SAND2013-2912C

April 5, 2013

Electrochemical Solution Growth of Gallium Nitride

Todd C. Monson, Karen Waldrip, Michael Russel, Viswanath Krishnamoorthy, Ana-marie Mollo, Linda E. Johnson

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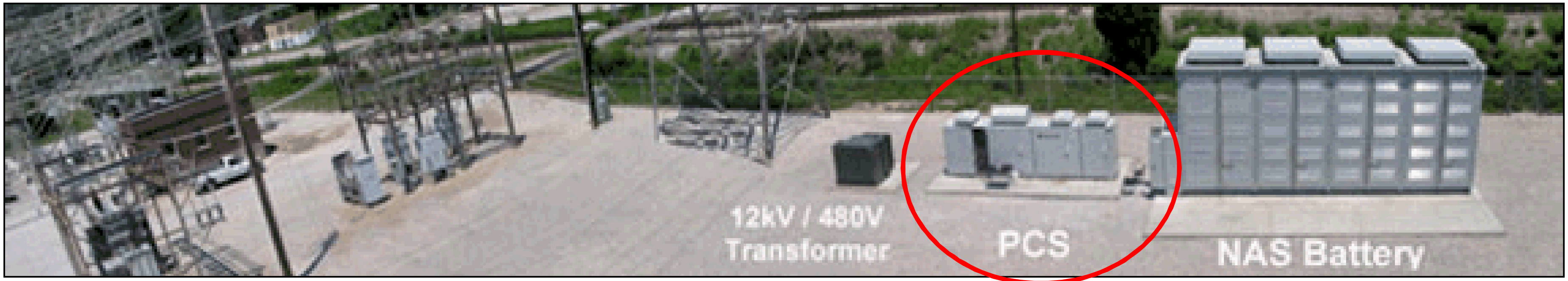
Project Objective



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

Motivation for Bulk Growth

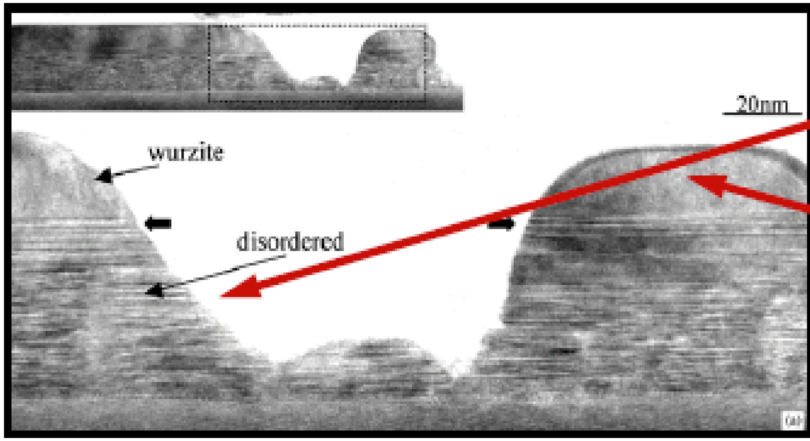
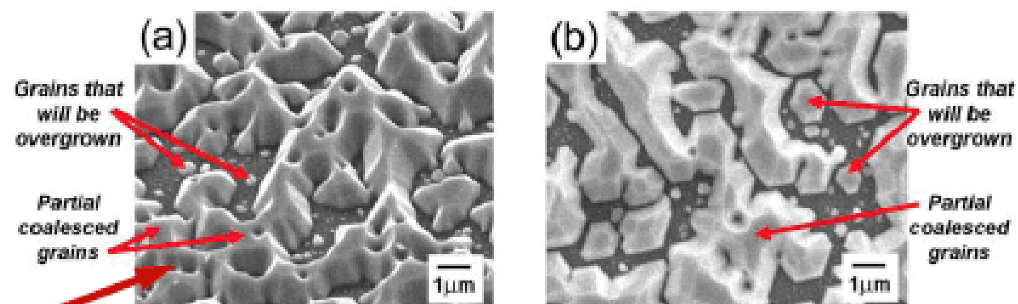


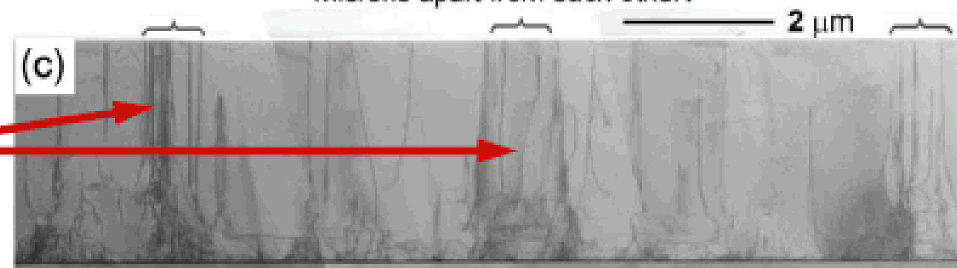
Figure from Lada et al., J. Crystal Growth 258, 89 (2003).

- 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.



TEM cross section

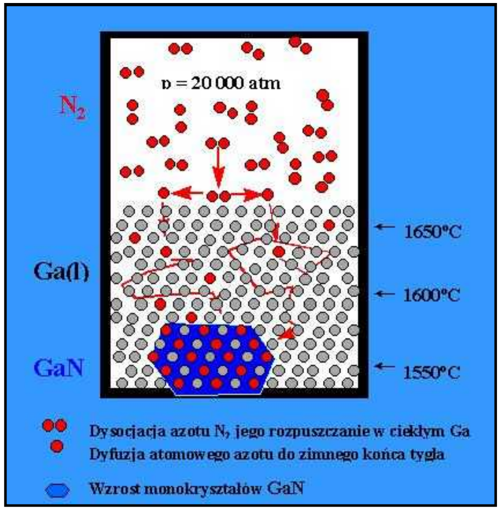
TEM courtesy of D. M. Follstaedt

- 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.

State of the Art in Bulk GaN Growth

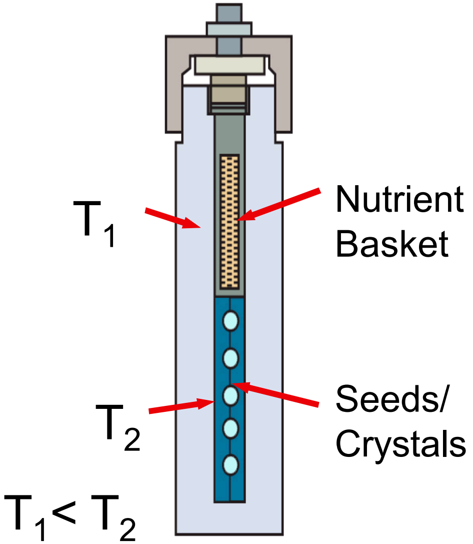
True bulk GaN not yet readily available

- **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



High Nitrogen Pressure Solution Growth

Ammono
IEEE Spectrum



Ammonothermal

Scalability Limited, Cost-Prohibitive

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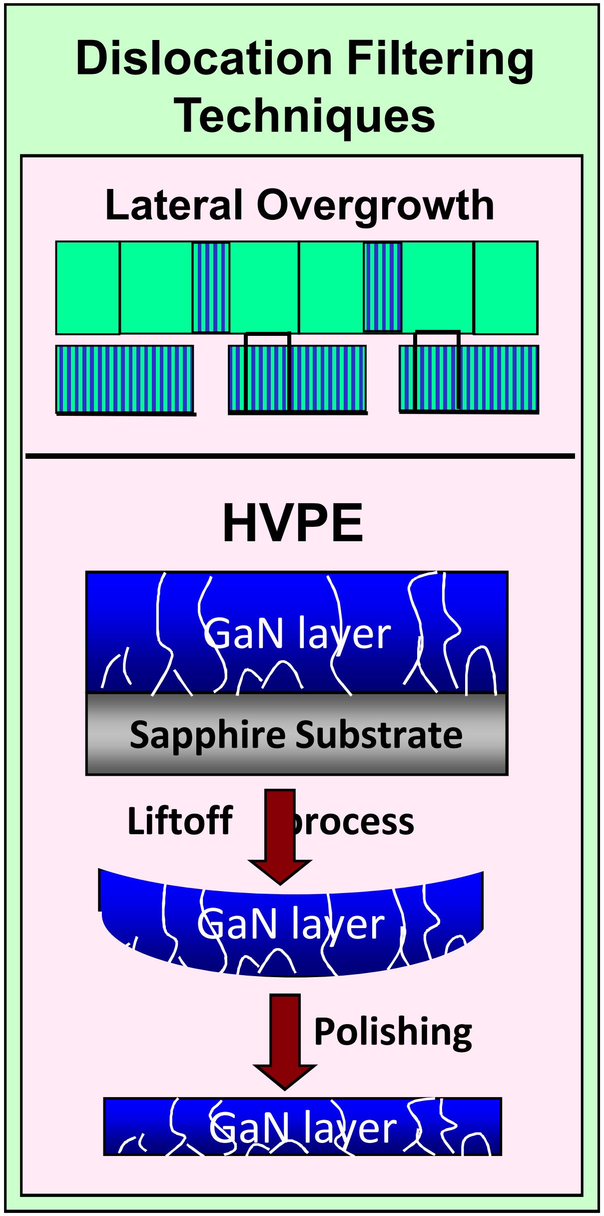
Hydride Vapor Phase Epitaxy (HVPE)



$$GaCl + NH_3 \rightarrow GaN + HCl + H_2$$

- **Gas phase approaches require high quality substrate**
  - *Sapphire or SiC, or bulk seeds*
  - *Quality not high, limited in size*
  - *Very expensive*
- **Difficulty with impurity incorporation on different crystal facets**

Desires/Requirements for a Bulk GaN Growth Technique

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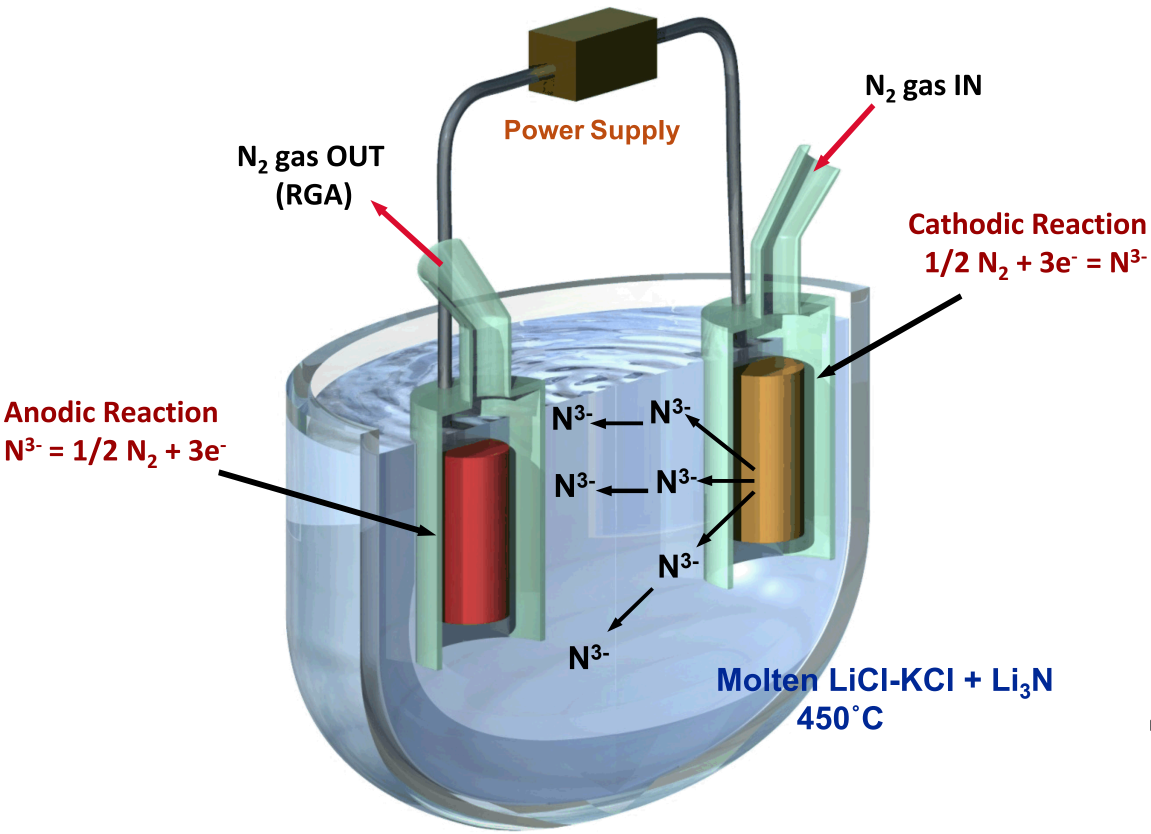
$1/2N_2 + 3e^- \rightarrow N^{-3}$: *The* Reactive Intermediate

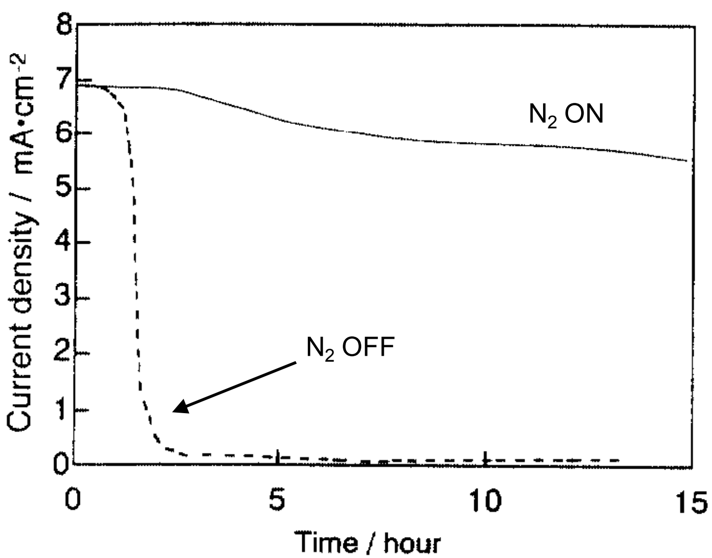
T. Goto and Y. Ito, "Electrochemical reduction of nitrogen in a molten chloride salt" Electrochimica Acta, Vol. 43, Nos 21-22, pp 3379-3384 (1998).

