Introduction to

Metalorganic Vapour Phase Epitaxy of III-V semiconductors

Selected experiments in MOVPE
Alok Rudra

III-N materials & devices
Nicolas Grandjean

Selective area epitaxy
Philippe Caroff

2D materials
Helge Weman

Scanning Probe Microscopy
Benjamin Dwir

Selected experiments in MOVPE

Outline

- Overview
  - History
  - Scientific & technical impact
  - Epitaxial techniques
- Instrumentation
  - System architecture
  - Hazards
  - Safe lab design
- Growth process
  - Growth regimes
  - Precursors
  - Carrier gases
- Surfaces & growth modes
  - Vicinal surfaces
  - Surface dynamics
  - Surface segregation
  - Surfactant mediated epitaxy
- Masked selective area epitaxy
  - Self-limited GaAs facet growth
  - In content modulation in InGaAs growth
  - GaAs nanowires
- Non-planar selective area epitaxy
  - Chemical Beam Epitaxy on non-planar InP substrates
  - GaInAsN dilute nitride alloys
  - InGaAs/GaAs quantum dot arrays

Epitaxy

- *$\varepsilon\pi\iota$ = over, $\tau\alpha\xi\iota\sigma$ = ordered arrangement*
- *Epitaxy:* deposition of a crystalline layer over a crystalline mother crystal
- *The purpose:*
  To create novel functionalities through materials and/or their combinations that do not exist in natural form
- *The challenge:*
  To control the structural, electronic and optical properties of materials down to the nanometer scale
- *The way:*
  - A thermodynamic unstability builds a driving force towards a phase transition
  - A mother crystal - the substrate - accomodates new atoms as building blocks
  - Physical & chemical processes on and near the surface allows the new crystal to be built

50 years of MOVPE development

1954 : T.R. Scott: Patent on InSb epi

1969 : H.M. Manasevit (Rockwell, Anaheim CA, USA)

The use of metalorganics in the preparation of semiconductor materials [1]

1970s : Work on home made reactors

Black box, intuitive, trial and error development

1980s : First commercial reactors

1981 : International Conference ICMOVPE I in Ajaccio (France)

2014 : ICMOVPE XVII

Lausanne, July 2014
ICMOVPE XVII

2022 : Major industrial fabrication technique

(1) *J. Electrochem. Soc. Vol. 116, N° 12 (1969) 1725-1731*

Materials, devices, applications

Consumer electronics, displays, TVs, cell phones, tablets, lighting, automotive, datacom, telecom, power management, photovoltaics, health, defense…

LEDs, lasers, solar cells, photodetectors, HBTs, FETs…

- GaAs, InAs, AlGaAs, AlInAs, GaInAlAs
- GaAsN, InGaAsN
- InP, GaP, AlInP, GaInP, GaInAsP, AlGaInP
- GaN, AlN, InN, InGaN, AlGaN
- InSb, GaSb, InAsSb, AlGaSb
- ZnSe, ZnS, HgCdTe
- Ge, GeSi
- Oxides, metals
- 2D materials (graphene)

Surface science

- Growth modes
- Vicinal surfaces
- Surfactants
- Selective area growth
- Non-planar growth…

Nanoscale engineering
QWs, QDs, NWs…

Blue: materials grown in LMSC2

MOVPE among other epitaxial techniques

- Liquid Phase Epitaxy (LPE)
  - High purity (AlGaAs), high growth rates
  - Poor uniformity, no super-lattice, not scalable

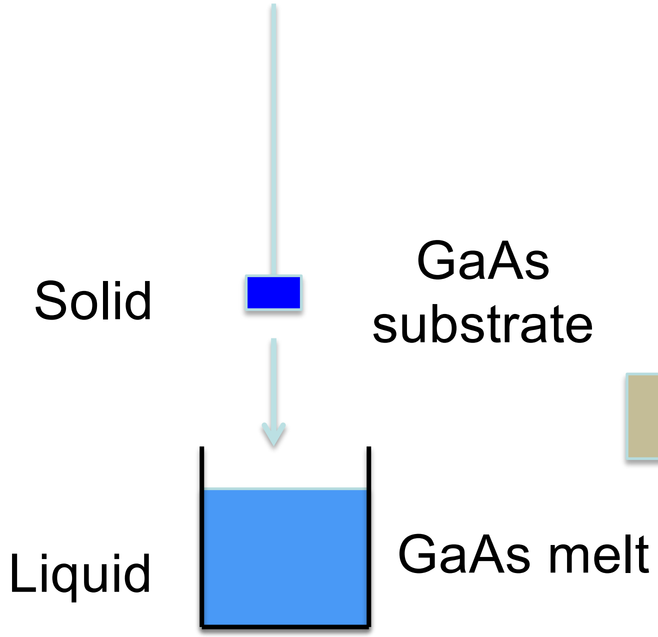
Vacuum epitaxy

- Molecular Beam Epitaxy (MBE)
  - High purity & uniformity, abrupt interfaces, in situ diagnostics
  - Costly & delicate equipment
- Chemical Beam Epitaxy (CBE)
  - InP based alloys, complex heterostructures, in situ diagnostics
  - Complex and costly, C uptake with Al-alloys, hazardeous sources

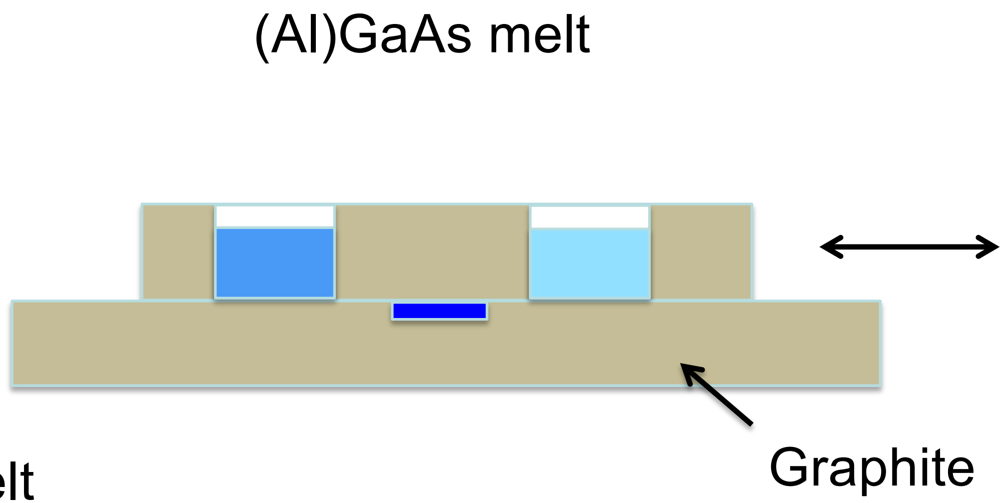
Gas phase epitaxy

- Vapour Phase Epitaxy (VPE)
  - Well studied, high growth rates
  - No Al alloys, no abrupt interfaces, no complex heterostructures
- Metalorganic Vapour Phase Epitaxy (MOVPE)
  - Versatile, abrupt interfaces, high uniformity & throughput, scalable
  - Hazardeous sources

Liquid Phase Epitaxy

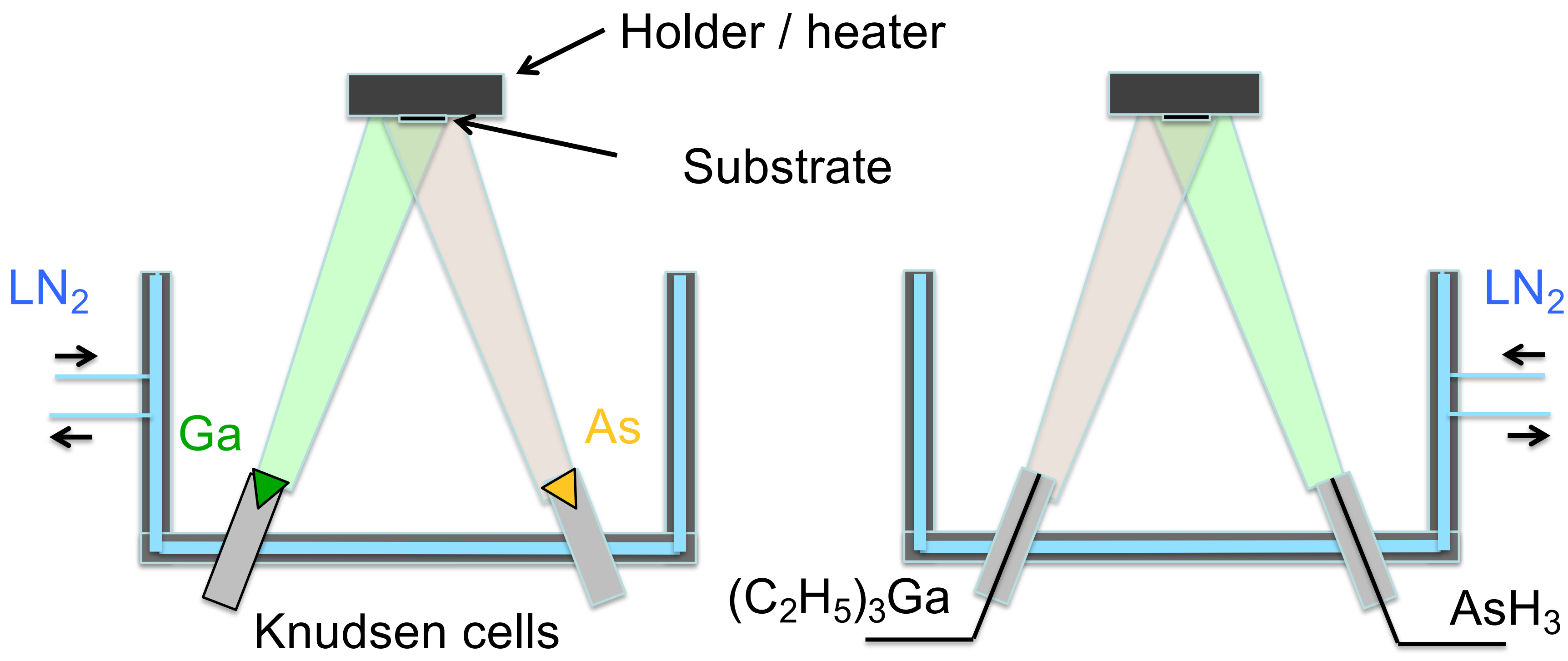


DIPPING



SLIDING

Vacuum Epitaxy

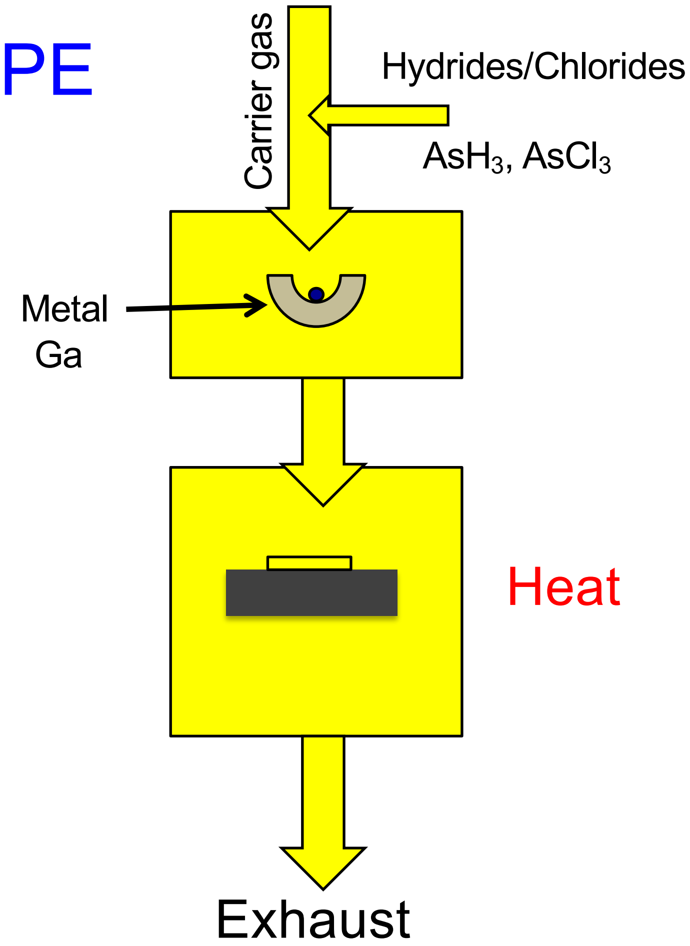


Molecular Beam Epitaxy
(MBE)

