Enabling Next-Generation Power Electronics:

Electrochemical Solution Growth (ESG) Technique for Bulk Gallium Nitride Substrates

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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.

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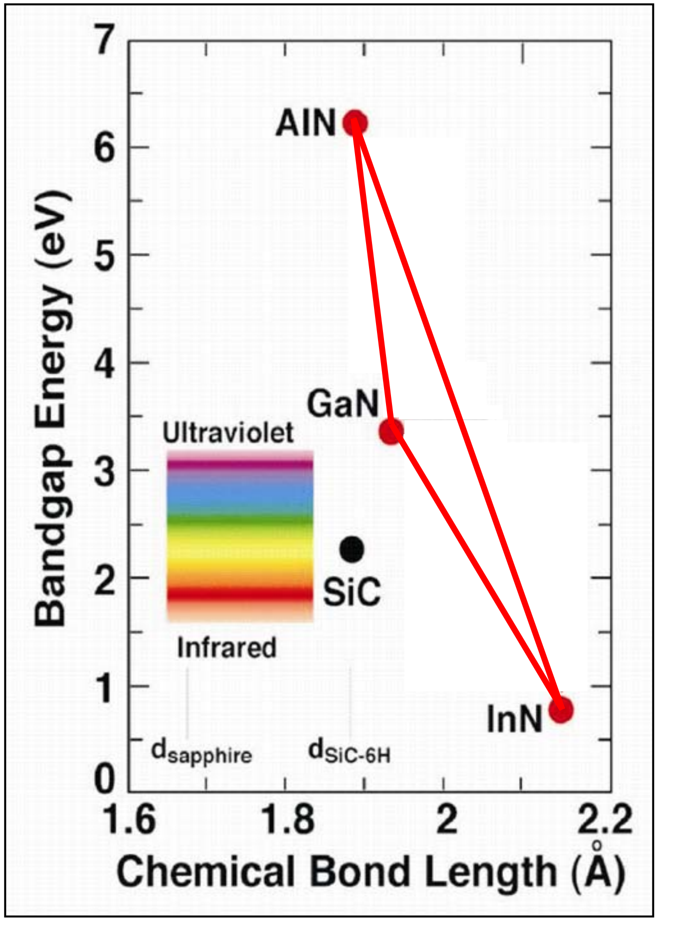
Motivation for GaN Power Devices

- **Footprint:** WBG power electronics offer advantages over silicon
  - No active cooling systems
- **Flexibility:** GaN offers additional device design options due to ability to alloy with AlN (higher standoff voltages) and InN (higher switching frequencies), new device architectures
- **Cost:** SiC expensive; GaN has market pull from solid-state lighting to reduce cost



Motivation for Bulk Growth

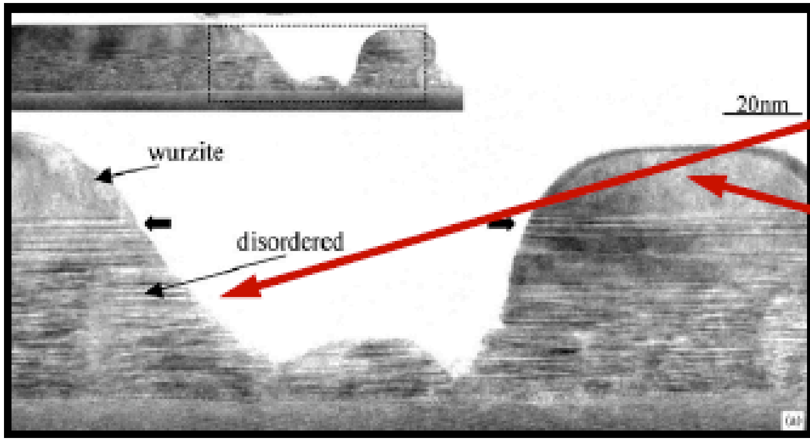
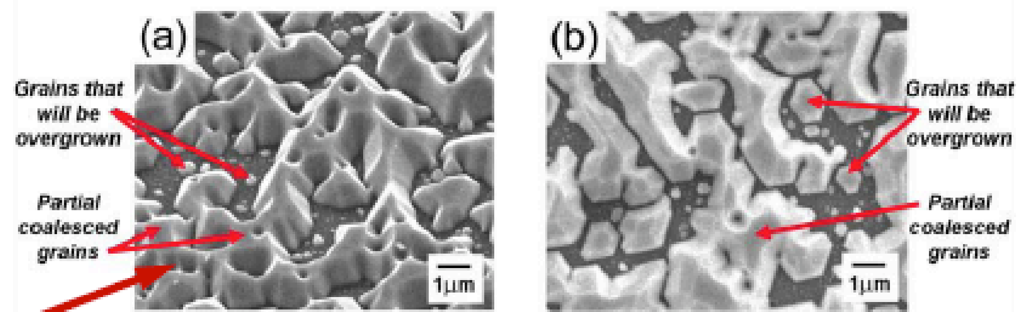


Figure from Lada et al., J. Crystal Growth 258, 89 (2003).