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



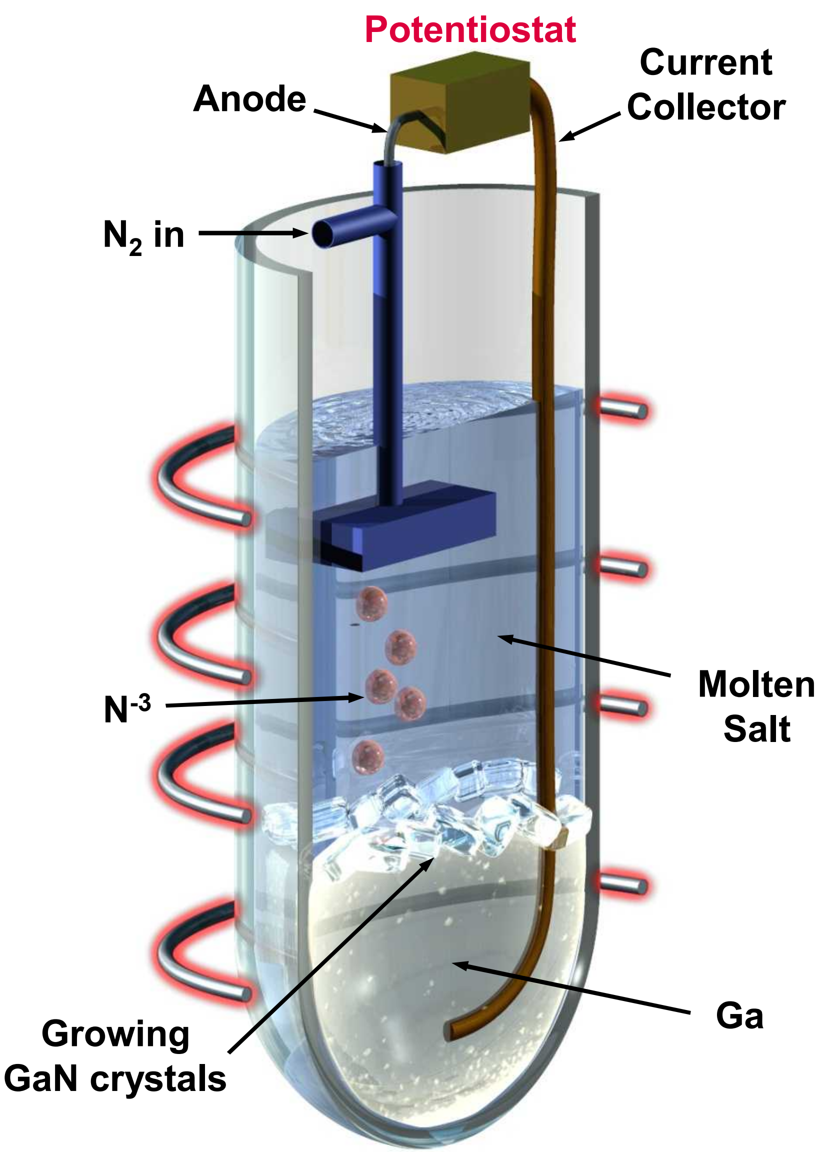
Advantages of using N_2 gas:

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



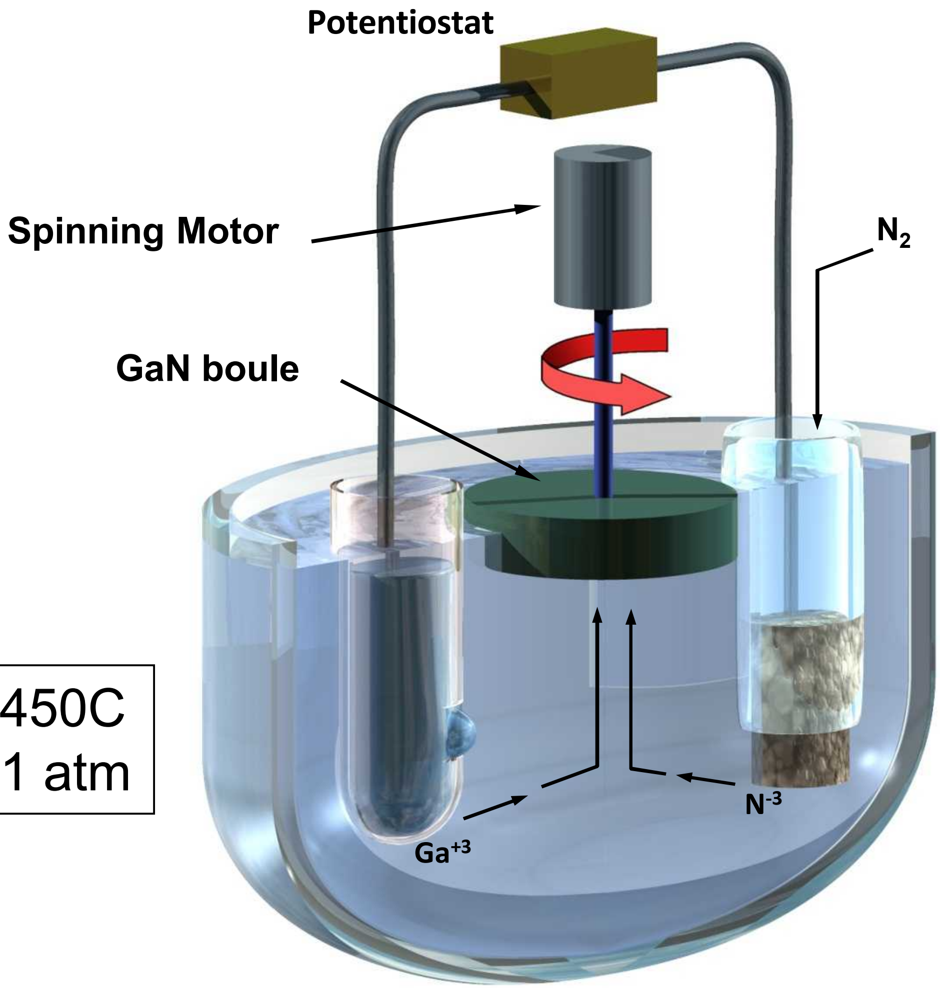
Report of nitride concentration in LiCl in literature: 12 mole %

Electrodeposition is Not a Viable Technique for Thick, Insulating, High Quality Crystals



- Tends to produce rough deposits for low-conductivity materials
- Gallium source on one side of crystal, nitride source on the other
  - Diffusion of either species through crystal very, very low
  - How to get Ga and N ions to same surface??
- However, it was a quick and inexpensive method for demonstrating viable chemistry and favorable kinetics
- Nitride ion available in large quantities… use this capability to our advantage

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

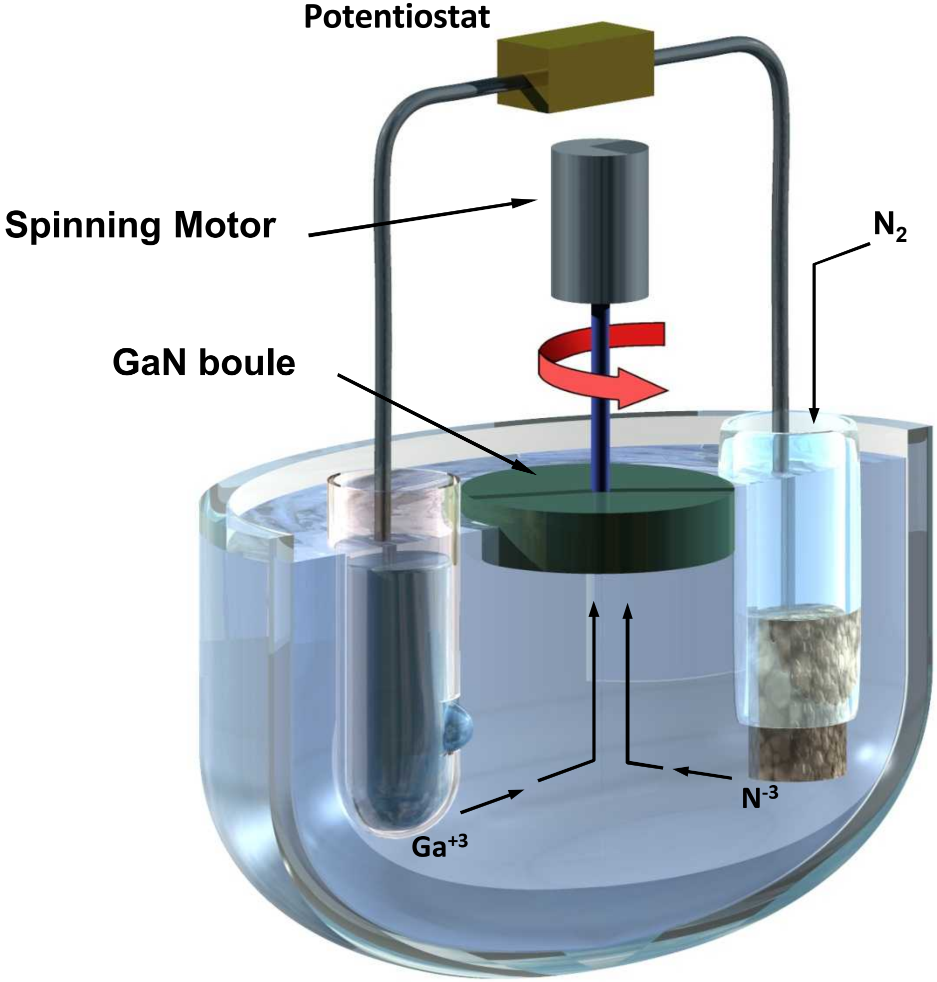
Increase growth rate through flux of reactants (increase spin rate)

Precursors can be replenished as they are consumed

Advantage: Continuous, isothermal or steady-state growth

U.S. Patent Issued October 2008

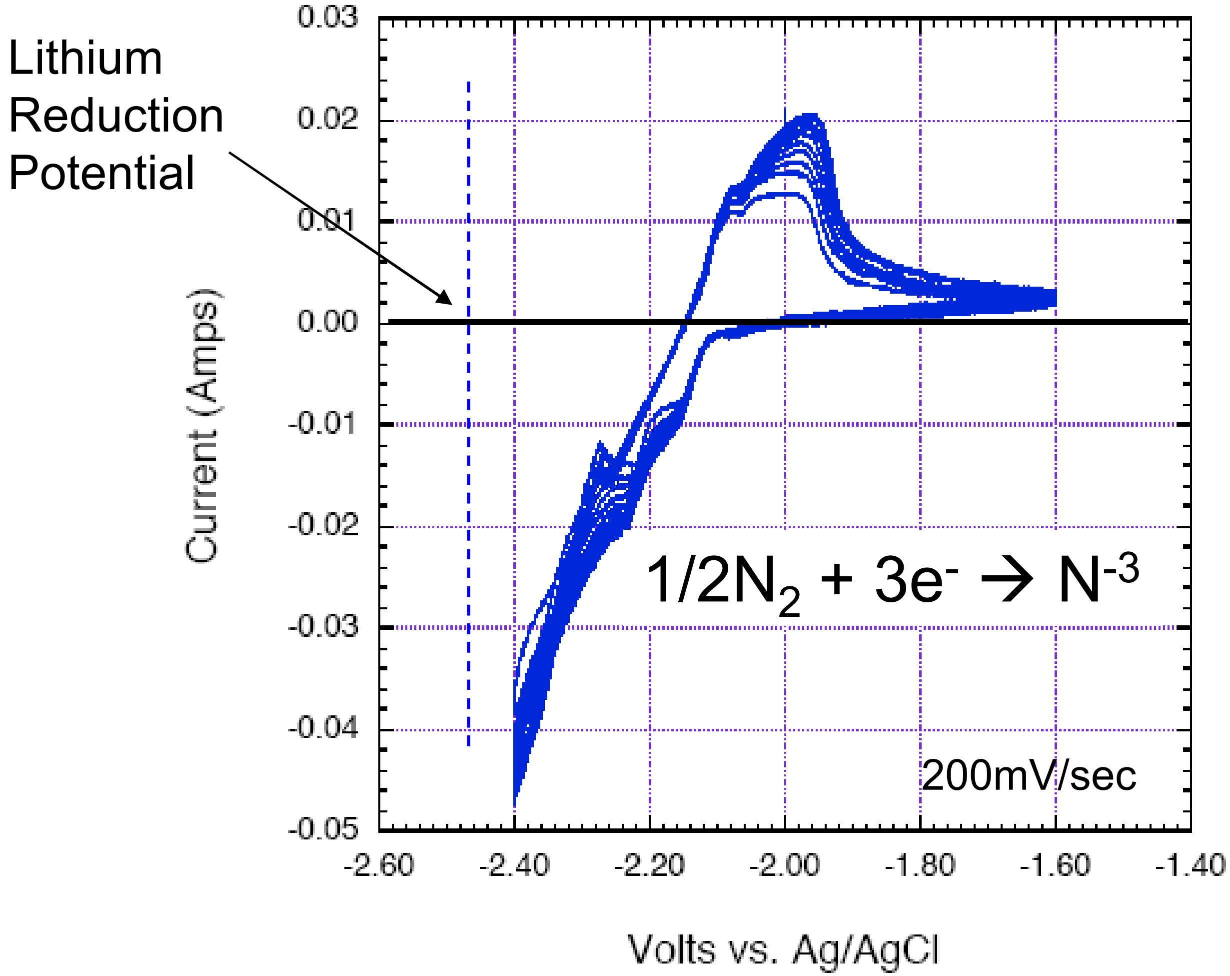
Electrochemical Solution Growth (ESG): Current Status



