Development of the Electrochemical Solution Growth (ESG) Technique for Native GaN Substrates

DOE Energy Storage & Power Electronics Research Program
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PI: Karen Waldrip

Advanced Power Sources R&D, Dept 2546

PM: Stan Atcitty, John Boyes

Sandia National Laboratories, Albuquerque, NM, 87185

Sponsor: Gil Bindewald, DOE Power Electronics & Energy Storage Program

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Outline

- Motivation
- Existing GaN Growth Technique
  - Epitaxial Lateral Overgrowth
  - Methods for Growing Bulk GaN
- Development of the Electrochemical Solution Growth Technique
  - Electroplating GaN from Ga^{+3} and N^{-3}
  - Electrochemical Solution Growth (ESG)
  - Initial Results

Project Objective

To develop a novel, scalable, cost-effective growth technique for producing high quality, low dislocation density bulk gallium nitride for substrates for GaN-based power electronics.

Project Start: 5/08

Previous Funding: DOE's Solid-State Lighting

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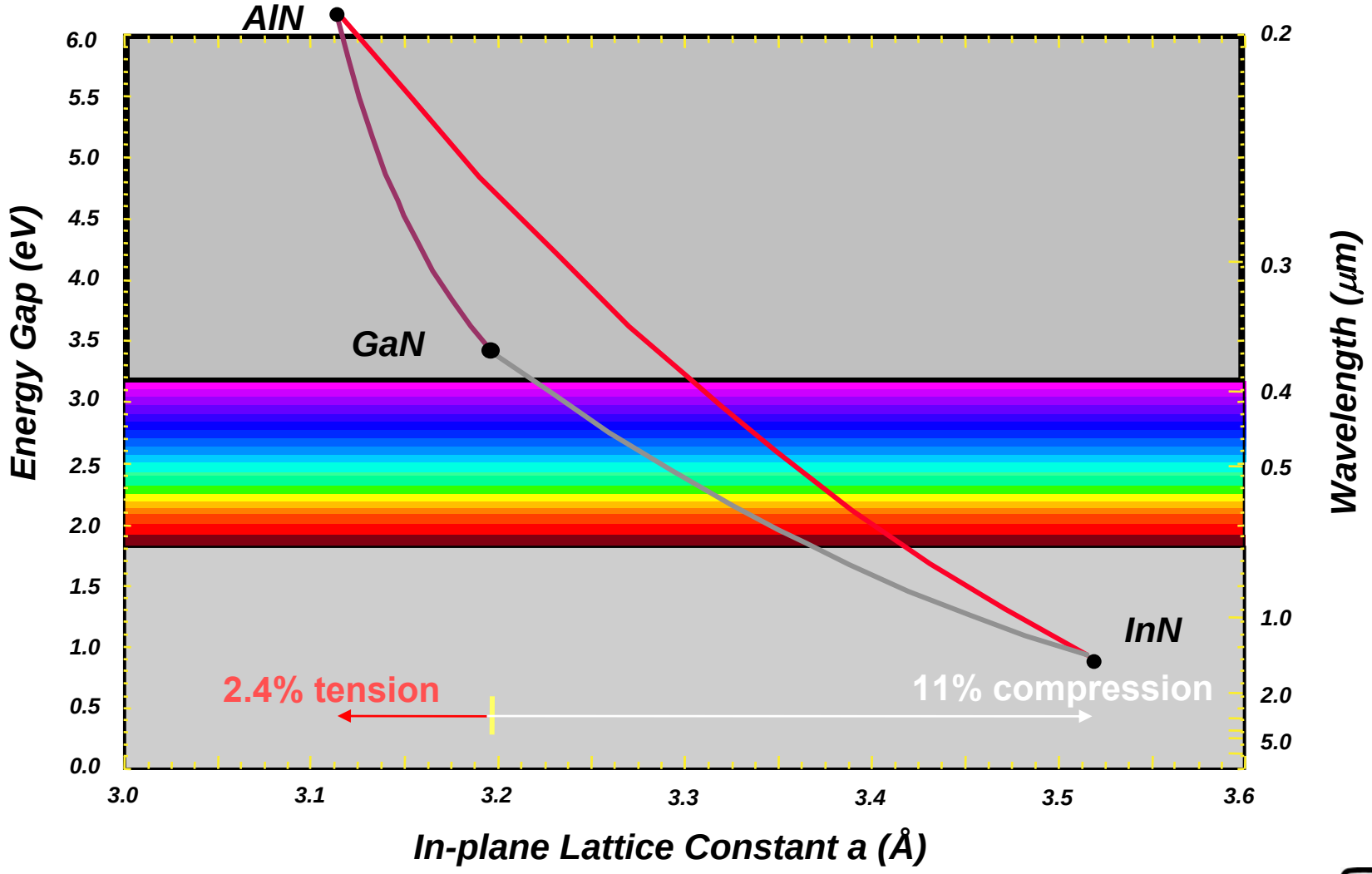
Combined Figure of Merit

	K (W/cm˚C)	E_c (MV/cm)	ε	μ (cm^2/Vs)	v_s	Combined Figure of Merit
Si	1.31	0.3	11.8	1350	1×10^7	1
SiC	4.9	2	10	650	2×10^7	136
GaN	1.3	3.3	9	1200	2.5×10^7	153

Energy gap - lattice parameter diagram of III-nitrides



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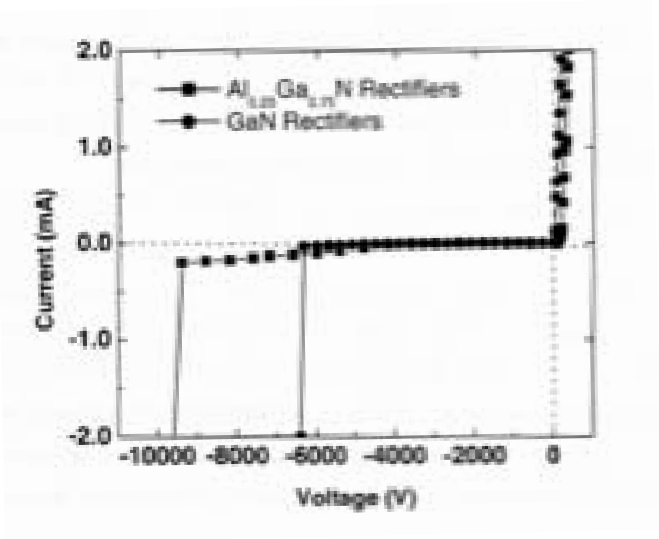
Heterostructure Rectifiers Offer Improved Breakdown Voltages



