Magnetron sputter epitaxy of GaN thin films and nanorods using liquid Ga target

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III-Nitride semiconductors

Photonic materials with versatile properties obtainable by band-gap engineering

- **Wurtzite structure (Stable phase)**
- **Direct bandgap**: deep UV – near IR
  - AlN: 6.2 eV (200 nm)
  - GaN: 3.4 eV (365 nm)
  - InN: 0.7 eV (1771 nm)
- **Tailoring of:**
  - band-gap: 
    \[ E_g(x) = xE_g(A) + (1-x)E_g(B) - bx(1-x) \]
  - Lattice parameter 
    \[ L(x) = xL_A + (1-x)L_B \]
Applications of III-nitride semiconductors

- **Wide direct bandgap**
- **Thermal Stability**
- **High breakdown**
- **High Electron mobility**
- **Piezo effect**

### III-Nitride Technology

- Laser diodes (Fiber-optical communication)
- Blue, green and white LEDs (Solid-state lighting)
- Automotive electronics (high-temperature electronics)
- Power Transmission Switching (high voltage electronics)
- Pressure Sensors (MEMS)
- Wireless base stations (RF Power transistors)
- **Applications of III-nitride semiconductors**
Growth Techniques for GaN

Chemical Vapor Deposition (CVD)
+ Commonly used in industry
+ Large area deposition
- High growth temperatures
- Harmful residual gases

Molecular Beam Epitaxy (MBE)
+ Lower growth temperatures ~700 °C
+ High film purity
- High running cost
- Scalability is an issue

Magnetron Sputter Deposition
+ Common industrial technique
+ Can handle very large substrates
+ Growth at low temperatures
- Highly energetic sputter species

Commercial PVD systems
http://www.pvdproducts.com/
Pulse magnetron sputtering (PSD) grown Si-doped GaN and AlGaN/GaN HEMT

- Blue, Green, and Red LEDs
- Electroluminescence (EL) spectra of the LED structure at forward currents ranging from 4 to 8 mA.
- No noticeable degradation upon bending

Si-doped GaN:
- RT electron mobility ($\mu_e$) >1000 cm$^2$/Vs

AlGaN/GaN HEMT:
- $\mu_e$:1360 cm$^2$/Vs, sheet carrier density: 1.3 x $10^{13}$ cm$^2$ and a sheet resistance of 386 $\Omega$/sq.


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Webinar, PVD Products, 2020
Deposition System for GaN Growth

- DC Reactive Magnetron Sputter Epitaxy
- Ultra-high vacuum (UHV) chambers - base pressure < 1x10^{-8} Torr
- Liquid Ga target (purity 99.9999%)
- RT -1000 °C
- N₂ + (Ar)
Deposition System for GaN Growth

Sputtering on a Ga Target

Condensation

Gas phase (in vacuum)

Solid phase

Al, Ga or In cathode

substrate

N₂⁺
Difficulties in sputtering liquid Ga target

New target-sold

Heating or sputtering - liquid

Proper design for crucible

- Ga melting point: ~29 °C
  - Horizontal placement for target
- High Surface tension of liquid Ga
  - Low wetability
  - Proper shape of crucible
- Sputtering: applying target bias

Formation of bubbles

Poison of target

Stabilization of target

- Conducting materials
- Stability
  - Proper cooling of target
  - Stabilization process - repetition of nitridation and removing of nitride layer

High-quality GaN epitaxial film on sapphire

- Film grown at 700 °C
- Low threading dislocation density ≤10 cm⁻²
- A sharp band edge emission: 3.474 eV; FWHM of 6.3 meV
- Low yellow band emission
- High quality and purity

M. Junaid, C.L.Hsiao et al., Appl. Phy. Lett. 98, 141915 (2011)
Why vertically aligned nanorods?

- Vertically aligned nanorods:
  - almost “free-standing” \( \Rightarrow \) independent of substrate material
  - low defect concentration
  - negligible mismatch of thermal expansion between GaN and substrate \( \Rightarrow \) large area without substrate bending
  - regular periodic array \( \Rightarrow \) photonic engineering

- Core-shell nanorods:
  - n-type core + p-type shell
  - Large active surface area
  \[
  \frac{A_{\text{core}}}{A_{\text{film}}} = \frac{2\pi r \cdot h}{r^2 \pi} = F = 4 \text{ (aspect ratio)} \ F
  \]
  - \( r \): nanorod radius, \( h \): height, \( F \): filling factor
  - \( F=0.5, \ AR=5 \Rightarrow 10 \text{ times} \)
  - Reduced current densities in the junction at constant total currents \( \Rightarrow \) less droop problems
  - c-oriented wurtzite nanorods \( \Rightarrow \) non-polar sidewalls \( \Rightarrow \) reduced internal electrical field
  - No quantitative comparison between commercial LEDs and Nano-LEDs