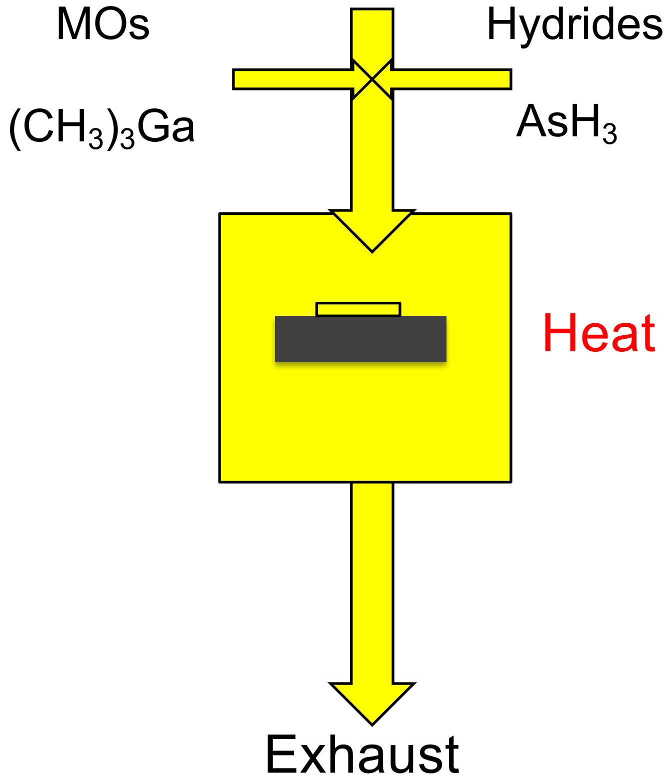
Gas Source MBE (GSMBE)
Chemical Beam Epitaxy (CBE)

Gas Phase Epitaxy

VPE



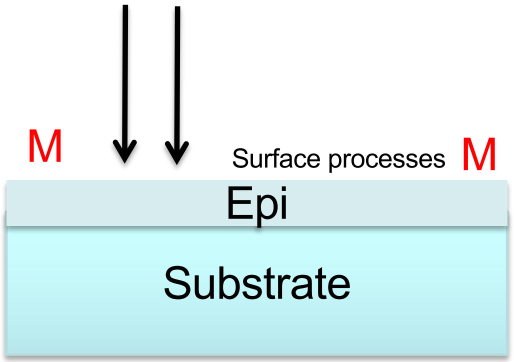
MOVPE



Vacuum vs Gas Phase Epitaxy

Vacuum Epitaxy
(MBE, *GSME, CBE*)

Atomic sources / precursors

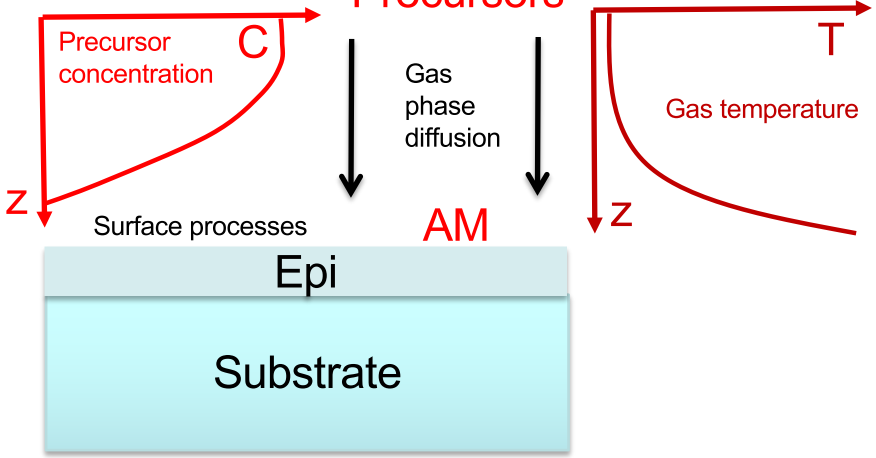


Sources (M) > adatoms (M) :

Ga, Al, In, Ge, Si,
Be, As, P, Zn, etc…

Gas phase Epitaxy
(HVPE, MOVPE)

Precursors

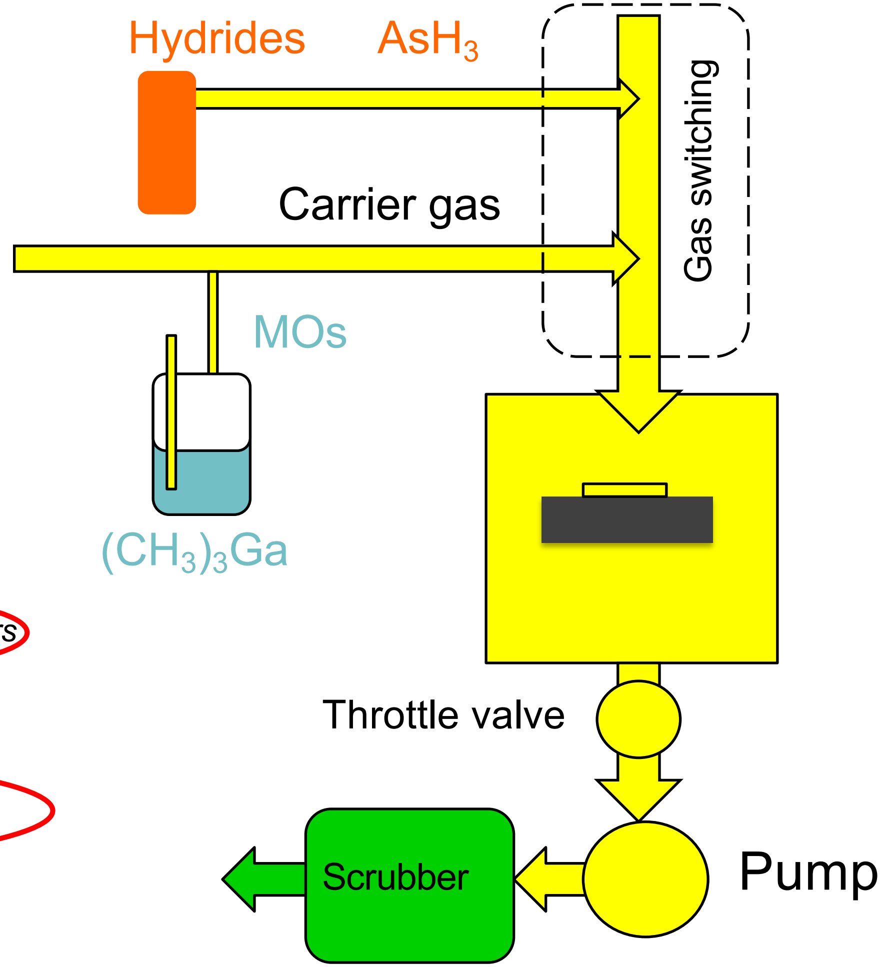


Precursors > Admolecules (AM):

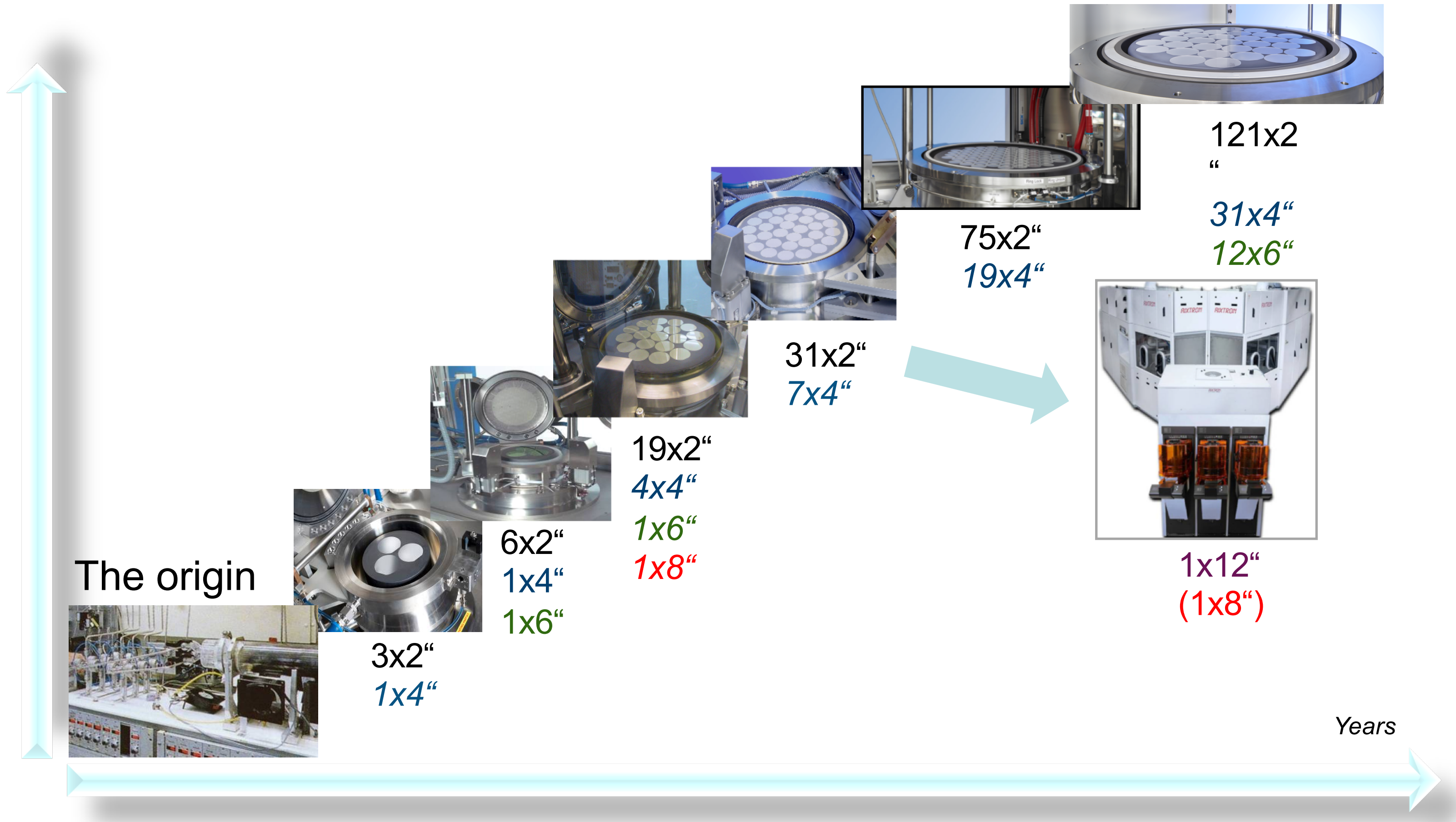
TMGa, TMAl, TMIn, $C_4H_{12}Ge$,
Si_2H_6, CBr_4, DEZn, etc…

MOVPE basic architecture

- Cold wall, open reactor:
  Gas mixture flows in and out
  Loading through glove box
- Susceptor: 500° C – 1500° C
- P: 5 – 800mbars
  Variable throughput pumping system
- Carrier gas: usually H_2, preferably N_2
  Transports the sources from storage point to reactor
- Gas mixing & switching system
  Fast gas composition switching for abrupt interfaces
- Chemical sources (precursors)
  MOs from bubblers, hydrides from pressurized cylinders
- Exhaust treatment
  Reduce toxic reaction products to acceptable levels
- Safety concept
  Survive your growth runs until & beyond your PhD

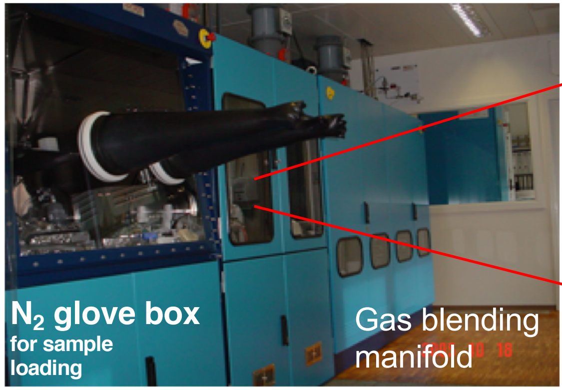


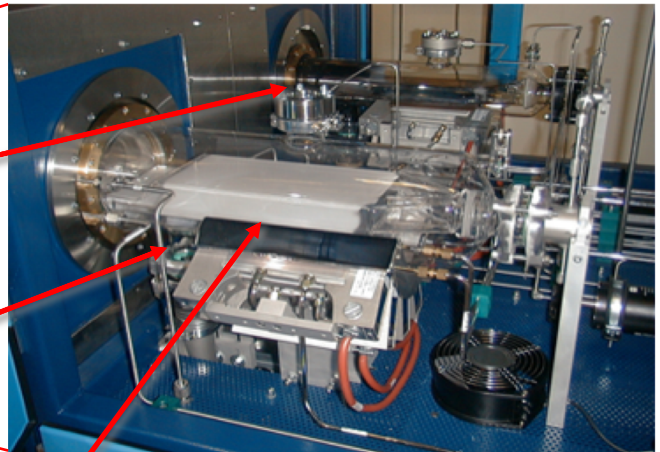
50 years of MOVPE Technology development