9.7 kV for $Al_{0.25}Ga_{0.75}N$

Leakage current due to bulk defects

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GaN is Grown Heteroepitaxially on Sapphire (and Silicon Carbide) Substrates

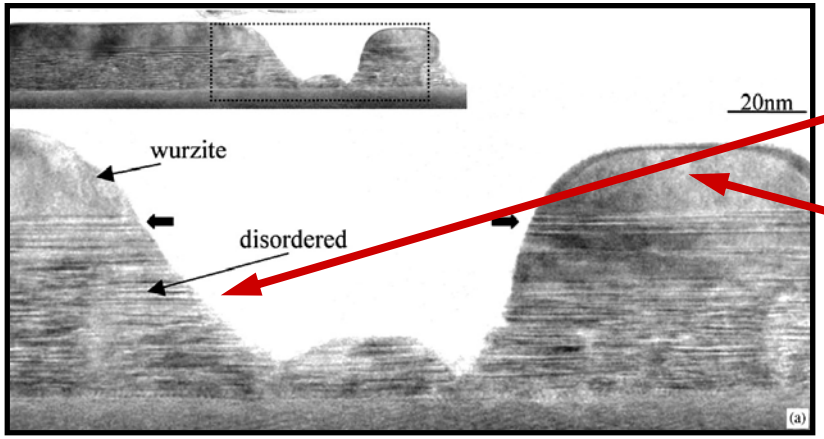
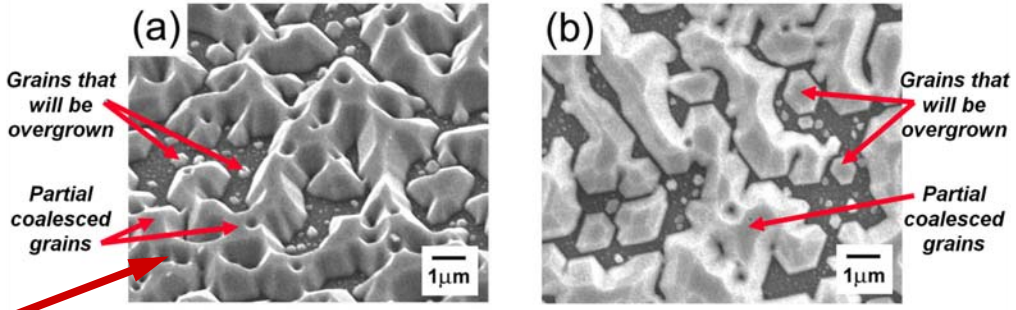


Figure from Lada et al., J. Crystal Growth 258, 89 (2003).

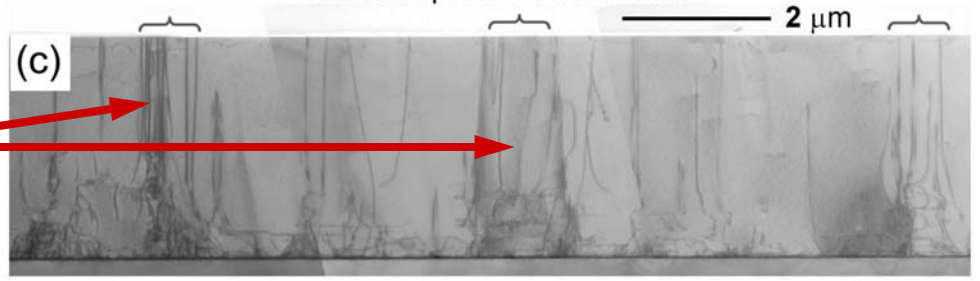
- **As grown GaN nucleation layers contain disordered GaN with many stacking faults.**
- **Once annealed, wurtzite GaN forms on top of disordered GaN NL, forming nano-sized GaN nuclei from which further high temperature GaN growth occurs.**

- **High temperature growth on the GaN nuclei produces GaN grains.**
- **Growth conditions can be varied to enhance the pyramidal growth mode or lateral coalescence. Dislocations are bent laterally on pyramidal facets.**
- **Dislocations are concentrated in bunches located microns apart.**

SEM Images of 3D GaN grain growth



The threading dislocation appear in bunches which are located a few microns apart from each other.