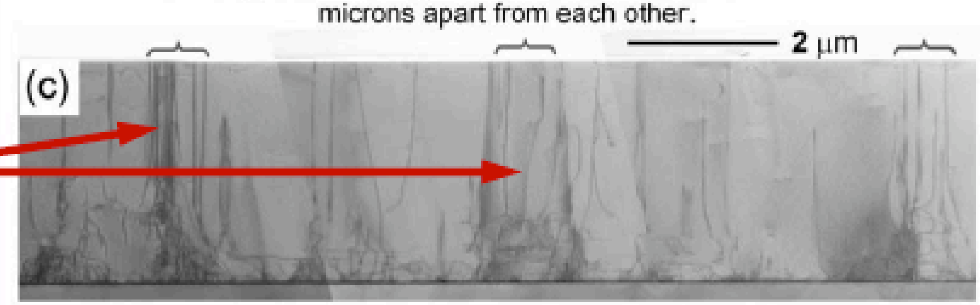
- As grown GaN nucleation layers contain disordered GaN with many stacking faults.
- Once annealed, wurtzite GaN forms on top of disordered GaN NL, forming nano-sized GaN nuclei from which further high temperature GaN growth occurs.

SEM Images of 3D GaN grain growth



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

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



TEM cross section

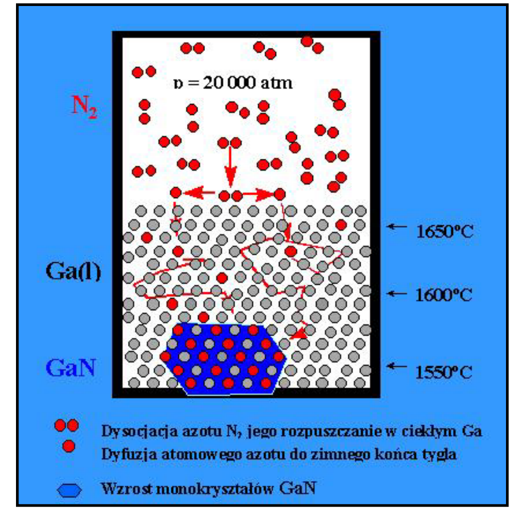
TEM courtesy of D. M. Follstaedt

State of the Art in Bulk GaN Growth

True bulk GaN not yet readily available

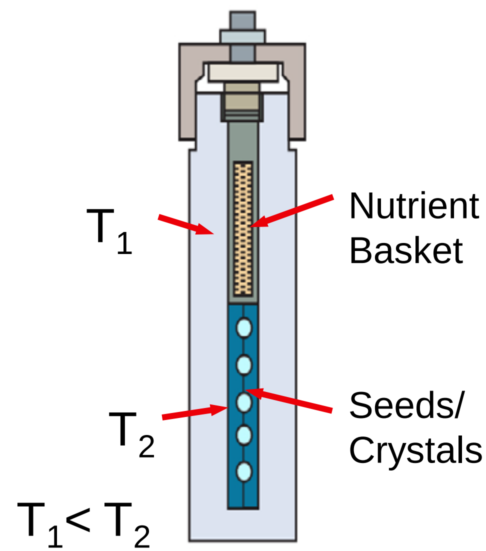
- **Traditional bulk growth techniques require high temperatures, high pressures**
  - **2500ºC**
  - **60,000 atm N_2 overpressure**
  - **Adaptations dissolve N_2 in Ga at 1500ºC, 20,000 atm**
- **Extremely difficult to dissolve**
  - **Liquid ammonia (500-800C, 4,000-5,000 atm)**
  - **Requires additional mineralizers**
  - **60 μm/day growth rates**
- **Gas phase approaches require high quality substrate**
  - **Sapphire or SiC**
  - **Quality not high, limited in size**
  - **Very expensive**

Scalability Limited, Cost-Prohibitive



High Nitrogen Pressure Solution Growth

Ammono
IEEE Spectrum



Ammonothermal

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Desires/Requirements for a Bulk GaN Growth Technique for Power Electronics

- **Good crystalline quality ($\rho \leq 1x10^{5}cm^{-2}$)**
- **High growth rate (~mm/hr): high throughput, high volume production**
- **Low impurity content**
- **Low background carrier concentration (~$1x10^{16}$ cm^{-3})**
- **Scalable**
- **Controllable**
- **Manufacturable**
- **Reasonably inexpensive**
- **Applicable to InN, GaN, AlN, and III-N alloys**

