminescence spectra taken at 4.6K of two different AlN crystals
  - m Sample R089
  - m Sample R091
- o Sample R091 shows a sharp peak near bandgap energy
  - m band-edge to impurity level transition



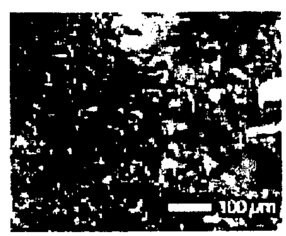
by R. Yakimova et al., Linkoping University, Sweden)

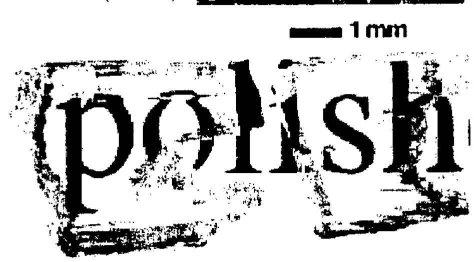
Polishing of AlN crystals

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

- o **Initial polishing work successful.**
- o **Typical polishing parameters:**
  - m 15 min, 240 grit SiC
  - m 1 hr, 600 grit SiC
  - m 1 hr, 5 μm Alumina
  - m 1 hr, 0.3 μm Alumina

Surface morphology after 30 min grinding with 600 grit SiC (right), and two crystals after final polishing step (bottom).



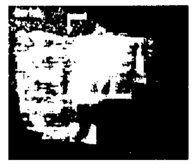


MURI Team Interactions

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

- **Samples sent for characterization to various MURI team members. Samples from representative growth runs were selected in an effort to correlate analytical results.**
  - **Dr. M. Dudley**
    - samples R089.2, R091-A
  - **Dr. B. Skromme**
    - samples R068-A, R068-D, R075-B, R088-A, R089.2, R091-A
  - **Dr. S. Mahajan**
    - samples R091-B, R089 (2 samples for TEM)
  - **Dr. J. Freitas**
    - samples R068-C, R075-A, R088-B
  - **Dr. A. Martinez**
    - source materials (AlN powders for XRD)
- **Cooperation with modeling teams**
  (Dr. H. Zhang, Dr. D. Brenner)
- **AlN seed preparation for ammonothermal growth**
  (Dr. J. Kolis)

R068-C



R075-B

R091-A

Research Plan (6 months)

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

- **Seed preparation:**
  - **Investigate growth of c-plates to be used as seed material.**
    - Gain control over growth in c-plane by growing in larger temp. gradients.
    - Increase surface area of spontaneously grown, thin c-platelets.
  - **Improve seed mounting technique.**
    - Improve thermal contact between the seed and crucible.
    - Optimize seed location and radial gradient to inhibit spontaneous nucleation.
- **Contamination issues:**
  - **Quantify contamination levels.**
  - **Investigate correlation between growth morphology and intentional contamination types and levels.**
- **Seeded growth:**
  - **Grow out c-platelets preferentially in c-direction.**
  - **Improve crystal purity.**

Sodium Flux Growth of GaN Crystals

Frank DiSalvo, Chris Hoffman, Koyota Uheda (as of Nov. 1) -
Dept of Chemistry, Cornell University

Hisanori Yamane - Tohoku University, Sendai, Japan

(10/31/01)

Our program is an outgrowth of developing flux growth methods for the preparation of single crystals of binary, ternary and quaternary nitrides.

Flux Growth of GaN Crystals

Scale-up of Na Flux Growth Method in Use at Tohoku Univ.

- **TSS Model HP Crystal Growing Furnace**
- **Pressure rating: 10^{-5} torr to 100 atmos.**
- **Temperatures up to 4000°C with RF heating**
- **0.81 cu. ft. internal volume**

- **Internal vessel to contain Na vapor (Cornell)**
- **Converting to resistance heating**

Flux Growth of GaN Crystals

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

Current Work

- If possible, a low vapor pressure flux would allow for an open crucible and possibly Czochralski growth techniques.

- Low melting/low vapor pressure: Cu, In, Ge, Sn, Pb, Bi
- Nitrogen activators: Mn, Fe, Co, Ni
- Nitrogen solubilizers/transporters: Li, Ca, Mg, Sr, Ba, La

Flux Growth of GaN Crystals

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

- Crystals from Tohoku University are being are being studied at ASU by Profs. Subash Mahajan and Brian Skromme.

Flux Growth of GaN Crystals

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

Work Plan for Next 6 Months

- New postdoc from Yamane Lab, Dr. Kyota Uheda arrives Nov. 1
- Continued studies of alternate fluxes
- New furnace testing
- First GaN crystal growth runs in large containers

Modeling and Simulation of Ammonothermal Growth

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

V. Prasad and Q.-S. Chen
Florida International University
CEAS 3430, 10555 W Flagler St.,
Miami, FL 33174
and
H. Zhang
Department of Mechanical Engineering,
SUNY at Stony Brook
Stony Brook, NY 11794-2300

Milestones and Goals

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

Goals – To analyze solubility and pressure dependence on fill and temperature, to build a thermal and mass transport model for ammonothermal growth of III-nitride crystals, and to optimize the growth conditions.

Short Term (one-year)

- Analyze pressure dependence on fill and temperature
- Develop a global model for thermal transfer, solute transfer, and growth kinetics.
- Develop a model for system design

Long Term (five-year)

- Analyze solubility dependence on mineralizer, fill and temperature
- Relate growth habit and defect formation to parameters, such as pressure, temperature difference, baffle opening
- Improve throughput and yield
- System optimization and control

Research Challenges

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

- Heat generation by resistant heating together with heat transfer in the system.
- Convection is highly coupled with heating conditions and baffle location, and is oscillatory and turbulent.
- Porous media flow.
- Dissolving, attack of nutrient by solvent.
- Temperature difference across the baffle to achieve supersaturation in the upper region.
- Supersaturation and deposition.
- Solubility coefficient with temperature.
- Crystallization, habit and defects.
- Irregular geometry, such as baffle, autoclave, seed and nutrient.

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Coupled Transport Model

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

Calculation ⇓		
Autoclave dimensions, ⇓	⇐	System optimization
Nutrient, solvent, ⇓	⇒	Chemical reaction
Thermodynamic analyses ⇓	⇐	Operating conditions
Pressure, temperatures ⇓	⇔	Conductive and convective heat transfer ⇓
Dissolving ⇓	⇔	Kinetics⇓
Species transport ⇓	⇔	Turbulent convection and porous media flow ⇓
Deposition ⇓	⇒	Habit, defects, stress

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Physical Properties in Ammonothermal Conditions

Conditions at ARFL: 70-90% NH_3 fill, pressure of 2-4 kbars, mineralizer of 1-2 N, temperature of 250-300°C, a typical run of 5-30 days, GaN platelets of 1mm in length.

Critical properties of Ammonia:

Tc=405.5K, Pc=11,280 kPa,

Properties of ammonia in ammonothermal conditions:

Reduced pressure and temperature:

Pr=2000/112.8=17.7, Tr=523/406=1.3

Viscosity and conductivity: $\mu / \mu_1 = 4.3$ $\quad k / k_1 = 5.0$

μ_1 and k_1 are the dynamic viscosity, and thermal conductivity at atmospheric pressure and same temperature (i.e. 250°C).

Governing Equations

- **Continuity Equation**

$$\frac{\partial(\varepsilon\rho_f)}{\partial t} + \nabla\cdot(\rho_f u) = 0 \qquad (1)$$

- **Conservation of Momentum**

$$\frac{\rho_f}{\varepsilon}\frac{\partial \mathbf{u}}{\partial t} + \frac{\rho_f}{\varepsilon}(\mathbf{u}\cdot\nabla)\frac{\mathbf{u}}{\varepsilon} = -\nabla p + \rho_f g\mathbf{k} + \nabla\cdot(\mu_e\nabla\mathbf{u}) - B[(\frac{\mu_f}{K} + \frac{\rho_f b}{K}|\mathbf{u}|\mathbf{u})] \qquad (2)$$

- **Conservation of Energy**

$$(\rho c_p)_e\frac{\partial T}{\partial t} + (\rho c_p)_f[(\mathbf{u}\cdot\nabla)T] = \nabla\cdot(k_e\nabla T) \qquad (3)$$

- **Species Transport**

$$\frac{\partial}{\partial t}(\rho\, c) + \nabla\cdot(\rho\,\mathbf{u}c) = D\nabla^2 c - B\alpha(c - c_0) \qquad (4)$$

Numerical Scheme

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

Momentum equation:

$$A_P u_P = (H_u)_P - \frac{fp}{fx} + A_P u_P^{0}$$

$$(H_u)_P = (a_E u_E + a_W u_W + a_N u_N + a_S u_S + b)/V_P + (A_P - a_P/V_P)u_P - A_P u_P^{0}$$