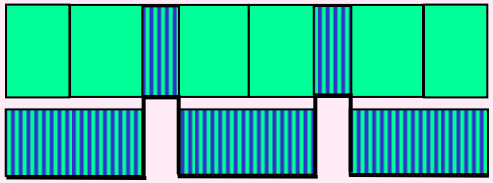
TEM cross section

TEM courtesy of D. M. Follstaedt

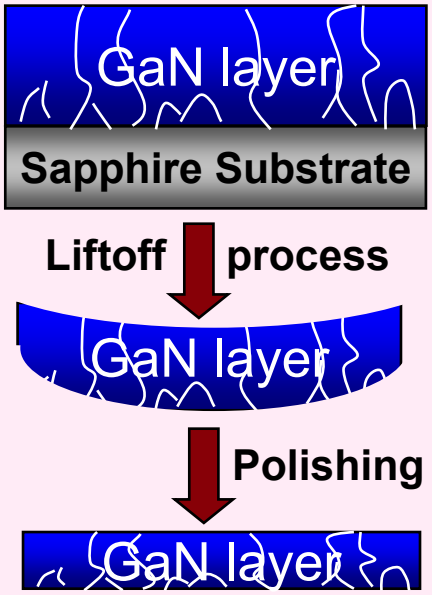
Methods for growing bulk GaN

Dislocation Filtering Techniques

Lateral Overgrowth

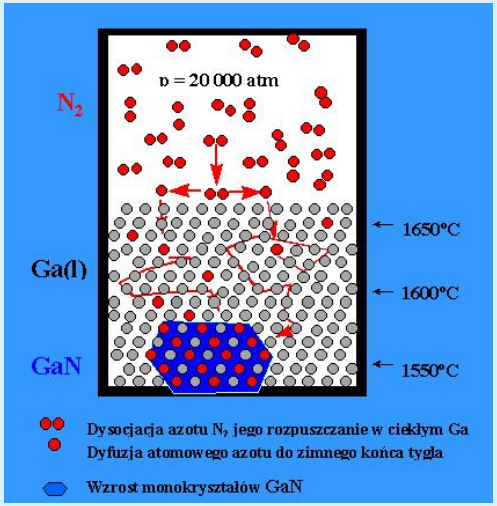


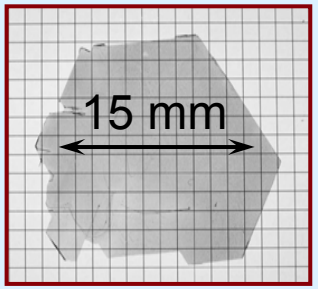
HVPE



"True" Bulk Techniques

High Nitrogen Pressure

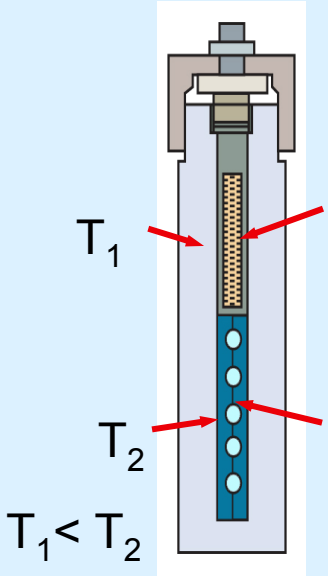




P = 10^5atm
T = 1500C
t = 100 hr
h = 100 μm

Dislocation density = 10^2cm^{-2}

Ammonothermal growth



$KNH_2 + GaN + 2NH_3 \rightarrow KGa(NH_2)_4$

$GaN + 2NaNH_2 + 2NH_3 \rightarrow Na_2Ga(NH_2)_5$

4,000 – 5,000 atm
T = 400 – 800°C
G.R. = 50 μm/day
Multiple seeds

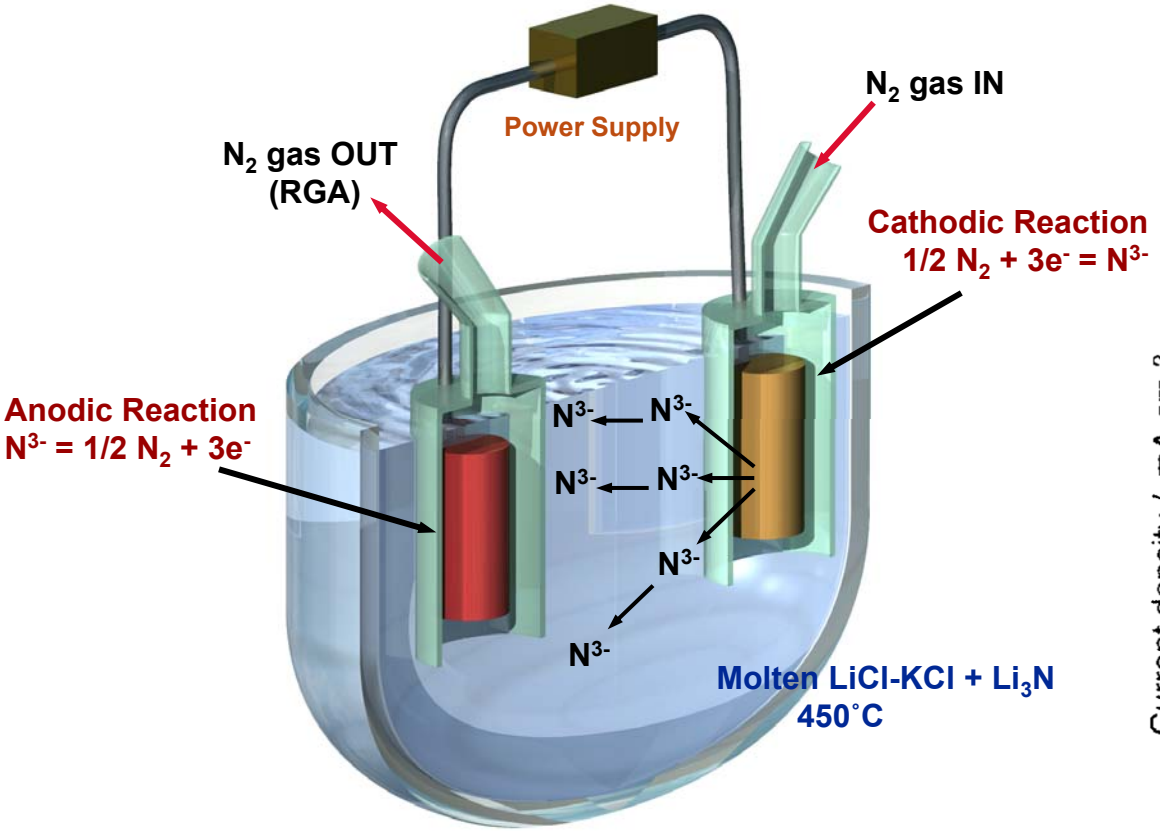
Desires/Requirements for a Bulk Growth Technique

- Good crystalline quality ($\rho \leq 1x10^5 cm^{-2}$)
- High growth rate (~mm/hr): high throughput, high volume production
- Low impurity content
- Scalable
- Controllable
- Manufacturable
- Reasonably inexpensive
- Applicable to InN, GaN, AlN, and III-N alloys

$1/2N_2 + 3e^- \rightarrow N^{-3}$: *The* Reactive Intermediate

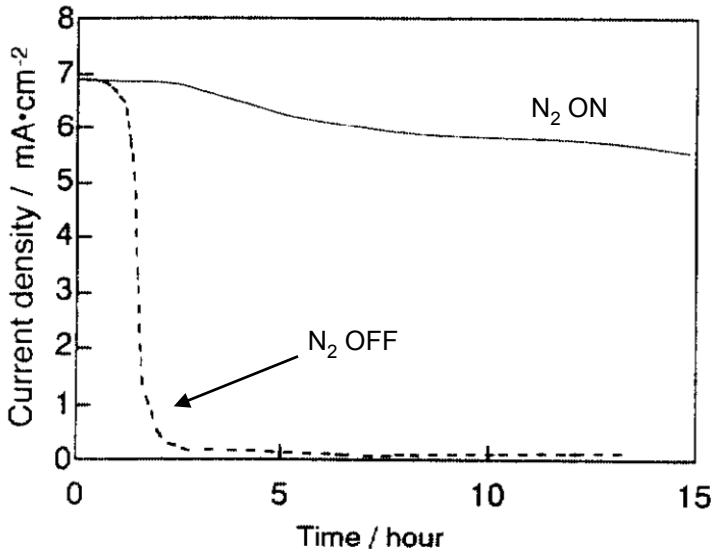
T. Goto and Y. Ito, "Electrochemical reduction of nitrogen in a molten chloride salt" Electrochimica Acta, Vol. 43, Nos 21-22, pp 3379-3384 (1998).

