Partial pressure curves for III-Nitrides

- For same temperature, the partial pressure of InN is the highest and AlN the lowest.
Substrates for nitride epitaxy: sapphire

Plane view of sapphire (rhombohedral)

Side view

Atomic arrangement of GaN on sapphire ($a_{\text{sap}} = 4.76 \text{ Å}$)

r-plane sapphire: non-polar GaN (a-plane)
c-plane sapphire: polar GaN (c-plane)
**Sapphire physical properties**

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
<th>Range</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lattice constant (nm)</td>
<td>$a = 0.4765$, $c = 1.2982$</td>
<td>$20 , ^{\circ}C$</td>
</tr>
<tr>
<td>Melting point (°C)</td>
<td>2030</td>
<td>$20 , ^{\circ}C$</td>
</tr>
<tr>
<td>Density (g/cm$^3$)</td>
<td>3.98</td>
<td>$20 , ^{\circ}C$</td>
</tr>
<tr>
<td>Thermal expansion coefficients (K$^{-1}$)</td>
<td>$6.66 \times 10^{-6}$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$9.03 \times 10^{-6}$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$5.0 \times 10^{-6}$</td>
<td></td>
</tr>
<tr>
<td>Percentages change in lattice constants</td>
<td>$a/a_0 = 0.83$, $c/c_0 = 0.892$</td>
<td>Heating from 293 to 1300 K</td>
</tr>
<tr>
<td>Thermal conductivity (W/cm K)</td>
<td>$0.23$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$0.25$</td>
<td></td>
</tr>
<tr>
<td>Heat capacity (J/K mol)</td>
<td>77.9</td>
<td>298 K</td>
</tr>
<tr>
<td>Young’s modulus (GPa)</td>
<td>452–460 in [0 0 0 1] direction</td>
<td>352–484 in the [1 1 2 0] direction</td>
</tr>
<tr>
<td>Tensile strength (MPa)</td>
<td>190</td>
<td>300 K</td>
</tr>
<tr>
<td>Poisson’s ratio</td>
<td>0.25–0.30</td>
<td>300 K</td>
</tr>
<tr>
<td>Hardness</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Knoop</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Nanoindentation (GPa)</td>
<td>$23.9 \pm 2.0$ [90]</td>
<td>300 K</td>
</tr>
<tr>
<td>Dielectric constants</td>
<td>$8.6$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$10.55$</td>
<td></td>
</tr>
<tr>
<td>Refractive index</td>
<td>1.77 at the rate of $\lambda = 577$ nm</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1.73 at the rate of $\lambda = 2.33$ $\mu$m</td>
<td></td>
</tr>
<tr>
<td>Energy band gap (eV)</td>
<td>8.1–8.6</td>
<td>300 K, experimental value</td>
</tr>
<tr>
<td>Resistivity (Ω cm)</td>
<td>$&gt;10^{11}$</td>
<td>300 K</td>
</tr>
</tbody>
</table>

For GaN: $a = 3.189$ Å, $c = 5.185$ Å, and $\alpha_a = 5.59$, $\alpha_c = 3.17$ ($10^{-6}$/K)
Summary of sapphire as substrate

- The growth of GaN on sapphire results in the rotation of the crystal directions by 30° to reduce strain between the substrate and the epilayer.
- The lattice mismatch with GaN is 13.9%.
- The steps for GaN growth includes: (a) Nitridation for few mins and (b) low temperature buffer layer (usually AlN) growth.
- Growth on c-plane of sapphire gives c-plane GaN, while growth on r-plane gives a-plane GaN.
- Energy gap of sapphire is > 8eV so light extraction possible from substrate side for LEDs.

Growth steps of GaN on sapphire:

1. AlN buffer or nucleation layer ($T_s = 600 - 700 \, ^\circ C$, $d(AlN) = 25-80 \, nm$)
2. Nucleation of GaN ($T_s = 950-1050 \, ^\circ C$)
3. Geometric selection ($d(GaN) = 50 \, nm$)
4. Island growth of GaN
5. Lateral growth ($d(GaN) = 200 - 300 \, nm$)
6. 2D-growth ($d(GaN) > 300 \, nm$)
Growth of GaN on SiC

<table>
<thead>
<tr>
<th>Properties</th>
<th>Polytype</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lattice constant (nm)</td>
<td>3C</td>
<td>$a_3 = 0.43596$</td>
</tr>
<tr>
<td></td>
<td>2H</td>
<td>$a_2 = 0.30736$, $c = 0.50480$</td>
</tr>
<tr>
<td></td>
<td>4H</td>
<td>$a_4 = 0.20736$, $c = 1.0683$</td>
</tr>
<tr>
<td></td>
<td>6H</td>
<td>$a_6 = 0.30696$, $c = 1.51173$</td>
</tr>
<tr>
<td>Linear thermal expansion coefficient ($\times 10^{-6}$/K)</td>
<td>3C</td>
<td>3.9</td>
</tr>
<tr>
<td></td>
<td>6H</td>
<td>4.46 $a$-axis</td>
</tr>
<tr>
<td></td>
<td></td>
<td>4.16 $c$-axis</td>
</tr>
</tbody>
</table>

- For GaN: $a = 3.189$ Å, $c = 5.185$ Å, and $\alpha_a = 5.59$, $\alpha_c = 3.17$ ($10^{-6}$/K)

No AlN layer: relaxed GaN, no 2D growth

With AlN layer: strained GaN

2D growth of AlN

- AlN nucleation layer (grown at high temperature) used for GaN growth. If not used, then 3D growth is possible, as relaxed GaN islands are created
- In situ hydrogen etching makes substrate smooth
- Usually, Ga-face GaN on Si-face SiC, and N-face on C-face
- Cubic GaN can be grown on 3C SiC due to similar stacking
Comparison of sapphire and SiC as substrates