Pressure equation:

$$a_P p_P = a_E p_E + a_W p_W + a_N p_N + a_S p_S + b$$

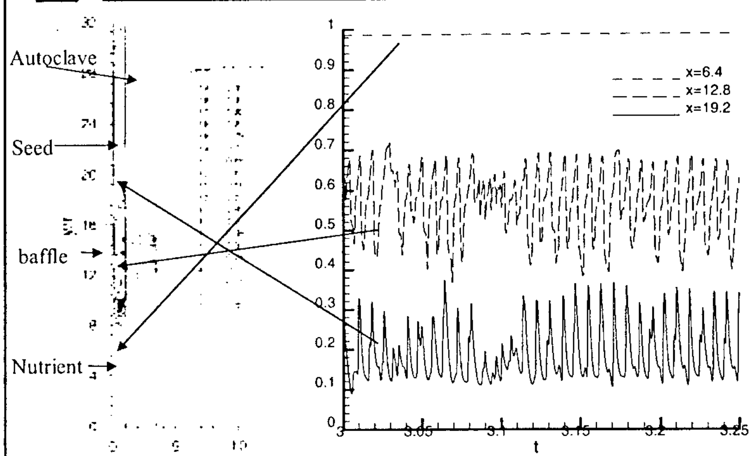
$$a_E = D_e \Delta\eta \qquad a_P = a_E + a_W + a_N + a_S \qquad D_e = [\rho\alpha_\xi/(h_\xi A_P)]_e$$

$$b = [(H_\xi h_\xi)_w / D_w + (\rho u_\xi \alpha_\xi)_w^{0}]\Delta\eta - [(H_\xi h_\xi)_e / D_e + (\rho u_\xi \alpha_\xi)_e^{0}]\Delta\eta$$
$$+ [(H_\eta h_\eta)_s / D_s + (\rho u_\eta \alpha_\eta)_s^{0}]\Delta\xi - [(H_\eta h_\eta)_n / D_n + (\rho u_\eta \alpha_\eta)_n^{0}]\Delta\xi + S_{NO}$$

- Pressure is obtained by solving Poisson Equation, and continuum is satisfied.
- Grid points: 157×47, time step: 0.002 S

Temperature Oscillation

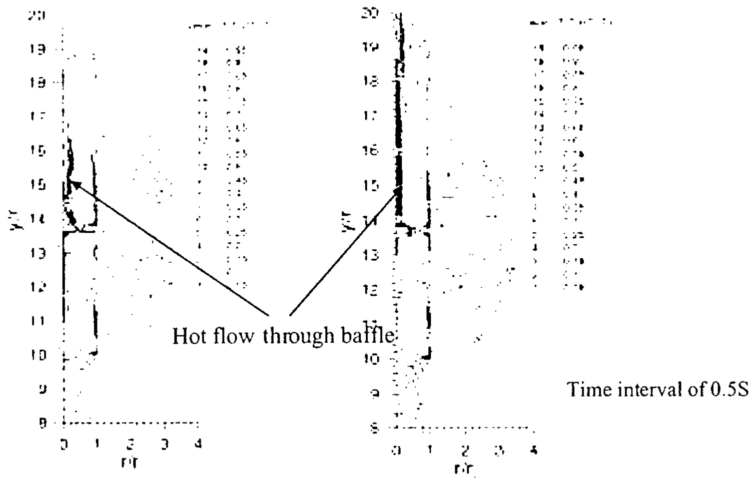
An Integrated Approach to the Bulk III-Nitride Crystal Growth and Wafering



Time scale: 464 S

Temperature Distribution at Different Times

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



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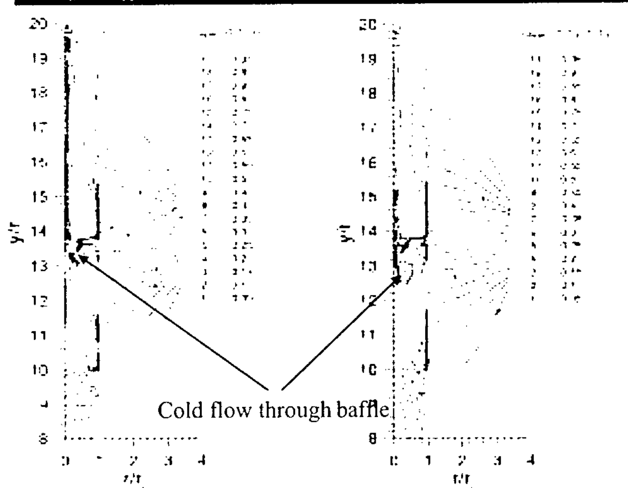
Temperature distribution at Different Times Con't

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



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Flow Field at Different Times

Time interval of 0.5S

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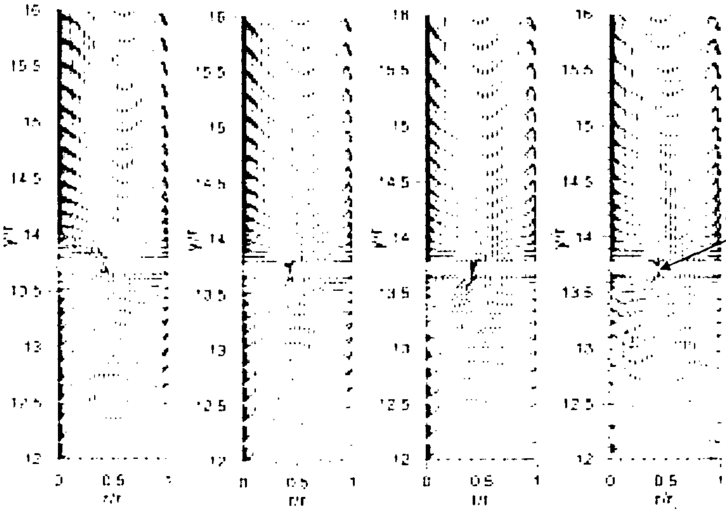

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Research Plan on Ammonothermal Growth

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

Dr. Qi-Sheng Chen at FIU is currently working on modeling and simulation of ammonothermal growth under the supervision of Dr. Prasad at FIU (moved recently from Stony Brook).

Modeling and Simulation of Ammonothermal Growth System at AFRL. We have developed a porous media based transport model which can simulate the fluid flow and temperature distribution in irregular domain with porous media. Calculations have been performed for the growth system at AFRL for which data were provided by Dr. Michael Callahan. We will continue to work with Dr. Callahan and provide simulation data to them for improvement of operating conditions.

Numerical Simulation of Growth System at Clemson. We will soon model the growth system at Clemson with the data provided by Professor Joe Kolis. The physical properties of ammonia, i.e., viscosity and conductivity, are obtained as a function of pressure and temperature. We will study the difference of transport mechanism between hydrothermal growth and ammonothermal growth.

Deposition of GaN in Ammonothermal Conditions. The solubility is related to solvent, temperature and pressure. The solubility coefficients of quartz and ZnO are usually positive in hydrothermal conditions. We will study the solubility coefficient of GaN in ammonothermal conditions and develop a growth model.

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

Growth of Bulk Group III Nitrides in Supercritical Ammonia

J. W. Kolis and E. W. Michaels

Clemson

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

Before April 2001

- GaN (powder) + KNH_2/KI → GaN (crystals)
- Crystals small (< 1mm) needles
- Conditions:

  Temperature: 600°C

  Pressure: 26.5 kpsi

  Density of NH_3: 0.67 g/mL

  Concentration of Mineralizer: $[KNH_2] = 0.4223M$

  $[KI] = 0.0052M$

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Mineralizer Optimization

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

- Both KN_3 and CsN_3 were synthesized successfully
- Ease of production and mineralization effectiveness of KN_3 have made it the mineralizer of choice
- GaN growth reactions have shown great improvement when 1.3M-1.6M KN_3 is used rather than KNH_2/KI or NaN_3
- Average GaN growth and transport over 14 days :
  - 2.28 mg using 1.3M NaN_3
  - 2.44 mg using 1.3M KN_3
  - 3.83 mg using 1.6M KN_3

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Effectiveness of Different Mineralizers

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

Mineralizer	T(°C)	Δm(g)	Δm/g NH_3	Density of NH_3
KNH_2/KI	600	0.0175	0.0045	0.691
	550	0.0279	0.0071	0.714
	450	0.0220	0.0053	0.755
	350	0.0115	0.0028	0.747
NaN_3	600	0.0295	0.0069	0.777
	550	0.0213	0.0053	0.731
	500	0.0118	0.0031	0.692
	450	0.0252	0.0068	0.675
KN_3	600	0.0352	0.0081	0.790
	550	0.0284	0.0066	0.782
	500	0.0327	0.0078	0.762
	450	0.0278	0.0070	0.722

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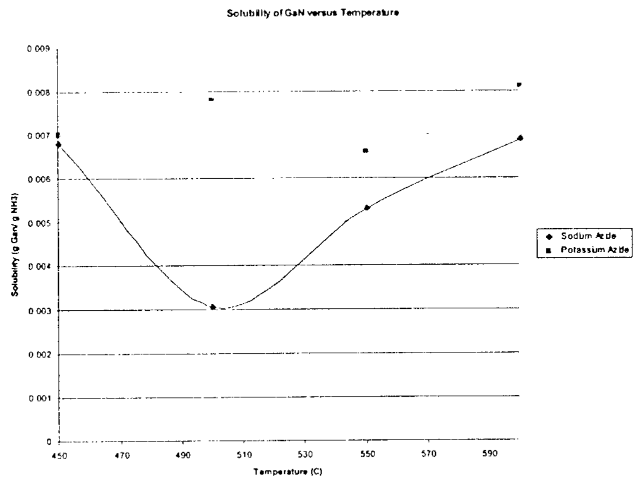
Solubility of GaN using NaN_3 and KN_3

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



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GaN Growth and Transport

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

- Use of KN_3 as the mineralizer has increased the rate of transport to GaN seeds, as well as, bulk growth
- Purity and size of GaN crystals has increased
  - Colorless plates (3-5 mm) and Pale polygons (1 mm)
- Growth conditions currently:
  - 500°C for 14 days
  - 16.5-19.0 kpsi
  - Density of NH_3: 0.672 g/mL
  - 1.3M-1.6M KN_3
  - 50:50 crystalline:powder GaN feedstock
- 3 sets of samples sent to both SUNY and ASU for analysis

