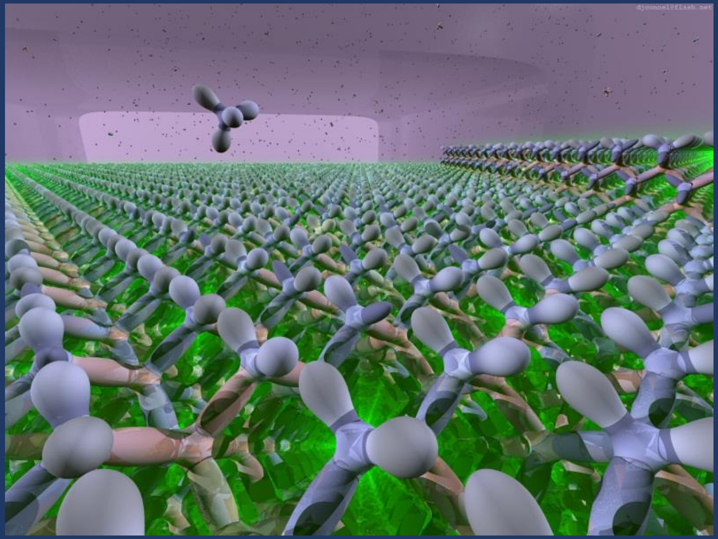
Epitaxial growth

Mattias Hammar
KTH Royal Institute of Technology



Dan Connely
http://oz.irtc.org/ftp/pub/stills/1998-08-31/epitaxy.jpg

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)

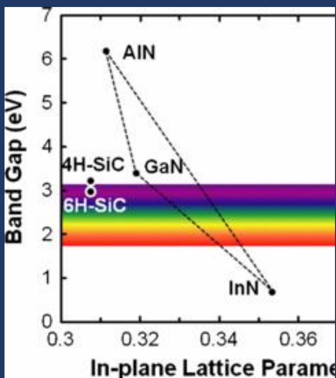
  Ex. ***InGaAs/GaAs***

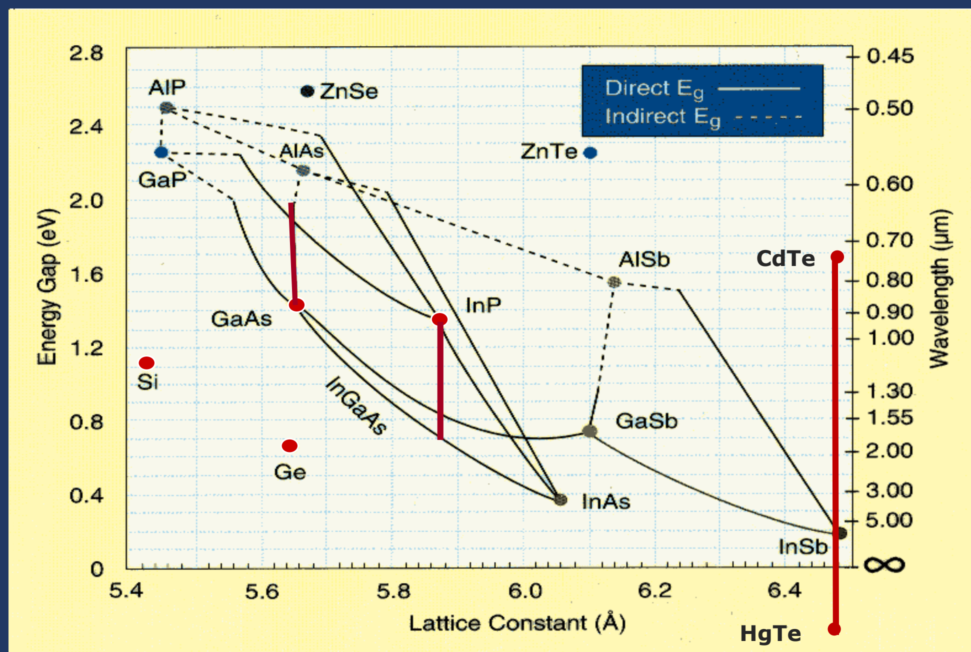
- Metamorphic growth

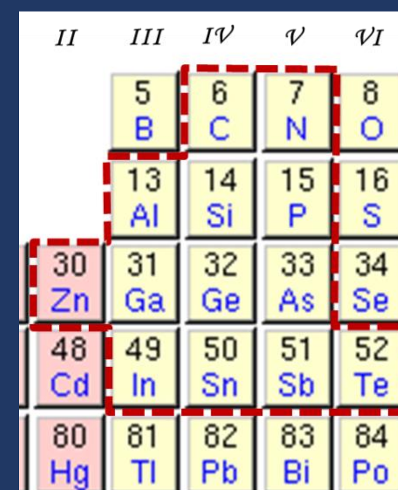
  Lattice-mismatched growth in the limit of large film thickness with high degree of plastic relaxation

  Ex. ***InGaAs/GaAs/Ge/Si***

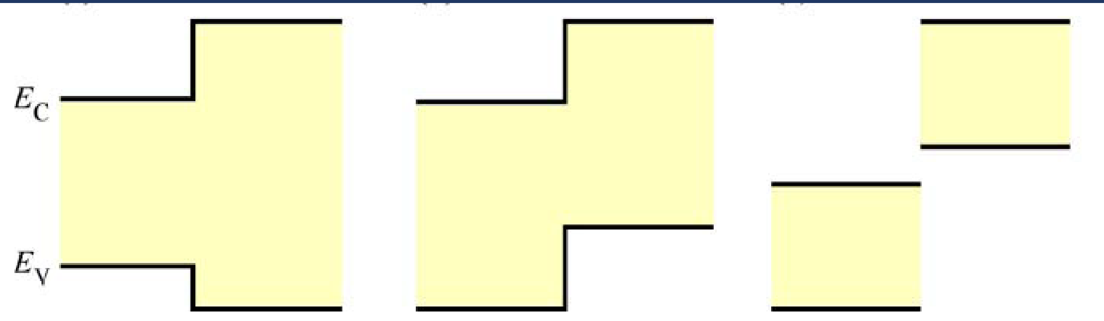
Semiconductor bandgaps vs lattice constants







Heterostructure band alignment



Stradding gap (Type I) | Straggered gap (Type II) | Broken gap (Type III)

nn, pp: Isotype junctions
np, pn: Anisotype junction

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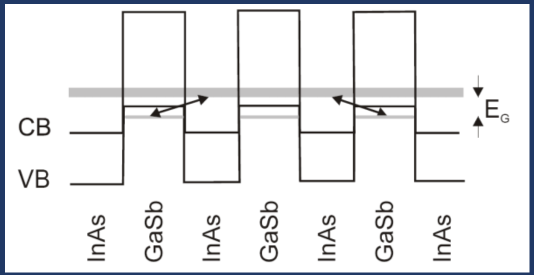
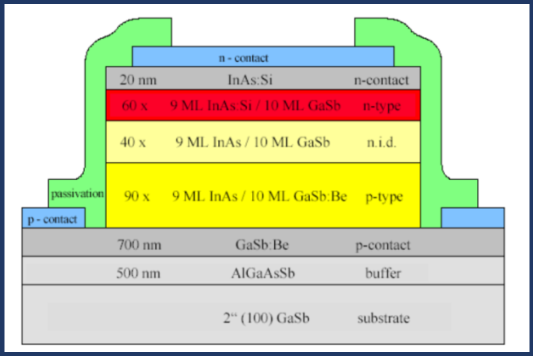
Example

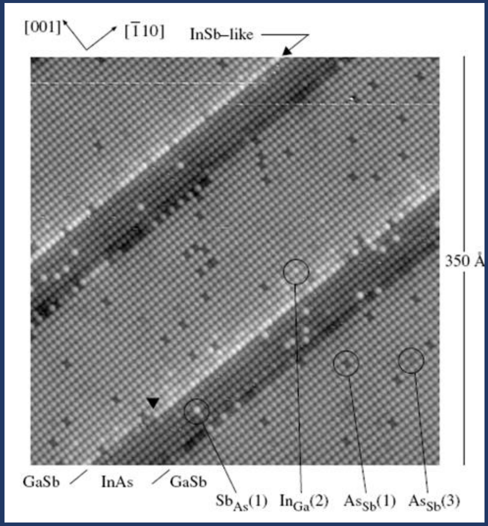
Strained-layer super lattice detector for LWIR imaging (T2SL)

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



Rehm, et al. Proc SPIE 5783, 123 (2005)