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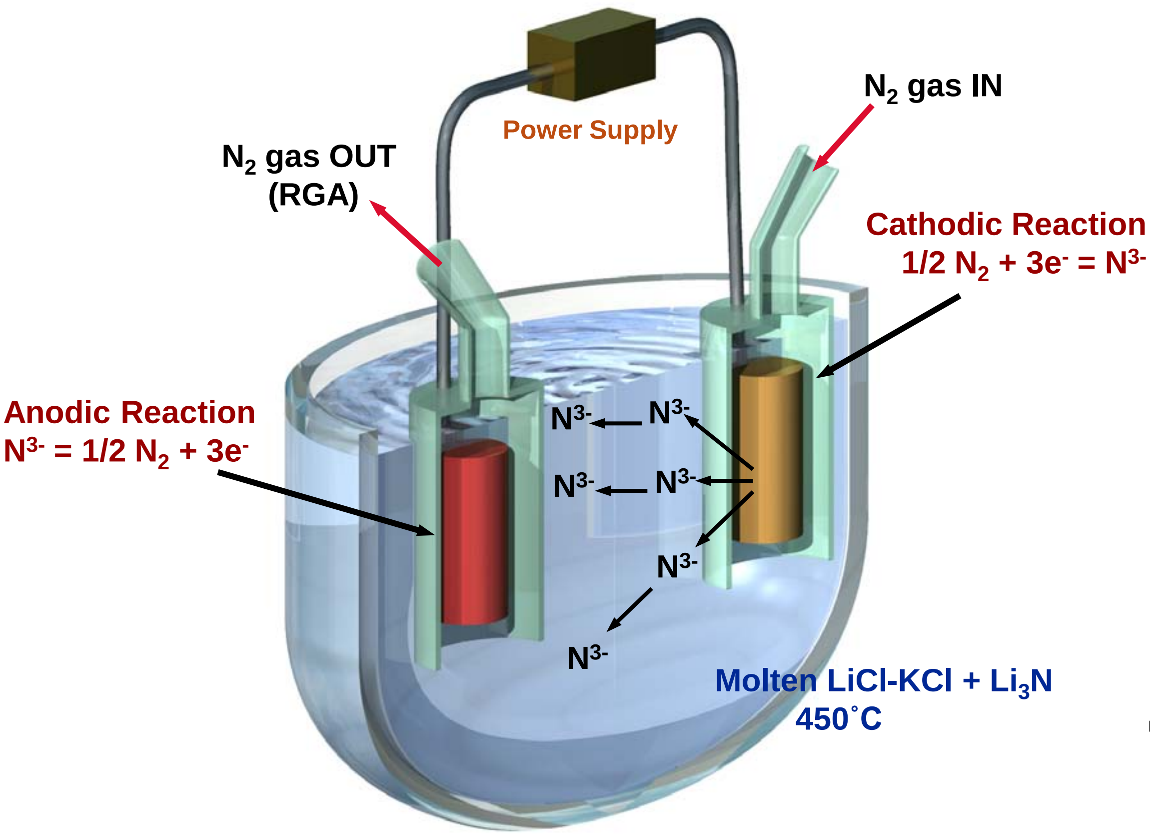
$1/2N_2 + 3e^- \rightarrow N^{-3}$: *The* Reactive Intermediate

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).

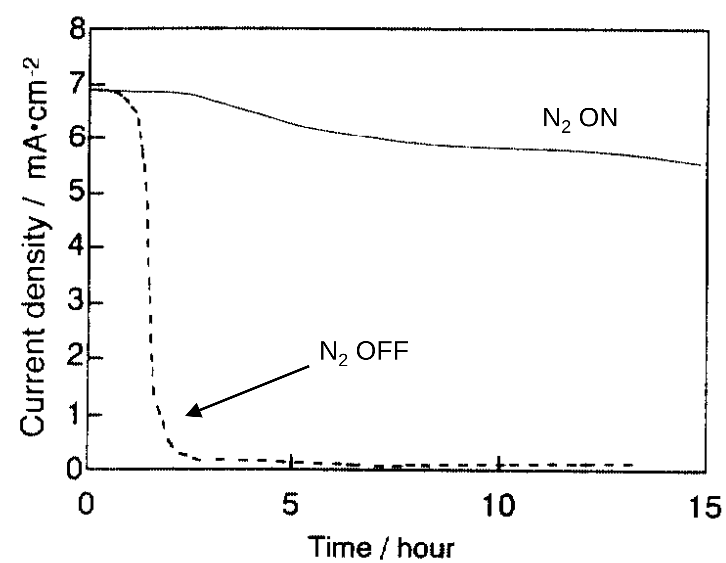
Found that nitrogen was continuously and nearly quantitatively reduced to nitride ions