- 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

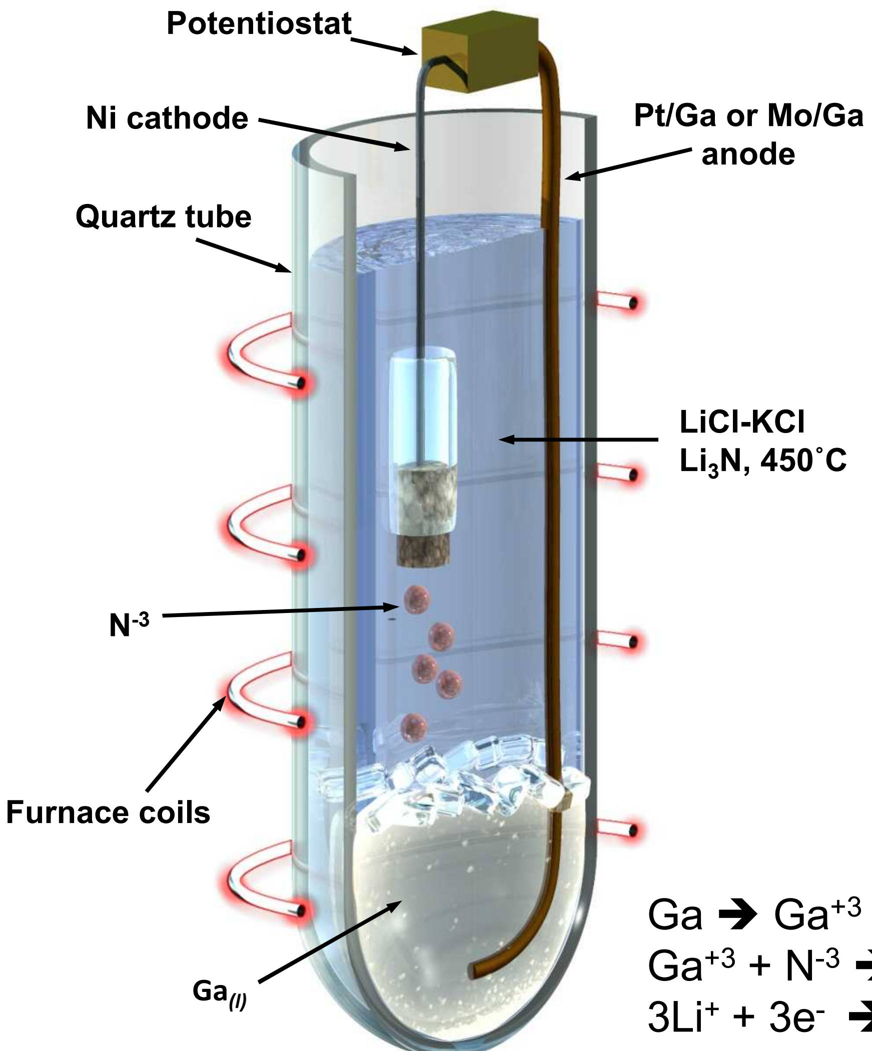
Next step: Developing quality of crystals

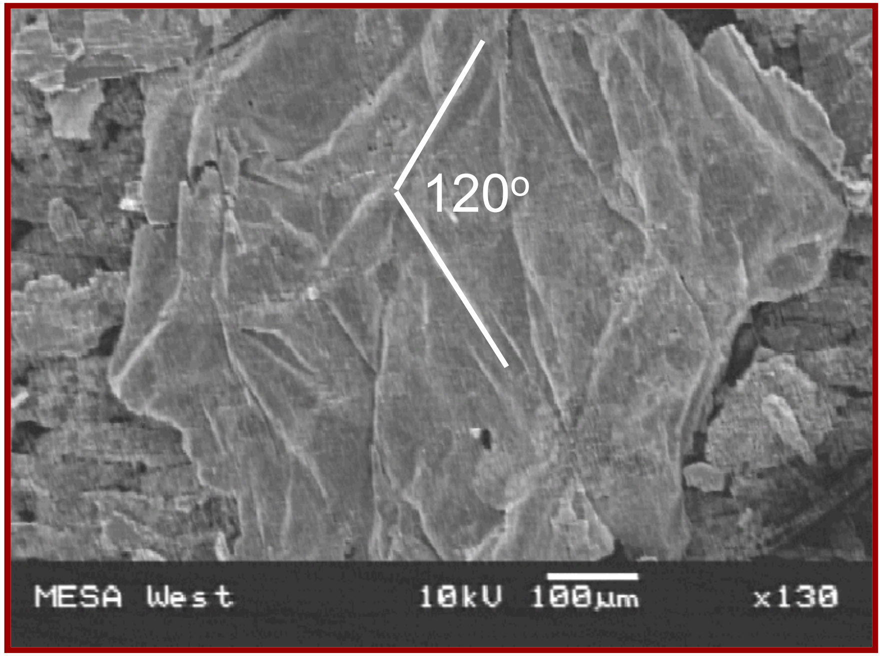
Example of Nitrogen Gas Reduction Cyclic Voltammograms



Autonucleation Experiments of GaN Produce mm-sized crystals in <2hrs.

Li_3N + Ga, 450˚C





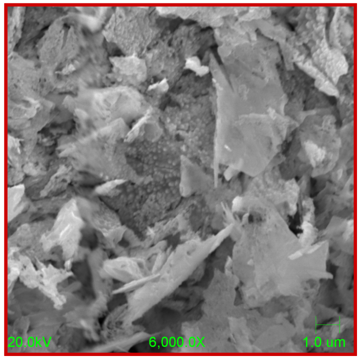
Produced numerous wurtzite GaN crystals;
This crystal was ~1.25mm long x 0.8mm wide