Found that nitrogen was continuously and nearly quantitatively reduced to nitride ions



Advantages of using N_2 gas:

- Clean
- Inexpensive
- Control over precursor conc.
- Continuous, controlled supply



Report of nitride concentration in LiCl in literature: 12 mole %

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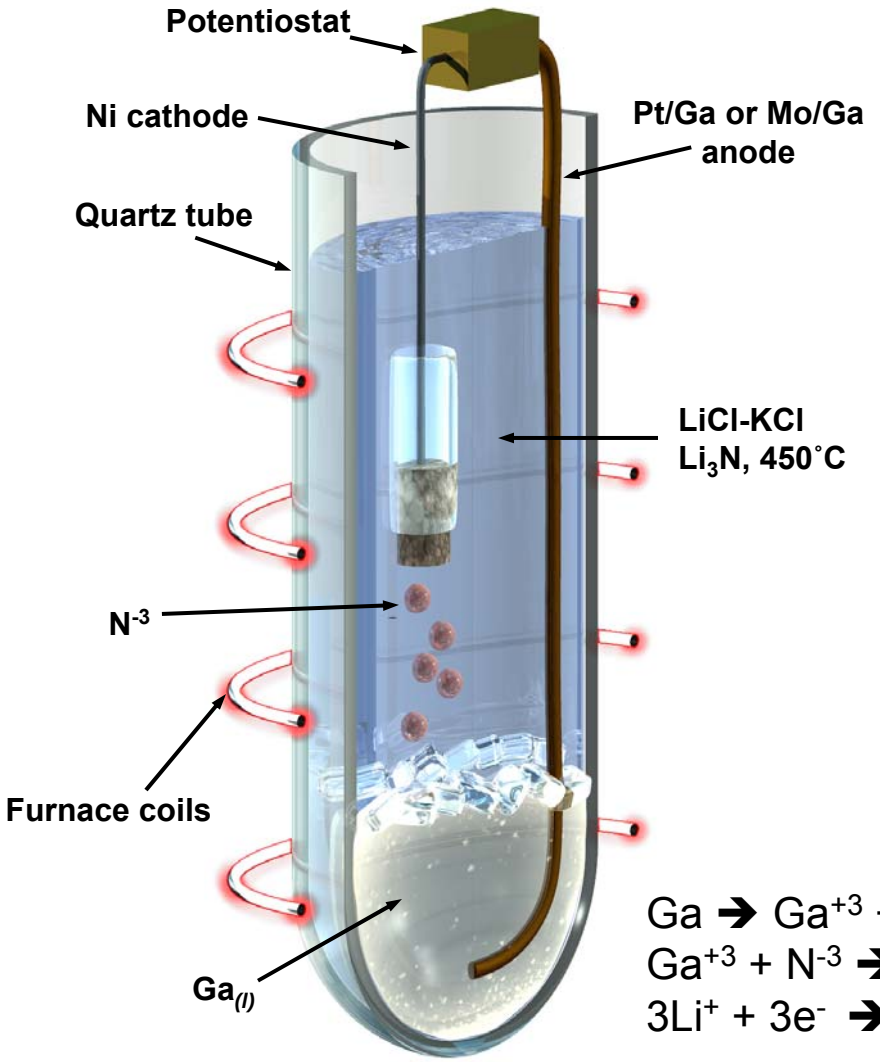
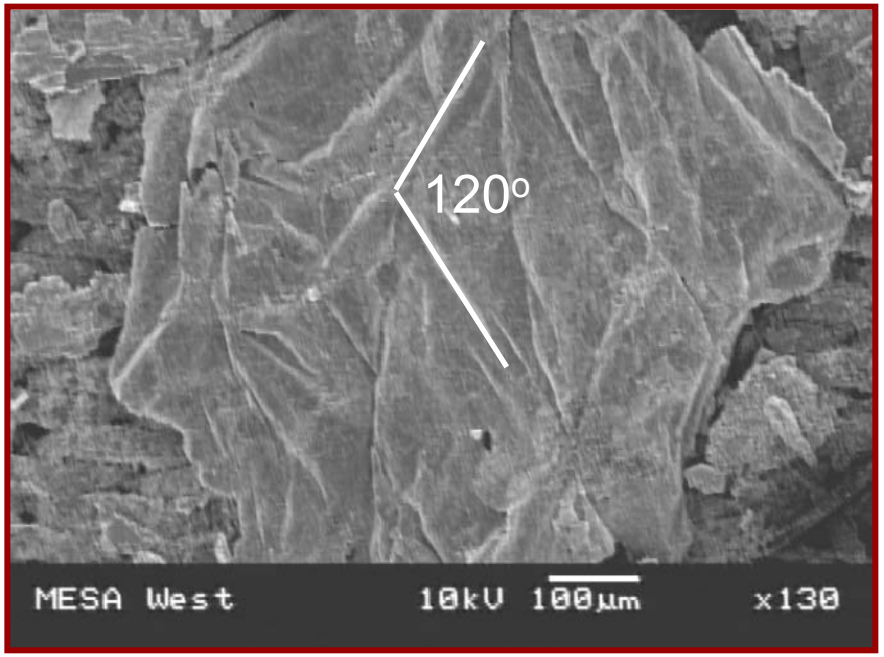
Initial Experimental Setup: Unseeded Growth of GaN in a Test Tube