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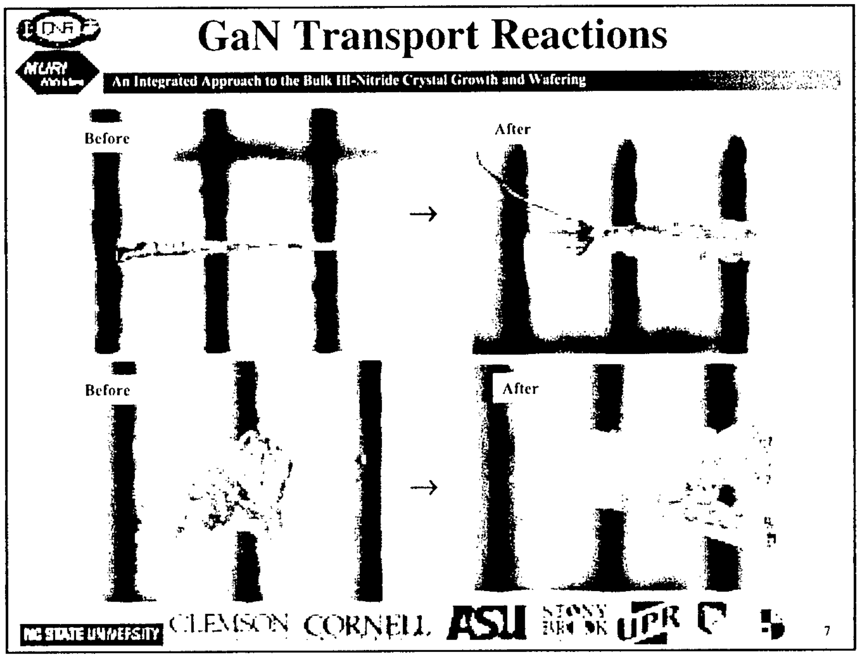
GaN Transport Reactions
An Integrated Approach to the Bulk III-Nitride Crystal Growth and Wafering
Before
After
Before
After
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ASU
UPR
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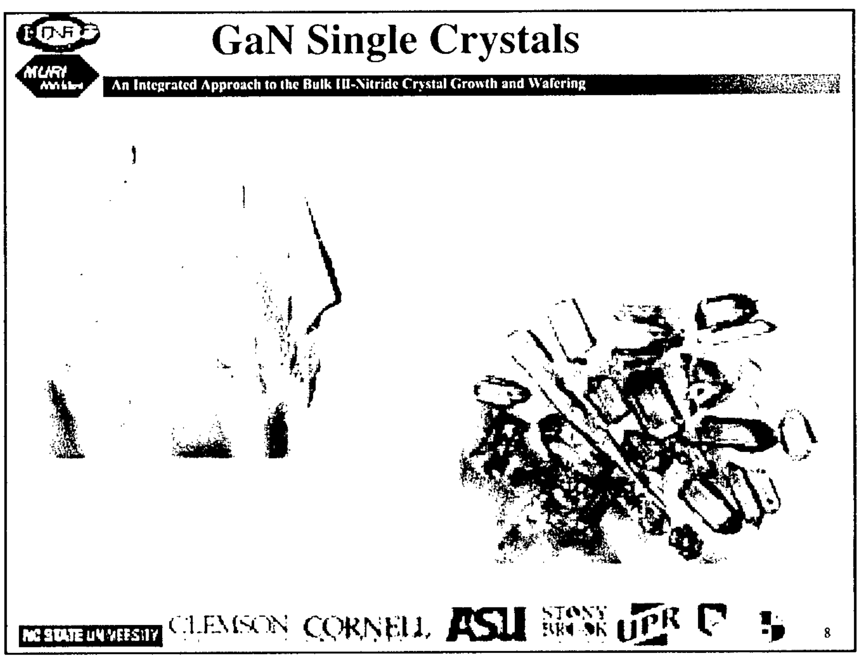
GaN Single Crystals
An Integrated Approach to the Bulk III-Nitride Crystal Growth and Wafering
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Future Goals

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

- Continue to find optimal conditions for transport of GaN to GaN (in house and Hanscom AFB), AlN (NC State), and SiC (commercial 6H) seeds
- Isolate and identify soluble intermediate in GaN reactions
- Continue solubility studies of GaN using KN_3 as the mineralizer to maximize transport and deposition
- Design cell for in-situ Raman spectroscopy

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Ammonothermal Processing for Bulk Gallium Nitride

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

M. Callahan, D. Bliss, R. Lancto
Air Force Research Laboratory,
Sensors Directorate,
Hanscom AFB, MA 01731, U.S.A.

Multi University Research Initiative
Bulk III-Nitride Crystal Growth and Wafering
Period 1 (7 months)

Requirements for Single Crystal Solution Growth of GaN

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

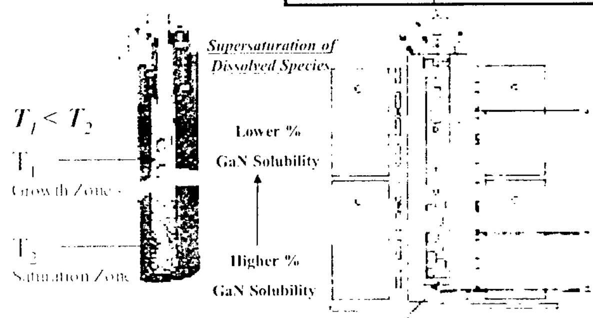
- Solubility of GaN in solvent must be adequate for growth.
  - Not high enough low growth rates will result.
  - Too high polycrystalline growth will result.
  - Obtained by adding proper complexing agent (mineralizer).
  - Typically solubility should be in 0.1-10 %.
- Solubility must be temperature dependent to achieve supersaturation.
  - This allows the transport of GaN to the seed interface to be controlled by varying the temperature gradient between the nutrient and seed.
  - Experiments now in process to determine solubility curves.
- GaN and desired phase (cubic or wurzite) must be thermodynamically favored at growth interface.
- A separate saturation zone and growth zone must be established by proper control of temperature and fluid flow.
- Temp. , Pressure, Mineralizer, and Geometry can be varied to achieve growth conditions above .

Ammonothermal Growth Mechanism

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

Typical Conditions
T1 : 450 °C ± 100 °C
T2 : 500 °C ± 100 °C
Pressure : 2- 5 kbars
Fill - 70-90% Vol.

A + E) Heaters	G,H, J, K) Thermocouples
B) GaN seed	I) Baffle
C) Insulation	L) Pressure Transducer
D) GaN Nutrient	M) Pressure Vessel
F) Liner (Optional)	N) Vessel Sealing Assembly



(assumes forward solubility - higher solubility with increasing temperature)

Growth Results of various Lewis acid/base ions in Ammononothermal Growth of GaN

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

Ion	*Mineralizers*	*Solubility of GaN*	*Phase of GaN grown*	*Size of GaN grown*	*Corrosiveness of Solvent*
NH_4^+ (H^+)	Ammoniums NH_4Cl, NH_4Br NH_4I	[illegible]	Hex, cubic mixed	um	[illegible]
NH_3	Ammines – $[Cu(NH_3)_4]^{++}$	Not attempted			
NH_4^+ and NH_2^-	NH_4I and KNH_2	**	Hexagonal	um- 10s um	****
NH_2^-	Amides - $NaNH_2$, KNH_2	*	Hexagonal	None	**
NH^{-2}	Imide - PbNH	Not Attempted			
N^{-3}	Azide – NaN_3 , KN_3	***	Hexagonal	um - 100s um	*

Red – Acidic system
Blue – Alkaline system

Azide mineralizers -- Yielded Best Overall Results to Date

Azide based mineralizers

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

- Many compounds bond with the N^{3-} ion.
- The alkali metal azides and some of the alkali earth azides are fairly stable.
- Usually prepared by neutralization of the hydroxide with hydrogen azide (hydrazoic acid.)
- Preliminary studies at Clemson indicates increased solubility of GaN with KN_3 than NaN_3.
- Boron, gallium , and aluminum azides have been prepared in past - I.E. $Ga(N_3)_3$.
- Azide containing ammonothermal solutions will react with Noble metals inhibiting solublization of GaN.
- Early indications are high normality azide based ammonthermal solutions can be run in high nickel content autoclaves with cone seals without appreciable corrosion of autoclaves.
- Still problem of transporting source material to seed over long distance (> 1cm)

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Insights and Directions

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

- Azide mineralizers show most promise to date.
- Noble metals complex with alkaline ammonothermal solutions.
  - Prevents Noble metals (Platinum, Gold, Silver) being used with alkaline solutions (I.E. amides or azides)
  - Large 0.875" autoclaves are sealed by noble metal disk Bridgeman type seal.
  - Alternative sealing disk with mechanical properties similar to the noble metals must be found if azide based ammonothermal solutions are to be run in a Bridgeman type seal.
- Bridgeman Seals can still be used with acidic solutions.
  - Must use either platinum liner fitted to autocalve or welded platinum can with a double fill system.
- Smaller Autoclaves are cone seal made out of Stainless Steel.
- Custom made larger scale autoclaves will have to be considered at some point with modified bridgeman seal.

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How to increase transport of GaN in ammonothermal growth ?

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

- Dielectric constant at *-33 °C* for ammonia = *22*
  - *The Dielectric constant effects solubility of GaN.*
  - *Increasing Dielectric constant will increase solubility of GaN.*
  - *Will mixed ammonia - azide or hydrazine solutions increase dielectric constant ? .*
- Viscosity at 25 °C for ammonia = *0.135* cP
  - *The Viscosity effects Flow Patterns of Ammononothermal Fluid.*
  - *How is viscosity related to flow patterns ?*
  - *Can viscosity be changed without contaminating the system by adding inert additives ?*
  - *Can geometry be modified in system to increase dynamic flow in both saturation zone and growth zone if viscosity and or other parameters that effect fluid flow cannot be adjusted?*
- *What other factors effect solubility and transport ?*
  - *Solubility of mineralizer itself (ability to ionize). (KN_3 and CsN_3 look promising)*
  - *Temperature gradient between saturation and growth zones must be optimized for slope of solubility curve vs. Temp.*
    (Want at least 10% change in solubility of GaN from source to seed.)
  - *Size and composition of source material*

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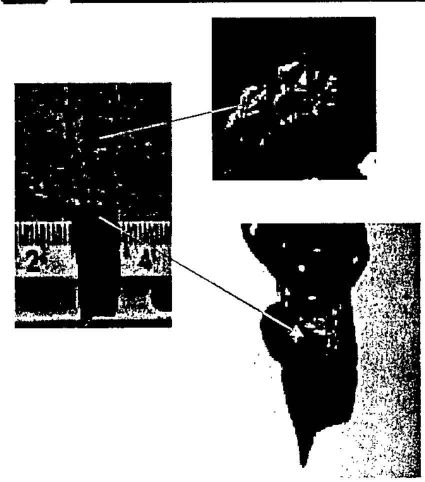
Polycrystalline GaN from Vapor Transport before ammonothermal growth.

