Epitaxial growth

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Outline

• Epitaxy basics
• Epitaxial growth techniques
• MOVPE basics and instrumentation
• Application examples (KTH)
• Process development
• Resources within the Nordic Nanolab Network
Epitaxy nomenclature

• **Epitaxy:** ~”arrange upon”
  Growth of a single crystal film on top of a crystalline substrate
  *Film A is grown on the substrate B*

• **Homoepitaxy**
  Film and the substrate are the same material
  *Ex. GaAs/GaAs*

• **Heteroepitaxy**
  Film and substrate are different materials
  *Ex. AlAs/GaAs*

• **Pseudomorphic growth**
  Lattice constant of film and substrate different, but coherently strained growth: In-plane lattice constant preserved (but distorted out-of-plane)
  *Ex. InGaAs/GaAs*

• **Metamorphic growth**
  Lattice-mismatched growth in the limit of large film thickness with high degree of plastic relaxation
  *Ex. InGaAs/GaAs/Ge/Si*
Semiconductor bandgaps vs lattice constants
Heterostructure band alignment

Straddling gap (Type I)

Straggered gap (Type II)

Broken gap (Type III)

nn, pp: Isotype junctions

np, pn: Anisotype junction
Example
Strained-layer super lattice detector for LWIR imaging (T2SL)

- Long-wavelength infrared detection (atmospheric transmission windows: 3-5, 8-14 µm) for thermal imaging
- Strained layer superlattices (InAs/GaSb) inter-miniband transitions


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Crystal growth methods

1. **Liquid phase epitaxy (LPE)**
   - Growth from the melt
   - Heterostructures and built-in doping variations
   - Moderate uniformity and thickness control
   - Work horse for optoelectronics (LEDs, PDs, etc)

2. **Vapor-phase epitaxy**
   - MOVPE (typically III/V) or LPCVD (typically Si/Ge)
   - Growth from the gas phase (liquid or gaseous sources)
   - Dominant for optoelectronics and Si-based electronics

3. **Molecular-beam epitaxy (MBE)**
   - Vacuum evaporation
   - Physical deposition (far from thermodynamical constraints)
   - Dominant for III/V-based electronics
   - Ultrasharp interfaces and versatility in materials
   - Popular research tool
Industry-scale MOVPE system

www.Aixtron.com
Molecular-beam epitaxy (MBE)

- Vacuum evaporation
- UHV conditions (base pressure $\sim 10^{-11}$ mbar)
- Elemental and/or gaseous sources
- Varieties: MBE, MOMBE, GSMBE, CBE
- In situ growth monitoring/surface characterization

www.Veeco.com
MBE production systems

RIBER MBE6000: 4x6" / 9x4"

VEECO GEN2000: 7x6" / 14x4"
<table>
<thead>
<tr>
<th>Growth control</th>
<th>MOVPE</th>
<th>MBE</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>High growth rate</strong></td>
<td>– Thick layer structures (optoelectronics)</td>
<td>– Interface control, ”δ-doping”, short-</td>
</tr>
<tr>
<td>– Better control of</td>
<td></td>
<td>period superlattices</td>
</tr>
<tr>
<td>compositional variations</td>
<td></td>
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</tr>
<tr>
<td>**Near thermodynamic</td>
<td>– Excellent quality/crystallinity</td>
<td><strong>Far from thermodynamic equilibrium</strong></td>
</tr>
<tr>
<td>equilibrium**</td>
<td>– Easier for P- and N-containing materials</td>
<td>– Metastable and ’difficult’ materials:</td>
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<tr>
<td>– Dilute nitrides,</td>
<td></td>
<td>dilute nitrides, antimonides, II/V:s,…</td>
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<tr>
<td>– Easier for P- and</td>
<td></td>
<td>– More straightforward for new materials</td>
</tr>
<tr>
<td>N-containing materials</td>
<td></td>
<td>→ Research tool</td>
</tr>
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<tr>
<td><strong>In-situ monitoring</strong></td>
<td><strong>Limited possibilities</strong></td>
<td><strong>Extensive possibilities</strong></td>
</tr>
<tr>
<td>– Optical reflectance</td>
<td></td>
<td>– Electron diffraction/spectroscopy, film</td>
</tr>
<tr>
<td></td>
<td></td>
<td>thickness monitoring, optical reflectance,</td>
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<tr>
<td></td>
<td></td>
<td>RGA, etc</td>
</tr>
<tr>
<td></td>
<td></td>
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<tr>
<td>**Maintenance and</td>
<td><strong>Shorter maintenance periods</strong></td>
<td><strong>Demanding vacuum conditions</strong></td>
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<tr>
<td>safety**</td>
<td>– Flexibility for setup variability</td>
<td>– Longer growth campaigns, less setup</td>
</tr>
<tr>
<td>– Higher safety risk</td>
<td>– H₂, toxic gases;</td>
<td>variability</td>
</tr>
<tr>
<td>– Subject to scrutiny</td>
<td></td>
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<tr>
<td>of legislative bodies</td>
<td></td>
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<tr>
<td>worldwide**</td>
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</table>
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Metal-Orgnic Vapor-Phase Epitaxy