Phys. Rev. Lett. 86 (14), 2953 (2000)

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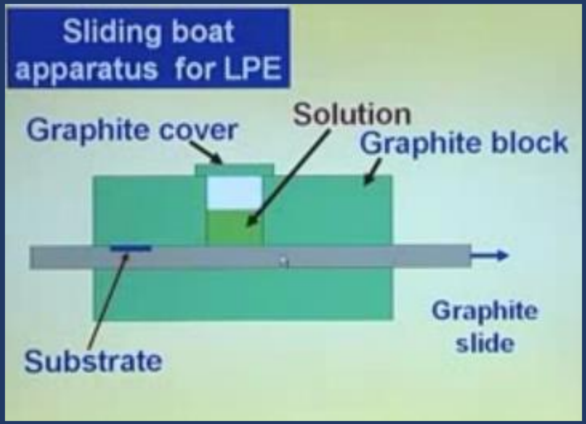
Crystal growth methods



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 eiptaxy
   - 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

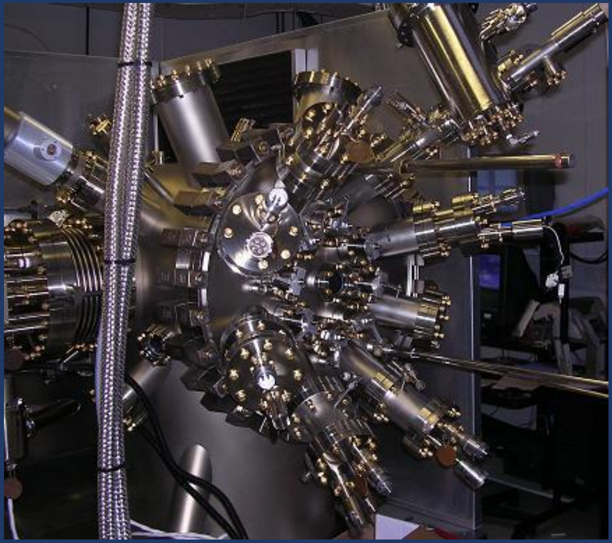
3. Molecular-beam epitaxy (MBE)
   - Vacuum evaporation
   - Physical deposition (far from thermodynamical constraints)
   - Dominant for III/V-based electronics
   - Ultrasharp interfaces and versatility in materials
     - Popular research tool

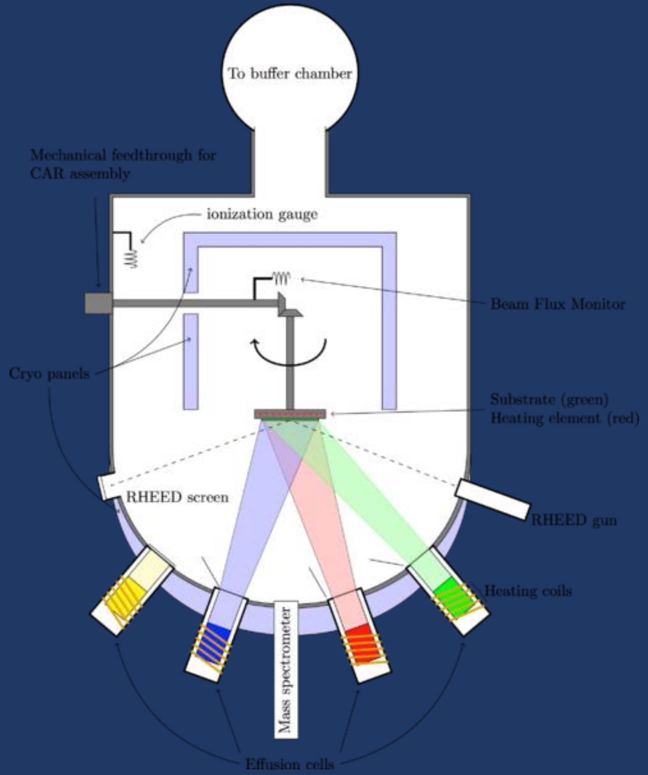
Industry-scale MOVPE system

www.Aixtron.com

Molecular-beam epitaxy (MBE)

- Vacuum evaporation
- UHV conditions (base pressure ~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"

	MOVPE	MBE
Growth control	**High growth rate** – Thick layer structures (optolectronics) – Better control of compositional variations **Near thermodynamic equilibrium** – Excellent quality/crystallinity – Easier for P- and N-containing materials	**Fast switching** – Interface control, ”δ-doping”, short-period superlattices **Far from thermodynamic equilibrium** – Metastable and ’difficult’ materials: dilute nitrides, antimonides, II/V:s, … – More straightforward for new materials → Research tool
In-situ monitoring	**Limited possibilities** – Optical reflectance	**Extensive possibilities** – Electron diffraction/spectroscopy, film thickness monitoring, optical reflectance, RGA, etc
Maintenance and safety	**Shorter maintenance periods** - Flexibility for setup variability **Higher safety risk** – H2, toxic gases; – Subject to scrutiny of legislative bodies worldwide	**Demanding vacuum conditions** – Longer growth campaigns, less setup variability

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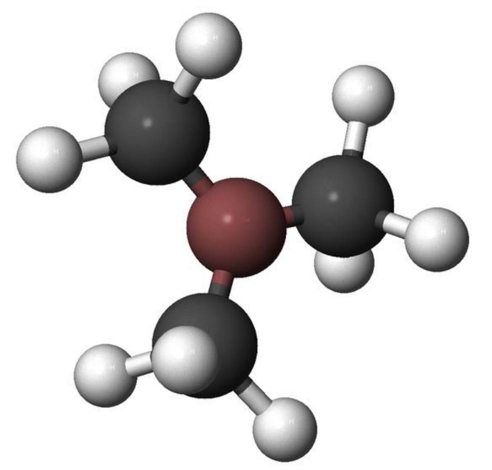
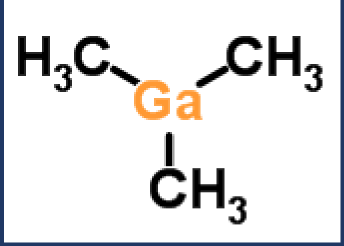
Metal-Organic Vapor-Phase Epitaxy MOVPE

- ... 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: $(CH_3)_3Ga + AsH_3 \rightarrow GaAs + 3CH_4$