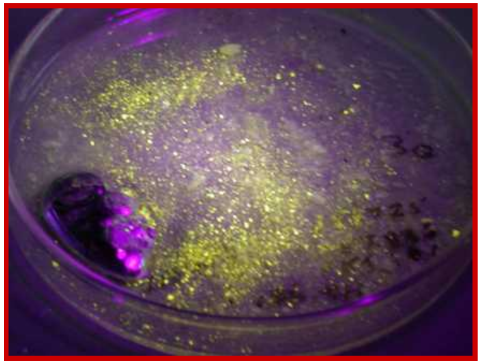
$Ga \rightarrow Ga^{+3} + 3e^-$

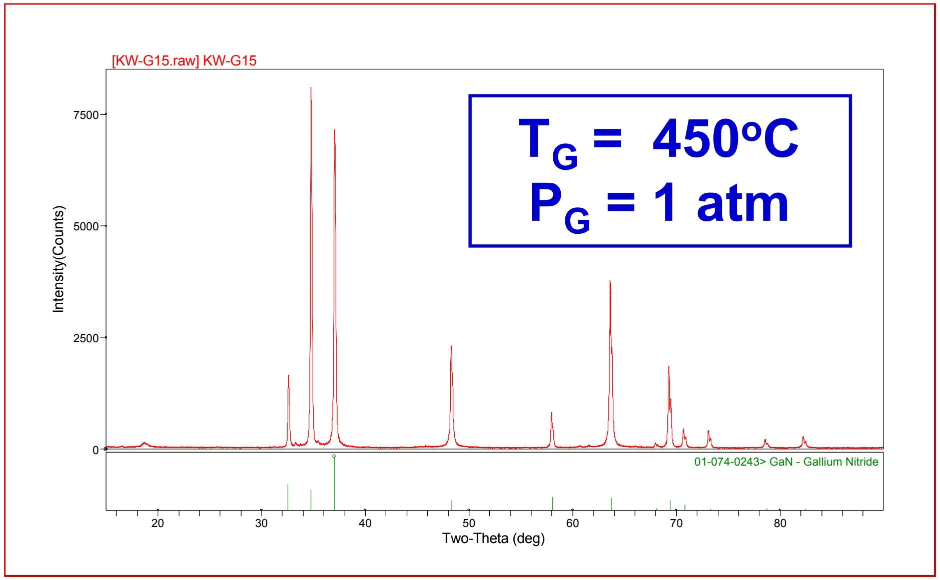
$Ga^{+3} + N^{-3} \rightarrow GaN$

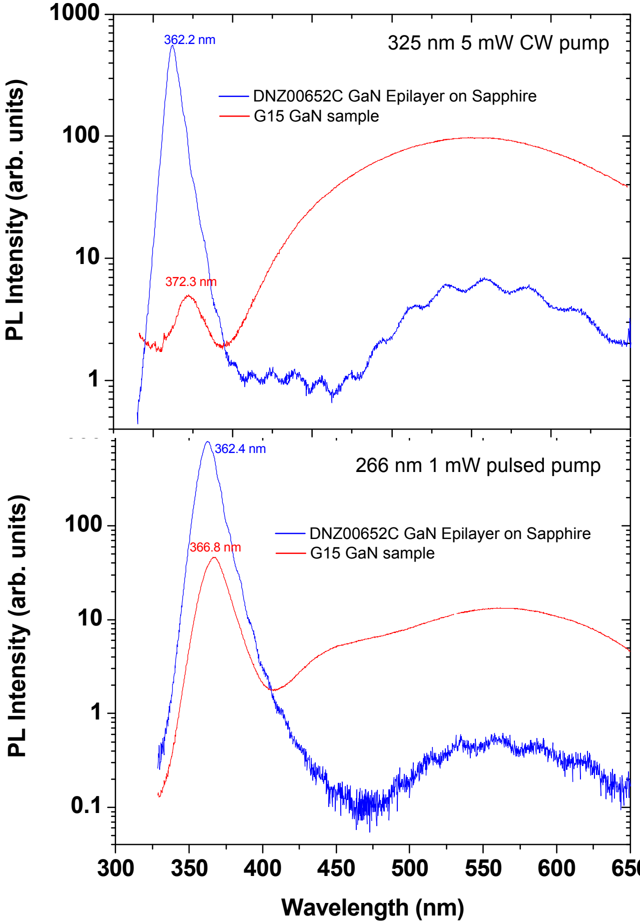
$3Li^+ + 3e^- \rightarrow 3\ Li$

GaN ESG Produces Photoluminescent GaN Crystallites









Mary Crawford, SNL

GNOEM Systems, Inc. Boulder Creek, CA

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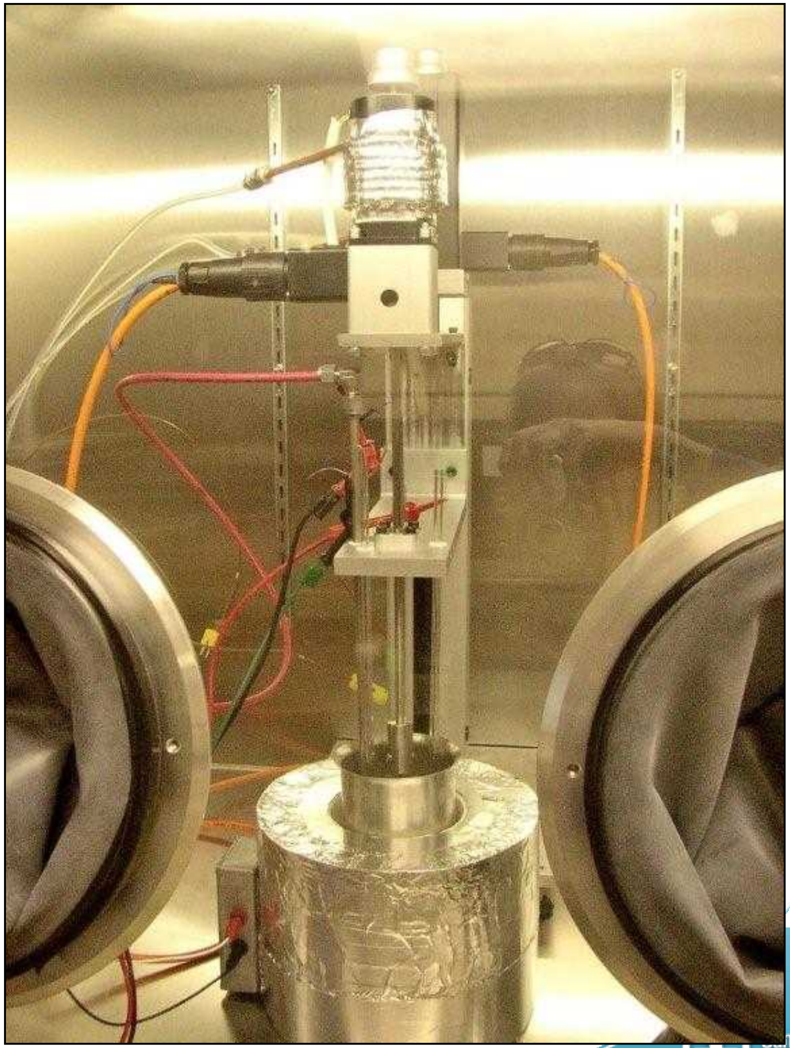
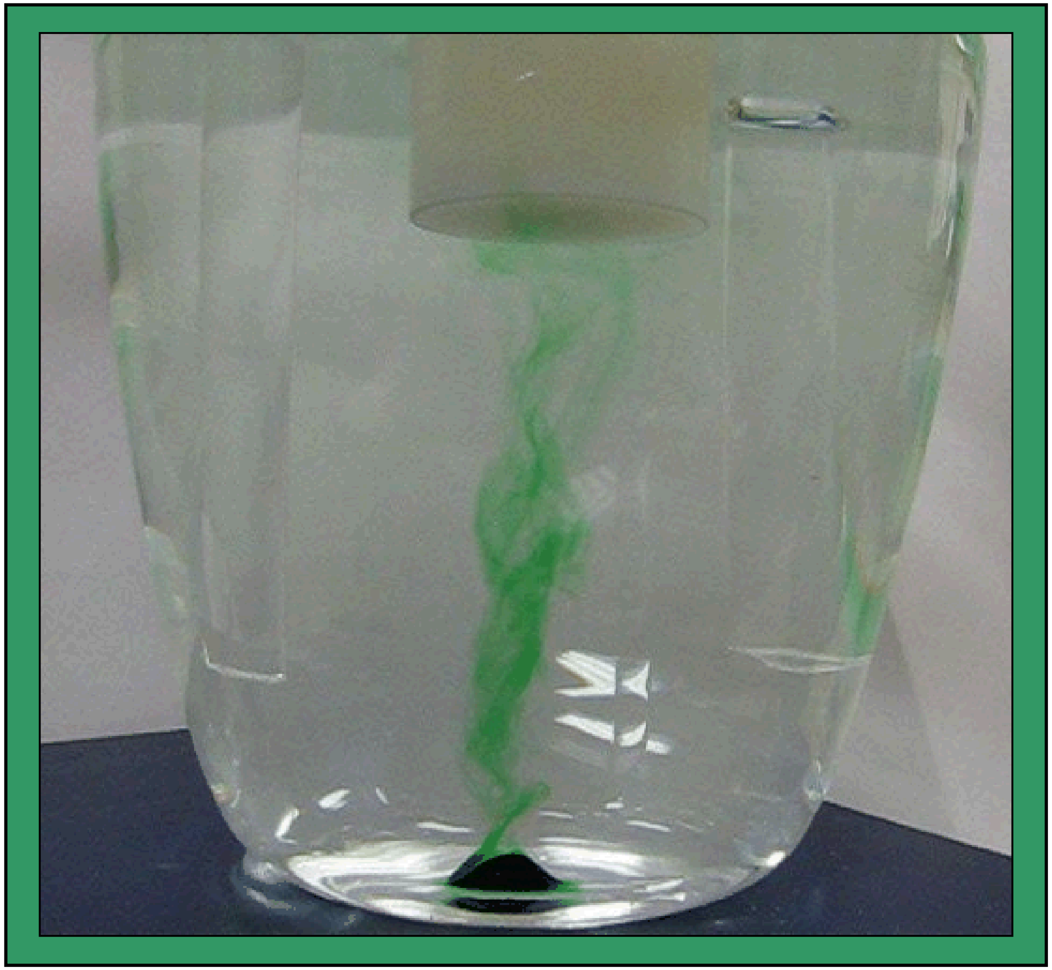
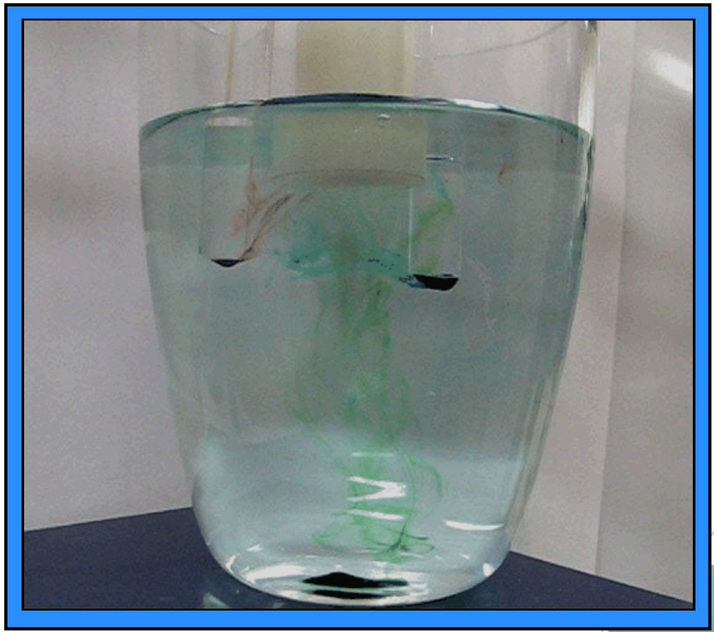
Gen-2 Boule Growth Reactor
Up to 1.5" diameter



Room Temperature Fluid Dynamics Experiments



Under laminar flow conditions, the spinning seed will draw nutrient-containing fluid to the surface– if the electrodes are properly shaped and located.



Innovative Manufacturing Initiative Award from the Department of Energy's Advanced Manufacturing Office (AMO)

- **Sun Edison (Michael Seacrist)/Sandia (Karen Waldrip)/GTRI (Prof. Russ Dupuis)**
- **3 year, $4.6M award with cost share, began 9/1/2012**
- **Major Year 1 goals:**
  - Develop reproducible ESG process on 1 cm^2 MOCVD-grown GaN seed crystal, evaluate growth rate
  - Develop and validate ANSYS growth models including electrochemistry
- **Major Year 2 goals:**
  - Scale up to 50 mm diameter seed crystal
  - Sustain growth to > 1mm
  - Grow and characterize epi layers on seed surfaces
- **Major Year 3 goals:**
  - Scale to 100 mm diameter
  - Demonstrate functional optical and electrical devices on ESG-grown material
  - Design, build and install 150 mm reactor

Conclusions

- Electrochemical reduction of N_2 and autonucleation of GaN in eutectic LiCl/KCl salt demonstrated
- Modeling and experiments show growth of GaN on seed substrate possible
- Scaling up process to grow GaN on 1 cm^2 (and greater) seed substrates

Acknowledgements:

- DOE Office of Electricity Delivery and Energy Reliability
- DOE Advanced Manufacturing Office (AMO)

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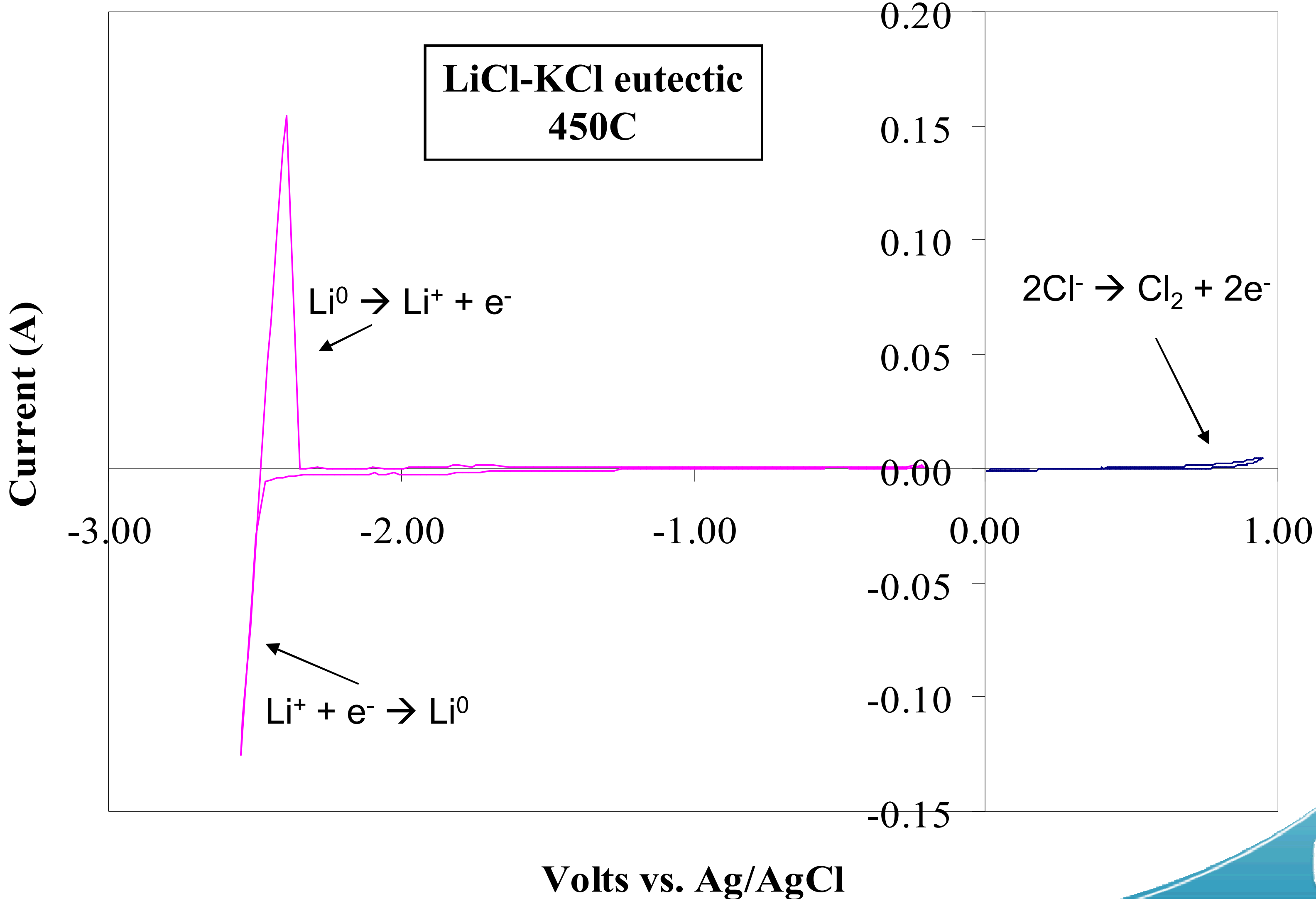
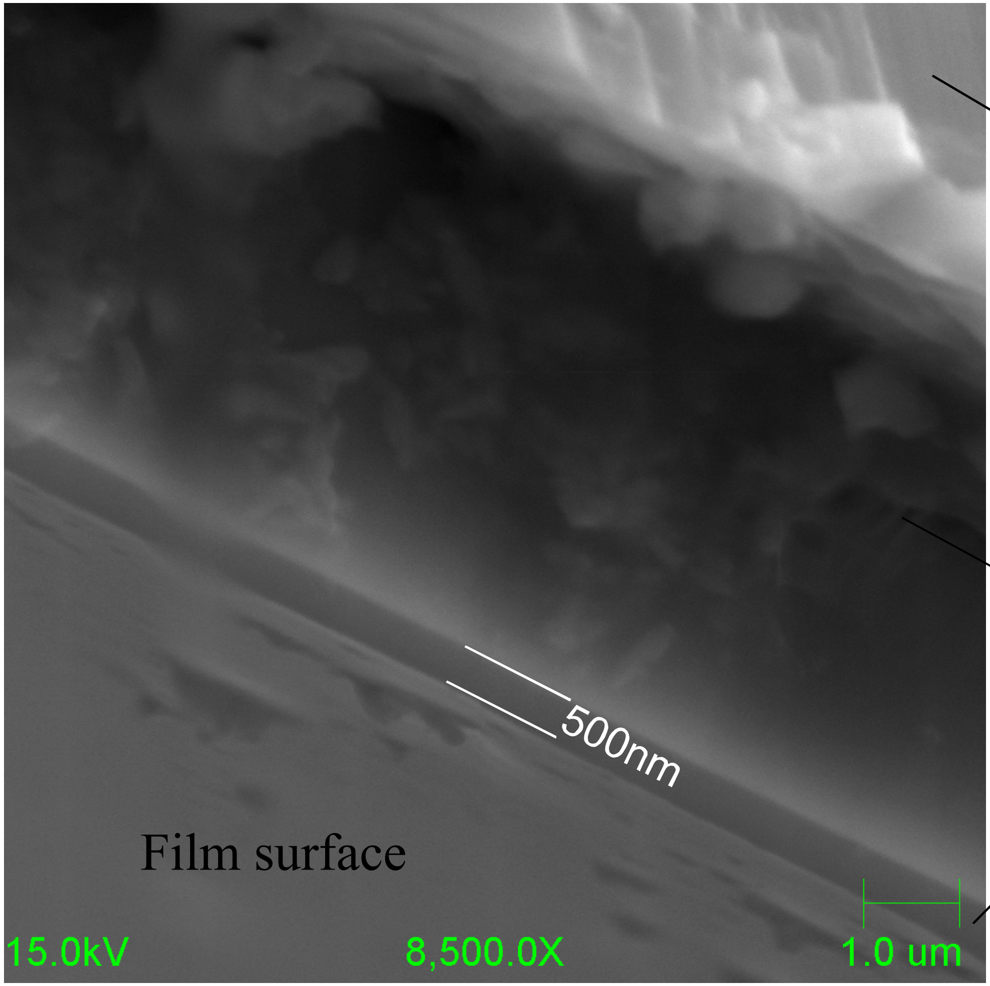
Extra Slides