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



- Material will be used at Hanscom, NRL, and Clemson for Scale Up.
  - Source material : 1mm^3 – 3mm^3
  - Seed material up to 1cm^3
  - Eventually Single Crystal Seeds will be needed.

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Collaborations

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

- Visit on November 24th to Clemson University.
  - Callahan (AFRL), Kolis (Clemson), Sitar (NCSU) and Chen (Florida International University) in attendance.
  - In-Depth Discussion on progress of ammonothermal to date.
  - Agreed to concentrate on Azide base mineralizer.
  - Discussed modeling of ammonothermal system and agreed to concentrate first on modeling flow properties of ammonia in attempt to make iterative adjustments to change flow dynamics in system to improve transport to seed.
- Verbal Discussions with Purdy (NRL) on doing closed platinum liner experiments with acidic solutions to enable better control of gradient.
- Once mm^3 or greater GaN samples are obtained. More characterization tools such as xray, Pl, Cl, and others can be used at AFRL, NRL, SUNY, and Arizona State.
- AFRL and NCSU sending vapor grown material to Clemson U. for seeds and nutrient.
- Free Standing GaN HVPE Single Crystal Seeds from other sources would enhance research.

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AFRL Work Plan for Second Period

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

- Obtain Post-Doctoral Student from Clemson to start in Jan-March Time frame at latest.
  - Possible candidate will visit AFRL lab at Hanscom during MRS meeting in November.
  - Will train 1-3 months at Clemson before working at AFRL.
- Concentrate on KN_3 and CsN_3 for Mineralizers in 15cc autoclave at high temperature and pressure.
  - Model MRA-438R can go to 650° C and 100,000 psi.
  - Obtain high temperature solubility curves 500 - 650° C for 0.5 - 5 Normal Solutions.
  - Merge data with temperature range from 300-500 ° C obtained from Clemson.
- Obtain 1-2 additional MRA-438R autoclaves (0.375" Diameter – 15 CC) and 2 Qnt. MRA-112R autoclaves (0.5" Diameter – 27 CC) for solubility and cm size growth experiments.
  - Contingent on AFOSR funding.
- Work on seal ring replacement for noble metal seal rings on 0.875" dia. Autoclaves.
- Obtain feedback from Dr. Chen on modeling flow patterns in order to improve transport from saturation zone to growth zone.
- Conduct acidic experiments in closed Pt liners with NRL to control normality, temperature gradient, flow patterns, and other parameters. (If time permits)
- Obtain > mm^3 size Ammonothermal GaN crystals for analysis.

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

Optical Characterization of Bulk GaN and AlN

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Overview of Progress

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

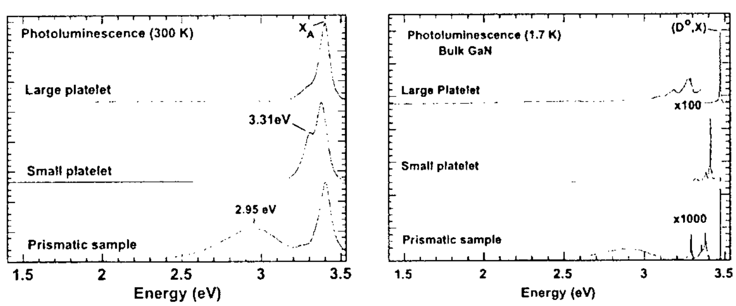
- Carried out room temperature & low temperature PL measurements on bulk GaN grown by
  - Na/Ga flux method (DiSalvo/Yamane)
  - Ammonothermal method (Kolis)
  - Freely nucleated HVPE (D. Bliss)
- Performed low T PL measurements on bulk AlN grown by sublimation (Schlesser/Sitar), using below gap excitation
- Performed Raman measurements on bulk GaN & AlN grown by above methods (undergraduate now assisting)

Overview of Progress

- Constructed system for reflectance on AlN (and GaN); will also allow excitation spectroscopy and possibly above gap excitation of AlN PL
- Modified CL system for short wavelength materials; expect to have first data shortly
- Constructed system for reflectance on AlN (and GaN); will also allow excitation spectroscopy and possibly above gap excitation of AlN PL; starting to use currently

Na/Ga Flux Material: Key Results

- Different crystal habits (from different growth conditions) have characteristically different spectra:

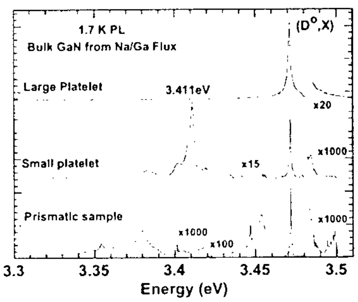


  - Zn acceptors observed in prisms; depends on polarity for platelets (discussed below)

Na/Ga Flux Material: Key Results

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

- Exciton spectra show new peak believed related to extended defects (stacking faults?) in thin platelets



Exciton peak positions imply strain is virtually zero

- Highly resolved excitonic spectra remarkable for bulk material!
- See sharp two-electron replicas up to n=3 state of donor, and sharp excited exciton states; should yield improved understanding of donors

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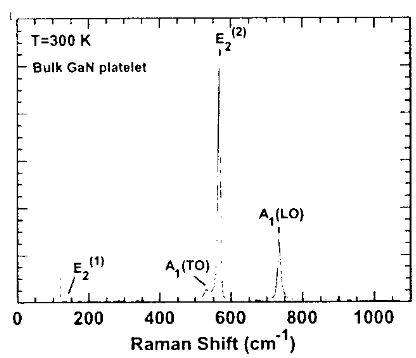
Na/Ga Flux Material: Key Results

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

- Raman spectra show sharp, unshifted A_1(LO) phonon peak; implies carrier concentration probably mid 10^{16} cm^{-3} or less (again remarkable for bulk: Na gettering?)



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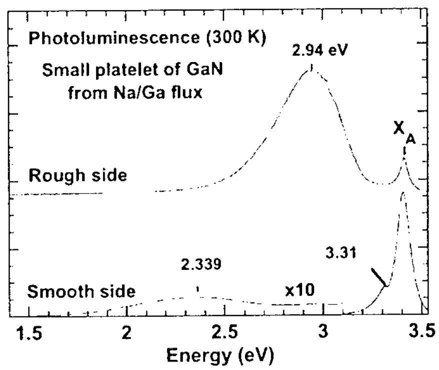
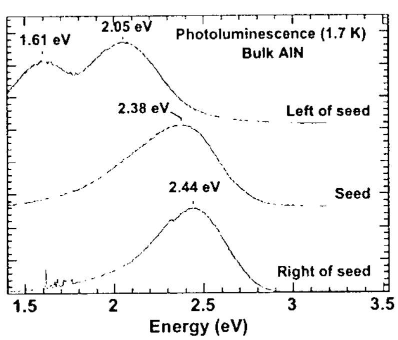
Na/Ga Flux Material: Key Results

- o Strong crystal polarity effect on material quality and Zn impurity incorporation



Bulk AlN Luminescence Properties

- o Excited Sitar/Schlesser crystals using Ar laser below gap; efficiently excites deep level PL!
- o See strong polarity effect on deep levels (opposite ends of seed)

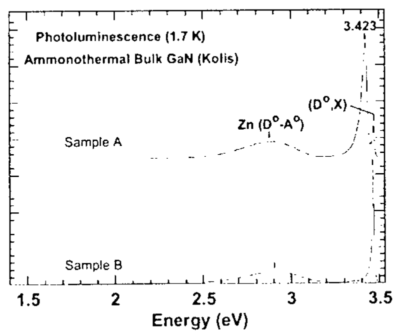


At least three deep levels; all deeper than the Al-vacancy-related "yellow" (really UV) band

Ammonothermal GaN Properties

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

- Studied various small crystals supplied by J. Kolis
- Some crystals in batches (not others) apparently have structural defects causing additional PL band

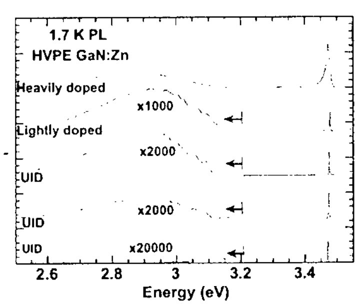


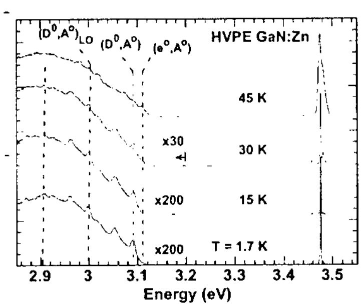
Again see Zn impurities as main acceptor

Related Work: Identification of Zn

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

- Studied Molnar HVPE with various [Zn] levels
- First ever resolution of separate (D^o-A^o) and $(e-A^o)$ peaks (no-phonon structure), as well as acceptor-bound exciton behavior