*

Hits in Google Scholar (2007-2017)	
MOVPE	16000
OMVPE	3060
MOCVD	28500
OMCVD	873

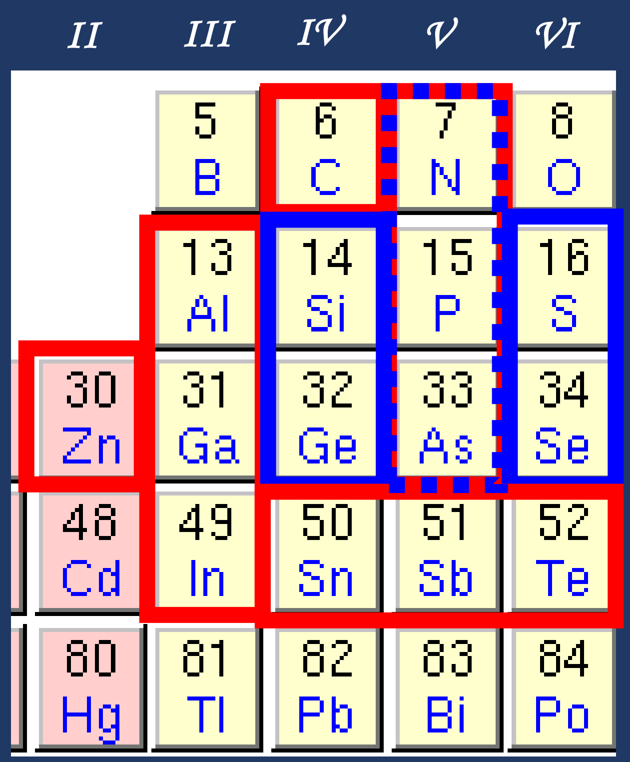


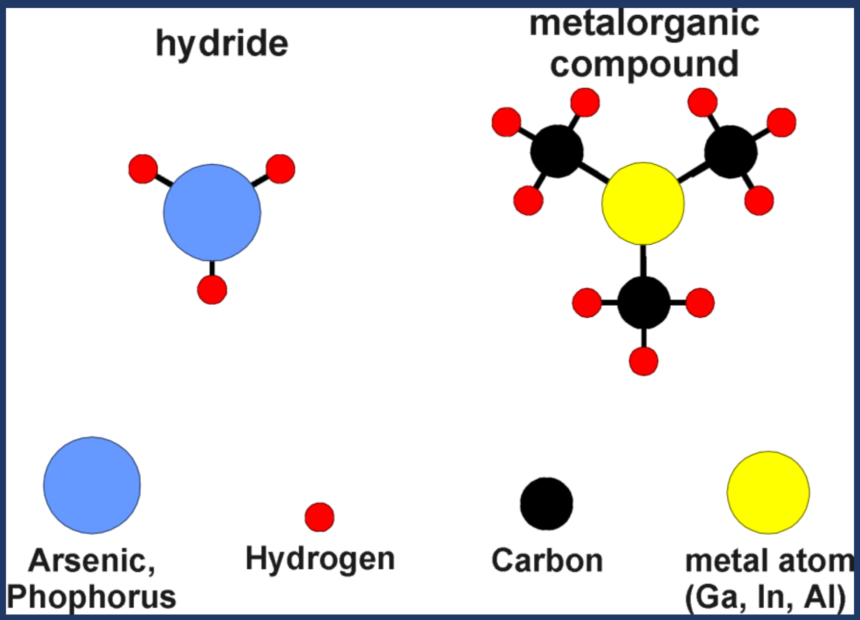


Trimethylgallium (TMGa)

MOVPE source molecules

Group III: Metal-organic precursors
Group V: often Hydrides





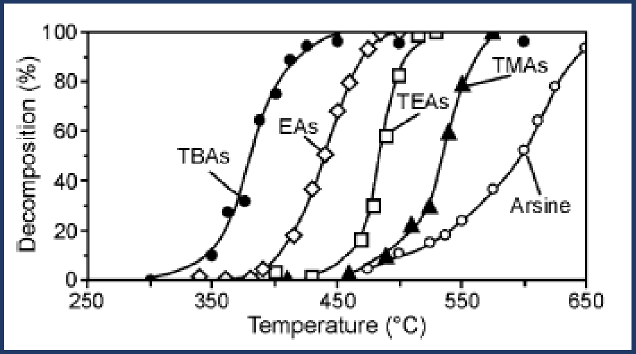
Pyrolysis and reaction mechanisms

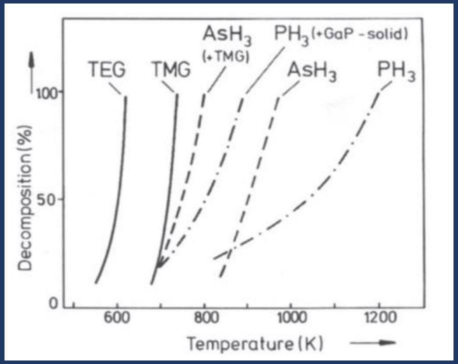
Hydrides: Strong catalytic effect on pyrolysis

Alkyles:

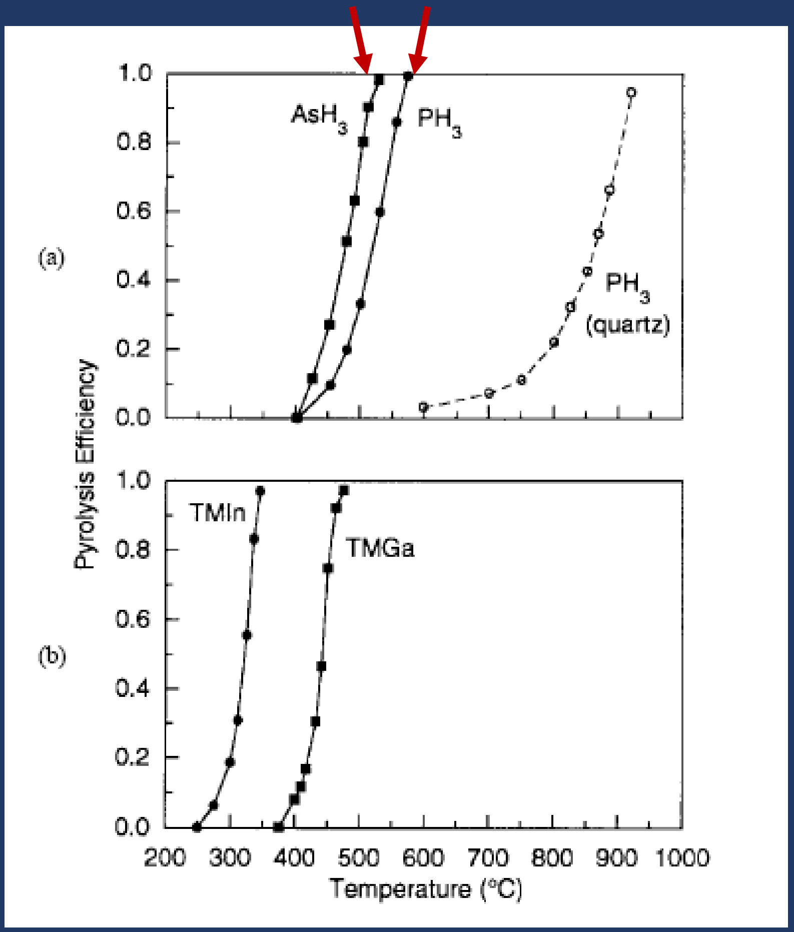
- Low temperature, steep sloopes
- Intermediate reactions

$(CH_3)_3In \rightarrow (CH_3)_2In \rightarrow (CH_3)In \rightarrow CH_3$





Presence of GaAs InP

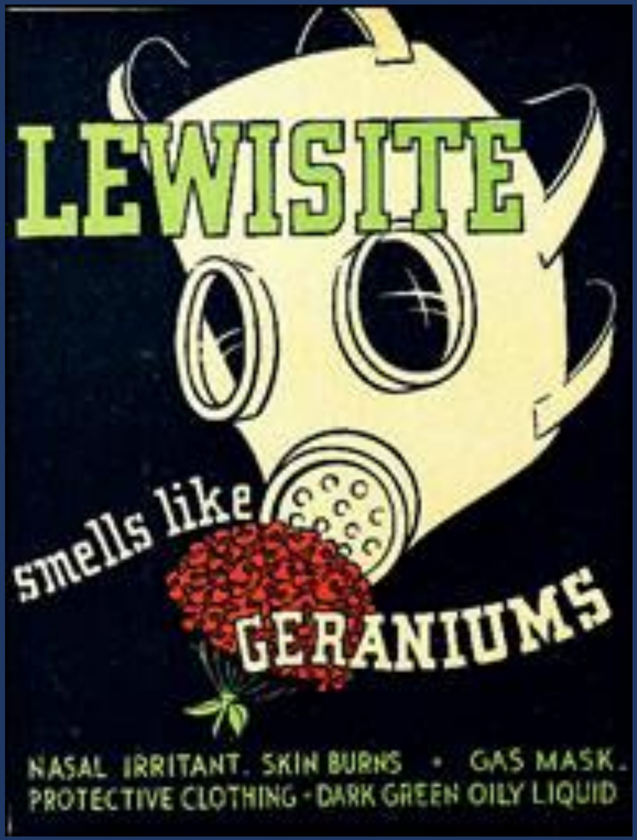


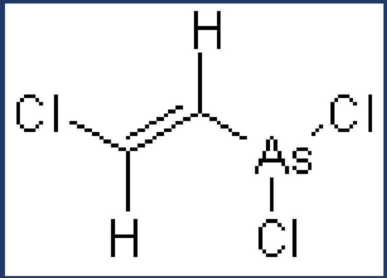
Arsine (AsH_3)

- Candidate as chemical war-fare wapon (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	leathal at long exposure
0.05 ppm	max allowd conc. in air



