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.
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

- 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.

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

SEM Images of 3D GaN grain growth

- Grains that will be overgrown
- Partial coalesced grains

The threading dislocation appear in bunches which are located a few microns apart from each other.
State of the Art in Bulk GaN Growth

*True bulk GaN not yet readily available*

- Traditional bulk growth techniques require high temperatures, high pressures
  - 2500°C
  - 60,000 atm N₂ overpressure
  - Adaptations dissolve N₂ in Ga at 1500°C, 20,000 atm
- Extremely difficult to dissolve
  - Liquid ammonia (500-800°C, 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*
Desires/Requirements for a Bulk GaN Growth Technique for Power Electronics

• Good crystalline quality ($\rho \leq 1 \times 10^5 \text{cm}^{-2}$)

• High growth rate (~mm/hr): high throughput, high volume production

• Low impurity content

• Low background carrier concentration (~$1 \times 10^{16} \text{cm}^{-3}$)

• Scalable

• Controllable

• Manufacturable

• Reasonably inexpensive

• Applicable to InN, GaN, AlN, and III-N alloys
1/2N₂ + 3e⁻ → N⁻³: The Reactive Intermediate


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

Advantages of using N₂ gas:
- Clean
- Inexpensive
- Control over precursor conc.
- Continuous, controlled supply

Report of nitride concentration in LiCl in literature: 12 mole %
Sandia’s Patented New Growth Technique: Electrochemical Solution Growth (ESG)

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$_3$N + 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
Seed Crystal Growth Experiments

• Motivation:
  – Better understand the experimental conditions under which GaN is formed

• Systematic set of electrochemical experiments conducted

• Ga oxidation, Li$_3$N as nitride source

• GaN formed only under one experimental condition

• Optimization straightforward

• DOEx setup performed

\[
\text{Ga} + \text{Li}_3\text{N} \rightarrow \text{GaN} + 3\text{Li}
\]
Seed Crystal Results

- **GaN + Ga**
- **No GaN**
- **No GaN**
- **No GaN**
Boule Growth Reactor Design

**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

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<th>Standard Order</th>
<th>Temperature (deg C)</th>
<th>Spin Rate (rpm)</th>
<th>Seed Depth (mm)</th>
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### 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 $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ Single Crystals from Solutions of Ionic Precursors

Giant crystal caves, Naica, Mexico

*Photo from National Geographic*