MOVPE

• ... or OMVPE, MOCVD, OMCVD (or even OMP – organometallic pyrolysis)*

• Relies on room-temperature transport of precursor molecules (usually metalorganic + hydride) in a cold-wall reactor with decomposition, reaction and growth on a heated substrate

• In competition with MBE the technology of choice for fabrication of sharp heterojunctions or QW-like structures in III/V compound semiconductors

• Example: \((\text{CH}_3)_3\text{Ga} + \text{AsH}_3 \rightarrow \text{GaAs} + 3\text{CH}_4\)


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<table>
<thead>
<tr>
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<tbody>
<tr>
<td>MOVPE</td>
<td>16000</td>
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<tr>
<td>OMVPE</td>
<td>3060</td>
</tr>
<tr>
<td>MOCVD</td>
<td>28500</td>
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<tr>
<td>OMCVD</td>
<td>873</td>
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</table>

Trimethylgallium (TMGa)
MOVPE source molecules

Group III: Metal-organic precursors
Group V: often Hydrides
Pyrolysis and reaction mechanisms

**Hydrides:** Strong catalytic effect on pyrolysis

**Alkyles:**
- Low temperature, steep slopes
- Intermediate reactions

\[
(\text{CH}_3)_3\text{In} \rightarrow (\text{CH}_3)_2\text{In} \rightarrow (\text{CH}_3)\text{In} \rightarrow \text{CH}_3
\]

- Presence of GaAs
- InP
Arsine (AsH₃)

- Candidate as chemical war-fare weapon (WW1)
  - Extremely toxic (lethal below limit for perception of Garlic-like smell)
  - Colorless
  - Heavier than air → "blanketing effect"
  - bp=-55°C
  - Flammable
- Adducts used for production of war-fare gases, e.g. Lewisite
- MO-sources considered for safety and low-T growth

**Toxicity (inhalation)**
- 250 ppm instantly lethal
- 25-50 ppm ½ hour lethal
- 10 ppm lethal at long exposure
- 0.05 ppm max allowed conc. in air
MOVPE system

Consist of

- Gas mixing cabinet
- Reactor
- Pump and scrubber system

1. MFC controlled hydride line
2. Bubbler configuration for MO sources
3. Vent-run manifold
4. H₂ or N₂ carrier gas
5. Quartz-tube reactor with heated graphite substrate holder (RF or IR)
6. Throttle valve for control of total pressure
7. System pump
8. Scrubber system for exhaust gases
MOVPE system

AIXTRON 200/4 – Horizontal cold-wall reactor, 3x2-inch configuration with gas-foil main and satelite rotation
Gas-blending system and interface control

- Large carrier gas flow (x100)
- Rapid switching of source gases at the injector block: three-way valve vent-run manifold and flow balancing
- Minimized distance between switching valves and reactor – no dead volumes
- All-laminar flow conditions (abrupt gas-phase interface)
- Flow rates adjusted by electronic mass-flow controllers (MFCs) under continuous flow for accuracy and reproducibility
- Electronic pressure controllers (EPCs) where accurate definition of pressures are required (e.g. MO sources)
MO gas-delivery configurations

1. **Standard MO source line, e.g. TMGa**
   - Small gas velocity at low flow rates
   - Modest dynamic range of concentration

2. **MO line with pusher flow**
   - Increased flow rate through vent/run line

3. **MO line with dilution configuration**
   - Greatly extended dynamic range
MOVPE principle

Growth rate determined by:
1. **Diffusion (mass transport)**: Gas phase transport of precursors/reaction products to interface
2. **Kinetics**: Reaction and incorporation at or near the interface
MOVPE growth regimes

- Zero-gas velocity boundary-condition → retarded gas velocity "boundary layer" close to substrate
- Heated susceptor → gas-phase depletion effect
- Column V species in excess → Growth rate determined by group III flow
Pressure dependence: LP-MOVPE