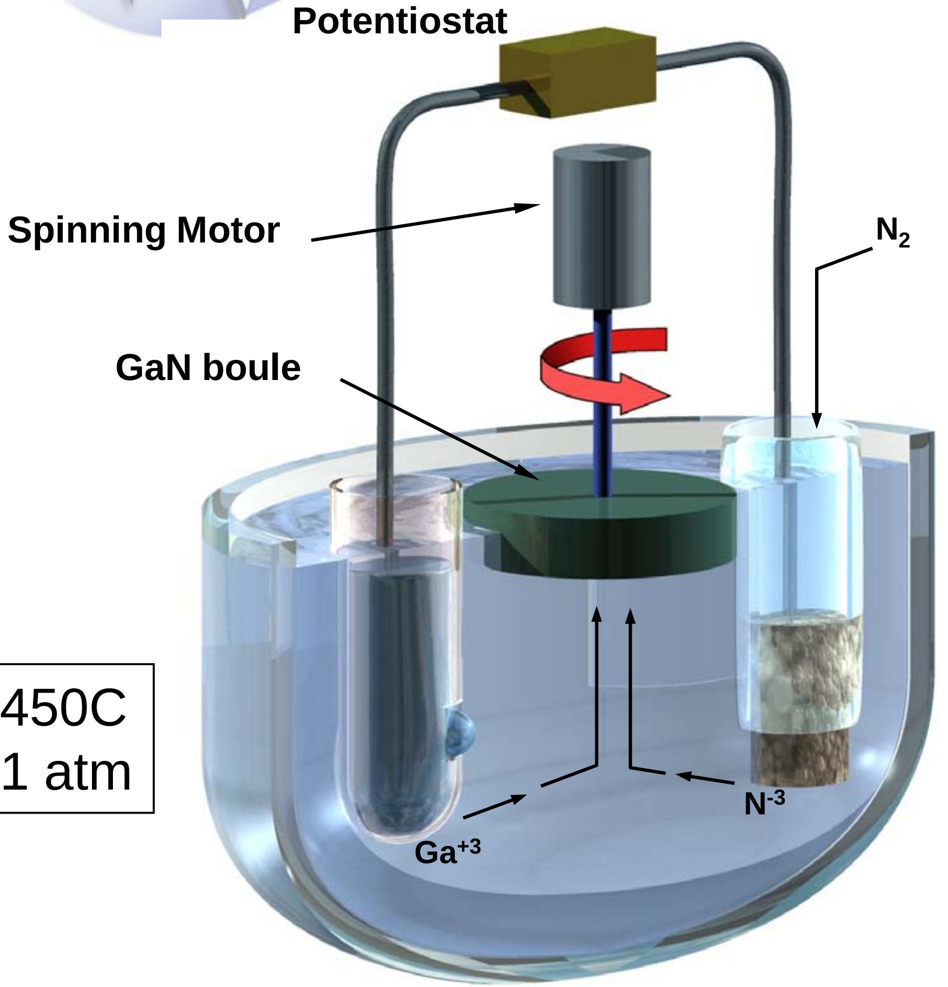
Report of nitride concentration in LiCl in literature: 12 mole %

Advantages of using N_2 gas:

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



Sandia's Patented New Growth Technique: Electrochemical Solution Growth (ESG)



450C
1 atm

Create Ionic Precursors Electrochemically:

$$2Ga \rightarrow 2Ga^{+3} + 6e^-$$

$$N_2 + 6e^- \rightarrow 2N^{-3}$$

$$Ga + N_2 \rightarrow Ga^{+3} + N^{-3} \rightarrow GaN$$

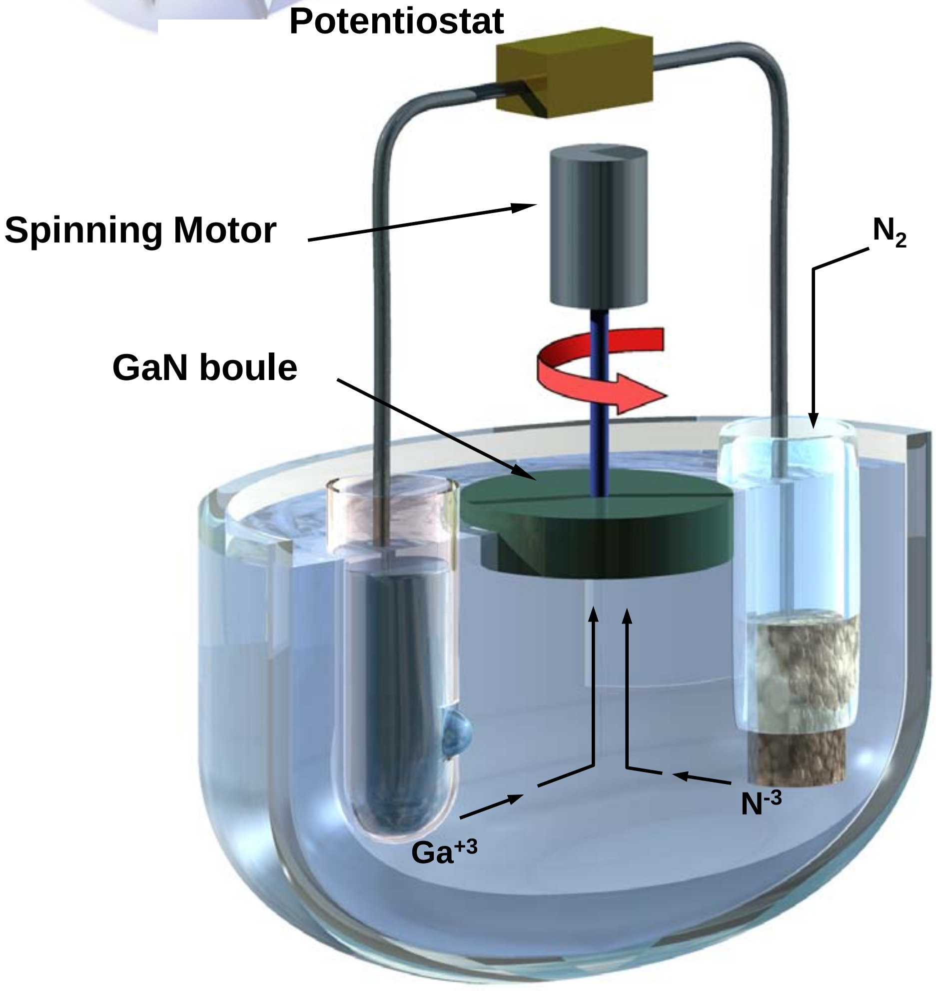
Use salt flow to deliver precursors to seed crystal surface