• Thermal conductivity of sapphire is much lower than SiC ⇒ High power devices can be fabricated
• Sapphire is much cheaper (> 10 times) compared to SiC. The cost of devices/ICs can be kept low.
• Growth of GaN on SiC is more lattice matched, so lesser dislocations expected (not seen very much in practice though!). Lower dislocations good for device performance.
• Sapphire is always semi-insulating but SiC has to be made semi-insulating. Semi-insulating substrate is good for high frequency performance.
• Polishing SiC substrates is tougher than sapphire substrates, but they can be etched in situ using hydrogen inside the chamber. Polishing is required for good growth.
Growth on other substrates

- **AlN**
  - **Advantages:** Similar lattice structure (no SMB), closely lattice and thermal match, higher thermal conductivity, electrically insulating
  - **Disadvantages:** Difficult to have large area substrate with good quality
- **LiGaO₂**
  - **Advantages:** Very low lattice mismatch (0.9%), polar, easy bulk growth, easy to etch away
  - **Disadvantages:** Low stability under MOCVD growth conditions, large mismatch, poor thermal conductivity
- **ZnO**
  - **Advantages:** Low lattice mismatch (2%), polar, conductive substrate
  - **Disadvantages:** Low thermal stability, difficult to grow
- **Si**
  - **Advantages:** High quality, low cost, extremely smooth surface, thermal stability, integration with optoelectronic devices
  - **Disadvantages:** Lattice and thermal expansion mismatch, tendency to form SiN
Bulk growth of GaN: direct synthesis

Melting conditions of semiconductors (without dissociating)

<table>
<thead>
<tr>
<th>Crystal</th>
<th>$T^M$ (°C)</th>
<th>$p^M$ (atm.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si</td>
<td>1400</td>
<td>&lt;1</td>
</tr>
<tr>
<td>GaAs</td>
<td>1250</td>
<td>15</td>
</tr>
<tr>
<td>GaP</td>
<td>1465</td>
<td>30</td>
</tr>
<tr>
<td>GaN</td>
<td>2500</td>
<td>45 000</td>
</tr>
<tr>
<td>Diamond (synthesis)</td>
<td>1600</td>
<td>60 000</td>
</tr>
</tbody>
</table>

Bulk crystal of GaN, grown at 10 – 20 Kbar, and 1400 – 1600 °C without seed, along the 10-10 direction. Growth rate 0.1 mm/hr. Squares grids have 1 mm sides.

2Ga (melt) + N$_2$ = 2GaN

Equilibrium curve for GaN
Summary of bulk of Nitrides

• Bulk GaN is not possible using standard techniques i.e. Czochralski or Bridgman method due to extreme melting conditions (extreme temperature and pressure to prevent dissociation)
• Growth of AlN bulk crystals is easiest and those of In is toughest due to difference in equilibrium partial pressures
• Growth rate of more than 100 μm/hr is considered viable for technological and economical purposes
• The growth processes can be made easier by
  – Quasi-bulk growth by Hydride Vapor Phase Epitaxy (HVPE) using a starting substrate such as sapphire
  – By Physical vapor transport of Ga vapors in a sublimation reactor using GaN powder as the starting material
• Main problems with bulk growth are the introduction of impurities from the sources. They also need to be polished for further epitaxy
MBE growth system

RHEED techniques for growth study
Reflection High-Energy Electron Diffraction (RHEED)

Purpose: To monitor the oscillations in the reflectivity and estimate the thickness and rate of growth of the epitaxial material.

http://britneyspears.ac/physics/fabrication/fabrication.htm
General MBE growth features

• Advantages
  – Precise layer by layer growth process
  – Excellent in-situ growth rate monitoring possible
  – Very abrupt (one atomic layer) growth possible
  – Can replicate starting layers in excellent manner

• Disadvantages
  – Growth occurs far from equilibrium and is not thermodynamically favorable
  – Growth temperature lower and so film quality is not as good
  – Slower growth rate than MOCVD; difficult design for multiple wafers
MBE growth of III-Nitrides

- Precursors for III: Solid sources of Ga, Al, In; V: NH₃ or N plasma (RF source (13.56 MHz.) or ECR source (2.45 GHz.) used for N-source activation)

- Difficult to find a good nitrogen source as N₂ or NH₃ does not dissociate at lower temperature

- Growth temperature usually in the range of 800 – 850 °C. Higher temperature causes lower growth rate as growth is governed by kinetics, i.e. both forward and reverse reactions are taking place simultaneously at , but at different rates.

- Higher V/III ratio increases the growth rate as it prevents GaN dissociation by providing enough vapor pressure of nitrogen

- The low temperature nucleation layer must be AlN to obtain Ga-face polarity. GaN nucleation layer gives N-face polarity
**MBE growth of Nitrides: Kinetics and Thermodynamics**

- **Energy for forward reaction**
  - energy from the vapor of group III atoms
  - rf or ECR plasma source for group V activation
  - The growth temperature

- **Energy for backward reaction**
  - The growth temperature

- **The growth temperature is limited by**
  - the rate of supply of activated N-species and
  - the kinetic barrier for GaN decomposition

GaN growth by MBE proceeds via competition of the forward and reverse reactions, where the reverse reaction is suppressed.

\[
2\text{Ga (l)} + \text{N}_2\text{(g)} \rightarrow \text{GaN (s)}
\]

- Kinetic barrier lowered by catalyst
- Kinetic barrier \(~1.3\) eV
- Thermodynamic barrier does not change with reaction path and catalysis

\[
\Delta G = 1.9 \text{ eV} \quad (@ \quad 800 \, \text{°C and} \quad 10^{-6} \text{Torr})
\]