S. Li and A. Wagg, JAP 111, 071101(2011).
Self-assembled GaN nanorods on Si substrates

Temperature effect

- Increase of axial growth rate with temperature
- Linear dependence of the NR length (L) on the inverse diameter (1/d)
  - \( L = C_1 (1 + 2C_2/d) \), \( C_1 \): film thickness; \( C_2 \): diffusion length
- Diffusion induced growth

*Energies 10, 1322 (2017)*
GaN nanorods grown on conducting substrates

- Diffusion induced growth: similar to direct growth on Si
- Template dependent growth: Different desorption temperatures of Ga adatoms

**Energies** 10, 1322 (2017)
Pressure dependence on nanorod growth

- Increase of axial growth rate with:
  - reactive N2 pressure
  - diluted Ar gas
- Nucleation density and aspect ratio of NR: highly related to $P_{Ar}$

**Total working pressure (pure N$_2$)**

- 5 mtorr
- 20 mtorr
- 1 mtorr

**Partial pressure ($P_{N_2}$) (N$_2$+Ar)**

- 5 mtorr

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Webinar, PVD Products, 2020


*Nanomaterials 8, 223 (2018)*
Microstructural and optical properties

Transmission electron microscopy (TEM)

Photoluminescence spectroscopy (PL)

High correlation between optical and structural properties

• Single crystal wurtzite structure
• Growth orientation: along c axis
• Sharpest emission: ~1.7 meV
• Free exciton: 3.485 eV
• Donor-bounded exciton: 3.479 eV
Self-assembled/induced nanorod growth (Bottom up)

Nucleation

Growth stage

Selective-area growth of GaN nanorods

Nano-sphere lithography

• Thin TiN mask layer (20 nm).
• Removal of the nanospheres → nanoopenings of ~ 150 nm in diameter.

Bird-view (left) and side-view (right) SEM micrographs of the GaN grown for different growth times.

Figures a - e, and g - h have the same scale.

- NRs formed by coalescence of multiple islands.
- After approximately 300 nm, the lateral diffusion is suppressed and the NRs grow along the $c$-direction.
- Longer NRs, grown for 2 hours have a preferential pencil-shaped termination.
• Equilibrium reshaping of the NRs as a function of growth temperature.
• SAG at temperatures ≥ 925°C – nucleation on the mask at lower temperatures.
• No growth at 1000°C.
Regular-array GaN nanorods

Focused-ion beam (FIB) lithography process

- milling current (2-50 pA)
- milling time (3-50 seconds)
- growth temperature
  → minimize substrate damage
Effect of interface

- Rough surface → multiple tilted nanorods

- Smooth surface → Single straight nanorods → minimize substrate damage
Surface diffusion

- Pitch shorter than 200 nm
  - Not very successful
  - Requires well patterning process
- Length and diameter increase with pitch
- Diffusion length decreasing with temperature

Temperature dependence of surface diffusion

Summary

• **Handling of liquid Ga target**
  • Difficult but not impossible
  • Require proper design of crucible and process of target’s stabilization

• **Epitaxial growth of GaN thin film on sapphire**
  • Direct growth without buffer, low-dislocation-density film ~ 500 nm, <10^{-10} cm^{-2}
  • Sharp PL emission ~6.7 meV

• **Self-induce growth of GaN nanorods**
  • Dislocation-free, single-crystal wurtzite structure
  • Growth on various functional templates/substrates
  • Sharp PL emission ~1.7 meV
  • Control Ga/N_{2} ration by tuning partial pressure of Ar/N_{2}

• **Selective-area growth of GaN nanorods**
  • Pre-patterning by NSL and FIBL, employing a TiN\textsubscript{x} mask
  • Well-defined single and uniform nanorods
  • Initial growth stages and time evolution → 5-step growth model
  • Temperature : surface diffusion, selectivity, coalescence, and morphology
  • Milling conditions: current and time → minimize substrate and mask damage
GANOX

A new paradigm for epitaxial GaN films and devices on large-area substrates

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Outline

• Introduction to Ion-Beam Assisted Deposition (IBAD) texturing
• GANOX technology
  
  GANOX = \textbf{GaN On} single-\textbf{Xtal} films

• Results on GaN to date (work with Sandia Labs)
• Implications and Novel Applications
Ion Beam Assisted Deposition

Materials property modification by ion bombardment during deposition (IBAD):

- Compositional effects by preferential sputtering
- Incorporation of (inert) ion species
- Compound formation by reactive ion species
- Improved step coverage
- Change of film stress
- Crystal alignment
IBAD induces in-plane and out-of-plane texture: IBAD TEXTURING or Ion Beam Crystal Alignment