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

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

U.S. Patent Issued October 2008

Electrochemical Solution Growth (ESG): Previous Work

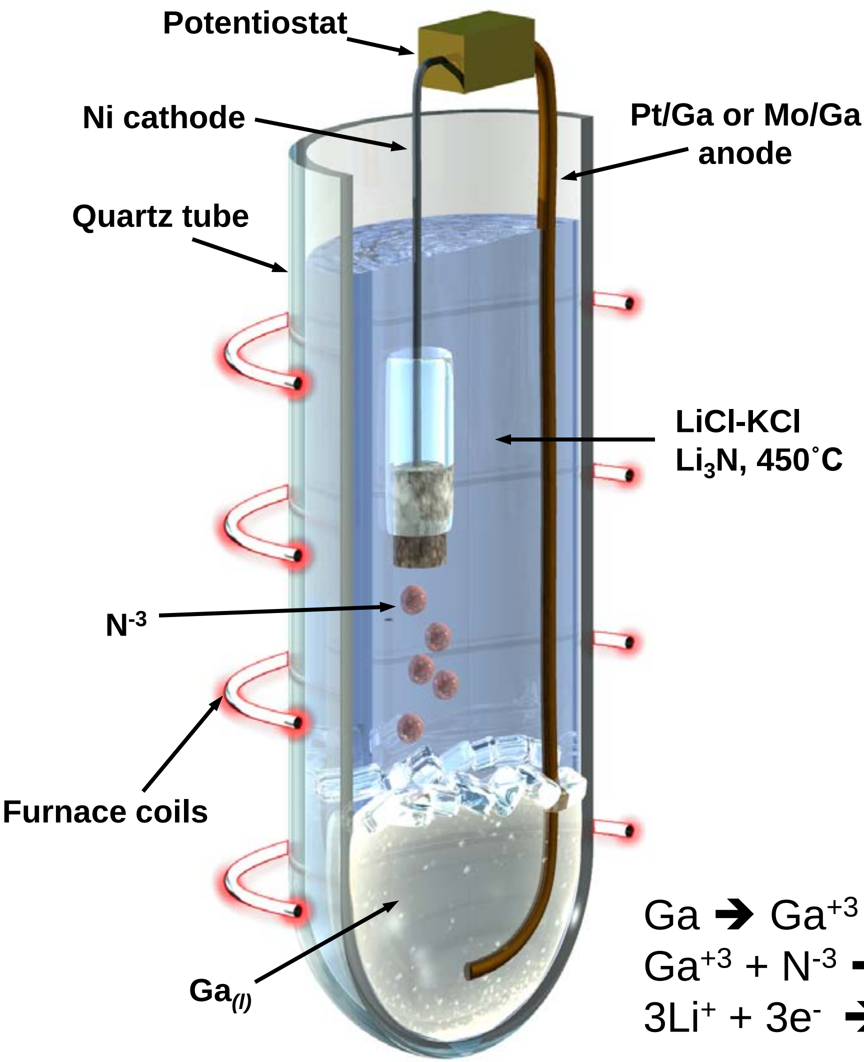


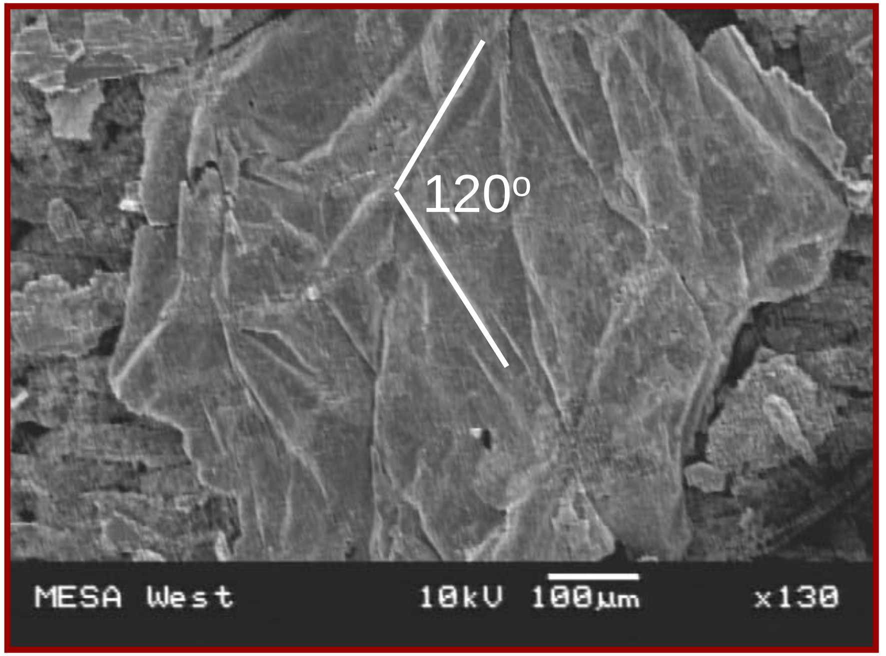
- Electrochemistry studies
- Preliminary fluid dynamics
  - Growth rates ~mm/hr
- Chemistry studies
- ESG autonucleation:
  - mm-sized crystals in 2 hrs
  - Bandedge photoluminescence
- ESG boule growth:
  - Deposition of GaN at seed surface

Next step: Developing quality of crystals