Low-pressure operation:
+ Laminar flow conditions for higher gas velocities – improved interface abruptness
+ Increased lateral diffusion $\rightarrow$ improved uniformity
+ Reduced parasitic reaction rate
+ Increased area-selectivity in growth (e.g., GaAs vs dielectric)

- Decrease of pyrolysis rate of group V hydrides $\rightarrow$ higher V/III ratios required
- More complex reactor design

$\Rightarrow$ Typical reactor pressure $\sim$100 mbar
Numerical modeling of MOVPE reactors and processes

Purpose
• Reactor design, process optimization
• Hydrodynamics, prediction of boundaries of flow instabilities
• Heat transfer
• Species transport and chemical reactions

Involves
• Solutions of coupled flow, heat transfer and mass transport equations
• Multicomponent mass transport of chemical species
• Gas phase chemical reaction kinetics
• Surface chemical reaction kinetics
Nitrogen vs Hydrogen as carrier gas

The properties of the carrier gas determines growth rate, uniformity, purity etc. Numerical simulations are used to find optimum flow conditions.

Heat distribution mainly affected by different optimal flow and thermal conductivity.

Growth rate for AlGaAs/GaAs

Without rotation

With rotation

- Improved uniformity with \( \text{N}_2 \) due to lower thermal conductivity and longer hydrodynamic entrance length (box-like profile - undeveloped gas phase)
- Improved purity with \( \text{N}_2 \) due to enhanced decomposition of hydrides and thereby increased concentration of atomic hydrogen at the surface
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KTH MOVPE setup

• Versatile MOVPE system
  – Aixtron 200/4
  – (AlGaIn)-(Ge)-(NPAsSb): C,Zn,Sn,Te
  – Not III-N:s
  – In-situ growth monitoring (EpiRAS)
  – Good measures against cross-contamination

• Electrum Laboratory + environment
  – Semiconductor processing facilities
  – Extensive materials/device characterization
  – Device design/system-related activities

• Variety of applications
  – Internal projects mainly optical communication
  – Excellent track-record with external partners
    • Academic: service epi/research collaborations
    • Industrial: Mainly long-term commitments using own personnel; commercial success stories
KTH MOVPE setup

Variety of materials and applications

Parallel developments and state-of-the-art results using arsenides, phosphides, antimonides and (by third party) growth of Au-assisted nanowire-based solar cells

➤ Flexibility and integrity against cross-contamination
Application examples KTH

**VCSELs for metro/access**
- 1300-nm GaAs-based VCSELs
- Challenges:
  - Long-wavelength InGaAs/GaAs MQW
  - 100s of heterointerfaces with high optical quality and high optical efficiency
  - Precision epi over +10 µm

Example: Optical diplexer for FTTH PON installations:

**QD-based interband photodetectors**
- LWIR photodetectors based on spatially indirect (Ga)InSb QD to InAs bulk transitions
- Challenges:
  - QD formation and control in immature materials
  - Requirement on thick multi-layer absorber

J. LIGHTW. TECHN. 25,(8), 2791 (2007)  

Infrared Phys. Techn. 61, 319 (2013)
Application examples KTH, cont.

Monolithically integrated EAT/SOA transceiver for 40-60 GHz RoF applications
- InP structure for 1.55-µm operation
- Challenges:
  - Epitaxial regrowth
  - Involved processing

Ultra-compact InP VCSELs for direct integration on silicon
- Transfer print and PhC mirrors/cavity
- Challenges:
  - Planar topography for high-quality fusion with PhC mirrors/cavity
  - Carrier injection through extremely thin InP membrane

Nature Photonics, 6, 615–620 (2012)
Scientific Reports, 6, 18860 (2016)
**HVPE at KTH**

Hydride Vapor Phase Epitaxy

- Hot-wall reactor
- Metal chlorides as III-group sources
- Hydrides ($\text{PH}_3$, $\text{AsH}_3$) as V-group sources
- High growth rates
- Selective epitaxy
Towards direct growth of high quality III-V on Si
Corrugated ELOG of InP on Si (CELOG)

Omanakuttan et al., Optical Materials Express, 9(3), 1488-1500 (2019).
InP:Fe Regrowth around Wet-etched Quantum Cascade Laser ridges

- 5.5 µm laser from Harvard University (R. Blanchard and F. Capasso)
- Wet-etched with mask overhang
- 9 µm deep
- Regrowth time: 13 minutes