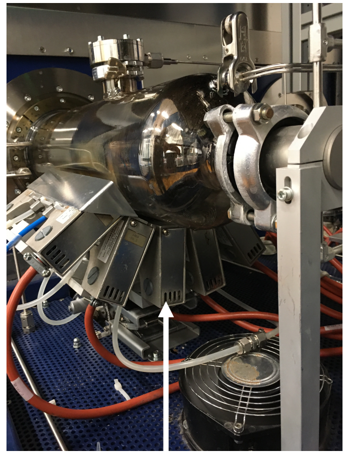


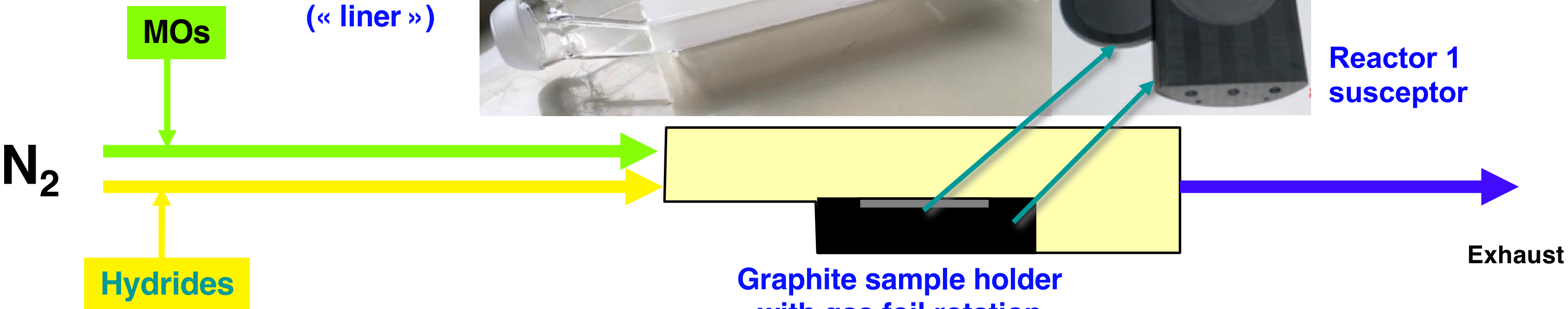
Courtesy of Aixtron A.G.

The III-V MOVPE facility @ LMSC2

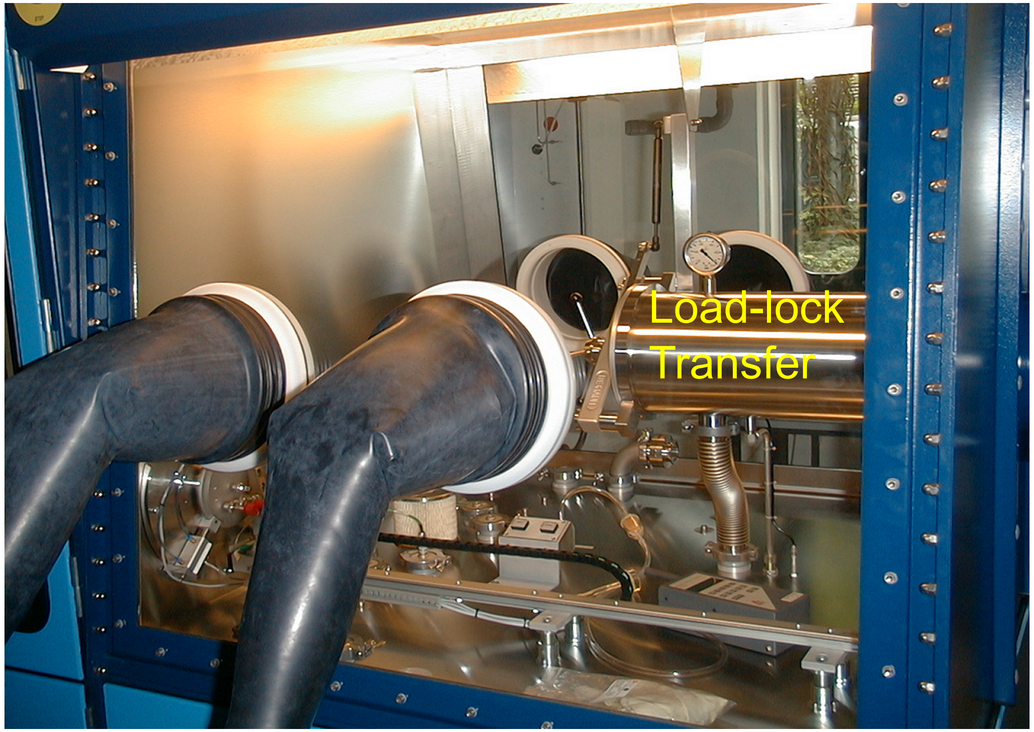








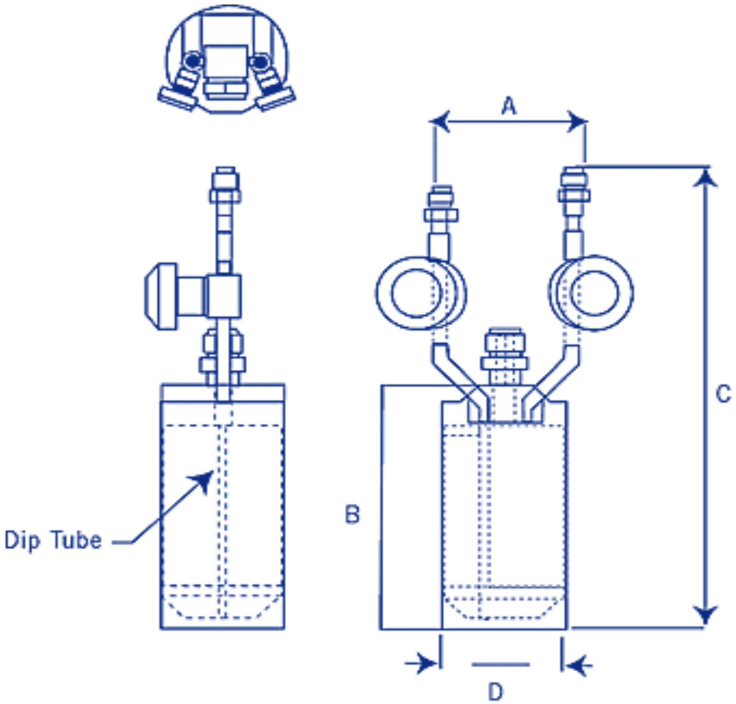
Safe, clean & flexible loading facility



- N_2 glove box with integrated purifier
- O_2 / H_2O < 1pp

- Reactor 2 susceptor in loading position
- 3 x 2'' or 1 x 3'' or 1x 4'' susceptor

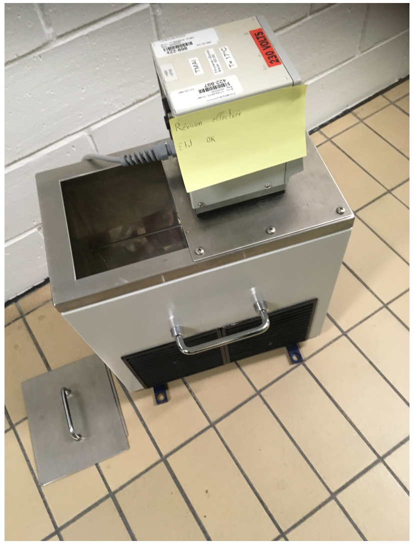
Metalorganic sources



MO pick up
through carrier gas

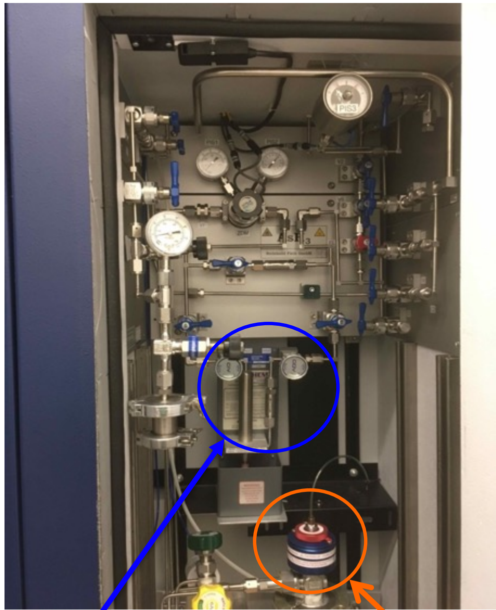
Example of MO bubbler

Courtesy of EMF Chemicals



Thermostatic bath

Hydrides gas cabinets

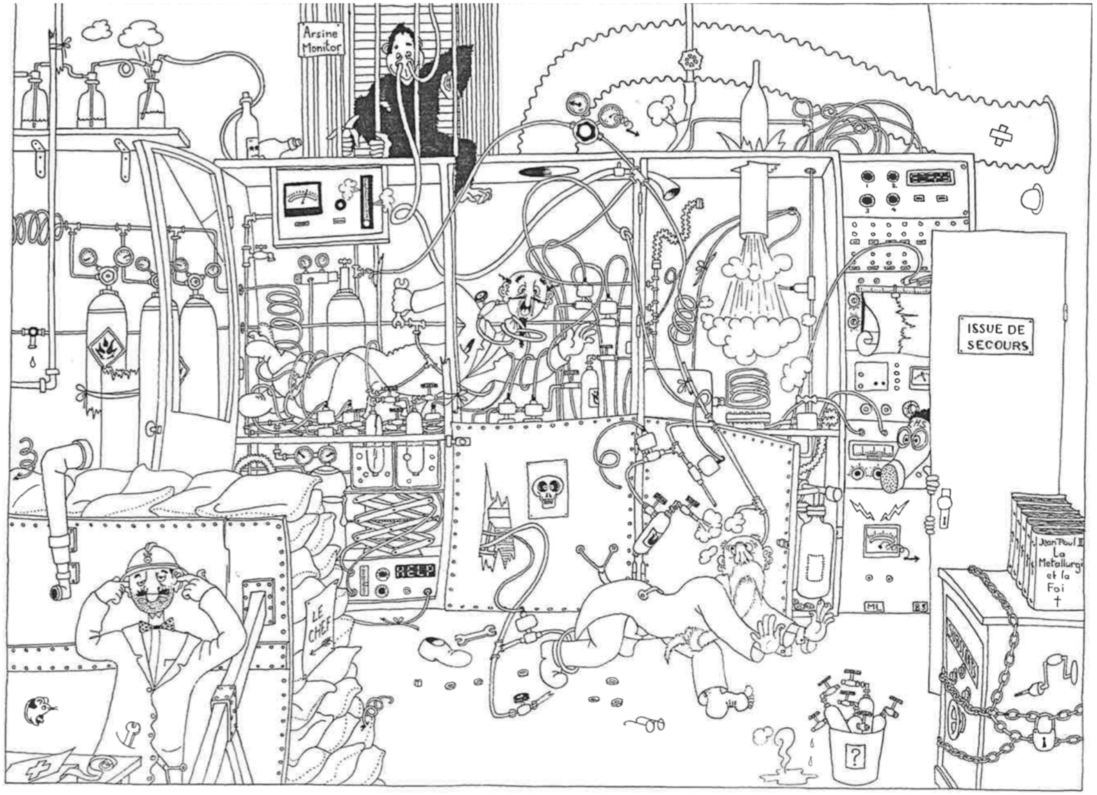


Purifier

- F90 fire resistant cabinets
- Separate AsH_3, PH_3 and Si_2H_6 cabinets
- Double piping connection to gas mixing cabinet
- Flow restrictor on cylinder (1l/mn)
- Cylinder pneumatic valve
- Permanent monitoring

Safe lab architecture

- Main Hazards
  - Chemical sources
  - Operation
  - Maintenance
- Basic safety principles
  - Passive
    - Segmentation
    - Containment
    - Exhaust management
    - Fail safe
  - Active
    - Dilution
    - Monitoring
    - Procedures



Courtesy of Mathieu Leroux, CNRS, France

Main hazards

Sources

Hydrides (pressurized gases)	• Arsine (AsH_3, 15 Bars): most toxic form of As, flammable – LC50 = 5-50 ppm, IDLH = 2 ppm, TLV = 50 ppb • Phosphine (PH_3, 40 Bars): toxic, flammable, – LC50 = 11-50 ppm, IDLH = 7 ppm, TLV = 300 ppb
Metalorganics (mostly liquids)	• Generally pyrophoric, violent exothermic reaction with moisture or oxygen, toxic fumes • Tertiarybutylarsine: LC50 = 70 ppm, TLV = 500 ppb

Operation

- High temperature, low pressure process: reactor strain
- H_2 as carrier gas: explosion hazard
- Exhaust gases contains toxic & flammable gases