Complete Electrochemical Background of Salt



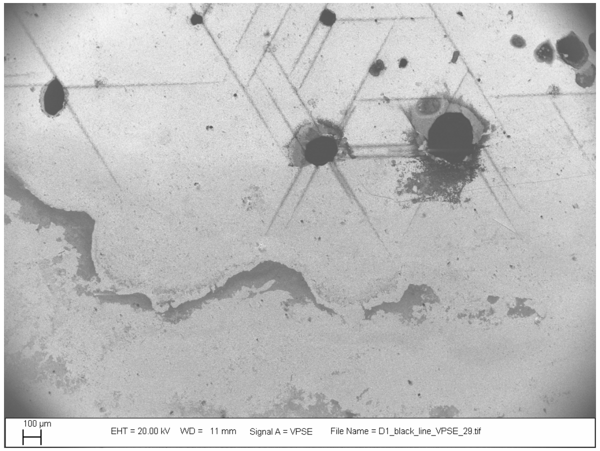
SEM of SNL RD-ESG Growth Run #1

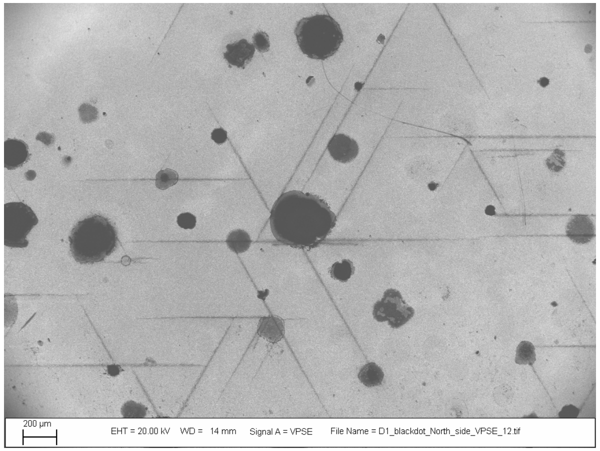


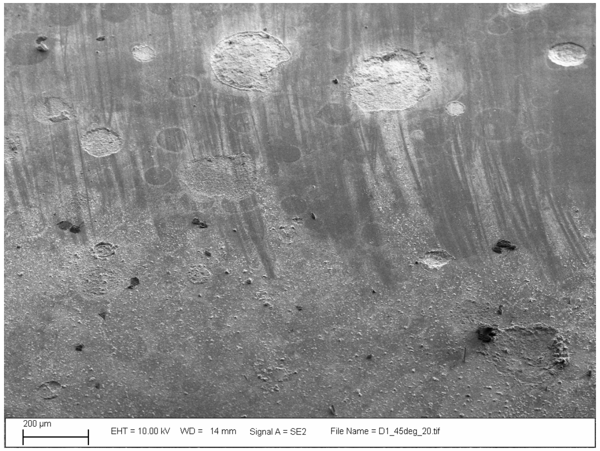
XPS and SIMS of SNL RD-ESG #1

- **XPS showed Ga, N, C, O, Si, Al, etc.**
- **SIMS revealed the layer to be a graphitic carbon layer, with Ga, N, and GaN clusters inside**
  - Ga,N content was about 10%
  - Profile was consistent with an increasing concentration
- **Problem with salt purity from supplier**
  - Developing in-house purification technique for reagent grade salt

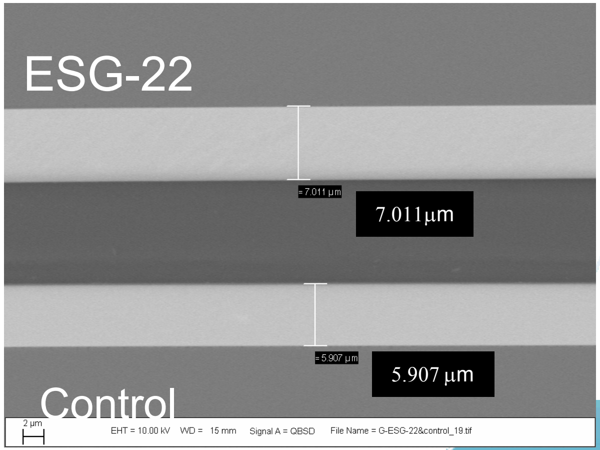
First GNOEM RD-ESG Experiment







- Growth at GNOEM Systems
- Hardware failure– susceptor sheared, not sure when
- Black line on sample surface delineated a thicker, specular region and thinner, roughened area
- *Defect selective etching observed* (several microns/hr)
- Highly encouraging for crystal quality
- Polished cross sections of control and experiment sample consistently measure about 1μm thicker for experiment



Bonnie MacKenzie, SNL

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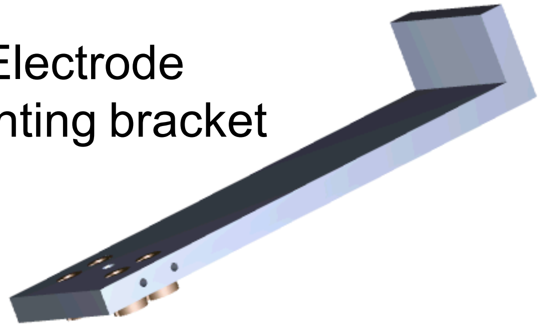
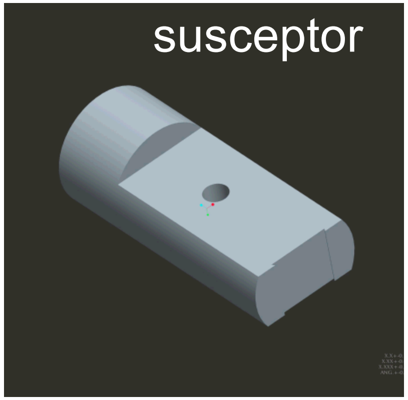
Boule Growth Reactor Design





Previous Setup	New Reactor
Ring Stand & Clamps -- irreproducible and clumsy	Positional and rotational control through computer-controlled stepper motors and machined mounting bracket
Temperature Control through variac power supply	Temperature Control through reactor temperature feedback to power supply
Quartz crucibles and electrodes	p-BN and/or stainless steel materials
Cement mounting of seed crystal	Precision-machined SS mechanical susceptor
Reactor located in secure area	Accessible to uncleared personnel

Acknowledgements: M.J. Russell, P. Michel

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

Giant crystal caves, Naica, Mexico
Photo from National Geographic

Growth Rate Calculations

From MBE:

ϕ = #atoms/(surface unit/monolayer thickness)*GR

$$\phi = (n/S/c/2)*GR$$

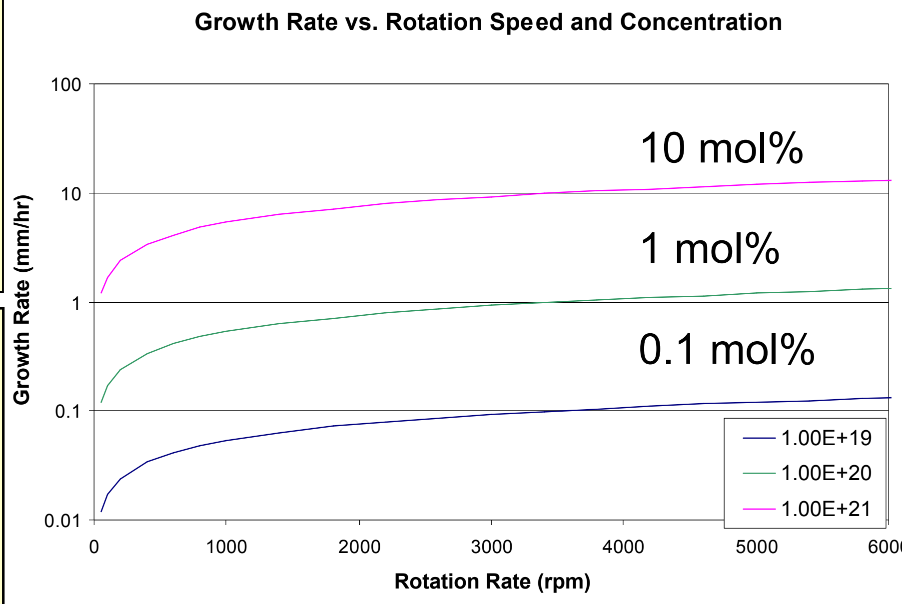
$$S = \frac{a^2\, c\, (3)^{1/2}}{4n}$$

$$GR = \frac{a^2\, c\, (3)^{1/2}\, \phi}{4}$$

Levitch Equation (from RDE):

$$i_{l,c} = 0.62nFAD_o^{2/3}\omega^{1/2}\nu^{-1/6}C_o^*$$

$$\frac{1}{A}\frac{dN}{dt} = \phi = 0.62D_o^{2/3}\omega^{1/2}\nu^{-1/6}C_o^*$$



$$GR\ (mm/hr) = \frac{a^2\, c\, (3)^{1/2} * 0.62D_o^{2/3}\omega^{1/2}\nu^{-1/6}C_o^*}{4}$$

Growth Rate Calculations

- Growth Rate = GR
- a, c = lattice constants
- ω = rotation rate (rpm)
- C_o* = bulk concentration
- D_o = diffusion constant
- y_h = hydrodynamic boundary layer thickness
- δ_o = diffusion layer thickness
- m_o = mass transfer coefficient
- ϕ = flux (at/cm^2-sec)
- n (or N) = # atoms
- v = kinematic viscosity

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Growth Rate Equations

From MBE:

ϕ = #atoms/(surface unit/monolayer thickness)*GR

$\phi = (n/S/c/2)*GR$

$$S = \frac{a^2\, c\, (3)^{1/2}}{4n}$$

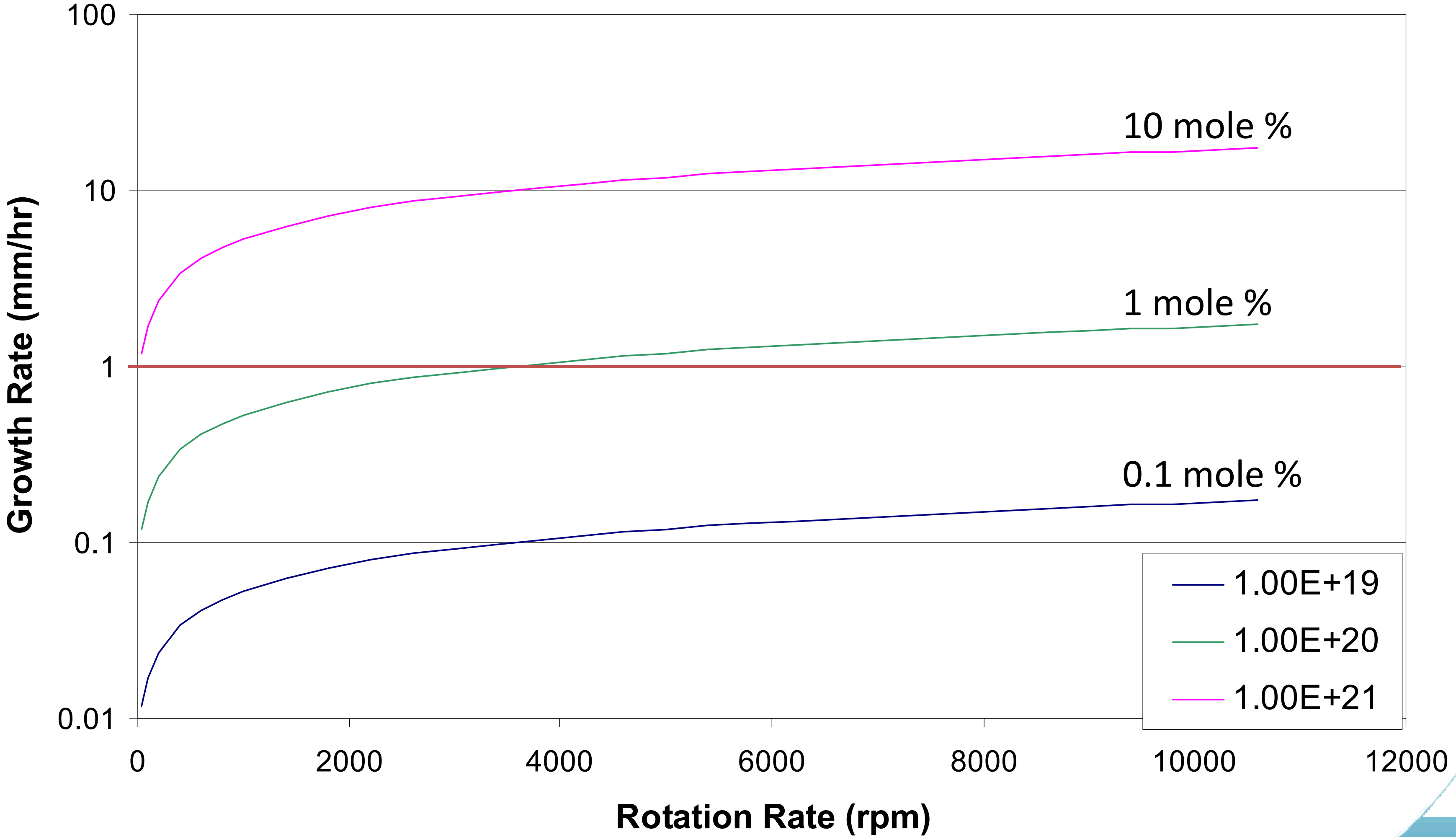
$$GR = \frac{a^2\, c\, (3)^{1/2}\, \phi}{4}$$

Levitch Equation (from RDE): $i_{l,c} = 0.62nFAD_o^{2/3}\omega^{1/2}\nu^{-1/6}C_o^*$

$$\frac{1}{A}\frac{dN}{dt} = \phi = 0.62D_o^{2/3}\omega^{1/2}\nu^{-1/6}C_o^*$$

$$GR\ (mm/hr) = \frac{a^2\, c\, (3)^{1/2} * 0.62D_o^{2/3}\omega^{1/2}\nu^{-1/6}C_o^*}{4} \times \frac{10mm * 3600s}{cm * hr}$$