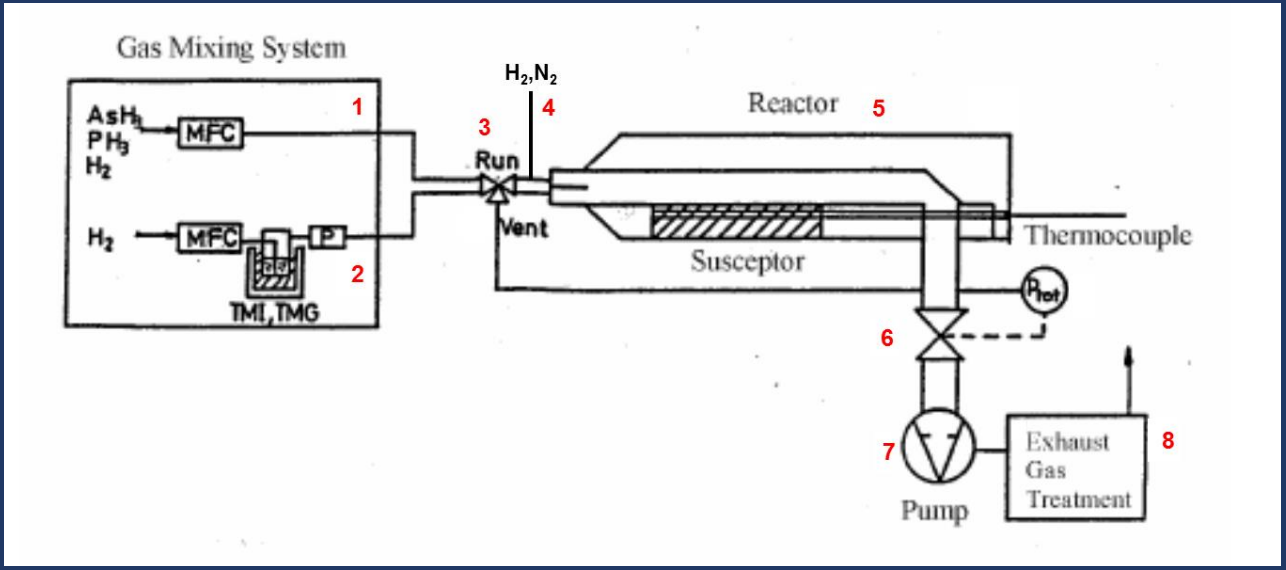


MOVPE system

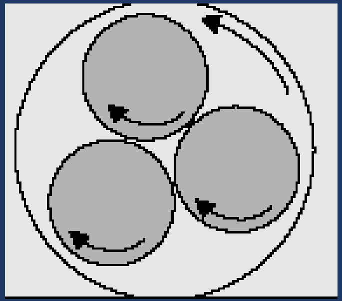
Consist of

- Gas mixing cabinet
- Reactor
- Pump and scrubber system

1. MFC controlled hydride line
2. Bubbler configuration for MO sources
3. Vent-run manifold
4. H_2 or N_2 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)

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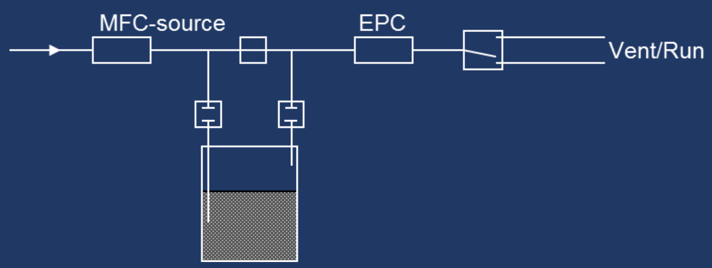
MO gas-delivery configurations

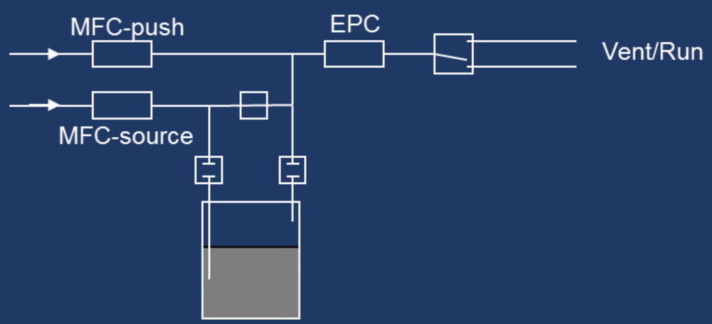
1. **Standard MO source line, e.g. TMGa**

   → Small gas velocity at low flow rates
   → Modest dynamic range of concentration



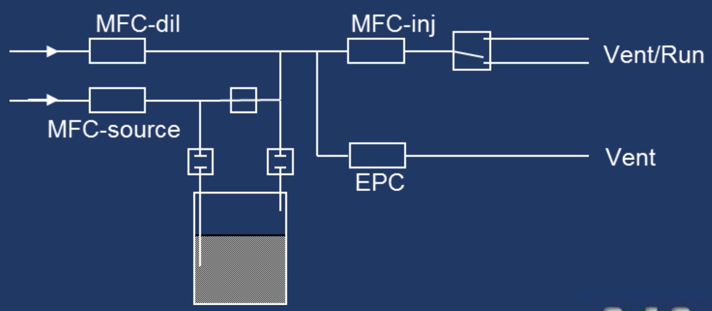
2. **MO line with pusher flow**

   → Increased flow rate through vent/run line



3. **MO line with dilution configuration**

   → Greatly extended dynamic range



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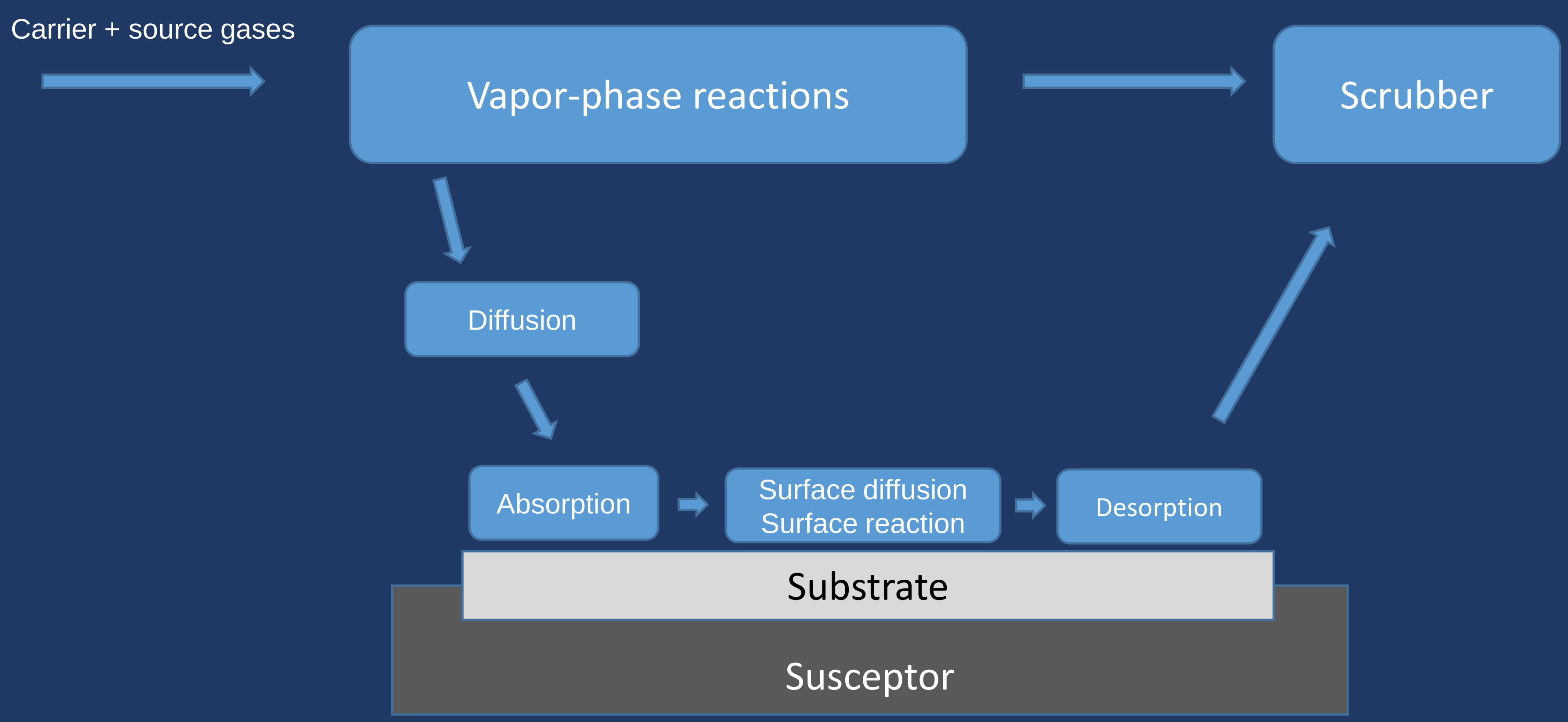
MOVPE principle