Seed Crystal Growth Technique Development

Li_3N + Ga, 450˚C





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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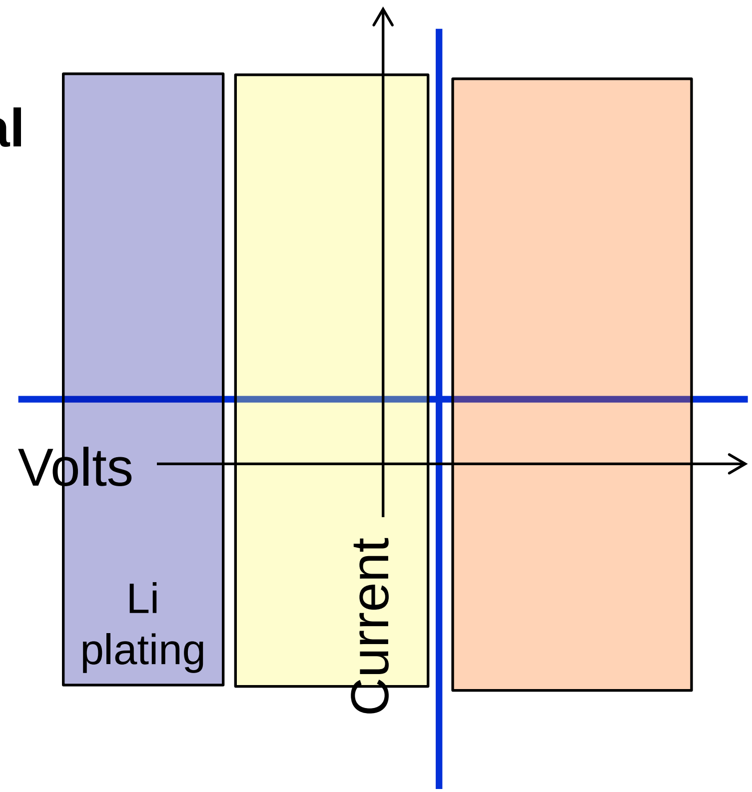
Seed Crystal Growth Experiments

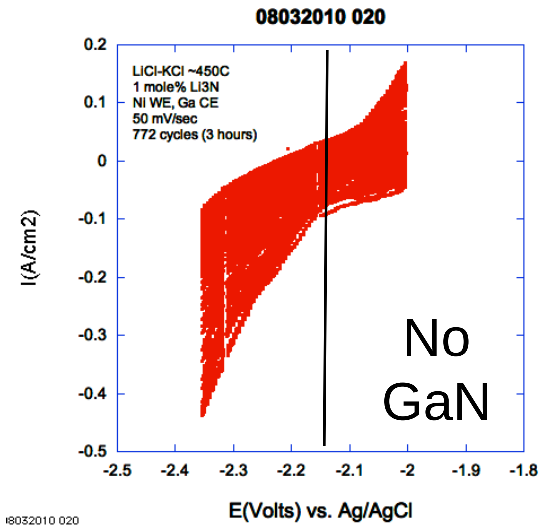
- **Motivation:**
  - **Better understand the experimental conditions under which GaN is formed**
- **Systematic set of electrochemical experiments conducted**
- **Ga oxidation, Li_3N as nitride source**
- **GaN formed only under one experimental condition**
- **Optimization straightforward**
- **DOEx setup performed**