Maintenance

- Servicing and cleaning of contaminated parts is hazardous
  Decomposition products are toxic, sometimes flammable
- Source exchange
- Scrubber cartridge exchange

Basic safety principles

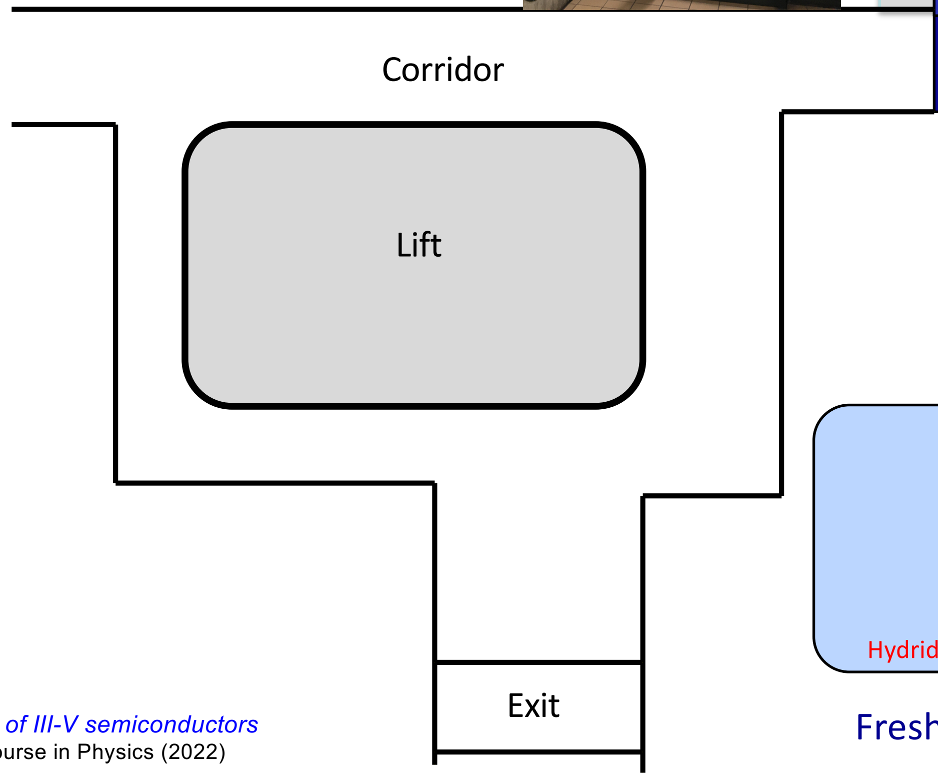
Passive

- Segmentation *don't put all your eggs in the same basket*
  - Dedicated volumes - rooms, cabinets, pipe segments...
  - Air flow management – pressure cascade
- Containment *give a second chance to avoid disaster*
  - Gas cabinets
  - Double wall piping
- Scrubbers: routine and emergency exhaust treatment
- Fail safe passive hardware
  - Shut off hazardeous gases, purge with inert gas
  - Stop heaters

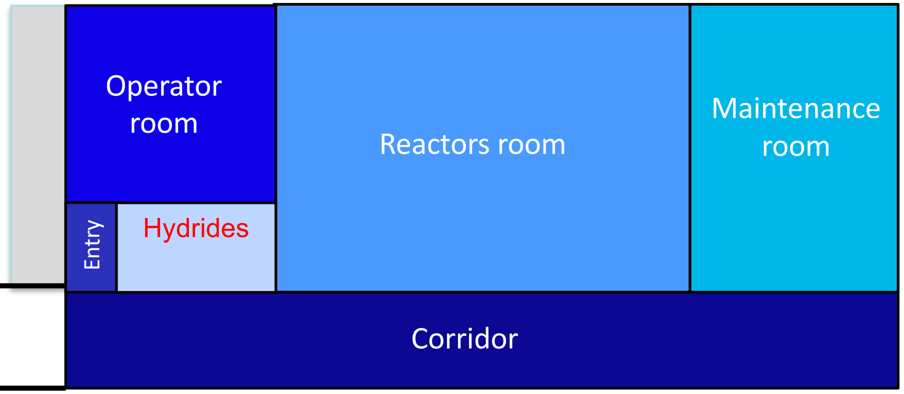
Active

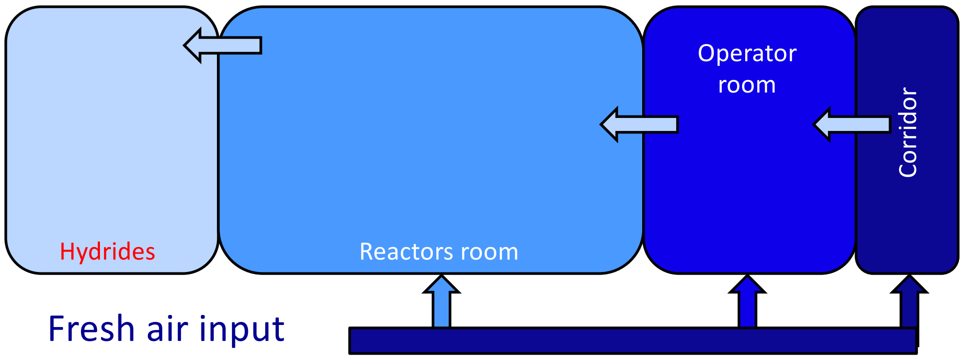
- Dilution of eventual toxic gas release through permanent ventilation
- Monitoring: continuous, reliable & selective at ppb levels
- Procedures: written operating procedures