Li_3N or (Li_3N + N_2) + Ga, 450˚C, current sweep, 2 hours





Produced numerous wurtzite GaN crystals;
This crystal was ~1.25mm long x 0.8mm wide

$Ga \rightarrow Ga^{+3} + 3e^-$

$Ga^{+3} + N^{-3} \rightarrow GaN$

$3Li^+ + 3e^- \rightarrow 3\ Li$

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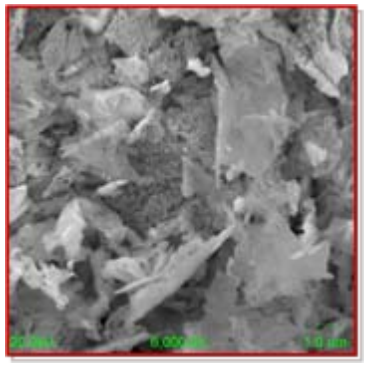
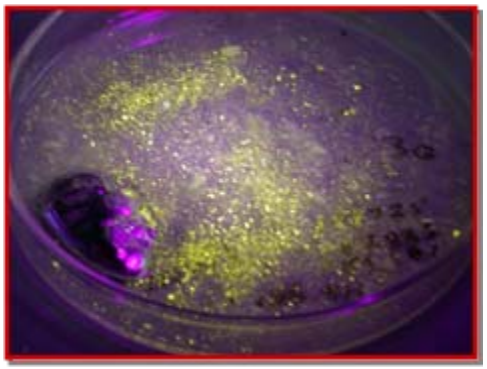
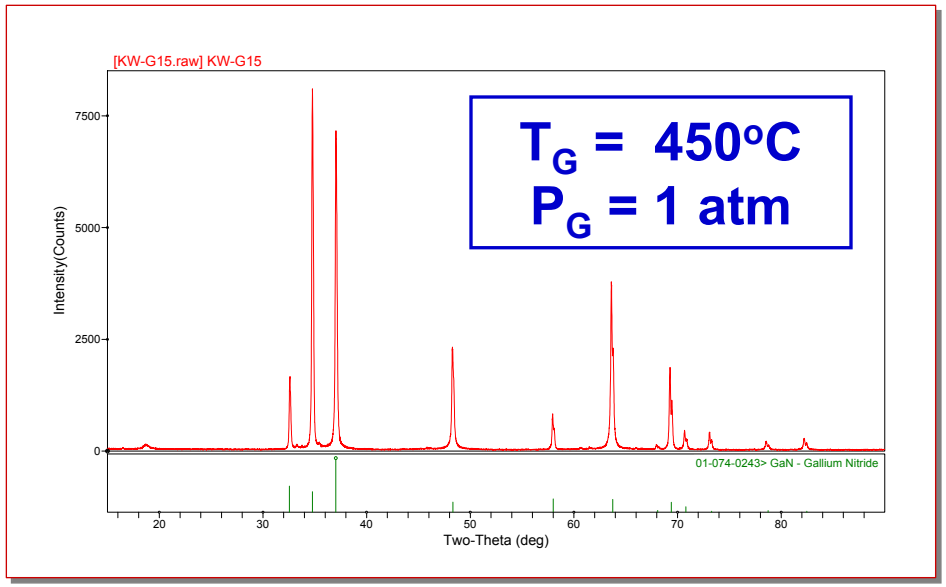
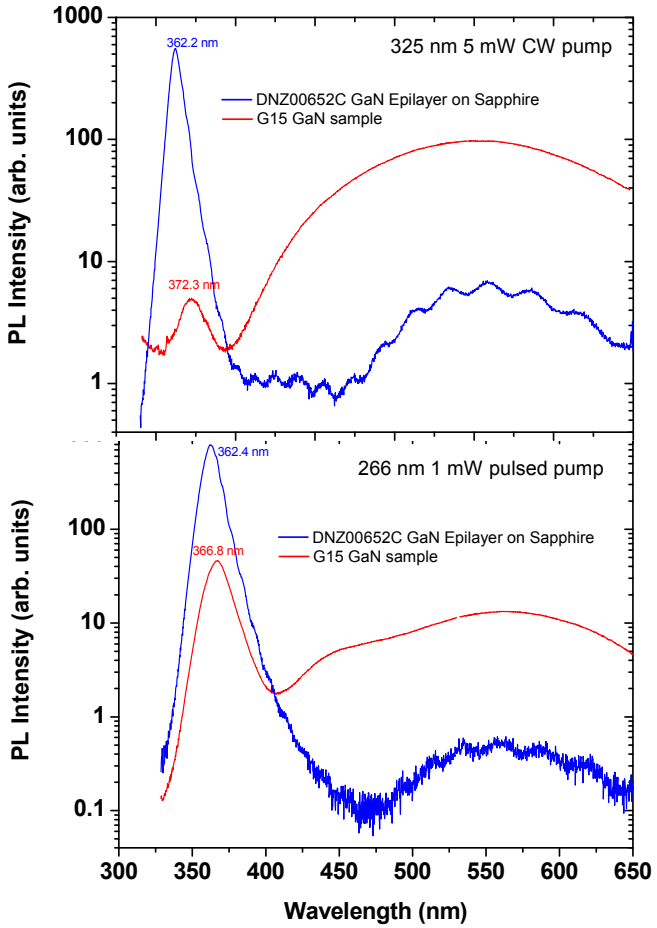
GaN ESG Produces Photoluminescent GaN Crystallites