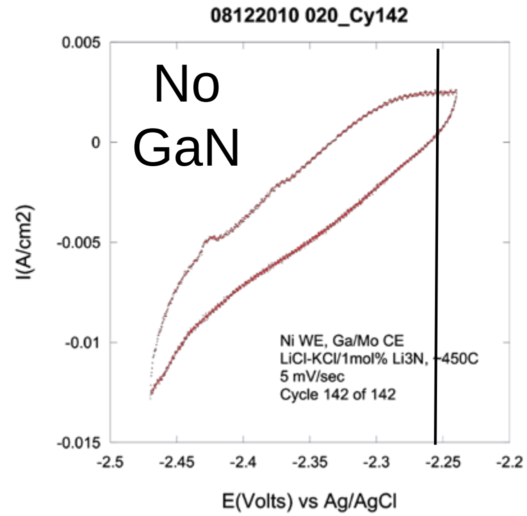


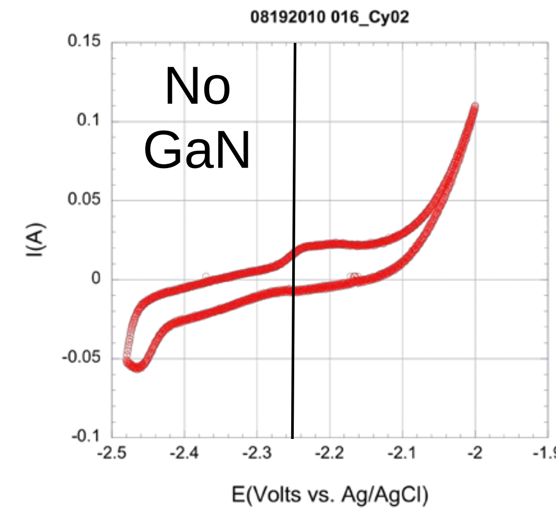
OCP

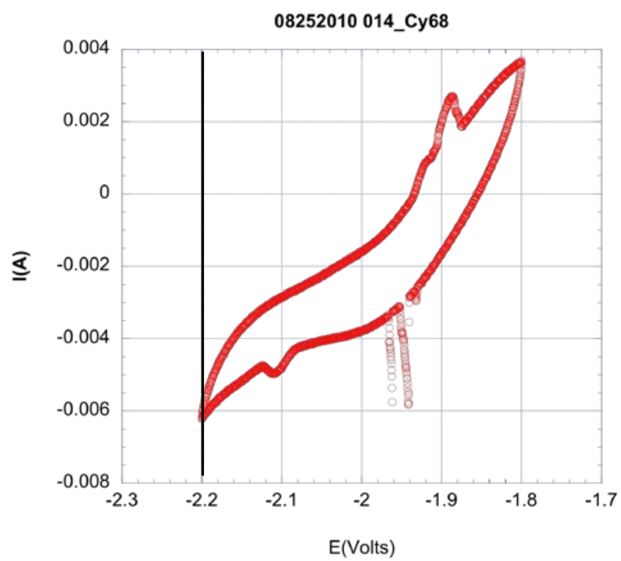
$$Ga + Li_3N \rightarrow GaN + 3Li$$

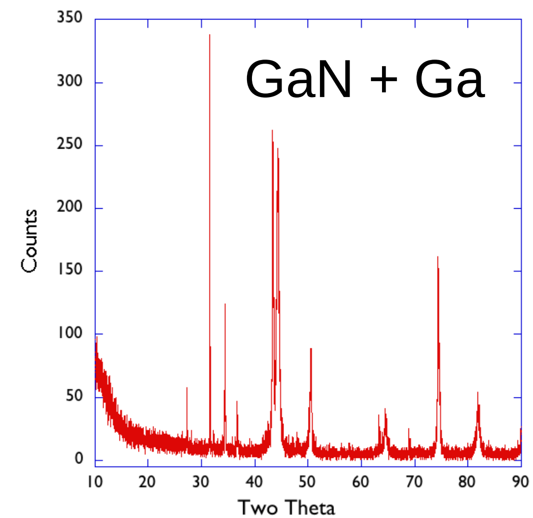
Seed Crystal Results











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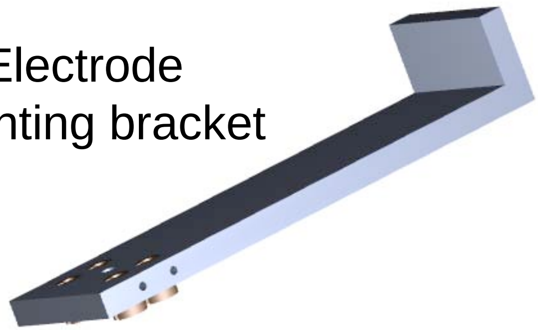
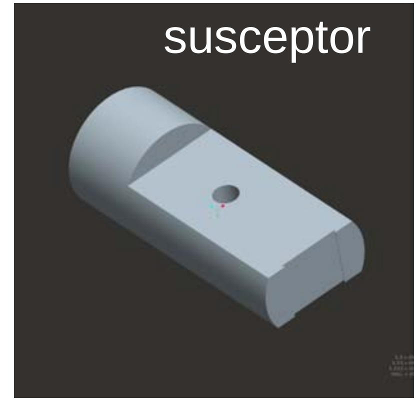
Boule Growth Reactor Design