Room layout

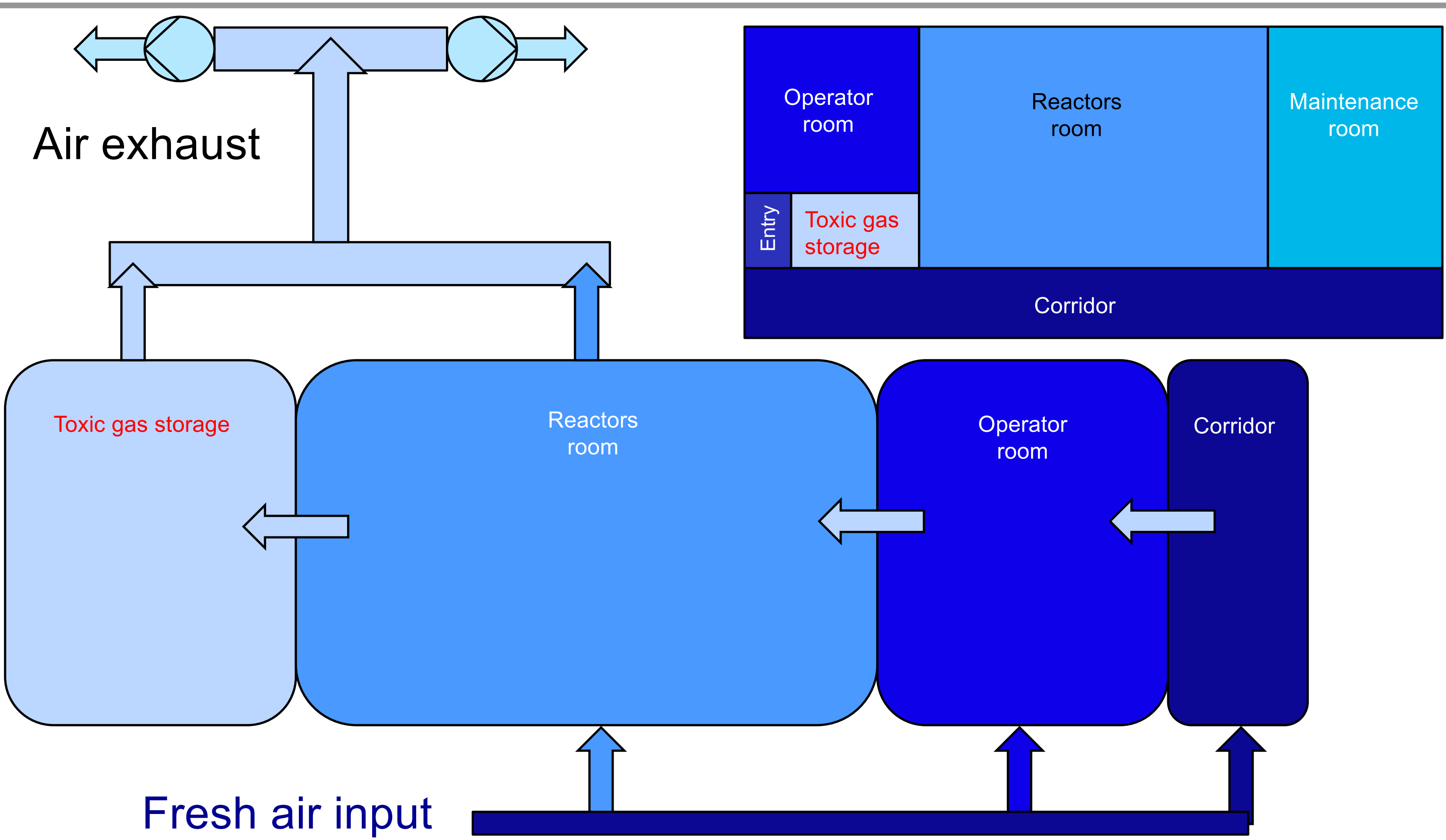


Segmentation

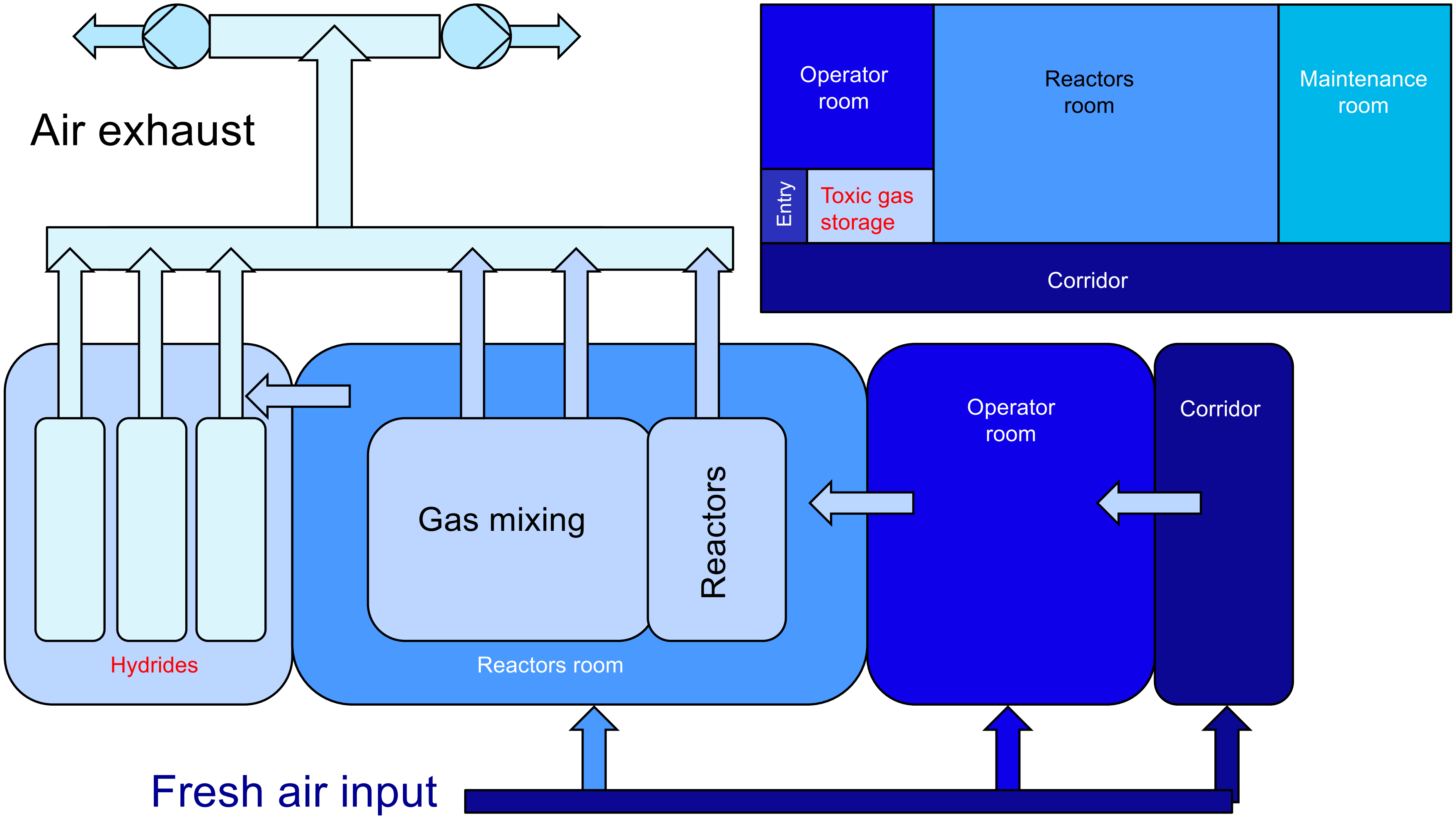




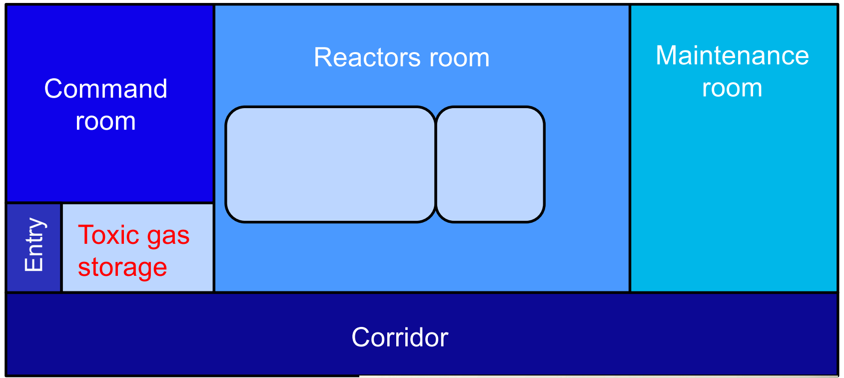
Room layout / segmentation



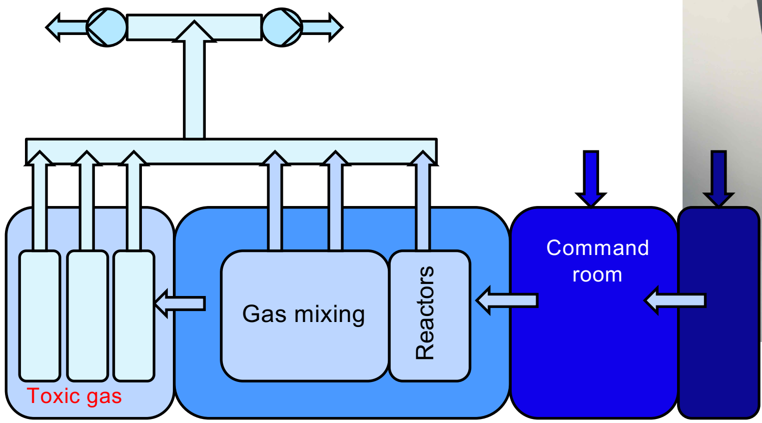
Segmentation & confinement



Air flow management



Pressure cascade from corridor to toxic gas storage room



Regular use dry bed scrubber

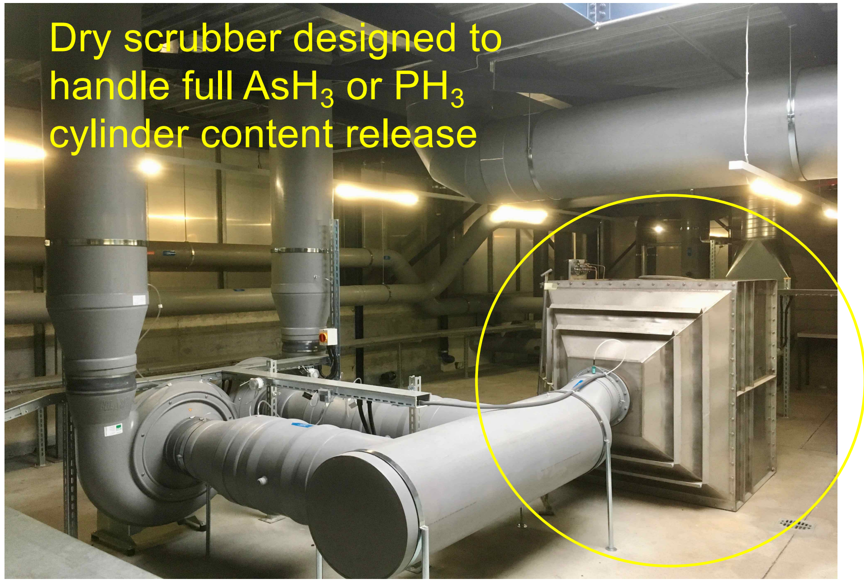
Operation:

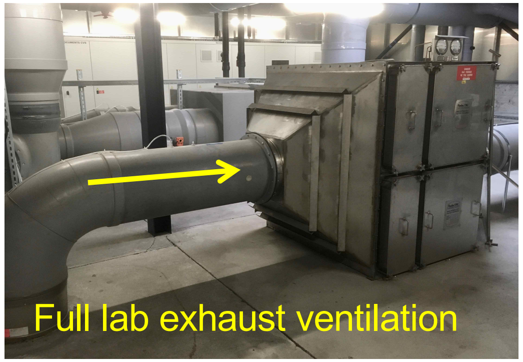
- Porous granulates with chemisorbed media
- Hydrides (gases) react with media to form stable solid by-products
- H_2 goes through, diluted in ventilation
- Periodic controlled air oxidation to complete chemical conversion
- Column temperature monitored
- Small bypass scrubber

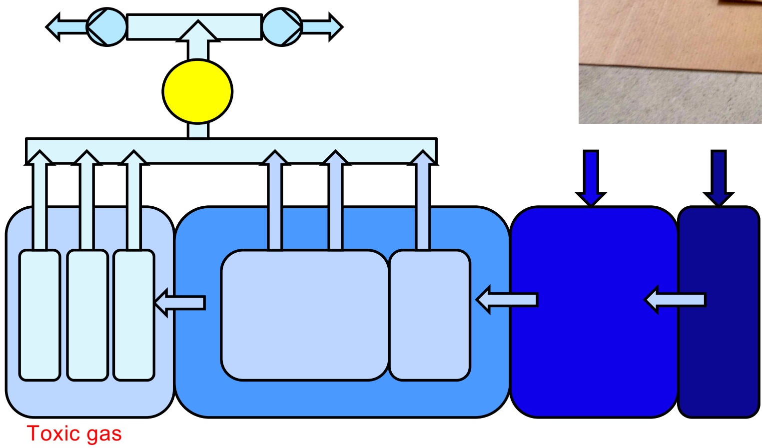
Columns maintenance:

- Exchanged & checked every 2 years
- Purged under N_2, filled with Ar for shipment
- Isolated when disconnected through valves
- Used granulates disposed at factory, replaced with fresh medium

Emergency scrubber







Toxic gas monitoring

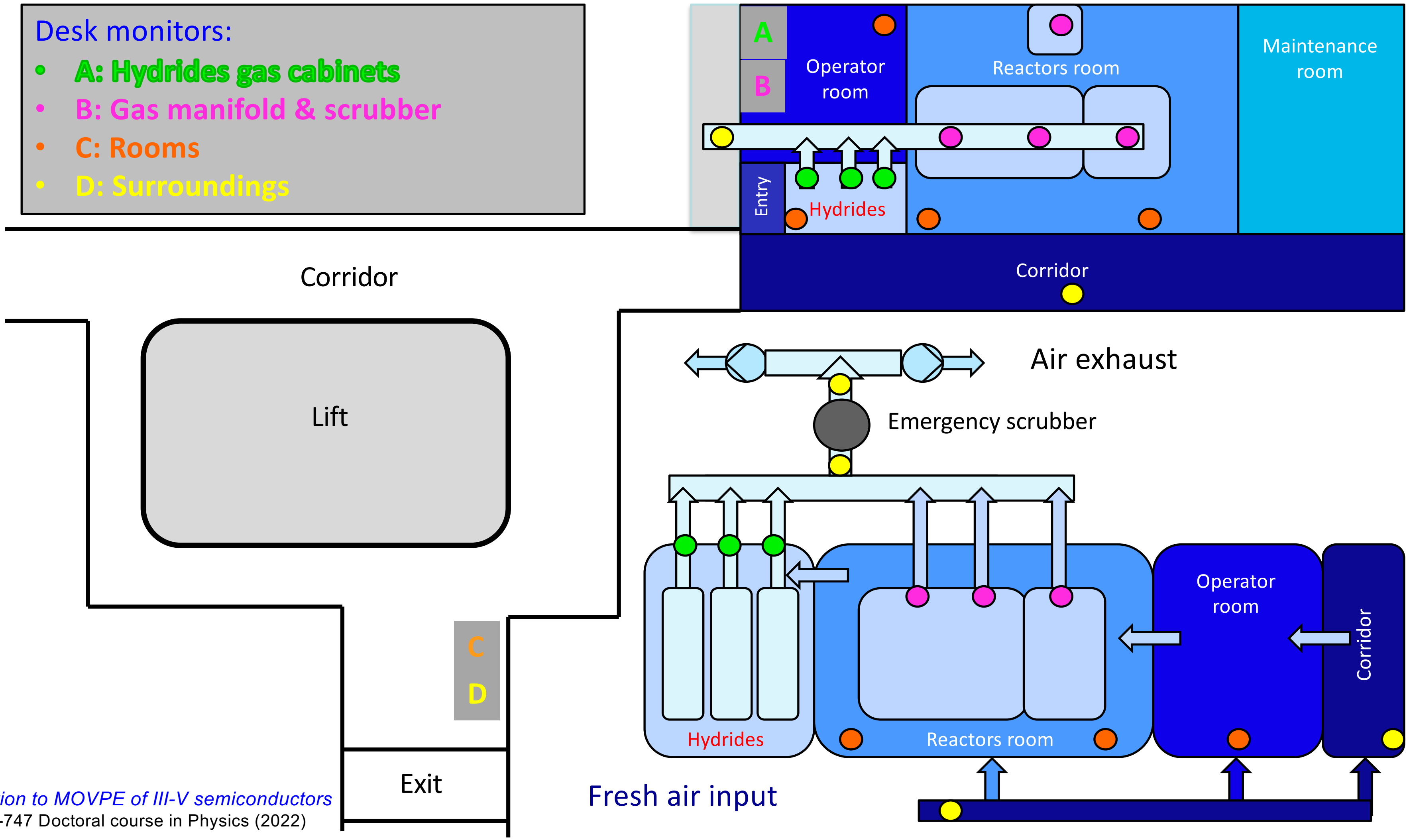
- Air pumped and flown through a sensitive tape
- Tape darkens on traces of hydrides
- Light reflection translated into gas concentration
- AsH_3/PH_3 detection limit 10ppb
- Optical calibration (no real gas needed)
- Single known interference: H_2S

4 points AsH_3/PH_3 desk monitor

Single point AsH_3/PH_3 portable monitor

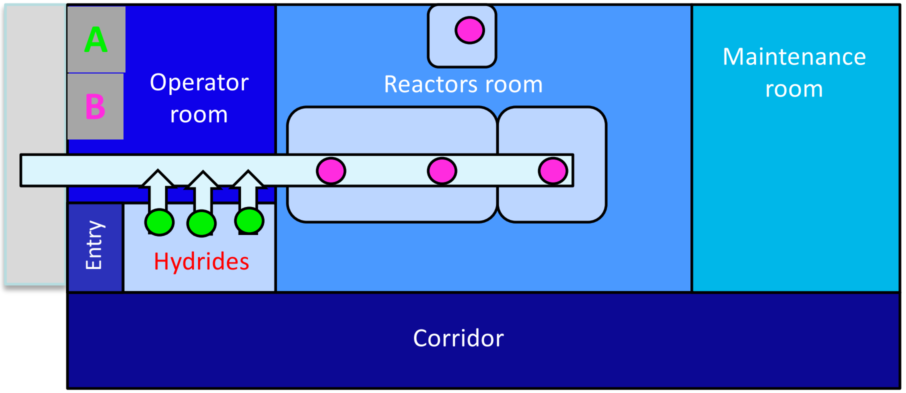
- 4 fixed monitors – 16 sensing points
- 2 portable monitors – 2 sensing points
- Weekly and monthly maintenance protocols

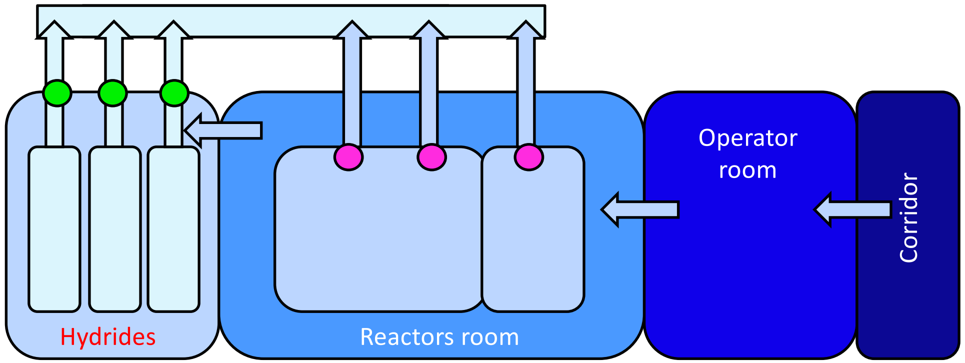
Toxic gas monitoring



Toxic gas monitoring: (A) Hydrides (B) Gas manifold & scrubber

Desk monitors:
- A: Hydrides gas cabinets
- B: Gas manifold & scrubber
- C: Rooms
- D: Surroundings