Mary Crawford, SNL

GNOEM Systems, Inc. Boulder Creek, CA

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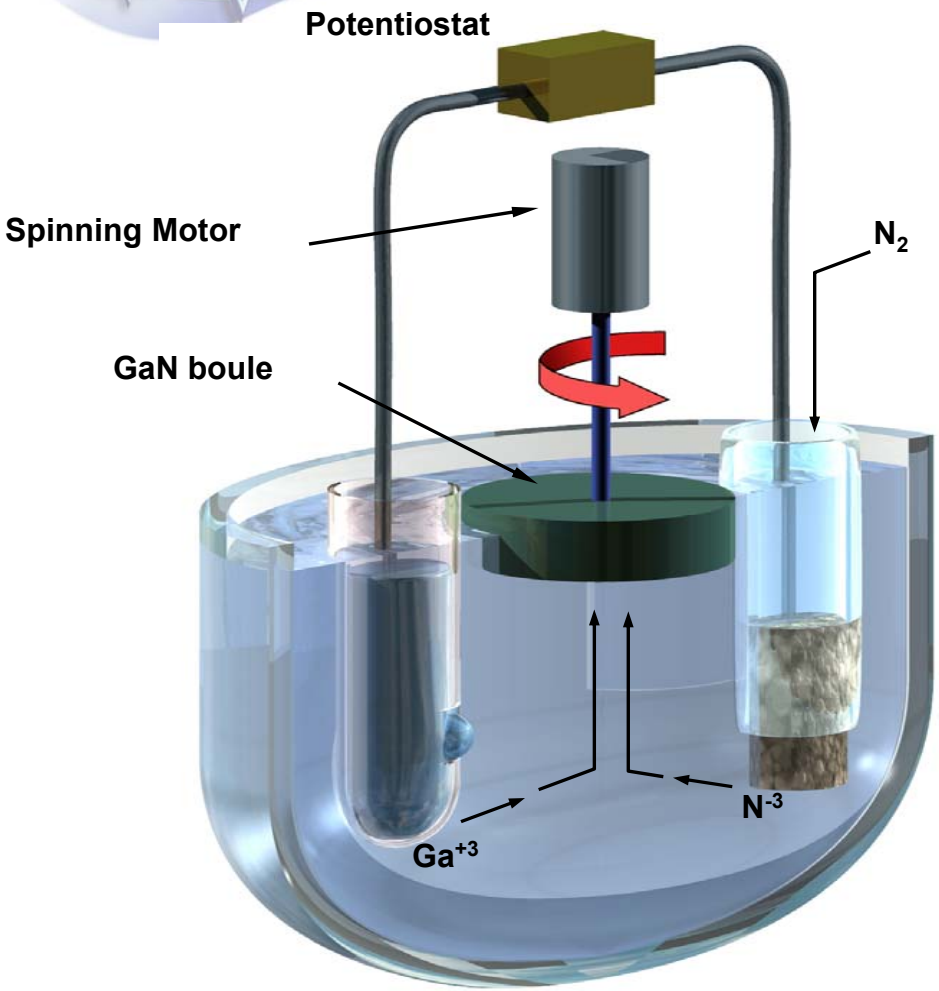
New Growth Technique: Electrochemical Solution Growth (ESG)



Use salt flow to deliver precursors

Increase growth rate through flux of reactants (increase spin rate)

- **Half-reaction 1:**
  - **$1/2N_2 + 3e^- \rightarrow N^{-3}$**
  - **N^{-3} concentrations ~12 mole %**
- **Half-reaction 2:**
  - **$Ga \rightarrow Ga^{+3} + 3e^-$**
  - **Ga^{+3} equilibrium concentrations ~1 mole %**

Precursors can be replenished as they are consumed
Advantage: Continuous, isothermal or steady-state growth

U.S. Patent filed April 11, 2005

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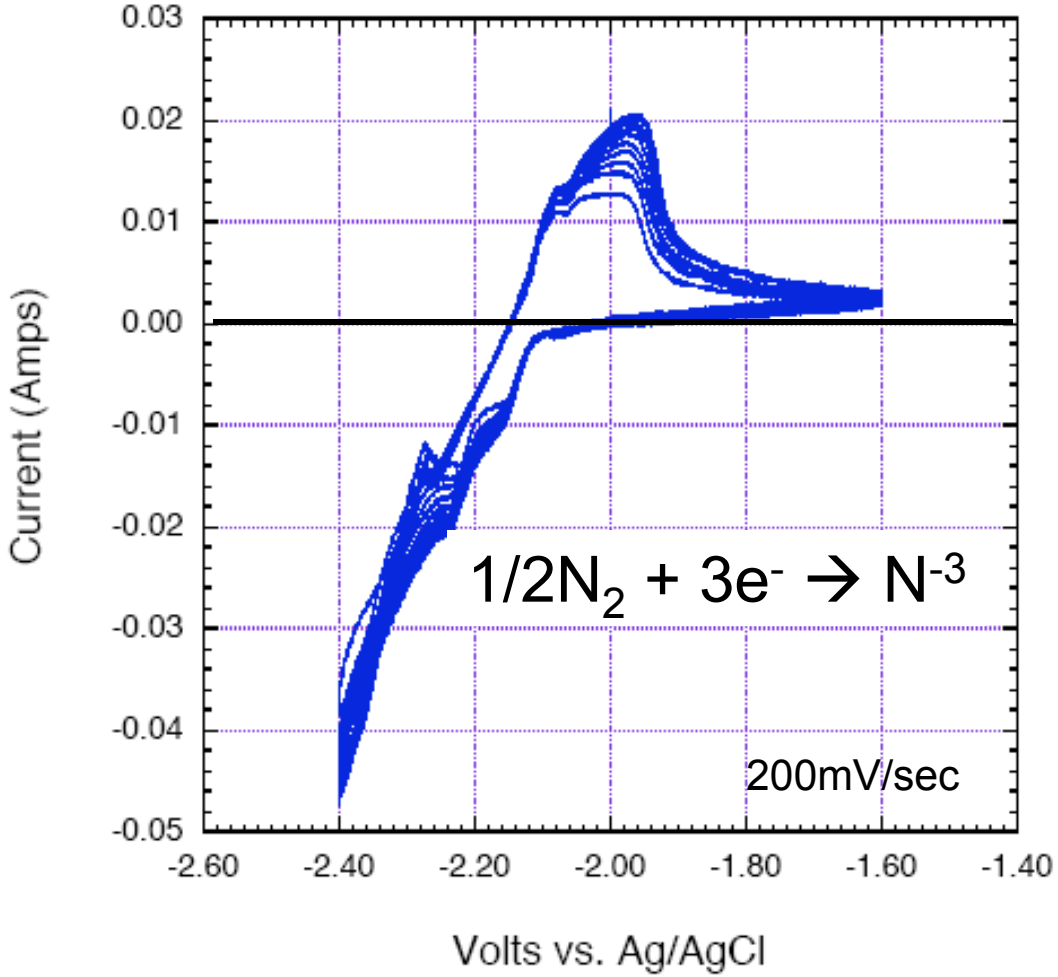
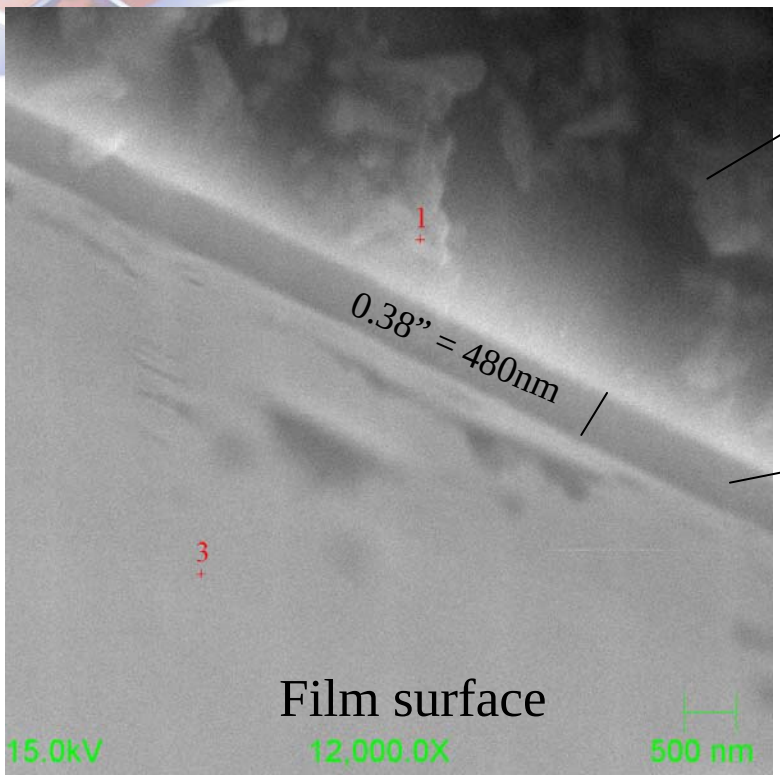
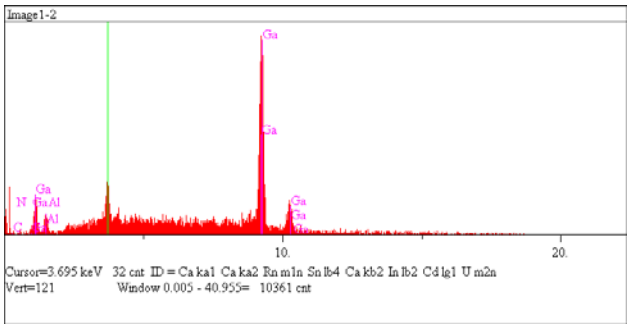
Example of Nitrogen Gas Reduction Cyclic Voltammograms



