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

DOE Energy Storage & Power Electronics Research 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
## Combined Figure of Merit

<table>
<thead>
<tr>
<th>Material</th>
<th>$K$ (W/cm°C)</th>
<th>$E_c$ (MV/cm)</th>
<th>$\varepsilon$</th>
<th>$\mu$ (cm²/Vs)</th>
<th>$v_s$</th>
<th>Combined Figure of Merit</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si</td>
<td>1.31</td>
<td>0.3</td>
<td>11.8</td>
<td>1350</td>
<td>$1 \times 10^7$</td>
<td>1</td>
</tr>
<tr>
<td>SiC</td>
<td>4.9</td>
<td>2</td>
<td>10</td>
<td>650</td>
<td>$2 \times 10^7$</td>
<td>136</td>
</tr>
<tr>
<td>GaN</td>
<td>1.3</td>
<td>3.3</td>
<td>9</td>
<td>1200</td>
<td>$2.5 \times 10^7$</td>
<td>153</td>
</tr>
</tbody>
</table>
Energy gap - lattice parameter diagram of III-nitrides
Heterostructure Rectifiers Offer Improved Breakdown Voltages

9.7 kV for Al$_{0.25}$Ga$_{0.75}$N

Leakage current due to bulk defects
GaN is Grown Heteroepitaxially on Sapphire (and Silicon Carbide) Substrates

- 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).
Methods for growing bulk GaN

**Dislocation Filtering Techniques**

- Lateral Overgrowth

**“True” Bulk Techniques**

**High Nitrogen Pressure**

- $P = 10^5$ atm
- $T = 1500^\circ C$
- $t = 100$ hr
- $h = 100 \, \mu m$

Dislocation density $= 10^2 \, \text{cm}^{-2}$

**Ammonothermal growth**

- $T_1 < T_2$
- $15 \, \text{mm}$
- $4,000 - 5,000 \, \text{atm}$
- $T = 400 - 800^\circ C$
- G.R. $= 50 \, \mu m/\text{day}$
- Multiple seeds

**Equations**

- $\text{KNH}_2 + \text{GaN} + 2\text{NH}_3 \rightarrow \text{KGa(NH}_2)_4$
- $\text{GaN} + 2\text{NaNH}_2 + 2\text{NH}_3 \rightarrow \text{Na}_2\text{Ga(NH}_2)_5$

**Techniques**

- HVPE
- Sapphire Substrate
- Liftoff process
- GaN layer
- Polishing

**Reactions**

- $\text{N}_2 \rightarrow 20,000 \, \text{atm}$
- $1550^\circ C$
- $1650^\circ C$
- $1600^\circ C$

**Environments**

- Seeds/ Crystals
- Nutrient Basket

**Substrates**

- GaN layer
- Sapphire Substrate
Desires/Requirements for a Bulk Growth Technique

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

Li$_3$N or (Li$_3$N + 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
GaN ESG Produces Photoluminescent GaN Crystallites

\[ T_G = 450^\circ C \]
\[ P_G = 1 \text{ atm} \]

GNOEM Systems, Inc. Boulder Creek, CA

Mary Crawford, SNL
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:
  - $\frac{1}{2}N_2 + 3e^- \rightarrow N^{-3}$
  - $N^{-3}$ concentrations $\sim 12$ mole %

- Half-reaction 2:
  - $Ga \rightarrow Ga^{+3} + 3e^-$
  - $Ga^{+3}$ equilibrium concentrations $\sim 1$ mole %

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

U.S. Patent filed April 11, 2005
Example of Nitrogen Gas Reduction Cyclic Voltammograms

\[
\frac{1}{2}N_2 + 3e^- \rightarrow N^-3
\]

200mV/sec
SEM of RD-ESG Growth Run #1

MOCVD-grown GaN

Ga, Al-containing layer

Film surface

0.38” = 480nm

• 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
Industrial Partner (GNOEM)
Hardware Development
• 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
Growth Rate vs. Rotation Speed and Concentration

- 10 mole %
- 1 mole %
- 0.1 mole %

Growth Rate vs. Rotation Speed

Rotation Rate (rpm)

Growth Rate (mm/hr)
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\textsubscript{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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