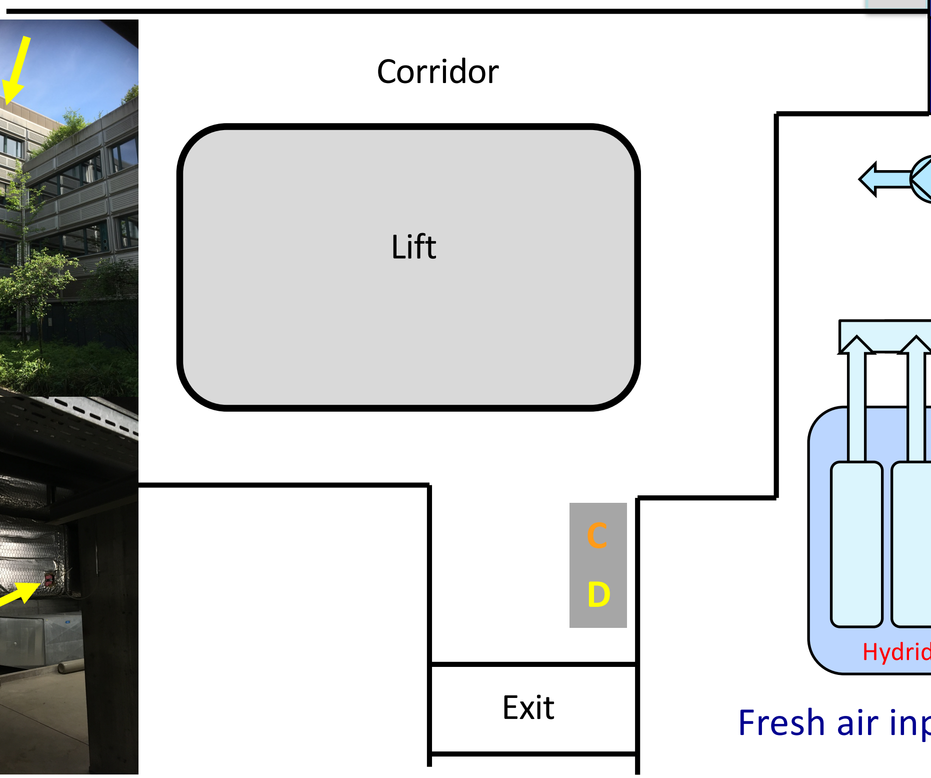


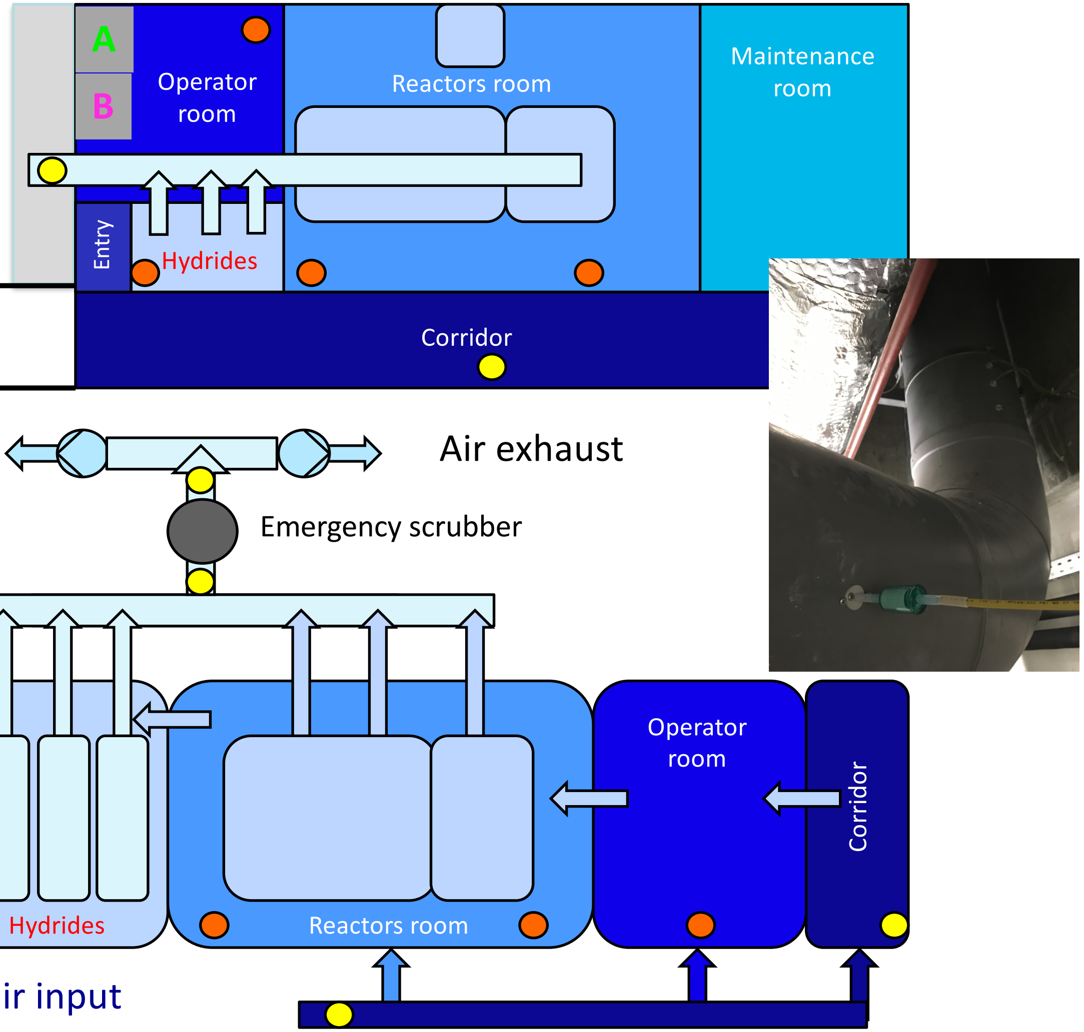


Toxic gas monitoring: (C) rooms (D) surroundings

Desk monitors:

- A: Hydrides gas cabinets
- B: Gas manifold & scrubber
- C: Rooms
- D: Surroundings





Flaw corrected in Physics building ventilation

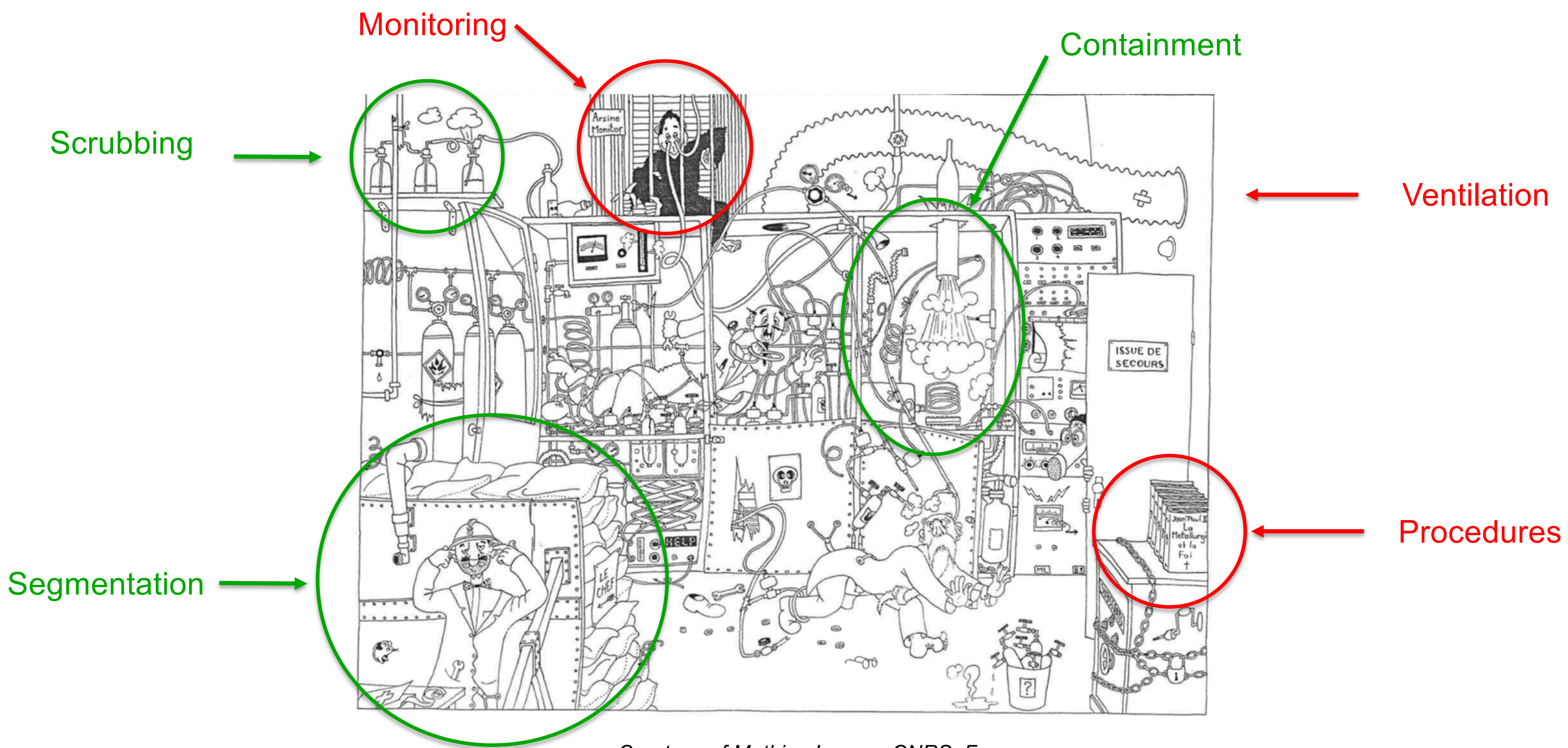
- 2 toxic gas detection systems installed at initial lab design
- Toxic gas alarm in the fresh air input in one group of detectors
- No alarm elsewhere in MOVPE Lab (other group of detectors)

→ Contamination attributed to an external source

- Part of ventilation was being recirculated for energy saving !
- Recirculation was stopped

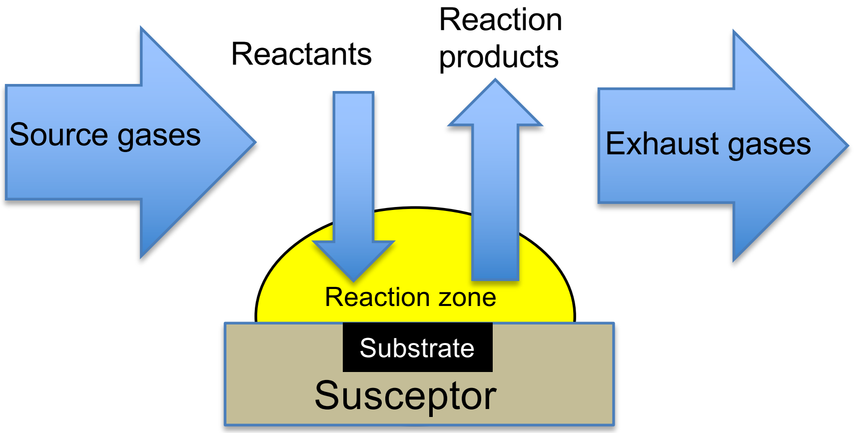
→ Toxic gas alarm disappeared !