Growth Rate vs. Rotation Speed and Concentration



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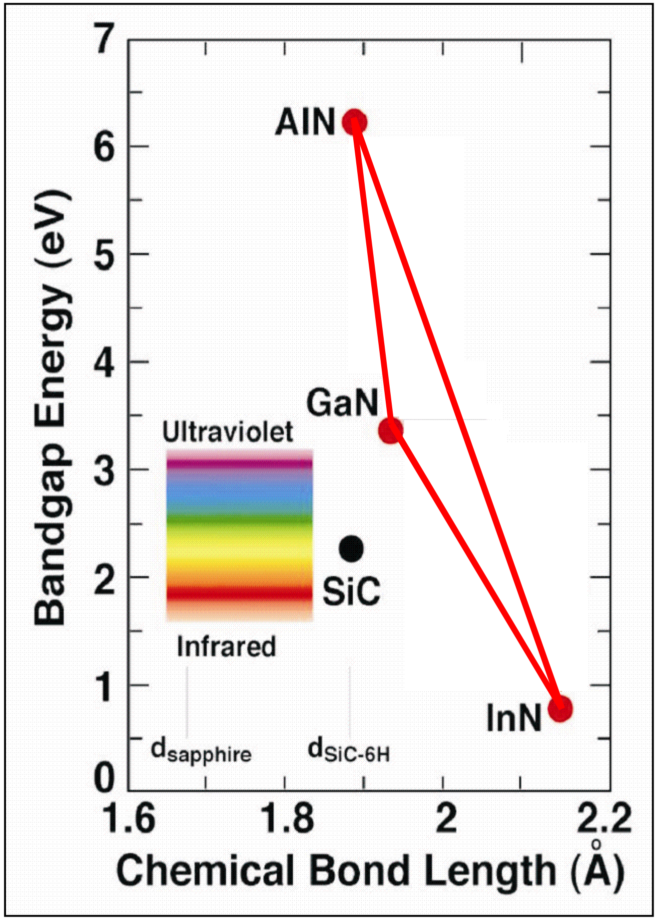
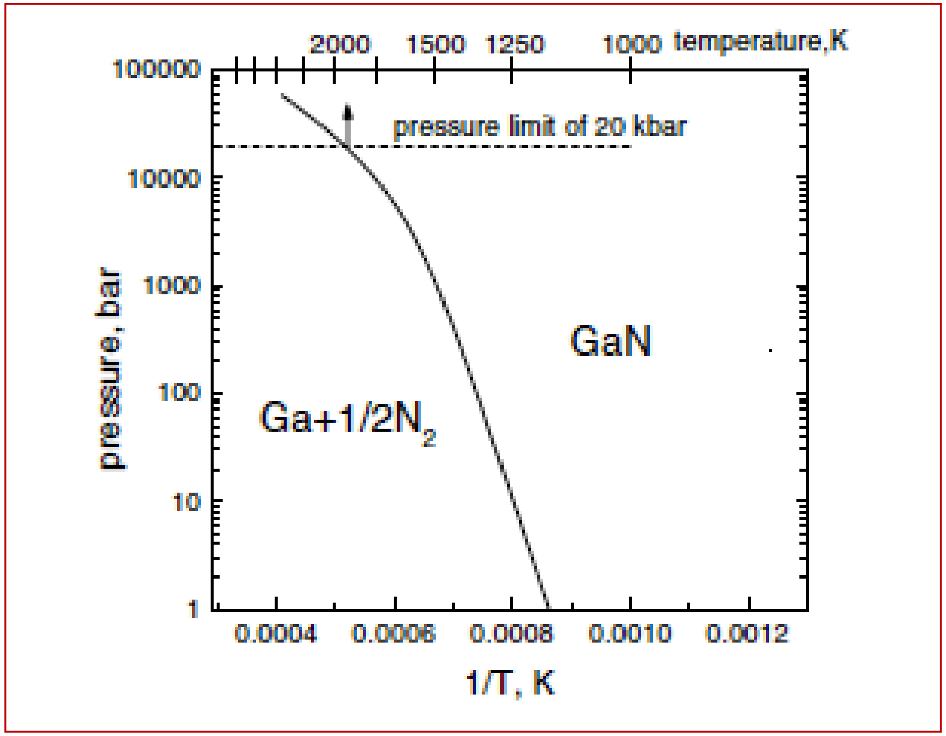
Motivation for GaN Power Devices

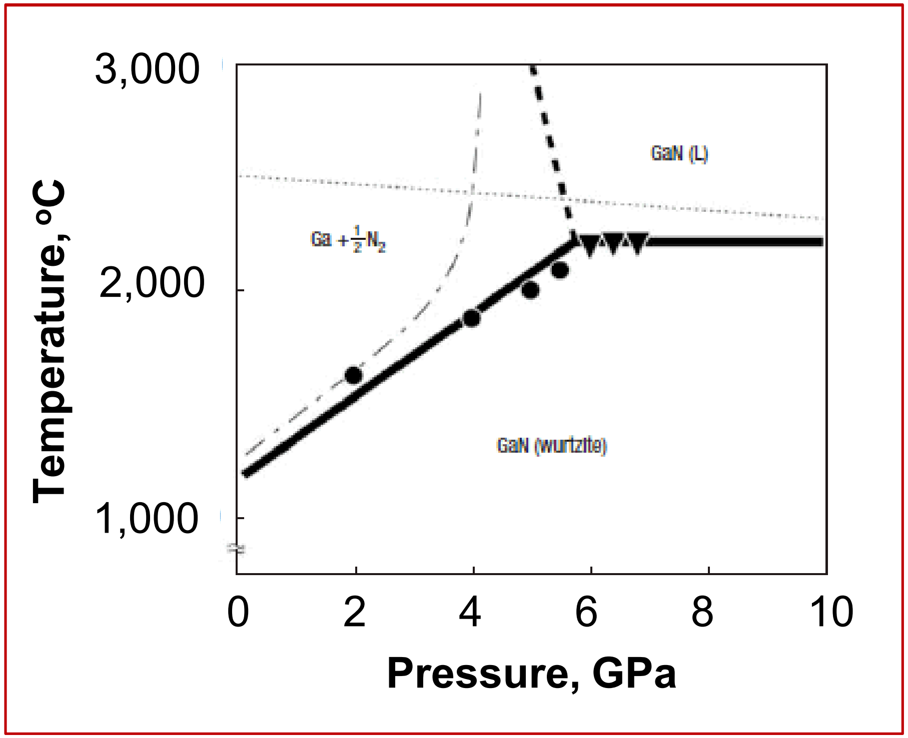
- **Footprint:** WBG power electronics offer advantages over silicon
  - No active cooling systems
- **Flexibility:** GaN offers additional device design options due to ability to alloy with AlN (higher standoff voltages) and InN (higher switching frequencies), new device architectures
- **Cost:** SiC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



GaN Thermodynamics
Melting point: ~2,225^{o}C at 6GPa



Grzegory et al, J. Phys. Cond. Matt. ***(14)****, 2002*



Utsumi et al, Nature Mat. Nov 2003

- **One report of congruent melting of GaN ca. 2003**
- **Many calculations of GaN melting conditions 2500C, 45,000 atm**

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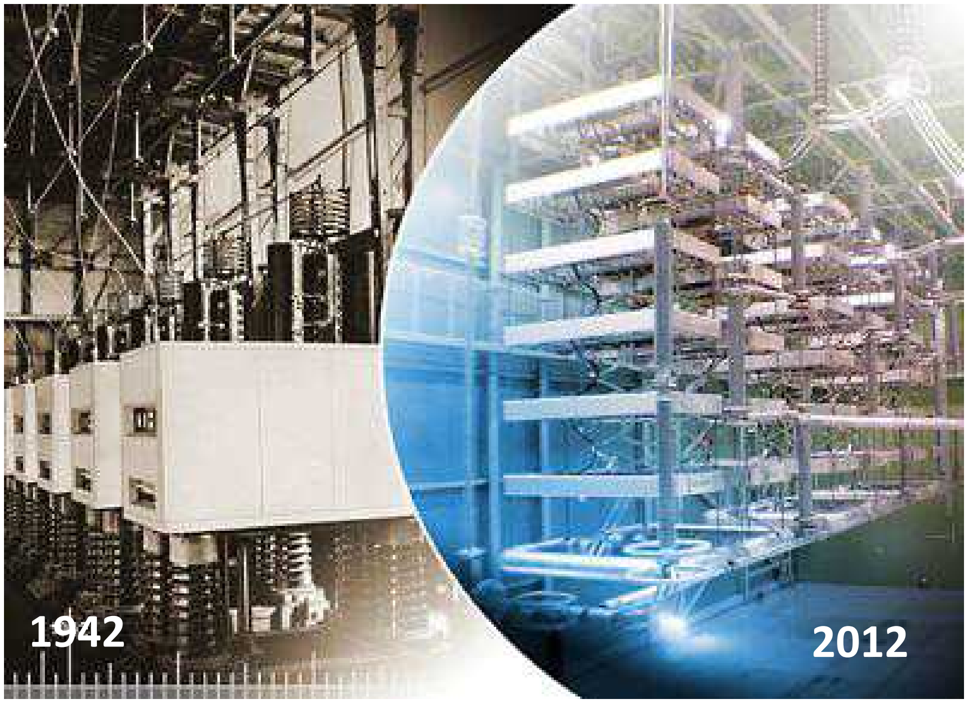
Historical Evolution of Power Electronics

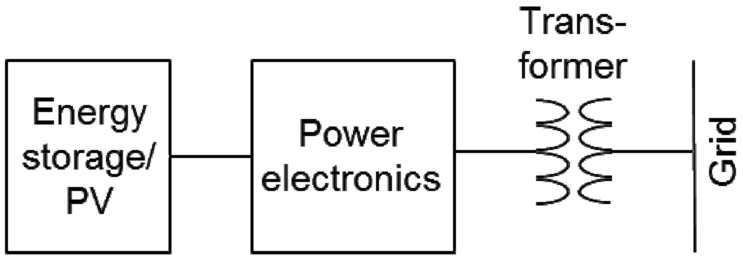


Hg-arc rectifier

Si thyristor

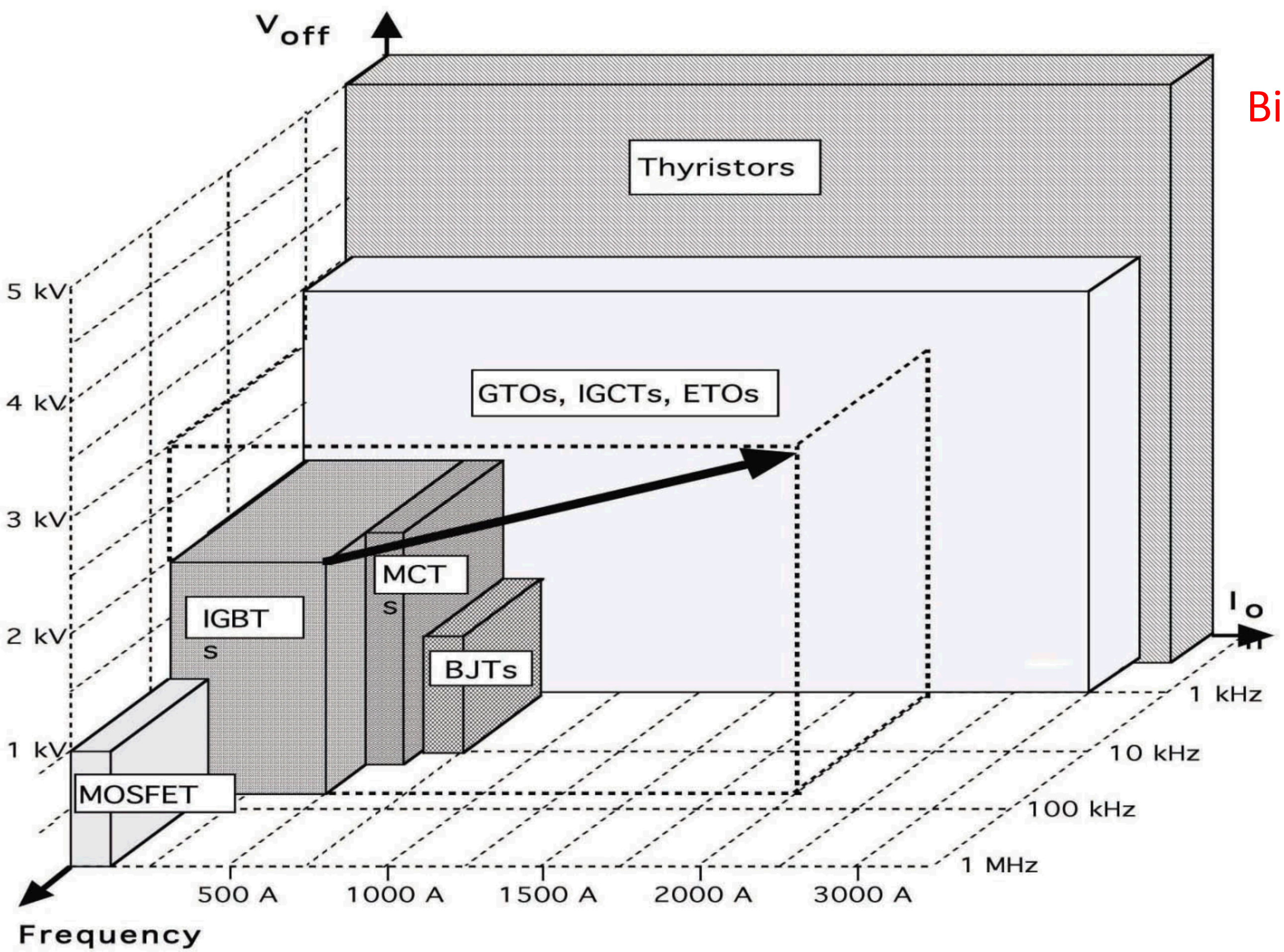
20??
SiC/GaN version
More compact
More efficient
Less cooling

Power Conversion System



- Renewable energy sources and energy storage need to interface with the electric grid through a power conversion system
- Heart of the power conversion system consists of semiconductor switches that determine overall cost, reliability, and performance (efficiency, power quality)
- Most systems today utilize silicon-based semiconductor switches (IGBTs, thyristors) – mature technology, incremental improvements
- Recent advances in the wide-bandgap materials Silicon Carbide (SiC) and Gallium Nitride (GaN) offer potential for improved performance, reduced cooling requirements, smaller system size, lower cost

Application Classes of Power Devices

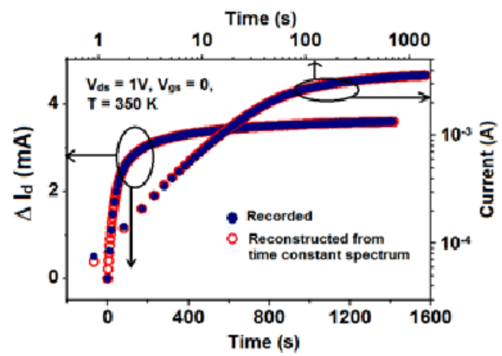


Bipolar

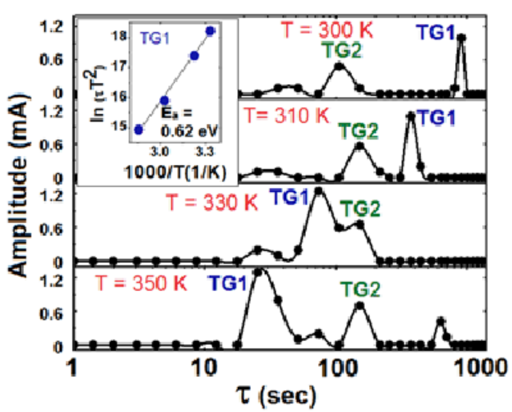
Unipolar

Figure from Mohan et al., “Power electronics: Converters, Applications, and Design” (Wiley, 2003).