Work Plan--Next Six Months

- Carry out more detailed studies of selected Na-flux crystals with sharp linewidths, including ERS and magnetospectroscopy
- Characterize a variety of AlN (and GaN) samples using panchromatic and spectral CL measurements
- Continue Raman studies on bulk GaN and AlN
- Characterize series of bulk GaN & AlN samples as a function of growth conditions, as they become available
- Begin implantation experiments to help identify spectral features for various impurities/defects

Synchrotron White Beam X-ray Topography (SWBXT) and High Resolution Triple-Axis X-ray Diffraction (HRTXD) of Widebandgap Semiconductors

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Beamline X-19C, National Synchrotron Light Source,
Brookhaven National Laboratory

Summary of 6 Month Accomplishments

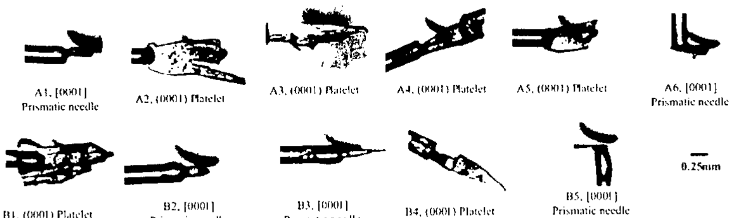
- In past six months SWBXT has been used to characterize defect distributions in
  - AlN crystals grown using spontaneous nucleation from the vapor phase by subliming AlN in a N_2 atmosphere by Raoul Schlesser and Zlatko Sitar
  - GaN crystals grown using the ammonothermal technique by Joe Kolis
- Results for AlN
  - 3-D defect distributions reconstructed to enable determination of their most likely origins
  - Surface ridges partially obscured SWBXT images from previous AlN crystals R047-3 and R047-4 which evidence for growth dislocations and growth bands. Subsequently grown crystals were subjected to a polishing process to remove the ridges. Images recorded from crystals R089-2 and R091-A indicate that the polishing was largely successful with few scratches apparent on only crystal R089-2 and clear images being recorded of growth dislocations, deformation dislocations, growth sector boundaries, inclusions and growth bands. The presence of growth dislocations, growth bands, inclusions and growth sector boundaries indicates the presence of small amounts of impurity in the growth system. Measures should be taken to identify and eliminate these. The deformation dislocations most probably arise due to the stress at the point of crystal attachment to the BN chamber. Stress modeling carried out on SiC by Hui Zhang at Stony Brook has shown that this is to be expected with the stress being very localized as observed in the case of AlN here.
- Results for GaN
  - 2H structure confirmed in all 11 crystals studied. Two growth morphologies observed: Basal plane platelets, and [0001] prismatic needles. Prismatic needles have lower mosaicity.

SWBXT of Ammonothermal GaN

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

Two batches of crystals grown using the ammonothermal technique were provided by Prof. Joe Kolis at Clemson.Many were fused masses of two or more crystals, but some were high quality single crystals which gave extremely good unit cells and peak profiles by ordinary single crystal X-ray diffraction on a simple 2 kW sealed tube.

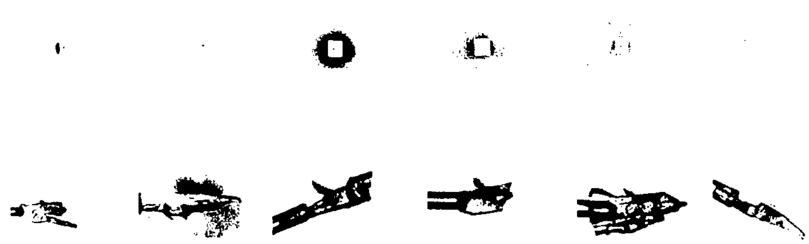
A total of 11 crystals from the two batches (A1-6 from batch 1, and B1-5 from batch 2) were examined using SWBXT. Generally crystals were observed to adopt one of two morphologies (habits): (0001) platelets parallel to the basal plane and prismatic needles aligned along [0001]. Laue patterns recorded confirm the 2H structure but indicate varying degrees of mosaicity.



SWBXT of (0001) GaN platelets

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

Transmission Laue Patterns from (0001) platelet crystals A2-5, B1, B4 (0001) face normal to the beam (recorded on 8"x10" high resolution X-ray film).

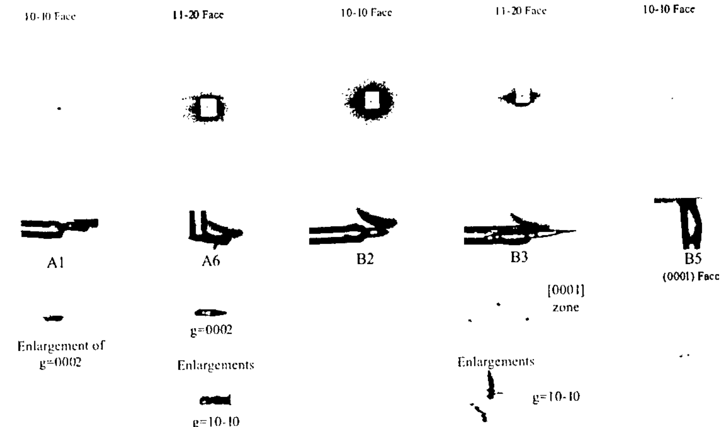


All platelet Laue patterns exhibit the expected 6-fold symmetry. Only crystal A3 shows well-defined Laue spots; the rest show varying degrees of asterism (streaking) indicative of mosaicity. Asterism obscures any detail within the Laue spots so no enlargements provided.

SWBXT of [0001] GaN Prismatic Needles

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

Transmission Laue Patterns from [0001] prismatic needle crystals A1, A6, B2-3, B5



All prismatic needle Laue patterns exhibit well defined Laue spots indicating an overall mosaicity smaller than that of the (0001) platelets

General Features from SWBXT of GaN

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

- Two kinds of growth morphology were found among the two batches of crystals: (0001) platelets, and [0001]-axis prismatic needles.
- Crystal sizes were of the order of 1mm in largest dimension.
- The [0001] prismatic needles were of highest relative quality, having the lowest mosaicities. Several of the individual Laue spots were of high enough quality to warrant enlargement, although no readily recognizable contrast features were identifiable.
- The (0001) platelets were generally of poorer quality than the [0001] prismatic needles with some having mosaicities as high as several degrees.

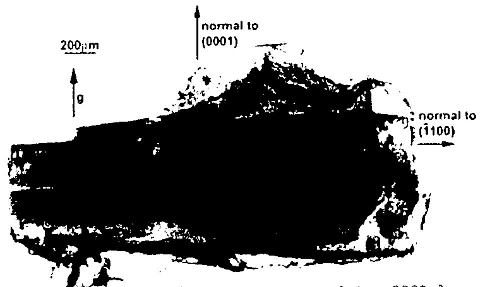
SWBXT of AlN Sample R089-2

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

R089-2: $(11\bar{2}0)$ surface orientation
Visual observation of the sample does not show any well-defined growth faces. X-ray topographs recorded in the transmission geometry show growth sector boundaries along the basal plane (0001). In the middle region, some inclusions can be seen. Several scratches are visible, probably left over from the polishing process.

2mm

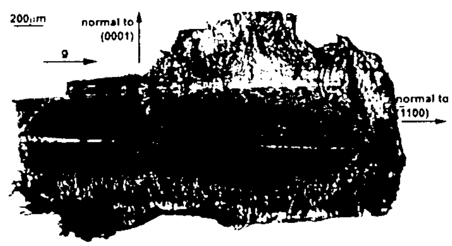
Optical micrograph of R089-2 sample.



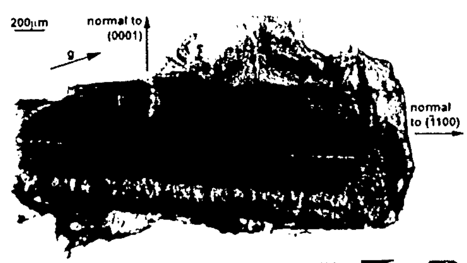
Transmission x-ray topograph (g = 0002, λ = 0.4333Å) of sample R089-2.

SWBXT of AlN Sample R089-2 (Contd.)

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



Transmission x-ray topograph (g = $\bar{1}$100, λ = 0.7499Å) of sample R089-2.



Transmission x-ray topograph (g = $\bar{1}$101, λ = 0.58Å) of sample R089-2.

SWBXT of AlN Sample R091-A

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

R091-A: $(11\bar{2}0)$ surface orientation

Visual observation of this sample shows well-defined growth faces. X-ray topographs recorded in the transmission geometry show growth sector boundaries along the basal plane (0001) and along $(\bar{1}10\bar{2})$. Observation of Pendellösung fringes at the right edge and the top edge indicates that dynamical diffraction conditions are operative and is indicative of ***very high crystal perfection***. Fringes at the top are spaced wider than those at the right edge indicating that the thickness gradient is more gradual. The slope angle is 11.628° $(12\bar{3}0)$ at top and 61.385° (approx. $(12\bar{1}\bar{3})$) at right edge as estimated from extinction distance calculations and fringe period measurement. Growth dislocations originating from the bottom edge are seen in the central region. No contrast from these dislocations is observed in the 0002 reflection indicating that these dislocations are of screw type. A line of inclusions is also seen along the $(\bar{1}100)$ plane in the middle section. This is likely to have been caused by some kind of growth accident (sudden but brief change in growth conditions). Some strain and deformation induced dislocations are observed near the bottom edge, perhaps associated with the point of attachment to the BN chamber. Stress modeling carried out on SiC by Hui Zhang at Stony Brook has shown that this is to be expected with the stress being very localized as observed in the case of AlN here.