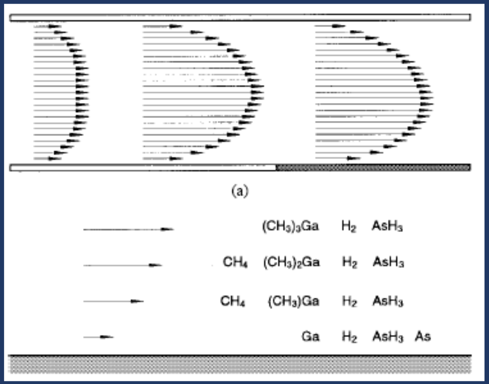


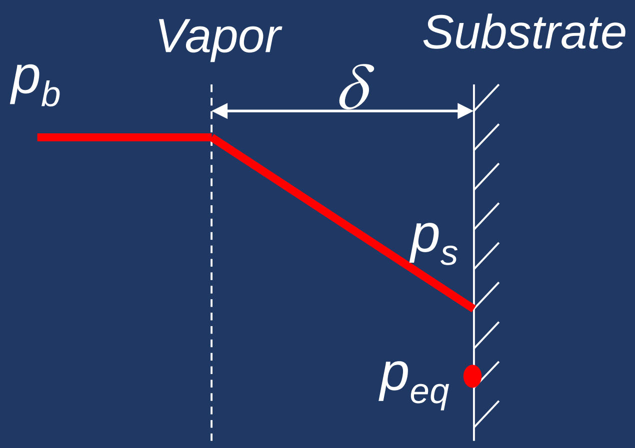
Growth rate determined by:

1. **Diffusion (mass transport)**: Gas phase transport of precursors/reaction products to interface
2. **Kinetics**: Reaction and incorporation at or near the interface

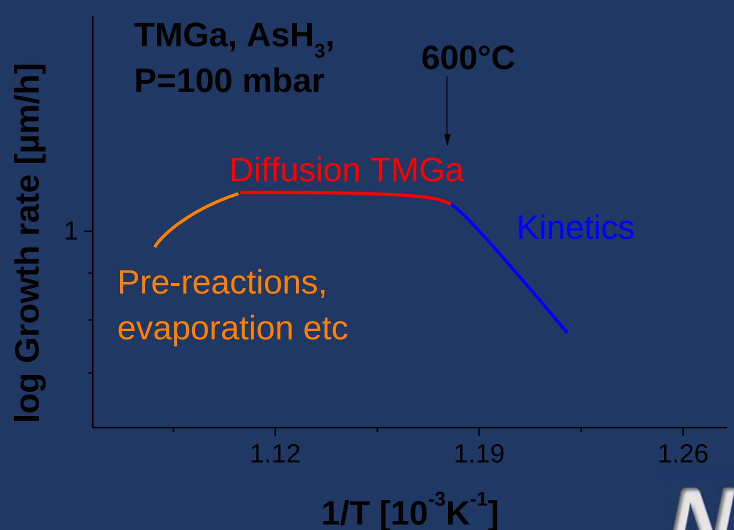
MOVPE growth regimes

- 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





Temperature dependence



Pressure dependence: LP-MOVPE

Low-pressure operation:

+ Laminar flow conditions for higher gas velocities – improved interface abruptness
+ Increased lateral diffusion → improved uniformity
+ Reduced parasitic reaction rate
+ increased area-selectivity in growth (e.g., GaAs vs dielectric)
- Decrease of pyrolysis rate of group V hydrides → higher V/III ratios required
- More complex reactor design

➔ Typical reactor pressure ~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

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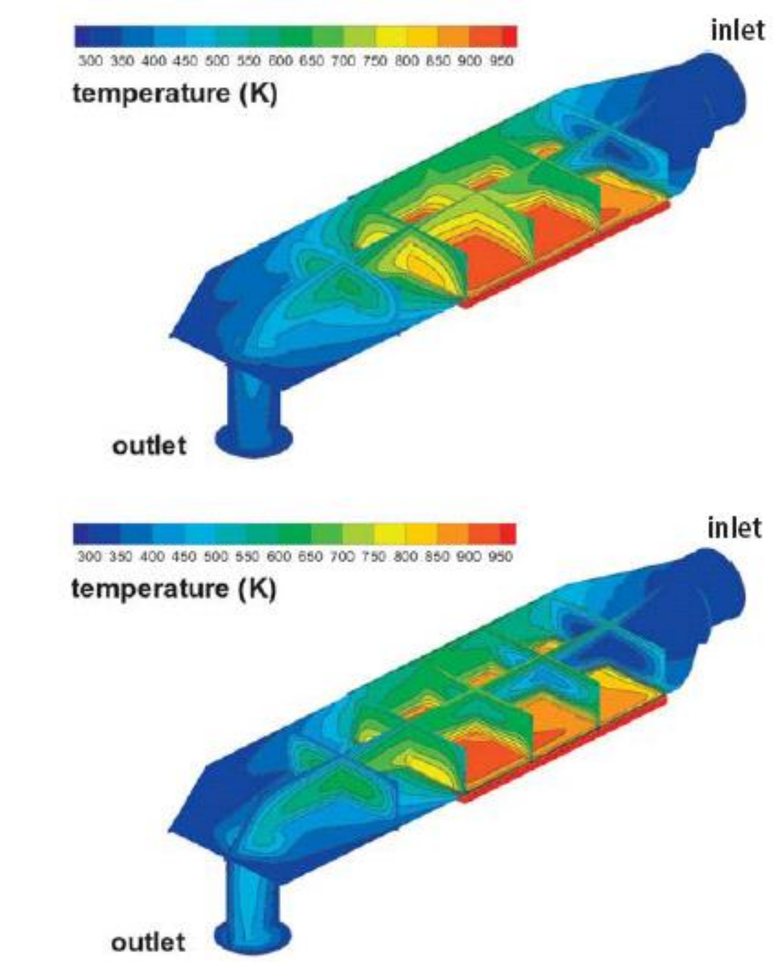
Nitrogen vs Hydrogen as carrier gas

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

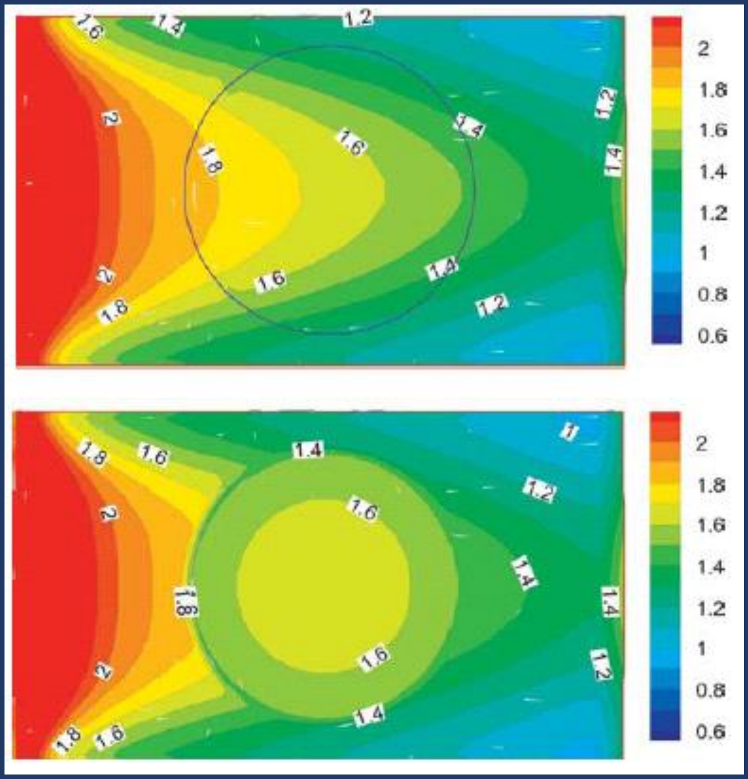
Heat distribution mainly affected by different optimal flow and thermal conductivity