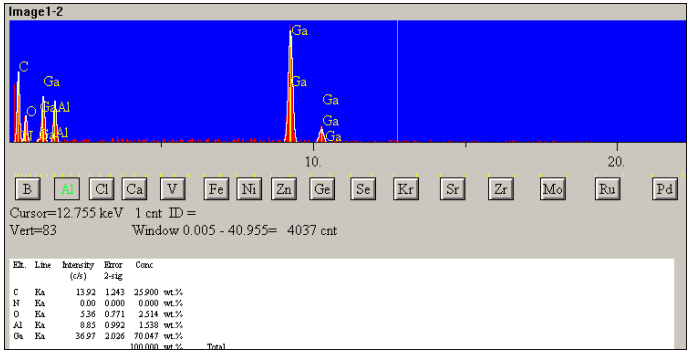
SEM of RD-ESG Growth Run #1



MOCVD-grown GaN



Ga, Al-containing layer



- **SIMS revealed the layer to be a graphitic carbon layer, with Ga, N, and GaN clusters**
  - **GaN content was about 10%**
  - **Profile was consistent with an increasing concentration**
- **Problem with salt purity from supplier**
  - **Working it out with supplier**
  - **Developing in-house purification technique for reagent grade salt**

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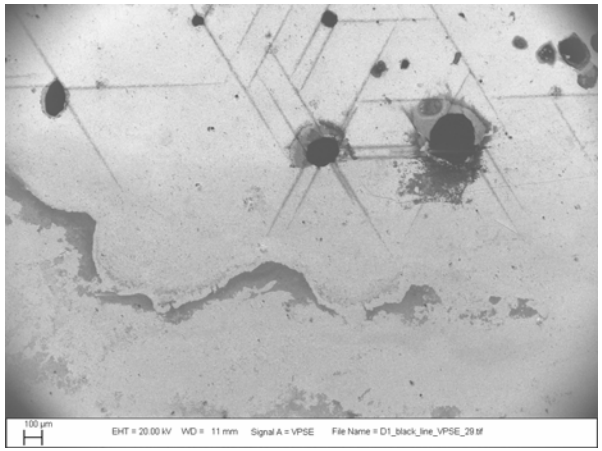
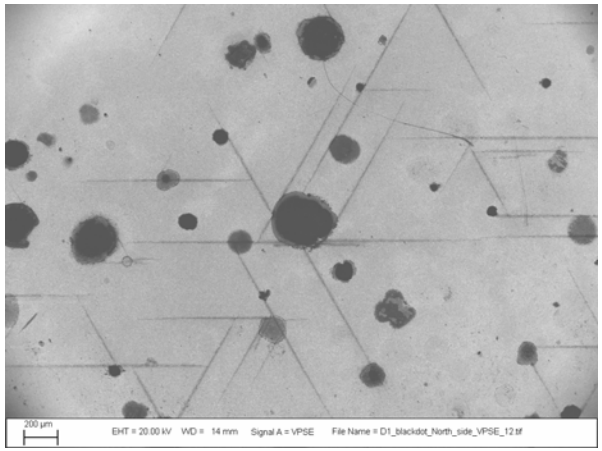
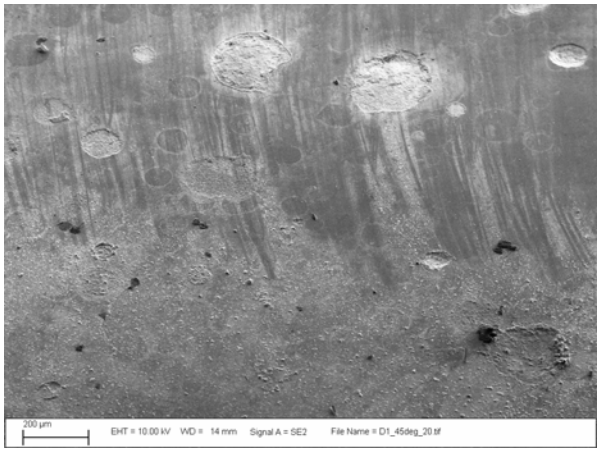
Industrial Partner (GNOEM) Hardware Development