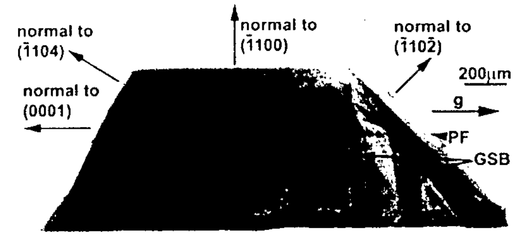
Optical micrograph of R091-A sample.

2mm

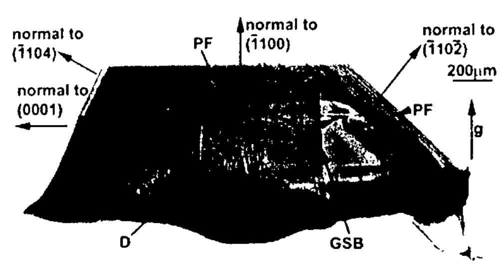
SWBXT of AlN Sample R091-A (Contd.)

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

Transmission x-ray topograph ($g = 000\bar{2}$, $\lambda = 0.4333$Å) of sample R091-A showing Pendellösung fringes (PF) and growth sector boundaries (GSB).



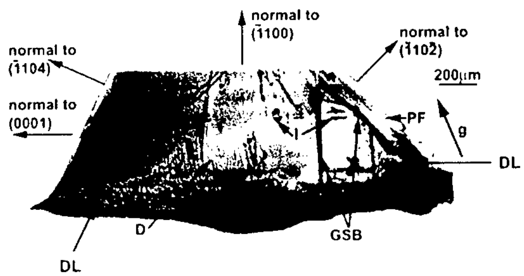
Transmission x-ray topograph ($g = \bar{1}100$, $\lambda = 0.7499$Å) of sample R091-A showing Pendellösung fringes (PF), growth sector boundaries (GSB), growth dislocations (D) and inclusions (I). Note the dark band of strain along the bottom edge.



SWBXT of AlN Sample R091-A (Contd.)

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

Transmission x-ray topograph ($g = \bar{1}101$, λ = 0.58Å) of sample R091-A showing Pendellösung fringes (PF), growth sector boundaries (GSB), growth dislocations (D) and inclusions (I). Near the lower edge of the crystal (probably where the crystal was attached to the BN chamber) there is evidence for localized strain and some plastic deformation with dislocation loops (DL) being visible. Stress modeling carried out by Zhang predicts such stress.



General Features from SWBXT of AlN

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

Summary of Observations from R089-2 and R091-A

SWBXT images of crystal R089-2 revealed mainly inclusions distributed throughout the crystal as well as growth sector boundaries.

SWBXT images of crystal R091-A revealed a very high degree of perfection. The overall dislocation density is around 10^{1}cm^{-2}; in the vicinity of the growth and deformation induced dislocations it is around 10^{4}cm^{-2}, but there are also regions completely devoid of dislocations. The growth dislocations, growth sector boundaries, growth bands and inclusions are evidence for slight impurity contamination. The strain and deformation induced dislocations observed at the bottom crystal edge are, according to research carried out on SiC by Hui Zhang of Stony Brook, expected from a stress modeling point of view due to thermal mismatch stress with the BN chamber.

The wedge shaped facets on the crystal and the overall wedge shape of the large faces (probably arising due to uneven polishing) create the opportunity for the production of thickness fringes. The presence of thickness or Pendelkösung fringes on the SWBXT images of crystal R091-A is indicative of an extremely high level of perfection. This is believed to be the first such observation in AlN. Pendelkösung fringes arise due to interference between wavefields (Bloch waves) associated with the two branches of the dispersion surface. These interference effects are extremely sensitive to local perfection and will be destroyed by the smallest lattice distortion. As a result they are only seen in crystals of the highest quality. In the lower right of each of the SWBXT images of this crystal, interactions between the Pendellösung fringes and the distortion fields associated with the deformation induced dislocation loops in that region can be observed. Fringe spacing changes and in some regions fringes disappear altogether.

Work Plan for Next 6 Months

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

- Characterization of AlN and GaN Crystals grown by ammonothermal and vapor transport techniques using SWBXT and HRTXD. Atomic Force Microscopy (AFM) and Optical microscopy studies will be carried out as necessary.
- Identification of the origins of the defects observed, e.g., growth dislocations versus deformation induced dislocations or point defect condensates, by detailed examination and analysis of defect morphologies observed on SWBXT images.
  - If growth dislocations are observed then it is likely that these can be minimized or eliminated by decreasing the impurity content in the growth system and for seeded growth by using more perfect seeds *(note: results obtained from vapor transport grown AlN crystals received from Raoul Schlesser indicate the presence of growth dislocations, inclusions and growth bands all indicating the presence of impurity)* Specific impurities will be investigated using Scanning Electron Microscopy (SEM), Secondary Ion Mass Spectroscopy (SIMS), and Infrared Spectroscopy carried out at Stony Brook. Results will be compared with Photoluminescence and Cathodoluminescence studies carried out at Arizona State and Naval Research Laboratory.
  - Growth dislocations can also be minimized by avoiding "growth accidents", i.e., sudden changes in growth conditions. This will be tested by requesting growers to make small known changes to growth parameters and observing the resulting defect nucleation phenomena using SWBXT. This will help establish the relationship between growth parameters and defect nucleation
  - If deformation induced dislocations are observed then stresses in the growth system must be minimized. For example where crucibles are used, stresses from thermal expansion coefficient mismatch must be avoided; where no crucibles are used, stresses arising from thermal gradients in the growth system must be minimized. Close collaboration with growth modelers will be established to understand these phenomena. *(Note: deformation induced dislocations were observed in one of the AlN crystals: the origins of these (likely to be associated with the point of attachment to the chamber) will be investigated).*
- Establishment of feedback loops with crystal growth and modeling groups to optimize growth parameters, understand defect nucleation and generation phenomena, and develop strategies for defect density minimization and/or elimination.
- Feedback of information regarding surface strain and strains associated with scratches etc., on wafers received. Scratches that might not be discernible optically or using AFM may be revealed through their associated strain fields in SWBXT. Diffuse scattering in HRTXD arising from surface localized polishing residual stress will also be closely monitored.

5 Year Milestones

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

- **Establishment of detailed relationship between crystal growth parameters in ammonothermal and vapor transport techniques and defect generation in crystals through feedback loops established above.**
- **Fine tuning of growth parameters in collaboration with crystal growers and modelers to optimize growth.**
- **Fine tuning of wafering and polishing technologies in collaboration with crystal growers and modelers.**
- **SWBXT and HRTXD characterization of thin films of GaN on GaN or AlN bulk substrates grown as part of the MURI. Comparison between substrate and thin film defect structures. In cases where high defect densities (e.g. dislocation densities in excess of 10^6 cm^{-2}) comparison will be made with results with Transmission Electron Microscopy (TEM) studies carried out at Stony Brook and Arizona State.**
- **Assessment of influence of defects observed on device performance. This requires establishment of close collaboration with crystal growers/device fabricators.**
- **Identification of defects most detrimental to device performance. Development of strategies for their density minimization or elimination**

Evaluation of GaN and AlN Bulk Crystals by Transmission Electron Microscopy

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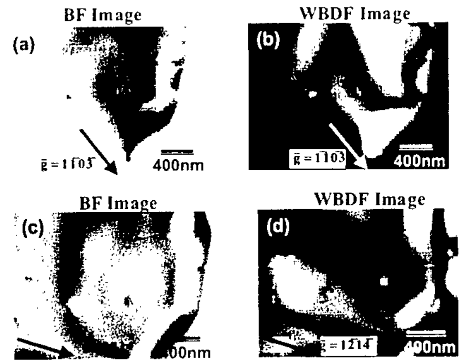
Arizona State University
Tempe, AZ 85287-6006

Objectives

- Two objectives of this study are:
  - (1) to understand the origins of dislocations in bulk GaN and AlN crystals, and
  - (2) to advise crystal growers on growth protocols that would lead to the reduction of dislocation densities.
- In the period under review, we examined GaN and AlN crystals supplied, respectively, by DiSalvo at Cornell University and Schlesser at North Carolina State University

Bulk GaN Sample from Cornell

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



Possible Burgers Vector: "c" or "c+a" type or $\frac{1}{3}[1\bar{2}10]$ or $\frac{1}{3}[\bar{2}110]$
Dislocation Density: 2 x $10^7/cm^2$

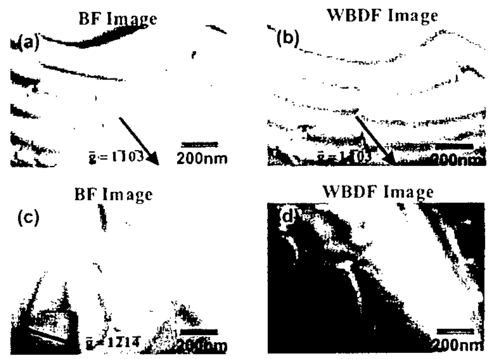
Figure 1. Micrographs illustrating diffraction contrast behavior of dislocations observed in a GaN crystal.

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

Figure 1 shows the diffraction contrast behavior of dislocations observed in GaN crystals for two different reflections. Both bright-field (BF) and weak-beam dark-field (WBDF) images are shown. Based on these results, the Burgers vectors of dislocations could be **c** or **c+a** or $\frac{1}{3}[1\bar{2}10]$ or $\frac{1}{3}[\bar{2}110]$. Dislocation density is estimated to be 2 x $10^7/cm^2$.