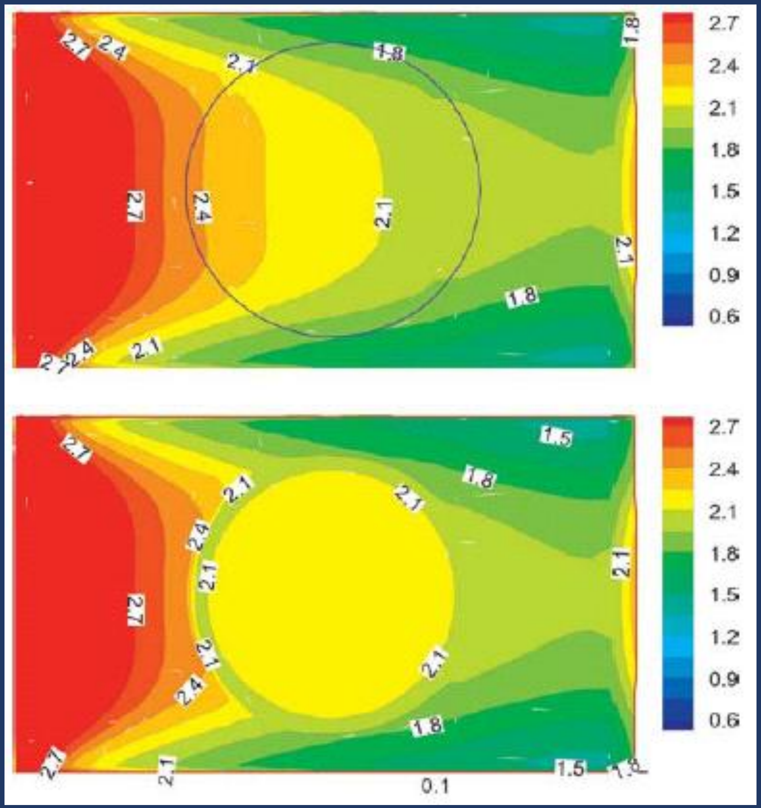


J. Daulsberg et al., J. Cryst. Growth 223, 23 (2001)

Growth rate for AlGaAs/GaAs

	H_2	N_2
Without rotation		
With rotation		





•**Improved uniformity** with N_2 due to lower thermal conductivity and longer hydrodynamic entrance length (box-like profile - undeveloped gas phase)
•**Improved purity** with N_2 due to enhanced decompostion of hydrides and thereby increased concentration of atomic hydrogen at the surface

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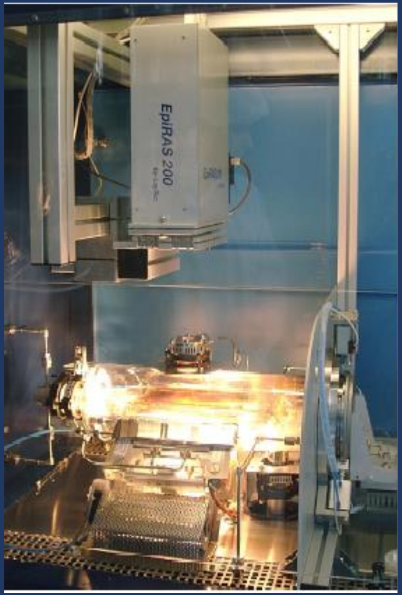
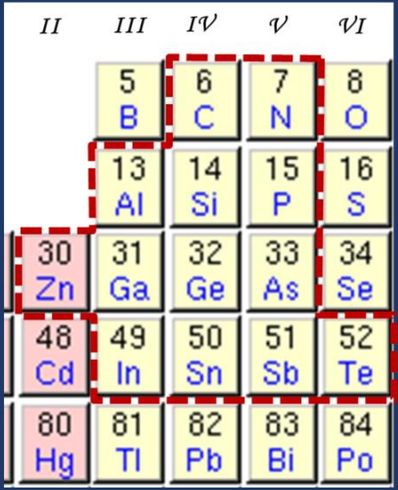
KTH MOVPE setup

- Versatile MOVPE system
  - Aixtron 200/4
  - (AlGaIn)-(Ge)-(NPAsSb): C,Zn,Si,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

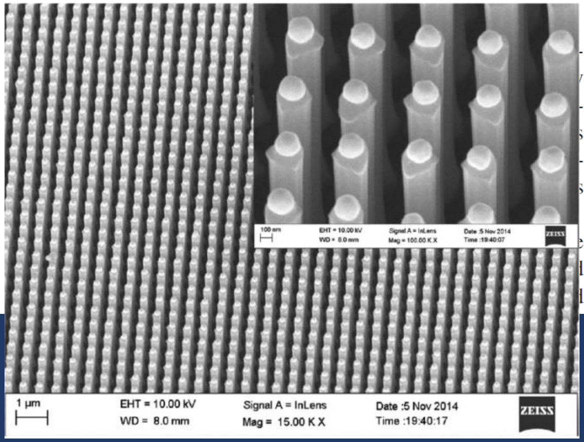
➔ Flexibility and integrity against cross-contamination

IEEE JOURNAL OF PHOTOVOLTAICS, VOL. 6, NO. 1, JANUARY 2016 185

A GaAs Nanowire Array Solar Cell With 15.3% Efficiency at 1 Sun

Ingvar Åberg, *Member, IEEE*, Giuliano Vescovi, *Member, IEEE*, Damir Asoli, Umear Naseem, James P. Gilboy, Christian Sundvall, Andreas Dahlgren, K. Erik Svensson, Nicklas Anttu, Mikael T. Björk, and Lars Samuelson

***Abstract*—A GaAs nanowire array solar cell with an independently verified solar energy conversion efficiency of 15.3% and open-circuit voltage of 0.906 V under AM1.5g solar illumination at 1-sun intensity has been fabricated. This is the highest published efficiency for nanowire array solar cells and is twice the prior record for GaAs nanowire array solar cells. The solar cell has been fabricated by substrate-based epitaxy but is structurally compatible with substrate-less aerotaxy fabrication, providing a path to high-volume manufacturing. The short-circuit current of 21.3 mA/cm^2 was generated with axial p-n junction GaAs cores covering 13% of the surface area, which is a volume of GaAs equivalent to a 370-nm-thick planar layer.**

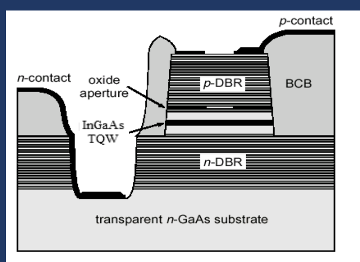


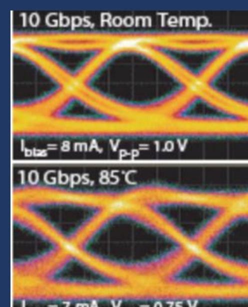
Application examples KTH

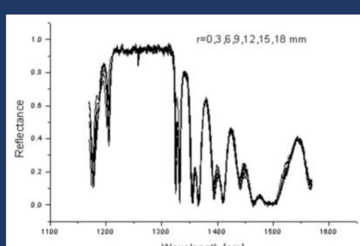
VCSELs for metro/access

- 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:



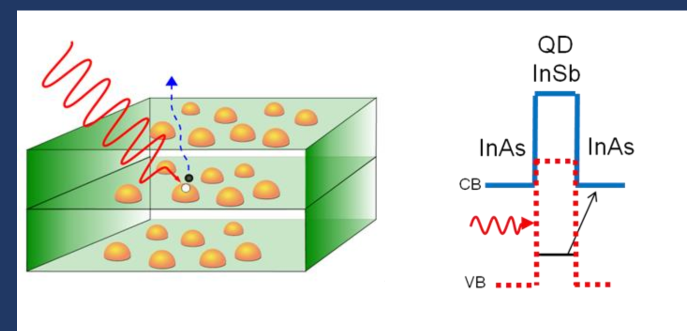


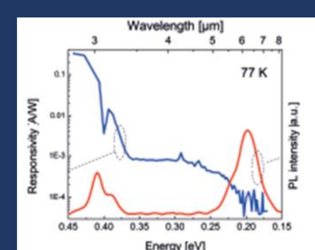


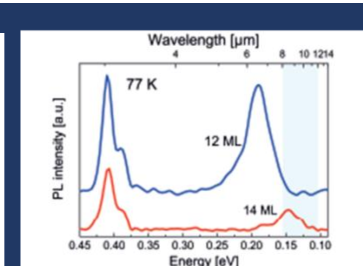
J. LIGHTW. TECHN. 25,(8), 2791 (2007)
Proc. of SPIE Vol. 6992, 699203, (2008)

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







Infrared Phys. Techn. 61, 319 (2013)

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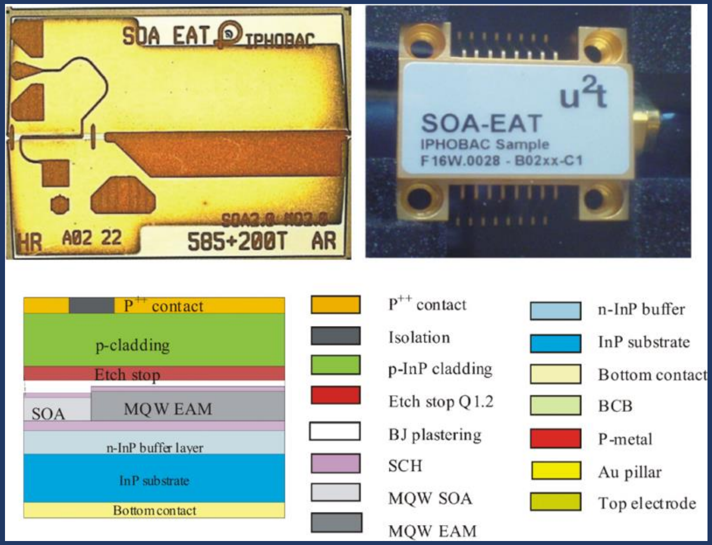
Application examples KTH, cont.