- Particular version of IBAD Texturing we call Ion Texturing at Nucleation; discovered originally at Stanford University
- Process is extremely fast, with only ≤ 5 nm of deposit required; demonstrated in < 1 second
- Process that allows formation of single-crystal like films on arbitrary but smooth substrates (such as glass, metal and plastic foils)
- Key parameters are ion-to-atom ratio, $r$, and ion beam energy
Ion Beam Assisted Deposition System

- Ion beam is incident during deposition: medium energy (500 – 1500 V) ions, typically Ar
- Source atoms/molecules can be evaporated/sublimed or deposited by sputtering
- In situ monitoring by RHEED (Reflection High Energy Electron Diffraction) is critical to determine crystalline orientation during deposition

iBeam Materials uses a deposition system specifically designed for IBAD and other depositions on long metal tape with in situ monitoring and diagnostics
There is a 1st order phase transition here

Region I: MgO is first deposited amorphous
• MgO crystallizes after 1-2 nm of deposit

Region II: Texture improves rapidly with additional IBAD – 2D region
• There is an optimum point after which there is no further improvement in texture

Region III: Texture improves further with homoepi, but much more slowly with thickness
How does IBAD change the game for Epitaxy?

- Deposit an ion-beam aligned single-crystal-like layer (few nm) on an amorphous or polycrystal substrate
- Substrates can have desired mechanical, thermal or electrical properties independent of lattice match
- Enables large-area substrates, such as glass, metal, plastic, including Roll-to-roll

By replacing single crystal wafers, IBAD reduces cost and enables Large area deposition and New functionalities
IBAD Texturing allows for Lattice Engineering

A) Lattice Orientation

<table>
<thead>
<tr>
<th>IBAD &lt;100&gt;</th>
<th>IBAD &lt;111&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>MgO – Prototype</td>
<td>CeO₂ – Prototype</td>
</tr>
<tr>
<td>Rock-salt structures</td>
<td>Fluorite and Bixbyite structures</td>
</tr>
<tr>
<td>NiO, CaO, SrO</td>
<td>ZrO₂, CaF₂</td>
</tr>
<tr>
<td>TiN, CrN, ZrN</td>
<td>Mn₂O₃, Sc₂O₃</td>
</tr>
</tbody>
</table>

B) Lattice Parameter Engineering

- IBAD texturing material can be chosen from a variety
- Lattice parameter can be further engineered with solid solutions of compounds (e.g. CaO-MgO solution)

Rock-salt structures

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GaN on IBAD Templates

- DOE ARPA-E funded project
- Lead was iBeam Materials, a technology startup company in Santa Fe, New Mexico
- iBeam worked with Sandia National Labs to develop GaN on IBAD substrates using metal foil

iBeam Materials
Template developed in R2R reactor

Sandia National Labs
GaN growth in wafer reactor

Los Alamos National Lab

University of New Mexico
Our approach to preparing epi-GaN on metal (GANOX)

iBeam’s GANOX, GaN on X, X = any substrate with a single-Xtal layer. Process consists of 3 steps:

1) Planarize the metal substrate using solution deposition planarization \( \text{(SDP}^{\text{TM}}) \)

2) Create textured and buffer layers using ion beam assisted deposition (IBAD) and physical vapor deposition

3) Deposit GaN and other device layers using Metal organic chemical vapor \( \text{deposition (MOCVD)} \)

Artificially aligned templates allow one to separate the substrate requirements from epitaxy lattice matching requirement
Solution Deposition Planarization (SDP)

- Chemical solution deposition planarizes by liquid layer surface tension
- Multiple coatings reduce roughness as much as required
- Typically roughness reduced to less than 1 nm RMS
- Start with a molybdenum metal foil with good CTE match
- Can use a variety of oxide materials (process done in air)
Lattice stack

RHEED images during deposition

Lattice parameter
- GaN (0001) 0.319 nm
- AlN (0001) 0.311 nm
- Zr (hcp) 0.323 nm
- Sc$_2$O$_3$ (111) 0.348 nm
- IBAD+epi CeO$_2$ (111) 0.383 nm

Texture Improves
- < 100 nm thick

Planarization Layer (amorphous) $R_q < 1$ nm

RMS Roughness
- $R_q > 50$ nm
IBAD Texturing of Templates for epi-GaN

- Fast IBAD <111> texturing: CeO$_2$
- 1000 eV Ar ions, e-beam evaporate CeO$_2$
- Epitaxial GaN deposited on a buffered template structure

![IBAD CeO$_2$ Layer (220) Pole figure](image1)

![MOCVD GaN (101) Pole figure](image2)

Rocking curve of < 1.5°
In-plane texture of < 4°

Rocking curve of < 0.2°
In-plane texture of < 0.7°
First Epi-GaN on Metal

- First-in-the-world epi-GaN fabricated completely on a polycrystalline metal foil
- Surface roughness < 1 nm
- GaN TDD of mid to high $10^8$/cm$^2$