Bulk GaN Sample from Cornell

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

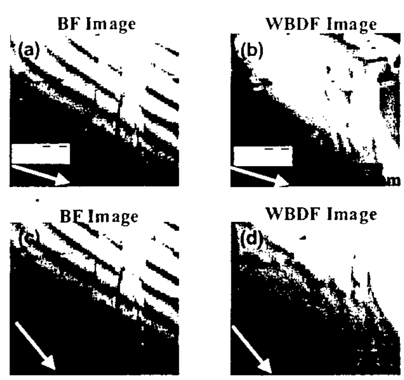


Possible Burgers Vector: "c" or "c+a" type or $\frac{1}{3}[1\bar{2}10]$ or $\frac{1}{3}[\bar{2}110]$
Dislocation Density: 1 x 10^8/cm²

Figure 2. Micrographs illustrating diffraction contrast behavior of dislocations observed in a GaN crystal.

Bulk GaN Sample from Cornell

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

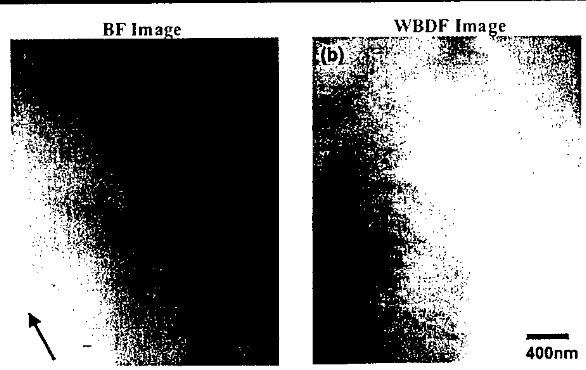


Possible Burgers Vector: "c" or "c+a" type or – or –
Dislocation Density: 3 x 10^8/cm²

Figure 3. Micrographs illustrating diffraction contrast behavior of dislocations observed in a GaN crystal.

Figures 2 and 3 show the diffraction contrast behavior of dislocations, observed in different regions of GaN crystals, for two different reflections. Again, both BF and WBDF images are shown. These results are consistent with the assignation of **c** or **c+a** or $\frac{1}{3}[1\bar{2}10]$ or $\frac{1}{3}[\bar{2}110]$ Burgers vectors to these dislocations, and their density is 1 x $10^8/cm^2$. Furthermore, dislocations appear to be randomly distributed and are not aligned along crystallographic directions.

Bulk AlN from NCSU



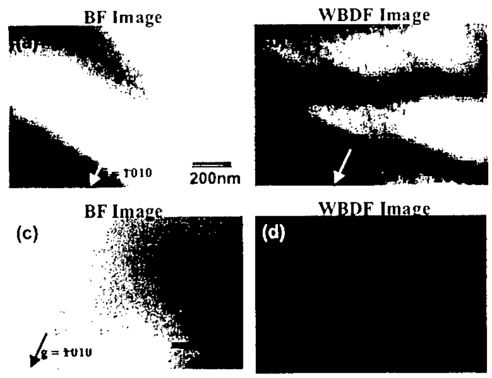
Extremely low dislocation density → less than $10^4/cm^2$

No dislocation was found in TEM

Figure 4. Micrographs showing BF and WBDF images obtained from a dislocation-free region in an AlN crystal.

Bulk AlN from NCSU

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



Extremely low dislocation density → less than $10^4/cm^2$

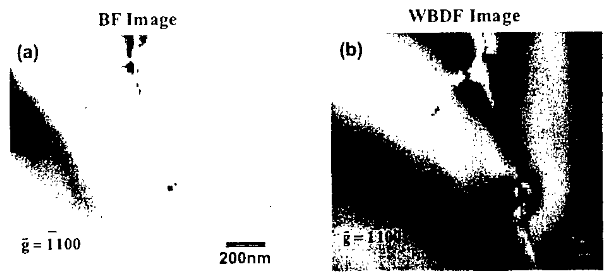
No dislocation was found in TEM

Figure 5. Micrographs showing BF and WBDF images obtained from dislocation-free regions in an AlN crystal.

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

Figures 4 and 5 show BF and WBDF images obtained from dislocation-free regions of AlN crystals, implying that these crystals are highly perfect. Furthermore, we do not see impurity striations that could be attributed to the incorporation of oxygen into the crystals.

Bulk AlN from NCSU



Dislocations were observed near a microcrack
Crack might be induced by sample preparation

Figure 6. BF and WBDF micrographs obtained from an AlN crystal. Dislocations are seen near a microcrack.

Figure 6 shows BF and WBDF images obtained from an AlN crystal. A couple of dislocations appear to emanate from a microcrack that could have been introduced during sample preparation. Based on these results, we could eliminate [0001], $\frac{1}{3}[11\bar{2}3]$ and $\frac{1}{3}[11\bar{2}0]$ Burgers vectors.

Discussion

- Two significant results emerge from the present study.
  - First, the dislocation density in GaN crystals grown by the flux method is fairly high.
  - Second, AlN crystals grown by vapor transport are of high quality.

Discussion (cont.)

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

- There are three sources of dislocations in seeded bulk growth:
  - (1) replication of dislocations present in seed crystals into growing crystals,
  - (2) incorporation of non-equilibrium concentrations of point defects into growing crystals, and
  - (3) multiplication of dislocations under thermal gradient-induced stresses.

Discussion (cont.)

Since our growths are not seeded and since dislocations in Figs. 2 and 3 are not aligned along specific directions, sources #1 and #3 may not be responsible for the observed dislocations. It is likely that non-equilibrium concentrations of point defects are incorporated into GaN crystals. These point defects could cluster together to form faults on (0001) planes. These faults could either coalesce to form **c** or unfault to form **a** dislocations. **c** and **a** dislocations could combine to form **c+a** dislocations.

Research Plan

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

- **We still need to resolve several scientific issues.**
  - **(1) What is the source and nature of point defects in flux-grown GaN Crystals?**
  - **(2) How do GaN and AlN crystals grow?**
  - **(3) Could dislocations in GaN and AlN crystals be delineated by etching?**

Research Plan (cont.)

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

To address the source issue, we will request Professor Frank DiSalvo to grow GaN crystals under different supersaturation. We plan to carry out collaborative positron annihilation experiments to address the nature of point defects. To resolve question #2, we will conduct AFM and Nomarski differential contrast studies on as-grown crystals.

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Research Plan (cont.)

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

Following the work of the Sony scientists, we have demonstrated that dislocations in GaN crystals can be delineated by vapor etching in an N_2/HCl mixture at 600°C. This study was carried out in our OMVPE system. To address question #3, we plan to extend this study to AlN crystals. If successful, this approach would complement X-ray topography for macroscopic characterization of bulk crystals where crystal thickness is not a limitation.

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Chemical-Mechanical Polishing of GaN and AlN

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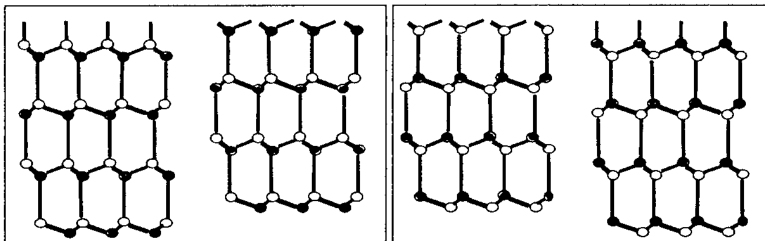
Introduction

- **Beaudoin team has extensive experience in SiO_2 CMP**
  - **Semi-quantitative models of polishing mechanics**
  - **Validated descriptions of wafer scale removal rate variations**
  - **Preliminary models for chemical effects**
- **Needs**
  - **Understand chemistry of GaN and AlN system (etching)**
  - **Understand mechanical structure of epitaxial and free standing crystals**
- **Goals**
  - **Protocol for polishing wafered samples**
  - **Protocol for polishing free standing crystals**

GaN and AlN Structures

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

- o **Understanding GaN and AlN structures**
  - m **Wurtzite structures expected**



Ga-polar GaN, (0001) oriented, +c type Ga -terminated surface (left) N - terminated surface (right)	N-polar GaN, (000-1) oriented, -c type Ga -terminated surface (left) N - terminated surface (right)

Epitaxial Films and Bulk Crystals

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

- o **MOCVD Films**
  - m **N - polarity, Ga - terminated surface "etchable"**
- o **MBE Films**
  - m **Both N (000-1) and Ga (0001) polarity**
  - m **Ga - terminated surface**
  - m **N polar "etchable", Ga polar "unetchable"**
- o **Bulk Crystals**
  - m **Both N and Ga polarity**

Sumiya, M.; Yoshimura, K.; Ito, T.; Ohtsuka, K.; Fuke, S.; Mizuno, K.; Yoshimoto, M.; Koinuma, H.; Ohtomo,A.; Kawasaki, M. , Growth Mode and Surface Morphology of a GaN film Deposited Along the N-face Polar Direction on c-plane sapphire substrate, Journal of Applied Physics, 88, No.2, pp. 1158 (2000).