<table>
<thead>
<tr>
<th>Ridge Width (µm)</th>
<th>Maximum output power under CW operation at RT (mW)</th>
<th>Maximum WPE (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td>725</td>
<td>5.3</td>
</tr>
<tr>
<td>6</td>
<td>1 475</td>
<td>8.7</td>
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<tr>
<td>8</td>
<td>1 500</td>
<td>8.5</td>
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<tr>
<td>10</td>
<td>2 000</td>
<td>8.4</td>
</tr>
<tr>
<td>12</td>
<td>2 400</td>
<td>8.8</td>
</tr>
<tr>
<td>14</td>
<td>2 400</td>
<td>7.6</td>
</tr>
</tbody>
</table>

W. Metaferia et al., Optical Engineering 53(8), 087104, 2014.
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Significance of in-house access

- Largely enabling: Major part of the device functionality relies on the epitaxial base structure
- Novel devices may typically rely on one or multiple regrowth steps
- Foundry-based epitaxy impractical (and overly expensive if even available) for development work
Process development / optimization

- Many calibration runs to generate “sharp” wafer, even if “well-known structure”

- Budget accordingly in terms of time, efforts and cost
Process development chart

Materials/device design

Choice of precursors
and overall growth conditions

Tuning of process parameters

Iterative runs based on fast-feedback characterization

Sharp runs

- Layer sequence
- Composition
- Thickness
- Doping
- Morphology

- Vs growth temp
- Pre-reactions
- Layer/growth integrity
- Doping efficiency

- Microscopy
- HRXRD
- PL
- Hall/CV
- ...

- Growth T
- Reactor P
- Source flows
- Reactor flow
- V/III ratio
- Growth rate ...

Need for “fresh” calibration runs!
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## III-V epitaxy resources within NNN

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<thead>
<tr>
<th>Lab</th>
<th>Equipment</th>
<th>Contact</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lund NanoLab</td>
<td>Aerotaxy (Nanowire growth)</td>
<td>Maria Huffman</td>
</tr>
<tr>
<td></td>
<td>Aixtron 200/4 (MOVPE)</td>
<td><a href="mailto:maria.huffman@ftf.lth.se">maria.huffman@ftf.lth.se</a></td>
</tr>
<tr>
<td></td>
<td>Aixtron CCS 18313 (MOVPE)</td>
<td></td>
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<tr>
<td></td>
<td>Epiquip MOVPE system</td>
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<tr>
<td></td>
<td>CBE system</td>
<td></td>
</tr>
<tr>
<td>Chalmers NFL</td>
<td>MBE-EPI 930 (III-V materials)</td>
<td>Mahdad Sadeghi</td>
</tr>
<tr>
<td></td>
<td>MBE-Riber C21 T-E (Sb materials, 11 port)</td>
<td><a href="mailto:mahdad.sadeghi@chalmers.se">mahdad.sadeghi@chalmers.se</a></td>
</tr>
<tr>
<td>NTNU, Trondheim</td>
<td>EpiQuest RF-PAMBE MOVPE</td>
<td>Bjørn-Ove Finland</td>
</tr>
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<td></td>
<td></td>
<td><a href="mailto:Bjorn.fimland@ntnu.no">Bjorn.fimland@ntnu.no</a></td>
</tr>
<tr>
<td>UiO, MINaLAB, Oslo</td>
<td>MOVPE (ZnO, ZnCdO, ZnMgO)</td>
<td>Vishnukanthan Venkatachalapathy</td>
</tr>
<tr>
<td></td>
<td></td>
<td><a href="mailto:vishnukanthan.venkatachalapathy@sxn.uio.no">vishnukanthan.venkatachalapathy@sxn.uio.no</a></td>
</tr>
<tr>
<td>DanChip</td>
<td>Veeco MOVPE (GaAs/AlGaAs)</td>
<td>Kresten Yvind</td>
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<tr>
<td></td>
<td></td>
<td><a href="mailto:kryv@fotonik.dtu.dk">kryv@fotonik.dtu.dk</a></td>
</tr>
<tr>
<td>Aalto</td>
<td>3xMOVPE (HVPE, III-V MOVPE, GaN)</td>
<td>Markku Sopanen</td>
</tr>
<tr>
<td></td>
<td>MBE (metal, oxides)</td>
<td><a href="mailto:markku.sopanen@aalto.fi">markku.sopanen@aalto.fi</a></td>
</tr>
<tr>
<td>KTH/ELAB</td>
<td>Aixtron 200/4 MOVPE</td>
<td>Mattias Hammar; <a href="mailto:hammar@kth.se">hammar@kth.se</a></td>
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<tr>
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