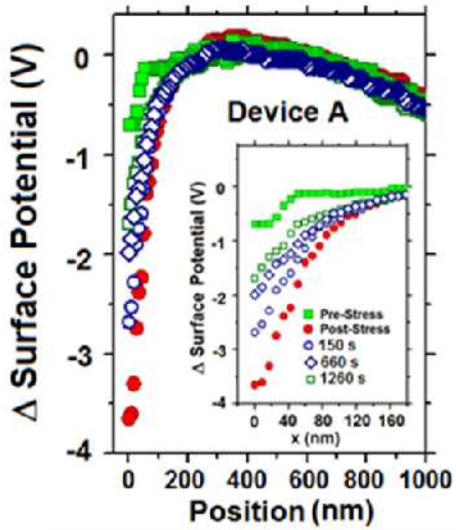
Analysis of Slow Transient Recovery of Drain Current – Deep Level Defects

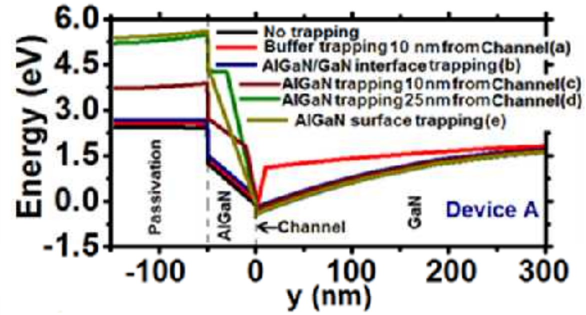


$$\Delta I_d = \sum_i A_i \left[1 - exp\left(-\frac{t}{\tau_i}\right)\right]$$



Passivated $Al_{0.15}Ga_{0.85}N/GaN$ HEMT



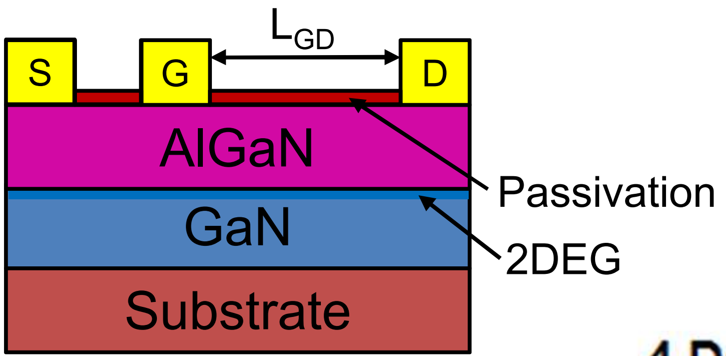


S. Dasgupta et al., submitted to IEDM

KFM surface potential measurements and device modeling to determine spatial location of traps

More understanding needed of defects responsible for current collapse and the dependence on composition, growth, and device structure; better understanding of surface effects and surface field engineering for high breakdown voltage

Lateral AlGaN/GaN Power HEMT



High Electron Mobility Transistor:

- Designed and fabricated at MIT
- Polarization induces high-m channel
- Normally-on device
- L_{GD} and Al% control V_{BD}

4 Device Types

- **$Al_{0.15}Ga_{0.85}N$ (C - doped buffer - V_{br} ~ 1800 V max)**
  - **Unpassivated**
  - **Passivated ($Al_2O_3/SiO_2/Al_2O_3$)**
- **$Al_{0.26}Ga_{0.74}N$ (Undoped Buffer V_{br} ~ 600 V max)**
  - **Passivated ($Al_2O_3/SiO_2/Al_2O_3$)**
  - **Unpassivated**

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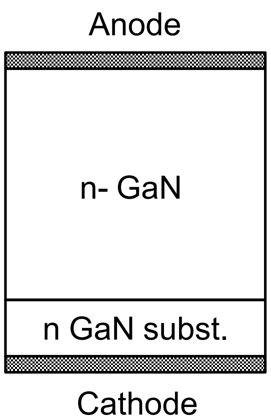
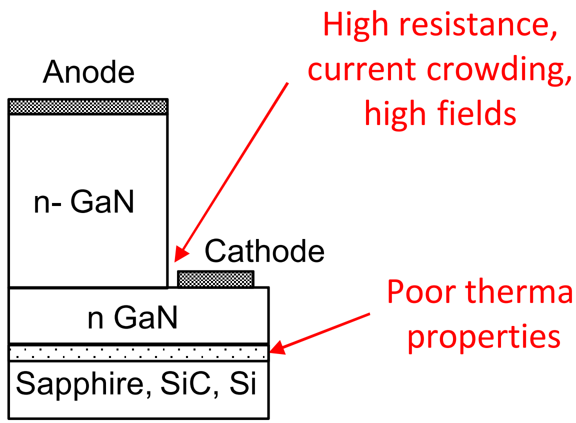
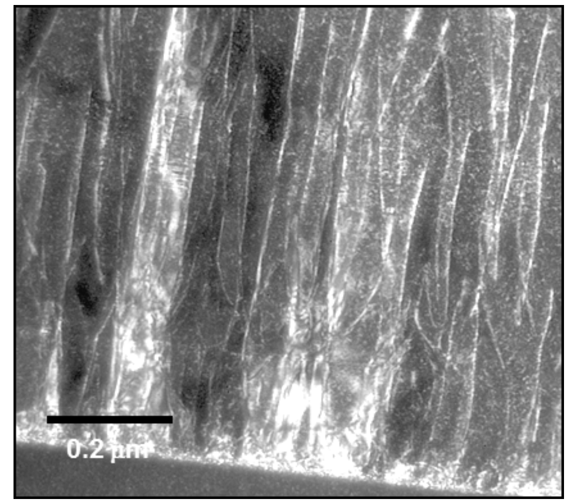
GaN Vertical Device on GaN Substrate

GaN substrate



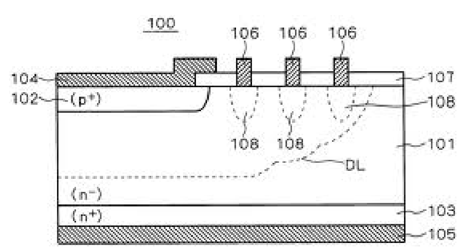




The science-based materials physics foundation for vertical GaN power devices grown on native GaN substrates is needed (e.g. breakdown, carrier lifetime and transport)

High dislocation density for heteroepitaxial GaN (10^9-10^{10} cm^{-2})

(Ammono)
GaN



- Premature breakdown
- Enhanced impurity incorporation
- Point / extended defect interaction

GaN Vertical Device – Previous Attempts

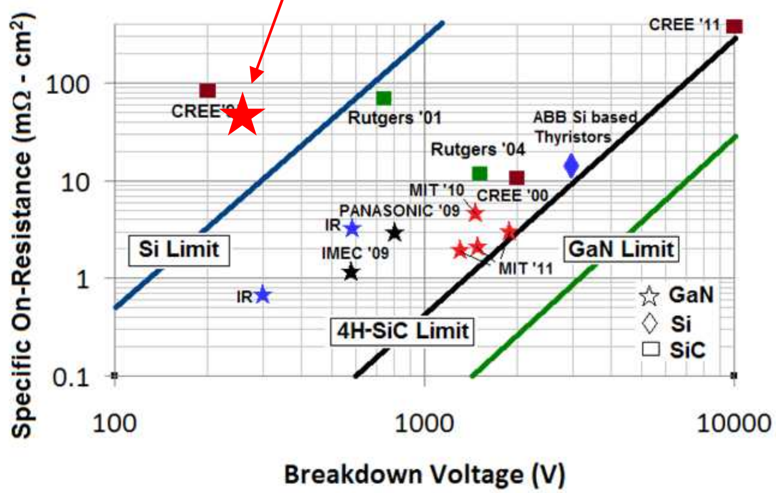
X. Cao et al., APL <u>87</u> 053503 (2005)

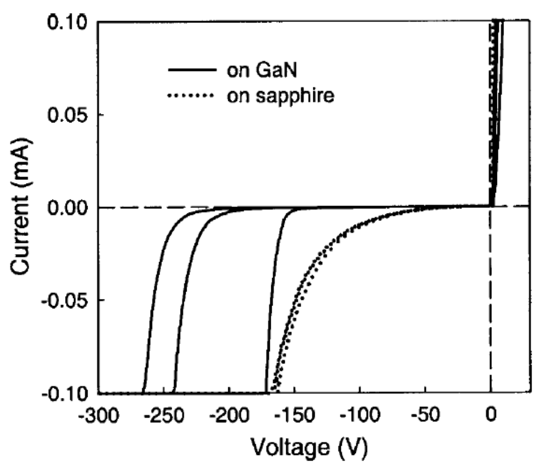
- MOCVD on HVPE GaN substrate
- PiN diode
- n ~ $1{\times}10^{17}$ cm^{-3}

In summary, homoepitaxy of GaN PiN rectifiers on a free-standing GaN yielded markedly improved material with a reduced dislocation density and impurity concentration, leading to better breakdown characteristics than similar devices grown on sapphire. However, the rectifiers still show relatively high reverse leakage, premature breakdown, and negative temperature dependence of the breakdown voltage. All of these findings reveal the presence of point and microdefects in the voltage-blocking layer. The microdefects are believed to originate from the substrate surface, and thus may be eliminated by improving the bulk GaN quality and surface preparation prior to the growth. Point defects in GaN, including common impurities (C, H, and O), N and Ga vacancies and antisites may act as dopants or compensation centers and need to be further reduced. To achieve high reverse-blocking capability, it is critical to precisely control the doping concentration in the drift region at low levels. Further work should focus on lowering the unintentional doping and compensation in homoepitaxial GaN.

Device problems are due to fundamental materials issues

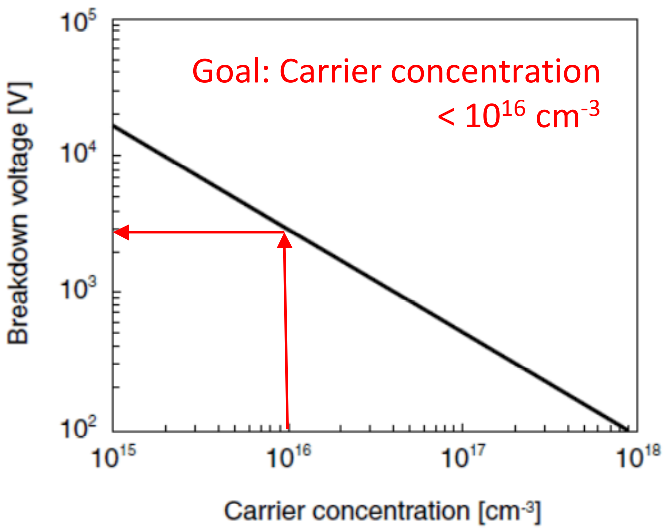
Device is far from theoretical limit





Significant variation between devices grown on GaN

Low and Controllable n-type Doping is Critical for Power Device



T. Tanabe et al., SEI Tech. Rev. **64**, 21 (2007).

$$V_B = \frac{\varepsilon E_C{}^2}{2qN_D}$$

High breakdown voltage requires low carrier concentration

- *Controllable* incorporation of Si donors in GaN
- Minimization of donor impurities / defects (O, V_N)
- Minimization of compensating acceptors (C, V_{Ga} – places a lower limit on effective carrier concentration under high electric fields)
- Requires scientific understanding of growth on GaN substrates and the impact of growth conditions on native point defects
- *Most knowledge of these issues to date is for heteroepitaxy on SiC, sapphire, or Si*