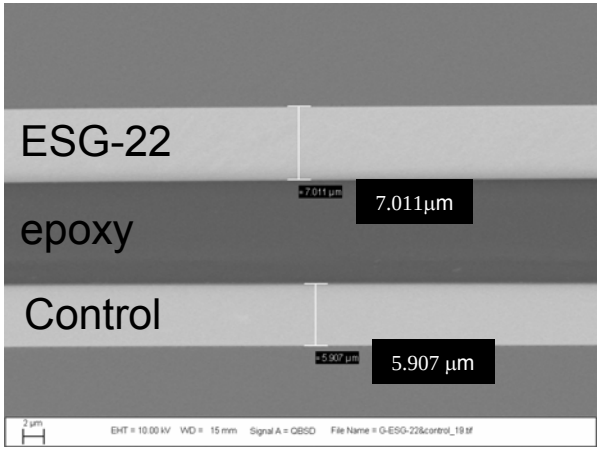
First GNOEM RD-ESG Experiment







- **Hardware failure– susceptor sheared, not sure when**
- **Black line on sample surface delineated a higher, specular region and lower, roughened area**
- **Defect selective etching observed (several microns/hr)**
- **Highly encouraging for crystal quality**
  - **Must identify the conditions under which this takes place**
- **Polished cross sections of control and experiment sample consistently measure about 1μm thicker for experiment**



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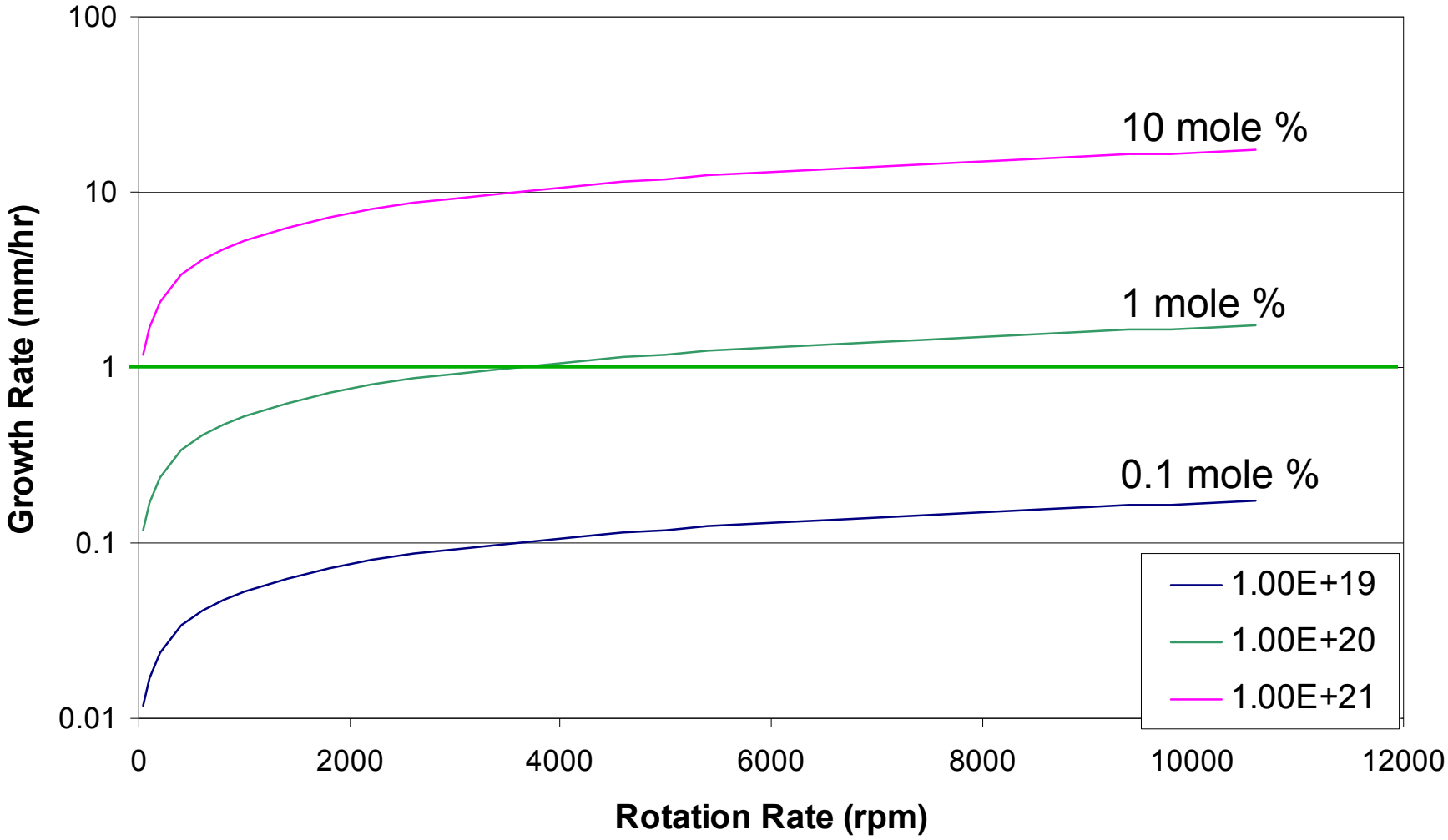
Growth Rate vs. Rotation Speed and Concentration



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Summary: Path For Development

- ✓ Demonstrate that chemistry is viable
  - Kinetics and thermodynamics are favorable in this setup
- ✓ Check for dissolution and precipitation approach
- ✓ Develop N_2 electrochemical reduction methods
- ✓ Develop initial fluid dynamics schemes
- ⇨ Deposit GaN on a seed crystal
- Improve crystal quality
- Optimize growth rate

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