Electrode
mounting bracket





Previous Setup

Ring Stand & Clamps -- irreproducible and clumsy

Temperature Control through variac power supply

Quartz crucibles and electrodes

Cement mounting of seed crystal

Reactor located in secure area

New Reactor

Positional and rotational control through computer-controlled stepper motors and machined mounting bracket

Temperature Control through reactor temperature feedback to power supply

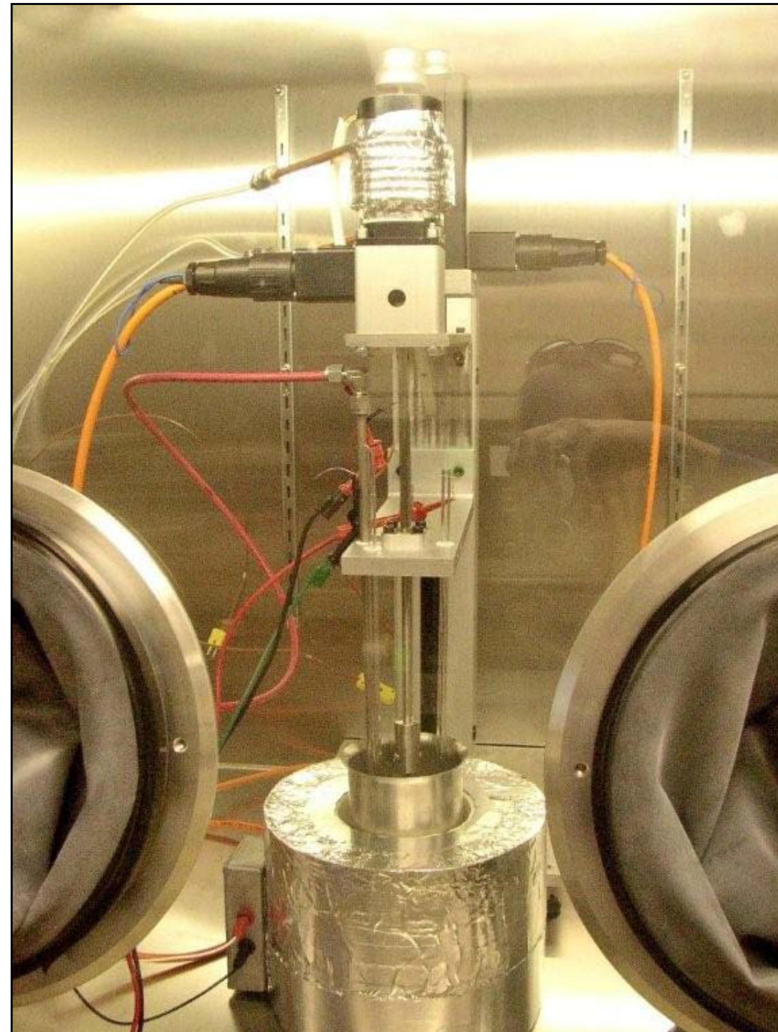
p-BN and/or stainless steel materials

Precision-machined SS mechanical susceptor

Accessible to uncleared personnel

Acknowledgements: M.J. Russell, P. Michel

Gen-2 Boule Growth Reactor
Up to 1.5” diameter



FY11: Design of Experiments
Boule and Seed Growth

Standard Order	Temperature (deg C)	Spin Rate (rpm)	Seed Depth (mm)	Static/ Dynamic	Li_3N Conc. (mole %)	Duration (hr)
1	375	0	2	Static	0	3
2	550	0	2	Static	10	3
3	375	400	2	Static	10	10
4	550	400	2	Static	0	10
5	375	0	18	Static	10	10
6	550	0	18	Static	0	10
7	375	400	18	Static	0	3
8	550	400	18	Static	10	3
9	375	0	2	Dynamic	0	10
10	550	0	2	Dynamic	10	10
11	375	400	2	Dynamic	10	3
12	550	400	2	Dynamic	0	3
13	375	0	18	Dynamic	10	3
14	550	0	18	Dynamic	0	3
15	375	400	18	Dynamic	0	10
16	550	400	18	Dynamic	10	10
17	450	200	10	Static	1	5
18	450	200	10	Dynamic	1	5

4-Factorial
Resolution IV
18 Runs
2 Replicates

Similar for Seed Growth

Growth: Y/N
Amount of growth
Dislocation density
Optical properties
Electrical properties

Each experiment duplicated = 36 experiments
Similar set (36 experiments) generated for Seed Growth

Acknowledgement: Steve Crowder

Nature Deposits $CaSO_4.2H_2O$ Single Crystals from Solutions of Ionic Precursors

Giant crystal caves, Naica, Mexico
Photo from National Geographic

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