Chemical Mechanical Polishing

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

- Chemical effects
  - Free etching chemical reactions
  - Kinetics, equilibrium
  - Process dynamics
- Mechanical effects
  - Wafer stress distribution
  - Abrasives, nanoindentation, scratches
  - Local stress distribution
- Both chemical and mechanical processes essential
  - Chemical etch only produces rough surface, slow polish
  - Mechanical abrasion only produces scratched surface

Preliminary Direction: CMP of GaN

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

- Form hydroxide layer by free etching (chemical effect)
- Resulting rough surface (hillocks) can be polished by applying a lateral force (mechanical effects)
  - More easily abraded than base material
- Both chemical and mechanical effects occur simultaneously
- Mathematical modeling for prediction and optimization of the GaN CMP
  - Free etching mechanism
  - Stress distribution and abrasives
  - Compile the results in an integrated model

Free Etching of GaN

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

- Wet etching
  - NaOH or KOH aqueous solution can etch the Ga terminated surface of N-polar GaN
  - Acid solutions can etch mostly at dislocations
- Observed phenomena
  - Etching rate is much higher at the dislocations
  - The overall etching rate decreases with time
  - After brief etching - hillocks on the surface have pyramidal shape with ~60° angle between the side-walls and the basis
- Ga atom on the surface has three dangling bonds and it is relatively more reactive than any other atomic configuration of GaN

Preliminary Etch Mechanism

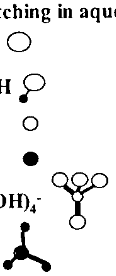
An Integrated Approach to the Bulk III-Nitride Crystal Growth and Wafering

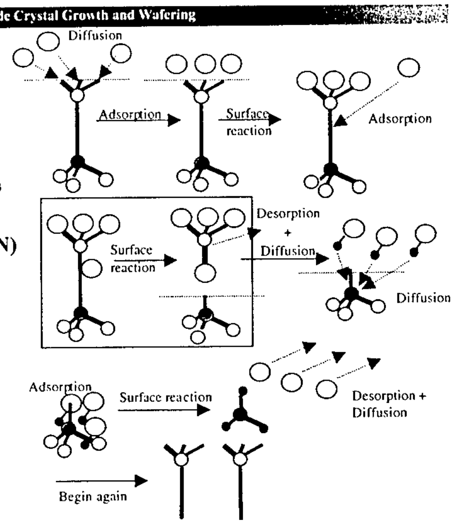
- Overall chemical reaction

$GaN + OH + 3H_2O = Ga(OH)_4^- + NH_3$

- Possible mechanism (MOCVD GaN) etching in aqueous KOH

OH-
H-OH
Ga
N
$Ga(OH)_4^-$
NH_3





Preliminary Etch Model

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

- Etch rate = k ($[A]^3[S]$-k'[C][S]/[A])
- [S] concentration of available active sites
- [D]= $[H_2O]$, [A] = $[OH]^-$, [C]=$[Ga(OH)_4]^-$, [E]=$[NH_3]$
- $[S]=[T]/(1+K_{a11e}[A]+K_{a11e}K_{a22e}[A]^2+K_{a11e}K_{a22e}K_{a33e}[A]^3 +K_c[C]+(K_c/K_{s2e})[C]+(K_c/K_{s2e}K_{a44e})[C]/[A]+K_{a55e}[D]+ K_{a55e}K_{a66e}[D]^2+K_{a55e}K_{a66e}K_{a77e}[D]^3+[E][S]/K_{D2e})$
- Assumes single site catalytic dissolution kinetics

Polishing Paradigm

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

- Basis: etching occurs much more rapidly at defects than at quality crystal sites, partially etched layer much less strongly bound than pristine crystal
- Induce selective, shallow (surface) damage on crystals
- Contact crystals with aggressive etchant, create partially etched surface layer
- Use mechanical abrasion with mild mechanical effects (stresses, indentation) to selectively remove surface layer without damaging sublayer

Work Plan--Next Six Months

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

- Characterize GaN etching
  - Temperature, solution composition, defects, crystal props.
  - Use Mahajan epitaxial films for benchmark
  - Preliminary model validation
  - Identify etching conditions conducive to polishing
- Characterize polishing of GaN
  - DI water, aqueous KOH, NaOH, alumina, ceria, silica
  - Use Mahajan epitaxial films
- Develop protocol for CMP for sample preparation
- Demonstrate proof-of-concept for damage mediated polishing

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Surface Preparation of Nitrides

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Robert F. Davis
Materials Science and Engineering
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Introduction

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

- Surface Preparation
  - Motivation for Surface Preparation
  - Ex-situ and In-situ Cleaning Techniques
  - Analytical Techniques Utilized
- Results Obtained
  - As Loaded
  - After Cleaning
- Discussion
- Future Work

Motivation for Surface Preparation

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

- MURI goal: AlN & GaN substrates for film growth
- Device quality films require substrate surfaces to be:
  - Atomically Clean
  - Undamaged
- The cleaning method must be applicable for MOVPE and MBE film growth process routes
- Present investigations on n-type, Si-doped GaN Films
  - 1 μm thick GaN(0001) films on AlN/SiC(0001) substrates

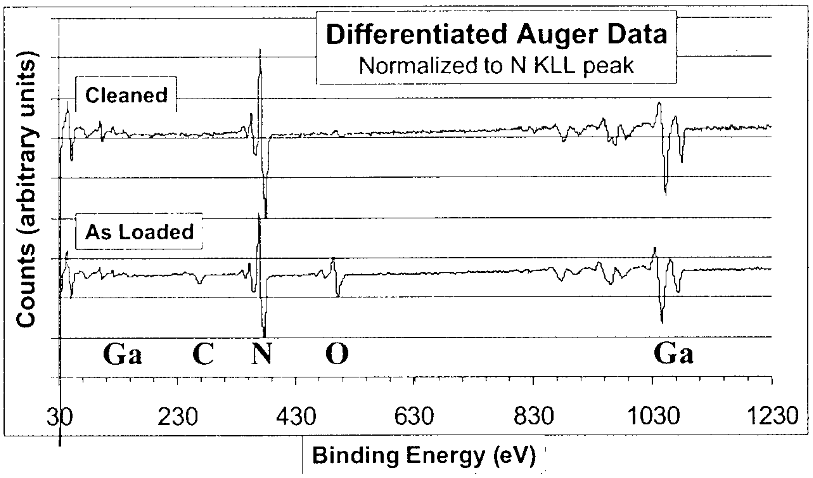
Experimental Procedures

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

- Cleaning Procedure
  - Ex-situ Wet Processing
    - 1 min each in trichloroethylene, acetone, and methanol
    - 10 min in 37% HCl
  - In-situ Chemical Vapor Clean
    - Heater ramped to 500°C in UHV (<1×10^{-7} torr)
    - GSMBE chamber filled to 1.0×10^{-4} torr with ammonia
    - Heater ramped to 1000°C, held for 15 minutes, ramped back to 500°C
    - Ammonia flow stopped, heater cooled to room temperature
- In situ Analytical Techniques Employed
  - Auger Electron Spectroscopy (AES)
  - X-ray Photoelectron Spectroscopy (XPS)
  - Low Energy Electron Diffraction (LEED)

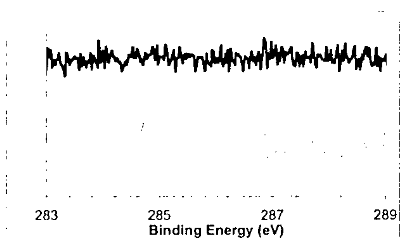
Auger Electron Spectroscopy Results

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



XPS Results

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



Carbon 1s Peak

After Cleaning

No Peak Detected

As Loaded

Peak Position 285.6 eV

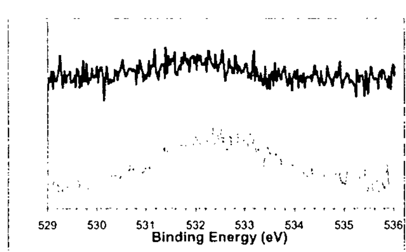
Oxygen 1s Peak

After Cleaning

Peak Position 532.05

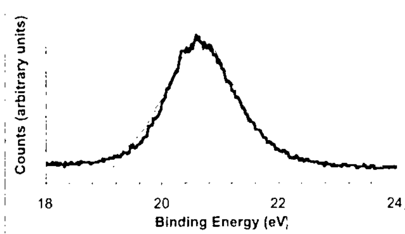
As Loaded

Peak Positions 531.76 and 532.88 eV



XPS Results

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



Gallium 3d Peak

After Cleaning

Peak Position 20.68 eV

As Loaded

Peak Position 21.06 eV

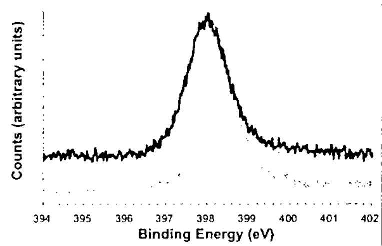
Nitrogen 1s Peak

After Cleaning

Peak Position 398.02 eV

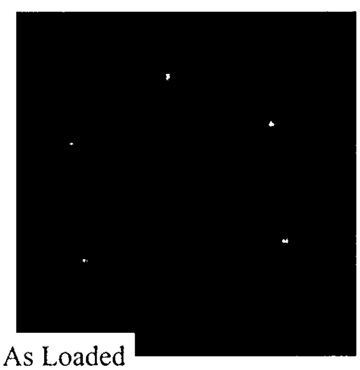
As Loaded

Peak Position 398.38 eV



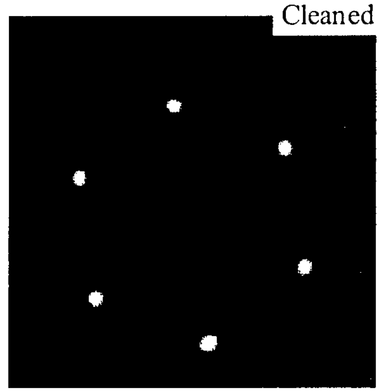
LEED Images

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



As Loaded

Cleaned



Results Following In Situ Cleaning

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

- Carbon removed by cleaning technique
  - Undetected by XPS
- Low coverage of oxygen remained
  - Oxygen coverage is lowered from as-loaded case
- Gallium/Nitrogen ratio dropped
  - Indicates removal of gallium rich phase from surface
- Ordered LEED pattern indicated no surface damage
- Ga and N peaks had higher XPS intensities after cleaning

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Future Work

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

- Chemical Vapor Cleaning:
  - Completely remove oxygen peak
  - Repeat process and compare results obtained from:
    - Undoped GaN
    - Mg-doped GaN
- Apply chemical vapor cleaning technique to AlN and $Al_xGa_{1-x}N$ surfaces
  - Determine suitable in-situ process routes for removal of O and C contaminants without surface damage

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