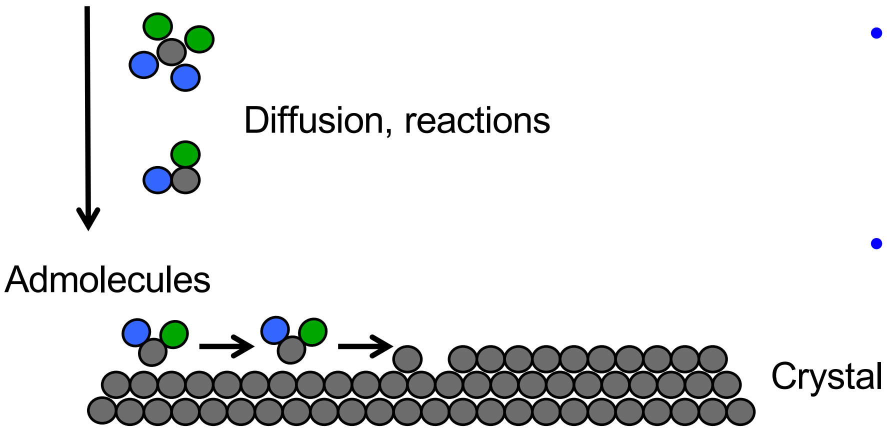
Passive & active safety



Courtesy of Mathieu Leroux, CNRS, France

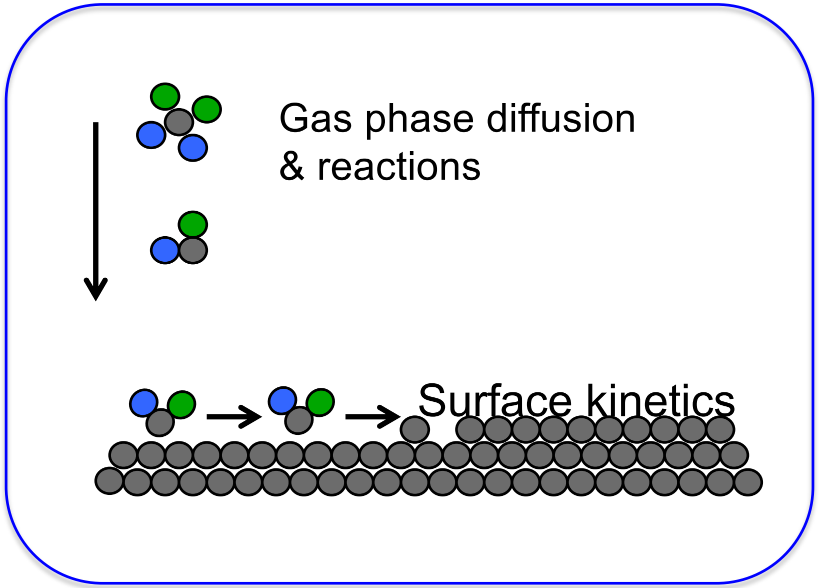
The MOVPE growth process





- Thermodynamics
  - Driving force for epitaxial growth
  - Precursors decompose at growth temperatures
- Mass transport
  - Diffusion through the gas phase to the growth surface
- Gas phase reactions
- Surface processes
  - Physical processes: physisorption, diffusion, evaporation, segregation
  - Chemical reactions: chemisorption, fragmentation, incorporation
- Sub-surface processes

The main MOVPE growth regimes



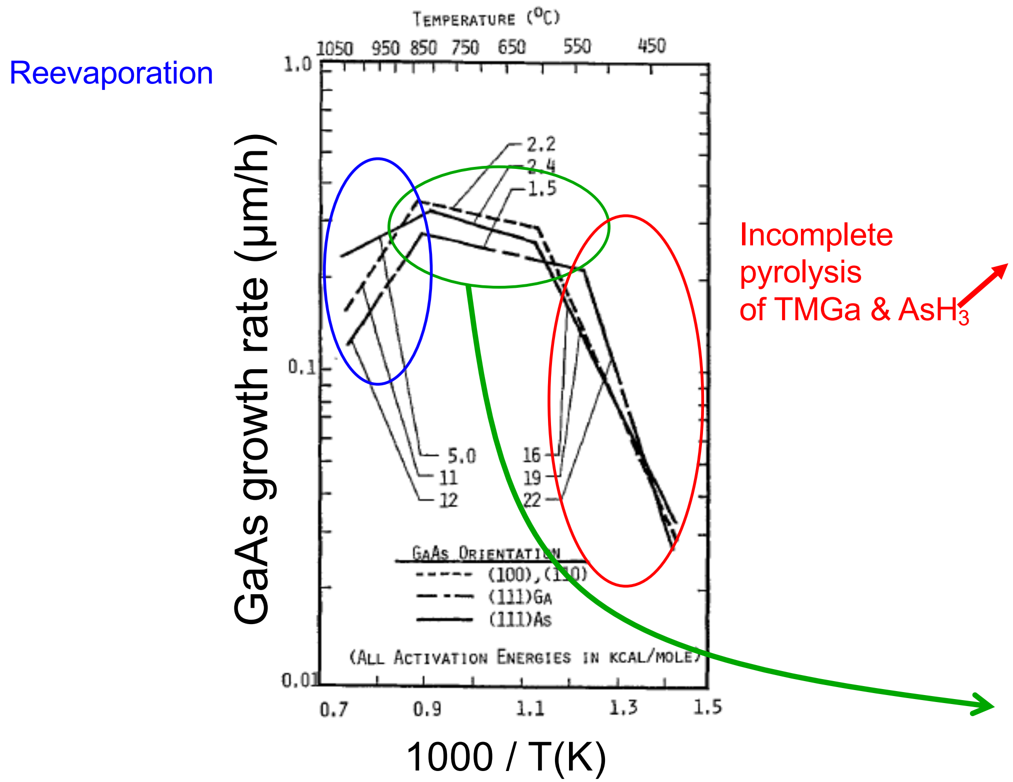
Diffusion limited growth:

- Surface kinetics faster than diffusion
- Near equilibrium at the interface
- Growth rate varies linearly with input group III flow
- Growth rate almost temperature insensitive

Kinetically limited growth

- Diffusion faster than surface processes
- Growth rate increases with temperature

GaAs growth regimes



D.H. Reep & S.K. Gandhi,
J. Electrochemical Society, 1983

- T < 550° C
- Growth rate increases with temperature
- Diffusion faster than surface processes

Kinetically limited growth

- 550° C < T < 850° C
- Growth rate almost temperature insensitive
- Growth rate varies linearly with group III input flow
- Surface kinetics faster than diffusion
- Near equilibrium at the interface

Diffusion limited growth

Main MOVPE precursors

Wish list

- Suitable vapour pressure: 0.01 - 10μ/h
- Stable at room temperature
- Unstable at growth conditions
- No *intrinsic* doping (C !)
- Pure (no *extrinsic* doping)
- No memory effect (short & long term)
- Dopants:

  large doping range, low diffusion coefficient, low growth parameters dependence
- Safe...!

Group V

As: AsH_3, $C_4H_{11}As$ (TBA)
P: PH_3, $C_4H_{11}P$ (TBP)
Sb: SbH_3
N: NH_3, DMHy

Group III, IV

Ga: $(CH_3)_3Ga$, $(C_2H_5)_3Ga$ (TMGa, TEGa)
Al: $(CH_3)_3Al$ (TMAl)
In: $(CH_3)_3In$ (TMIn); $(C_2H_5)_3In$ (TEIn)
Ge: IBuGe

Dopants

Donors: Si, S, Se, Te, Sn

Si_2H_6, SiH_4, H_2S
$(C_2H_5)_2Te$ (DETe)
$(C_2H_5)_4Sn$ (TESn)

Acceptors: C, Zn, Mg

(Al)GaAs	*InP*	*GaN*
CBr_4 $(CH_3)_2Zn$ (DMZn) Cp_2Mg	DMZn	Cp_2Mg

Blue: precursors in use in our lab

Ethyl- vs methyl- precursors: intrinsic C uptake

Inst. Phys. Conf. Ser. No. 63 : Chapter 3
Paper presented at Int. Symp. GaAs and Related Compounds, Japan, 1981

Acceptor incorporation in high-purity OMCVD grown GaAs using trimethyl and triethyl gallium sources

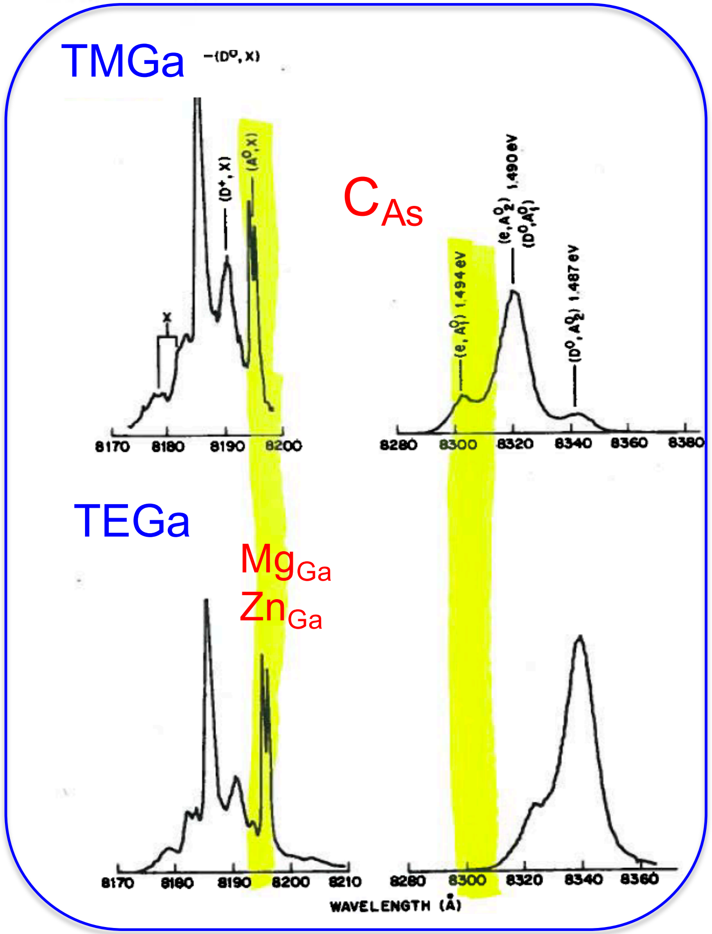
R. Bhat, P. O'Connor, H. Temkin, R. Dingle and V. G. Keramidas

Bell Laboratories, 600 Mountain Ave., Murray Hill, N.J. 07974, USA

- TMGa: $(CH_3)_3Ga$
- TEGa: $(C_2H_5)_3Ga$

- Extrinsic C present with both precursors
- C_{As} with TMGa, NOT with TEGa
- Reduced intrinsic C uptake in (Al)GaAs
- Ga-C bond stronger in TMGa than in TEGa
- TEGa decomposes at lower temperatures

8° K PL
GaAs epi



The choice of carrier gas: N_2 vs H_2

Wish list

- Enables laminar flow in growth chamber
- < 10^{-8} impurities
- Inert towards the transported chemicals
- Inexpensive
- Safe

H_2

- H_2 enables laminar flow at atm. pressure
- Mature H_2 purifier technique (Pd foil diffusion)
- H_2 selected against N_2, He and Ar from tests in early atmospheric reactors
- Most widely used, mandatory for nitrides
- Explosion hazard

N_2

- Low pressure (<100 hPa) > laminar flow
- Getter purifiers developped in the 90s
- Improved uniformity in AlGaAs/GaAs [1] and InGaAsP/InP [2]
- Lower O, C uptake in (Al)GaAs [3]
- Improved N uptake in InGaAsN [4]
- Higher p-(In)GaAs doping (TMGa+CBr_4) [5]
- Lower growth rates

N_2 vs H_2

- Higher density: N_2: 28g/mole; H_2: 2g/mole
  > Lower diffusion through the more viscous N_2 gas phase
  > Lower (x0.6) group III concentration on surface
  > Lower growth rates
- Higher viscosity
- Lower thermal conductivity
  > lower heat transfer
  > steeper temperature profiles

(1) Dauelsberg *et al.*, J. Crystal Growth (2001)
(2) Roehle *et al.*, J. Crystal Growth 170 (1997) 109- l 12
(3) Hardtdegen *et al.*, III-Vs review (2001)
(4) Ougazzaden *et al.*, Jpn. J. Appl. Phys. Vol. 38 (1999) 1019–1021
(5) Keiper *et al.*, J. Crystal Growth 197 (1999) 25-30

Gas phase temperature profiles: N_2 vs H_2

Modeling and experimental verification of deposition behavior during AlGaAs growth: a comparison for the carrier gases N_2 and H_2

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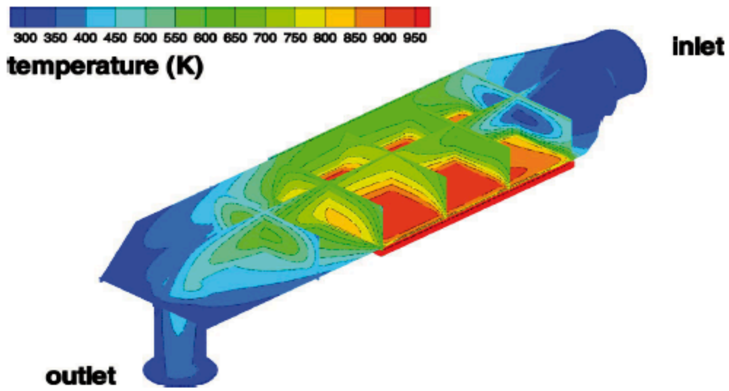
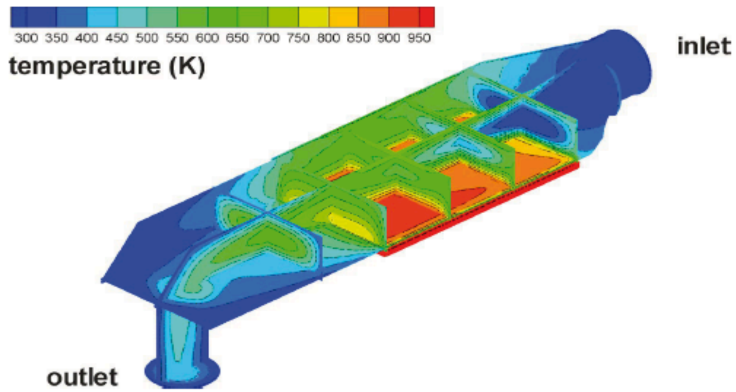
Journal of Crystal Growth 223 (2001) 21–28