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GANOX LEDs on Metal Foil

- First LEDs demonstrated: 70% of IQE from PL compared to sapphire LEDs
  - There is plenty of room for improvements: Better lattice match, optimize GaN growth, optimize reflectance, optimize planarization, can control miscut angle
- Mechanical flexibility demonstrated down to radius of 7 mm

50 µm Parallel Arrays

50 µm Series Arrays

50 µm LED

10 µm LED

30 µm LED

LED Structure

p-GaN
MQW
n-(In,Ga)N
n-GaN

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First Transistor Device Fabricated using GANOX

*First-in-the-world* demonstration of a GaN/AlGaN HEMT on a metal foil (2019)

- **Metal Foil Substrate**: 60 µm
- **iBeam IBAD stack – 250 nm**
- **25 nm epi-AlGaN barrier**
- **3 µm undoped epi-GaN buffer**

*Smaller device sizes than TFTs are possible, giving higher aperture ratios in an active matrix*
How does making GaN devices with GANOX change the game?

Fabricating epi-GaN devices directly on IBAD substrates *fundamentally* changes:

1) **How devices can be manufactured**
   - In large areas, no longer limited to small, rigid wafers
   - ROLL-TO-ROLL (R2R) for certain substrates
   - Simplifies backend fabrication (pre-packaged on substrate)

2) **How devices (LEDs) can be utilized**
   - In large areas, sheets of integrated devices

3) **Volume of production and concomitant cost reduction**
   - Single factory can replace today’s whole world-wide production volume (needed for microLEDs)
   - Cost reduction in epi-GaN can be >20x
Key Features of the iBeam LED Design

• Fabricate GaN sheets on metal foil
• Very simple LED structure
• LED package fabricated directly on metal – completely new platform
• Greatly simplifies packaging steps
• Allows LED integration via printing technology on sheets of LEDs
• Flexibility and scale
Large-area LED Epi Deposition using GANOX

GANOX enables large-area substrates:

1) Large area deposition on rigid substrates such as glass or ceramics

1) R2R deposition on metal substrates
   - Appropriate substrate can be used R2R (5 orders of magnitude scale up)
   - Thermal advantages of metal substrates
Mo alloy foil substrate is a good CTE match to GaN

- Coefficient of thermal expansion (CTE) of the molybdenum alloy can be engineered to match GaN as closely as possible
- Standard single crystal substrates are not nearly as good a match
- This yields GaN films that are not stressed as they are on single crystal wafers
Metal substrate is an excellent thermal conductor

- Mo metal is a 25x times better thermal conductor at GaN growth temperature (~1000°C) compared to sapphire

InGaN LED wavelength uniformity comparison

**PL mapping of LED 2” Sapphire Wafer**

- 5 cm sapphire wavelength variation (Sandia reactor): ± 10 nm

**PL map of iBeam LED across 9 cm Metal Tape in same reactor**

- 9 cm metal foil: ± 6 nm
- Improved uniformity using a metallic substrate!
Future of GaN devices: Roll-to-Roll Manufacturing

- GANOX process scales GaN production to **kilometer lengths**
- Enables low-cost doubling of global LED capacity needed for microLED displays
- Ultimate Scale-up: reduce Epi cost by >20x
- Metal substrate improves LED wavelength uniformity in production

Example: R2R Deposition system from PVD Products
R2R Process Steps for GANOX Technology

1. Clean + SDP (planarize)  
   \[R2R\]

2. IBAD + PVD Buffers  
   \[R2R\]

3. HVPE (or other)  
   Thick GaN Buffer  
   \[R2R\]

4. MOCVD LED Active layers  
   \[S2S\]  
   \(\text{Step and Repeat}\)
iBeam’s GANOX Technology for microLED Display

- **Monolithic integration** of LEDs for µLED displays with NO TRANSFER
- Yield and Reliability improve greatly compared to mass transfer approaches
- Overlayed TFTs or epi-integrated GaN transistors to control LEDs
- QD downconversion for red and green colors, easily exceeding DCI-P3 gamut
- **Paper thin and flexible substrate**
IBAD Substrate: A completely new platform for LEDs

- We demonstrated the first InGaN LEDs and GaN/AlGaN HEMTs fabricated directly on metal foil using Ion Beam Crystal Alignment (IBAD)
- IBAD templates are a path to Large-area deposition of GaN and R2R Processing
- Epi-GaN cost can be significantly reduced and new functionalities and products can be enabled
- Materials improvement key challenge ahead
- We welcome collaborations from the community

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Innovative Techniques and Applications for Gallium Nitride Devices

Q&A

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Thank you!

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