Monolithically integrated EAT/SOA transceiver for 40-60 GHz RoF applications

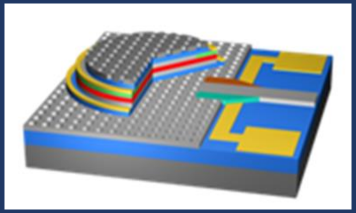
- InP structure for 1.55-µm operation
- Challenges:
  - Epitaxial regrowth
  - Involved processing

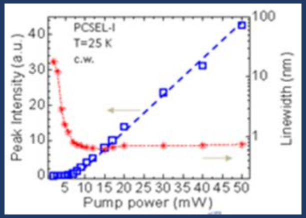


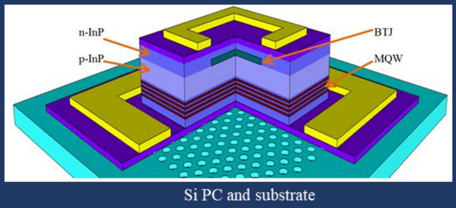
Sem. Sci. Technol. 26, 014042 (2011)

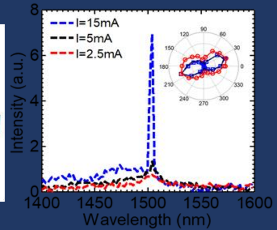
Ultra-compact InP VCSELs for direct integration on silicon

- Transfer print and PhC mirrors/cavity
- Challenges:
  - Planar topography for high-quality fusion with PhC mirrors/cavity
  - Carrier injection through extremely thin InP membrane







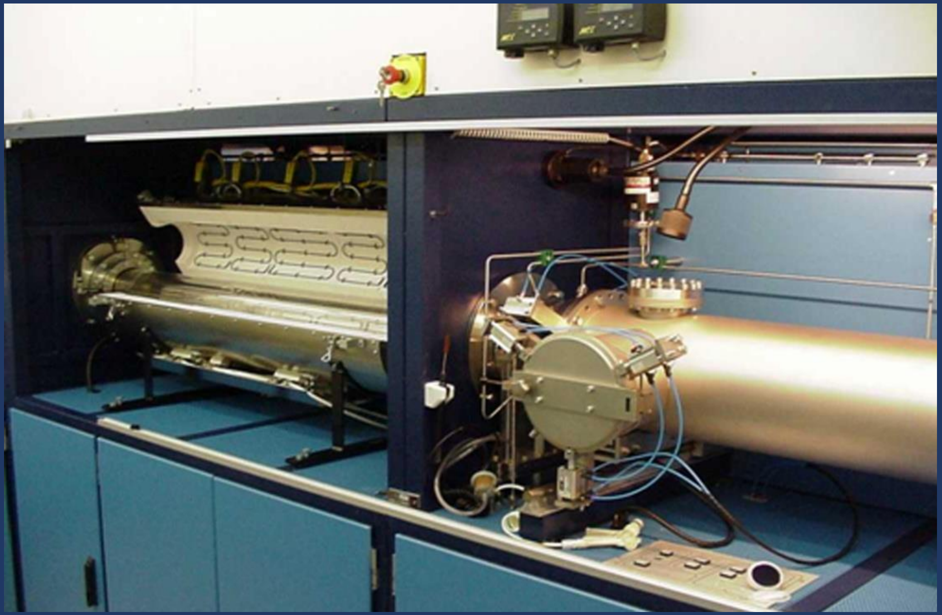


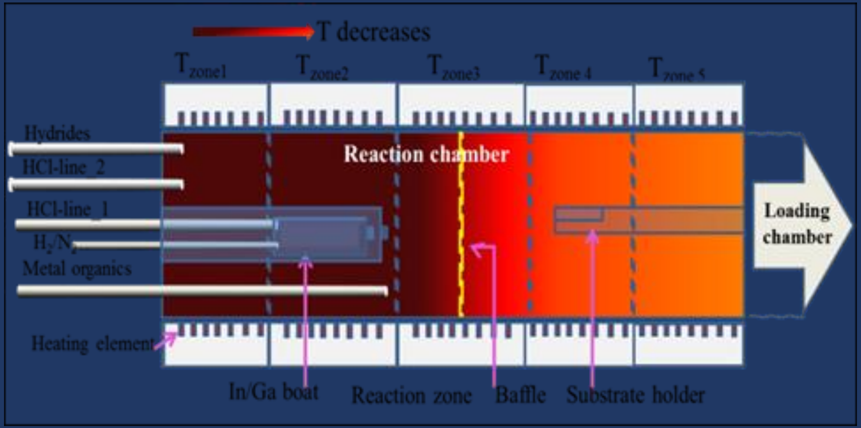
Nature Photonics, 6, 615–620 (2012)
Scientific Reports, 6, 18860 (2016)

HVPE at KTH

Hydride Vapor Phase Epitaxy

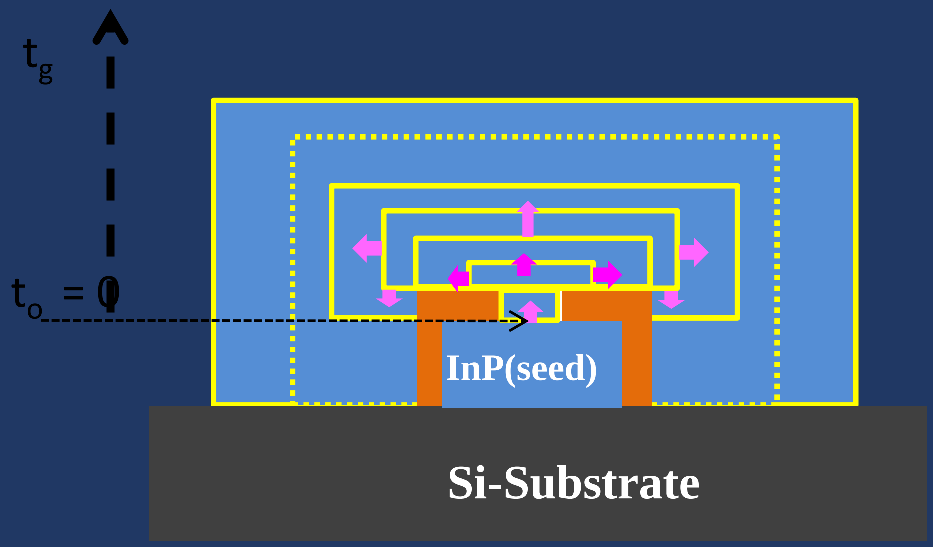
- Hot-wall reactor
- Metal chlorides as III-group sources
- Hydrides (PH_3, AsH_3) as V-group sources
- High growth rates
- Selective epitaxy