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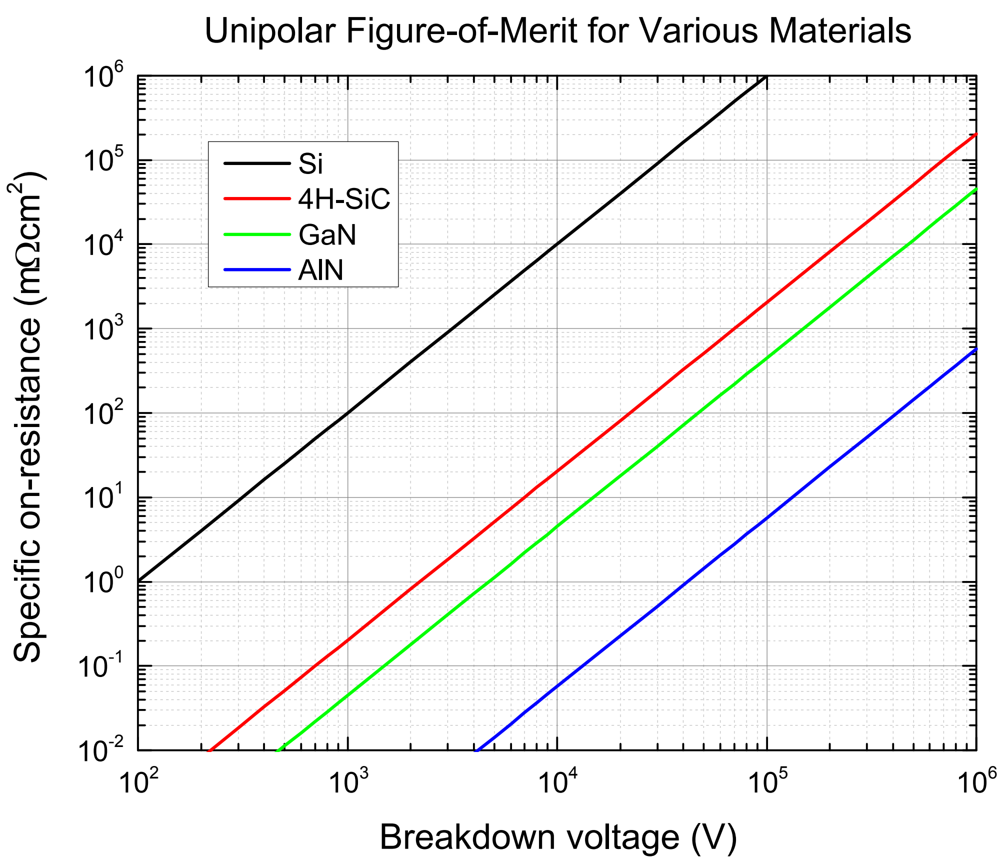
Theoretical Performance of Ultra-Wide-Bandgap AlN Unipolar Device



Outstanding performance *in theory* – but numerous material physics problems must be solved, similar to GaN:

- Growth on AlN substrates for vertical devices
- Low, non-compensated n-type doping
- Minority-carrier transport
- Gate oxide

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Conclusion: Key Materials Physics Issues for WBG Power Electronics

- Native substrates: Need large-area, defect-free wafers to achieve yield and reliability approaching that of Si devices
  - Enable high voltage and current for grid-scale devices
  - GaN and AlN substrates for vertical III-N devices
- Fundamental III-N material properties
  - Controllable low-doped n-type drift layers
  - Ultra-wide bandgap and high critical field
  - Bipolar devices: Carrier lifetime, mobility
  - Charge trapping, deep level defects, and extended defects
  - Dependence of switching speed on materials properties
  - Breakdown mechanisms (avalanche vs. others, e.g. surface)
  - Novel heterojunction engineering (e.g. graded composition)
- Gate oxides for MOSFETs and IGBTs
  - SiC/SiO_2 low channel mobility, bias-temperature instability
  - Gate oxides on III-N materials

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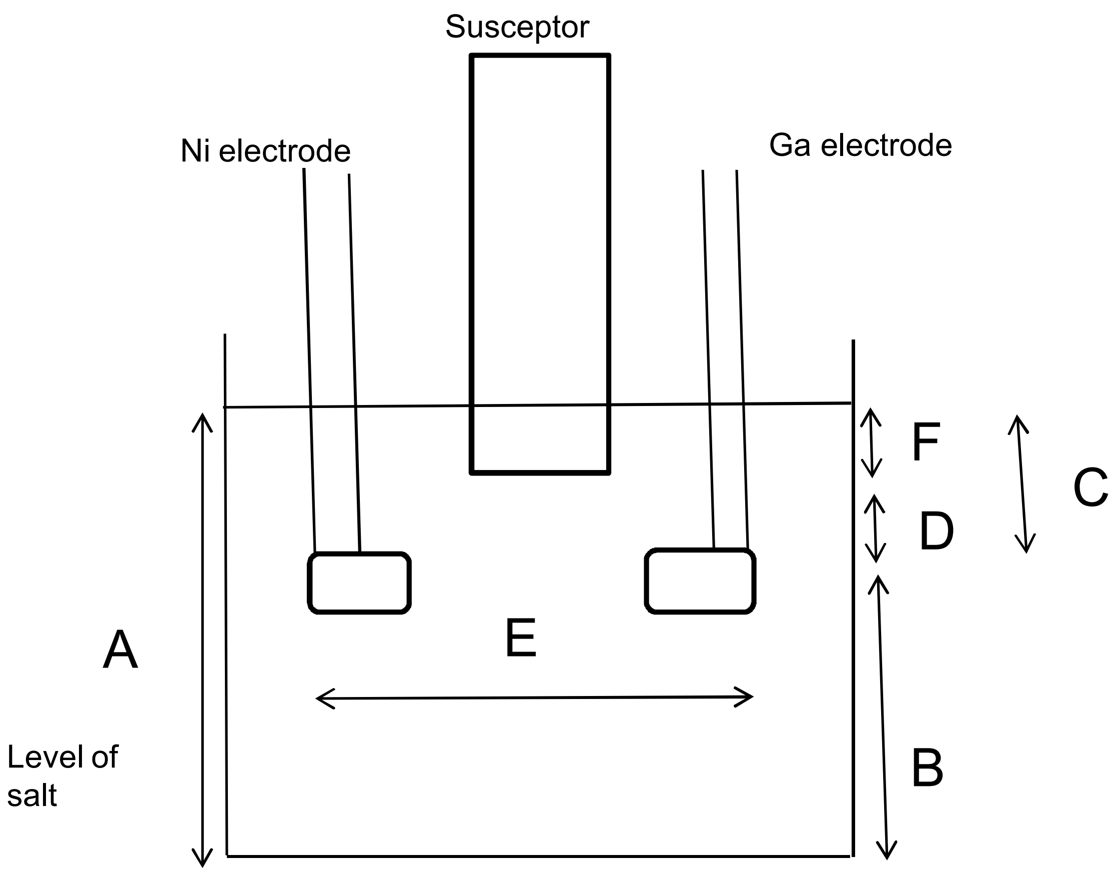
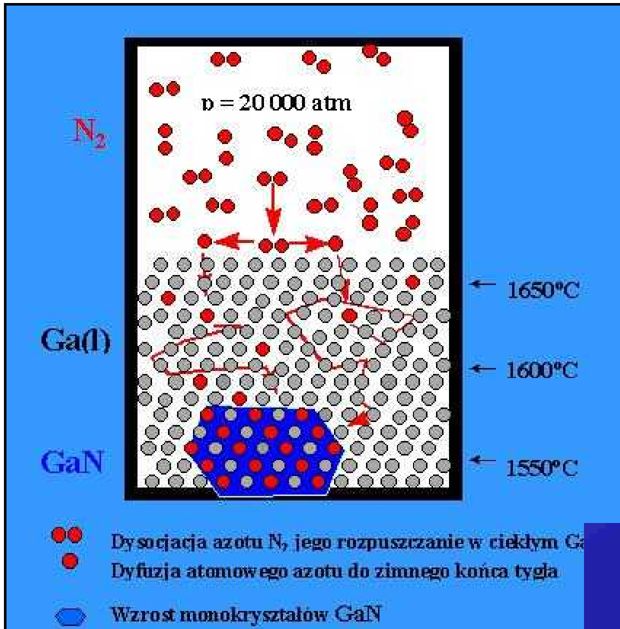
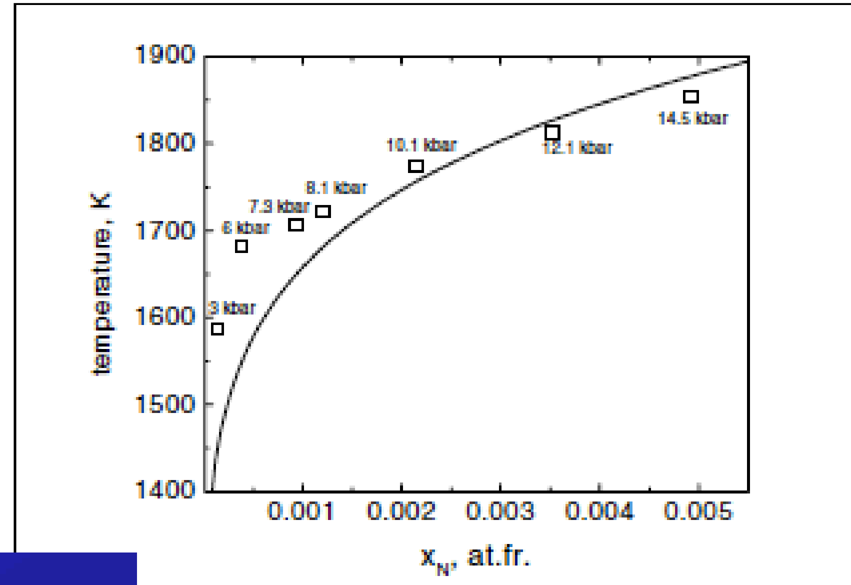
Thermal Battery Salt (no filtration)

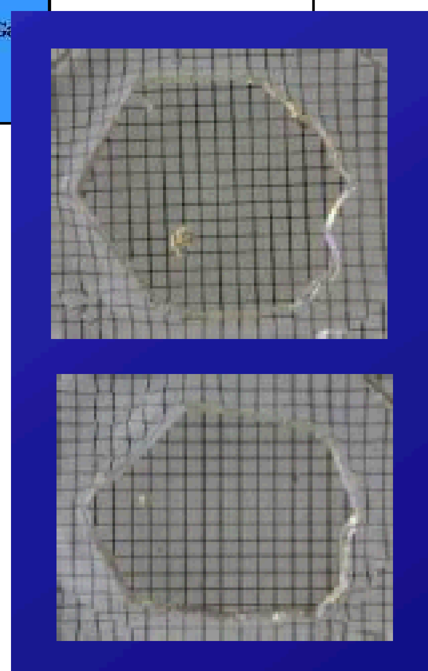
Experimental Set Up



High Nitrogen Pressure Solution Growth







unipress

S. Porowski, I. Grzegory et al.

Institute for High Pressure Physics
Warsaw, Poland

Dissolve atomic N in molten Ga (1500C, 20,000 atm)

2" diameter is physical limit

First blue LD grown (Nakamura)

Dislocations <100 cm^2

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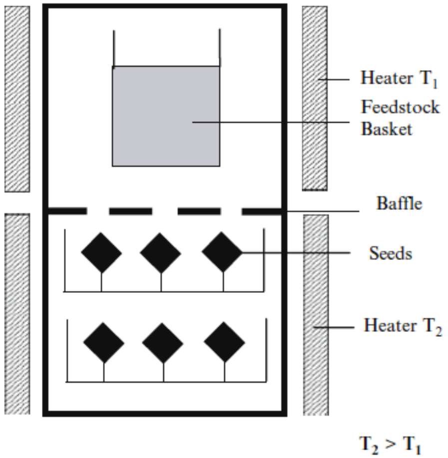
Ammonothermal Growth

- **GaN is extremely difficult to dissolve**
  - Supercritical ammonia (500-800C, 4,000-5,000 atm)
  - Requires additional mineralizers
  - Acidic or basic approaches
- **Major players:**
  - Dwilidinski & Doradzinski: Ammono
  - Nakamura: Soraa
  - Haskell & Fini: Inlustra
- **Up to 60 μm/day growth rates**



- **Another solvent: Molten LiF (850C, 240atm)**
- **B. Fiegelson, NRL**

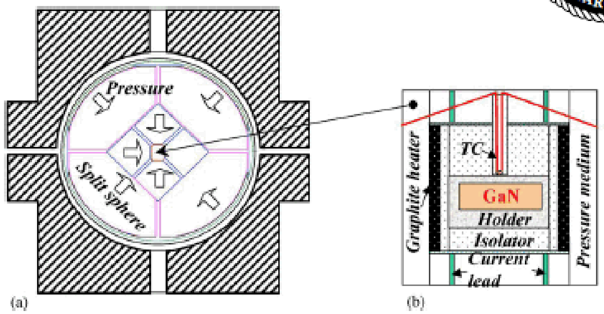
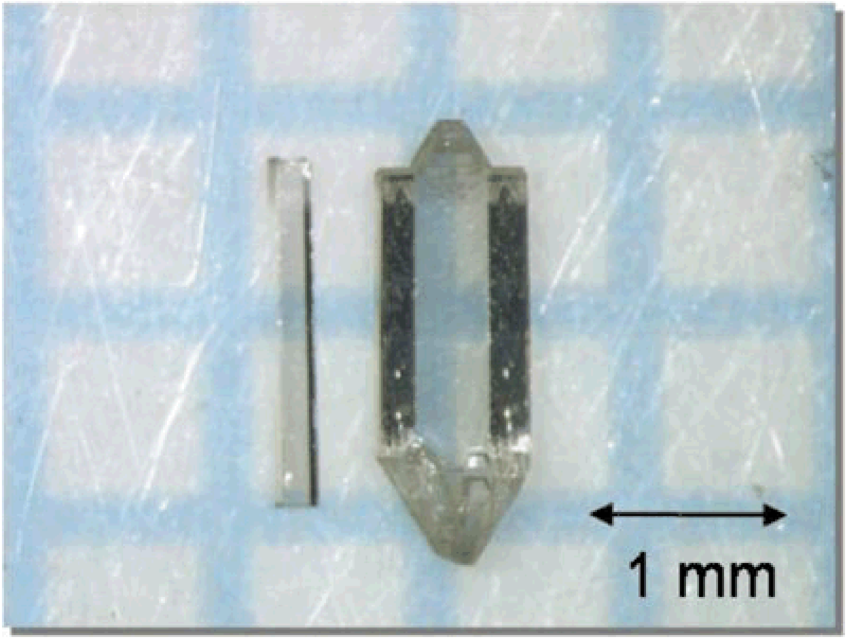


Fig. 1. Schemes of the (a) multi-anvil split sphere high-pressure apparatus, and (b) high-pressure cell.

Alkali Metal Flux/LPE

- Sodium Flux/LPE
- Na dissociates N_2
- 750C, 50 atm
- Growth rates ~2µm/hr
- Additives

Yamane et al., 2006



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