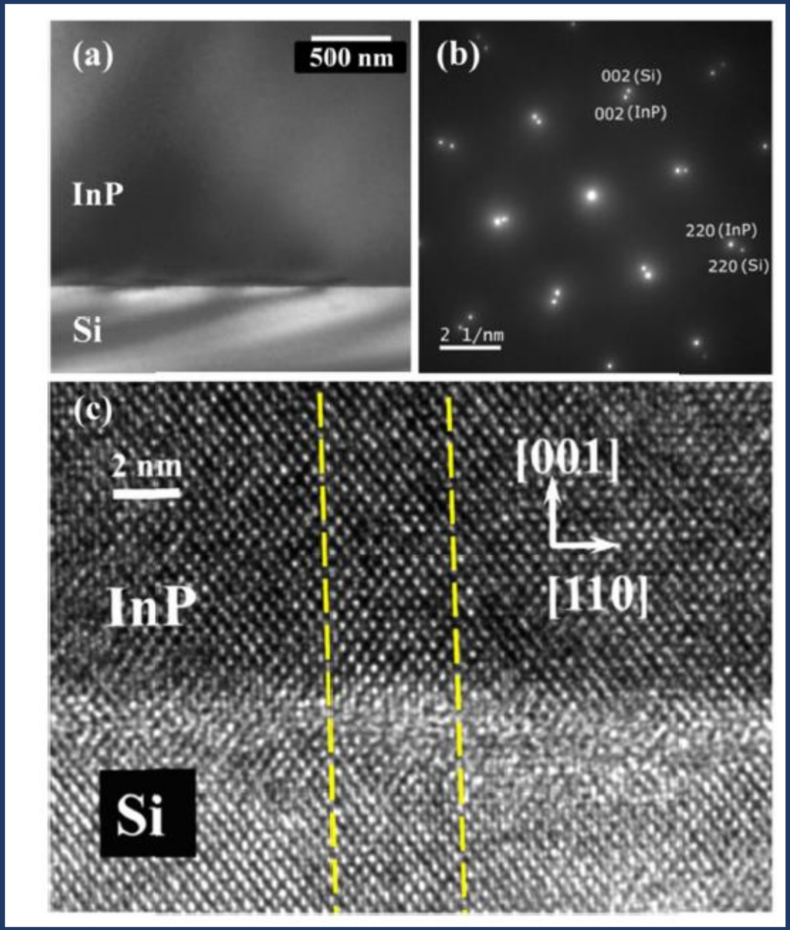




Towards direct growth of high quality III-V on Si

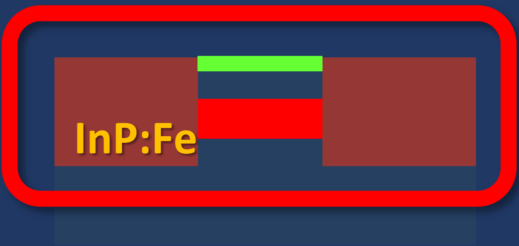
Corrugated ELOG of InP on Si (CELOG)

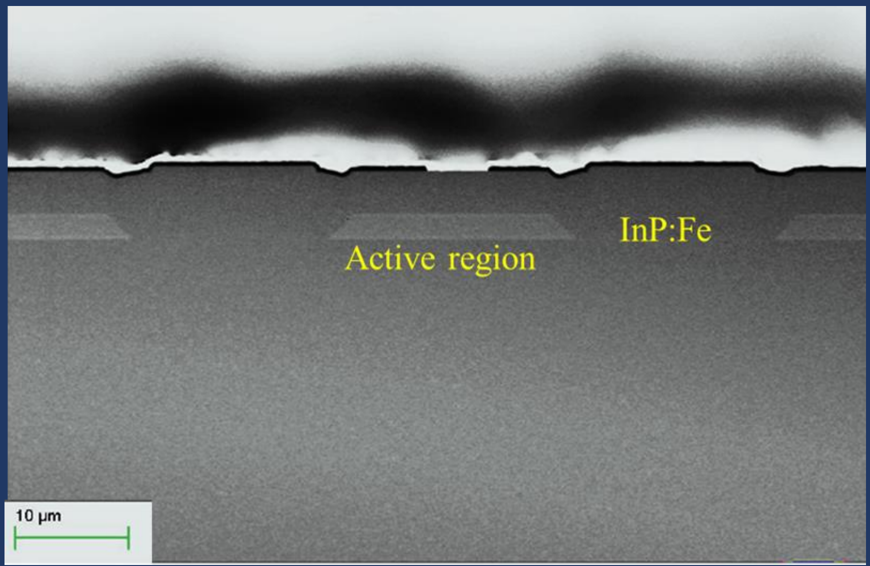




Omanakuttan et al,, Optical Materials Express, 9(3), 1488-1500 (2019).

InP:Fe Regrowth around Wet-etched Quantum Cascade Laser ridges





Ridge Width (µm)	Maximum output power under CW operation at RT (mW)	Maximum WPE (%)
4	725	5.3
6	1 475	8.7
8	1 500	8.5
10	2 000	8.4
12	2 400	8.8
14	2 400	7.6

- 5.5 µm laser from Harvard University (R. B
- Wet-etched with mask overhang
- 9 µm deep
- Regrowth time: 13 minutes

W. Metaferia et al., Optical Engineering 53(8), 087104, 2014.

Outline

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

Significance of in-house access

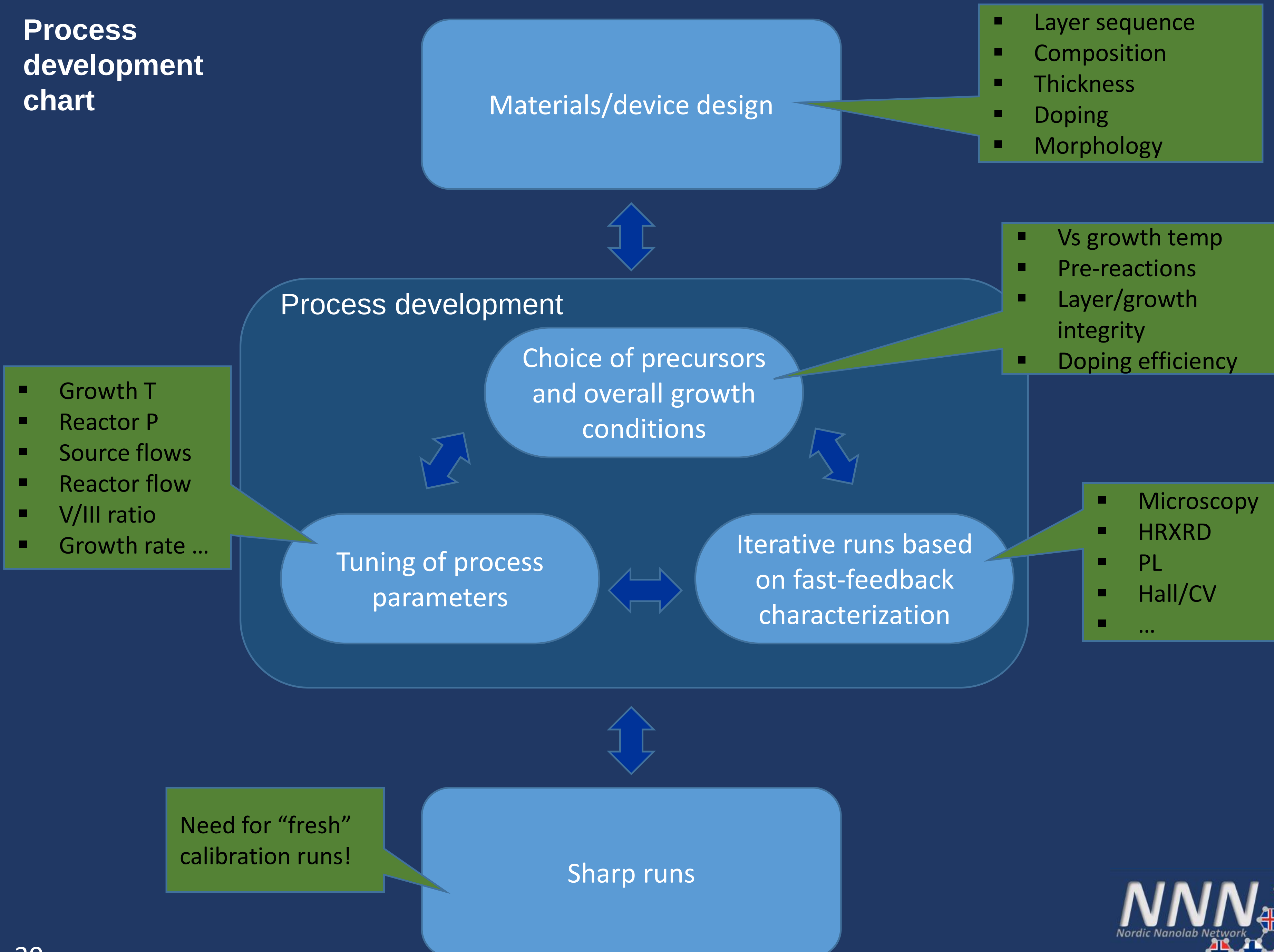
– Largely enabling: Major part of the device functionality relies on the epitaxial base structure
– Novel devices may typically rely on one or multiple regrowth steps
– Foundry-based epitaxy impractical (and overly expensive if even available) for development work

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



Outline

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III-V epitaxy resources within NNN

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

NNN Nordic Nanolab Network