H_2



N_2

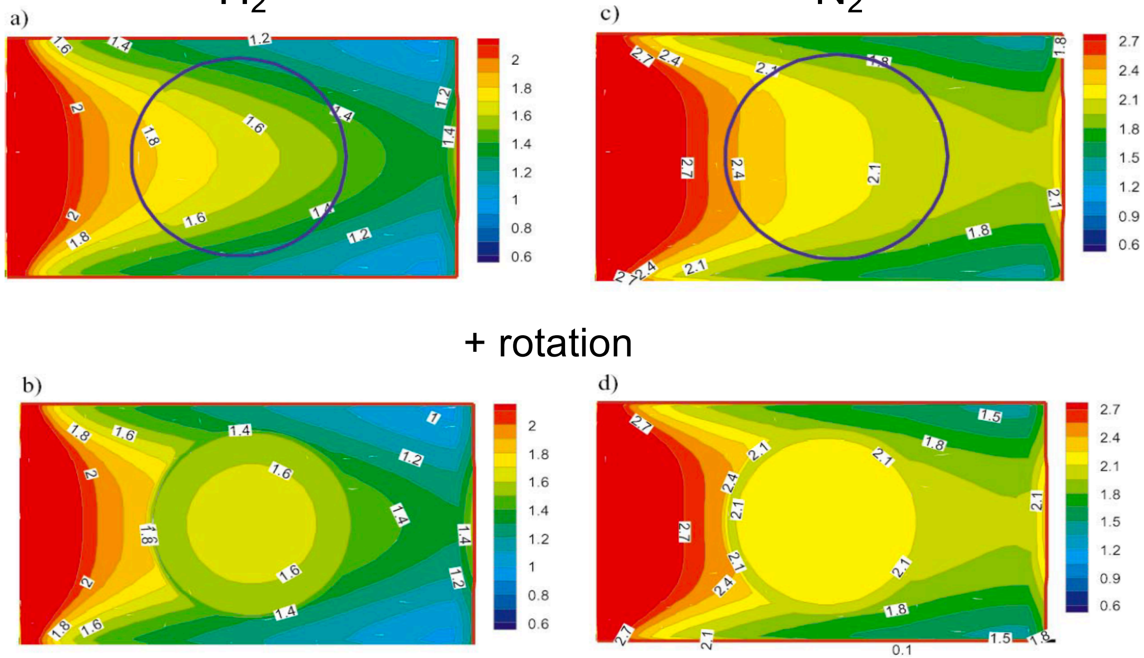


N_2
lower thermal conductivity

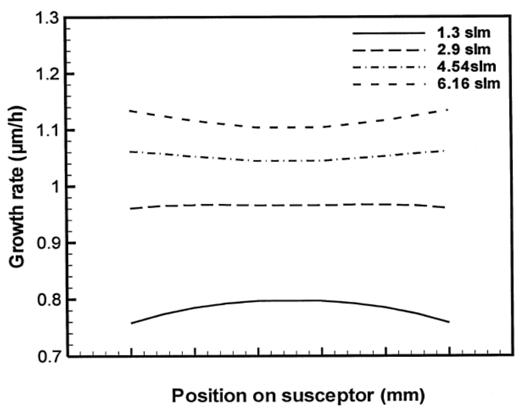
- lower heat transfer
- cold finger in the reactor axis – need to reduce gas velocity
- Steeper temperature gradient above the susceptor

AlGaAs growth rate profiles: N_2 vs H_2

H_2 N_2



TMAl, TMGa, AsH3,
700° C, 20 hPa



Fully developped parabolic profile,
steep gradient
orthogonal to reactor axis

Bloc-like profile
reduced orthogonal gradient

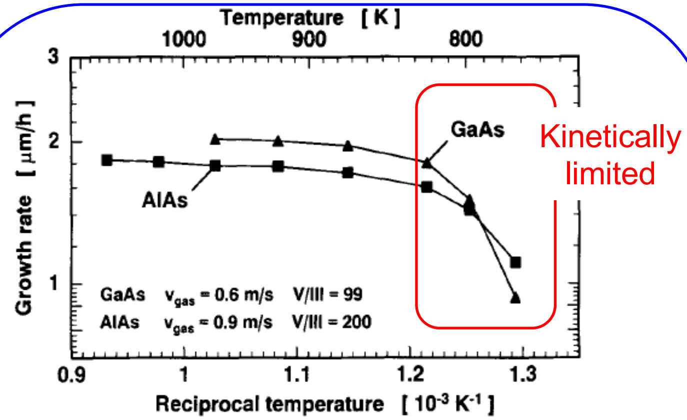
Optimized uniformity
through total flow
adjustment

Rotation does not compensate
for orthogonal gradient

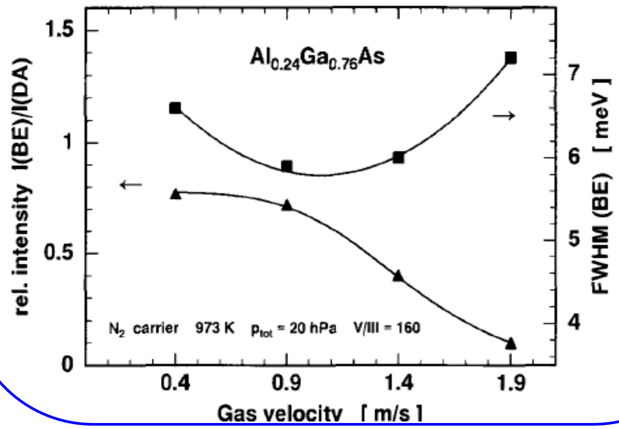
Rotation compensates
for axial gradient

Dauelsberg *et al.*, J. Crystal Growth (2001)

Growth of AlGaAs using N_2 as carrier gas



M. Hollfelder *et al.*,
J. Electron. Materials (1994)



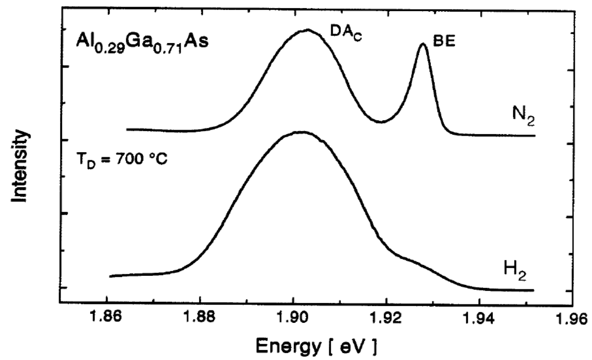


Figure 4. 2K photoluminescence spectra of $Al_{0.3}Ga_{0.7}As$ deposited by the nitrogen (upper spectrum) and hydrogen (lower spectrum) processes at 20 mbar and 700°C. The higher intensity ratio of the bound exciton transition (BE) to donor acceptor transition $(DA)_C$ indicates the lower carbon and deep level impurity concentration in the layers, when N_2 is used as the carrier.

H.Hardtdegen *et al.*,
III-Vs reviews (1005)

Higher As and H^+ surface coverage from AsH_3 decomposition (not from H_2)

⬇

Lower C and O incorporation

⬇

Improved optical and transport properties

Surfaces & growth modes

Basics of surface structure

- TSK model
- Vicinal surfaces
- Ehrlich & Schwoebel statistics

Homoepitaxy

- 2D island nucleation
- Step flow mode
- Step bunching

Heteroepitaxy

- Strain
- Elastic relaxation
- Plastic relaxation

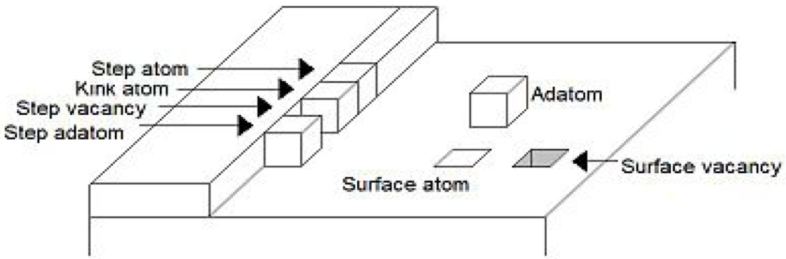
Vicinals

2D / 3D transition

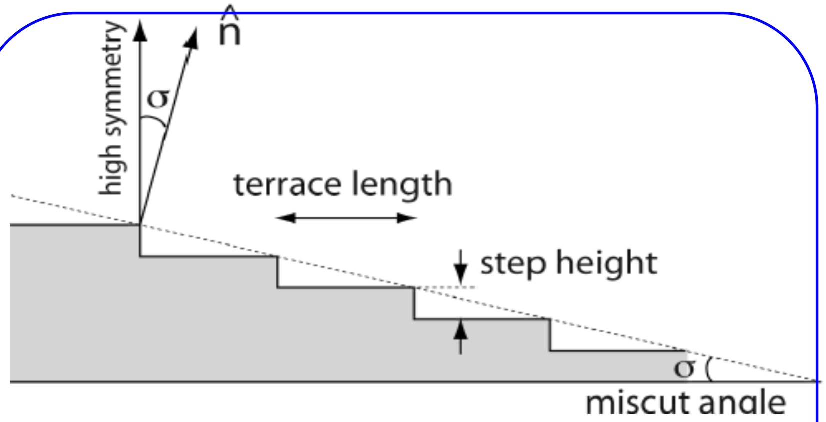
Basic surface structure

Terrace Step Kink (TSK) model

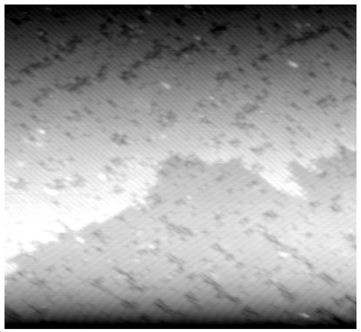
(Kossel & Stranski, 1927)



- Names refer to the position of atoms on the surface (cubic lattice):
- Energy of an atom's position is determined by its bonding to neighboring atoms
- Transitions involve the counting of broken and formed bonds
- Describes surface processes: diffusion, roughening, vaporization, growth

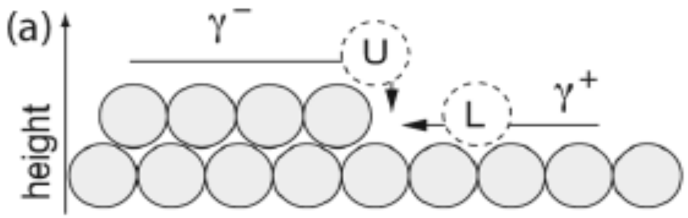


Residual or intentional misorientation:
vicinal surfaces



Scanning tunneling microscope image of a clean silicon (100) surface showing a step edge as well as many surface vacancies.

Ehrlich & Schwoebel statistics

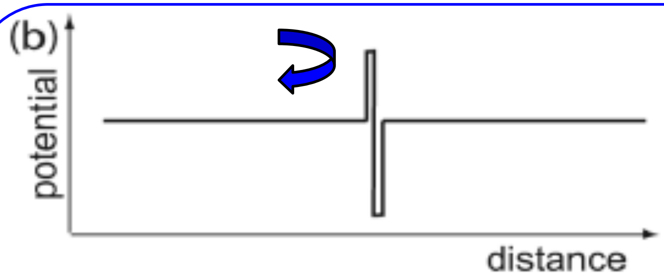


Adatom approaches surface step
from upper (U) or lower (L) terrace

Adatom to step sticking probability

γ^+ : from lower terrace

γ^- : from upper terrace



Difference in nearest neighbors seen by a diffusing adatom creates a potential barrier at the step upper edge

$\gamma^+ > \gamma^-$

- Small terraces grow faster
- Uniform step separation develops
- Step flow mode

$\gamma^+ < \gamma^-$:

- Large terraces grow faster
- Catch up with lower, smaller ones
- Step bunching

Ehrlich and Hudda, J. Chem. Phys. **44**, 1039 (1966)
Schwoebel and Shipsey, JAP **37**, 3682 (1966)

Ethyl- vs methyl- sources and doping: InGaAs:C

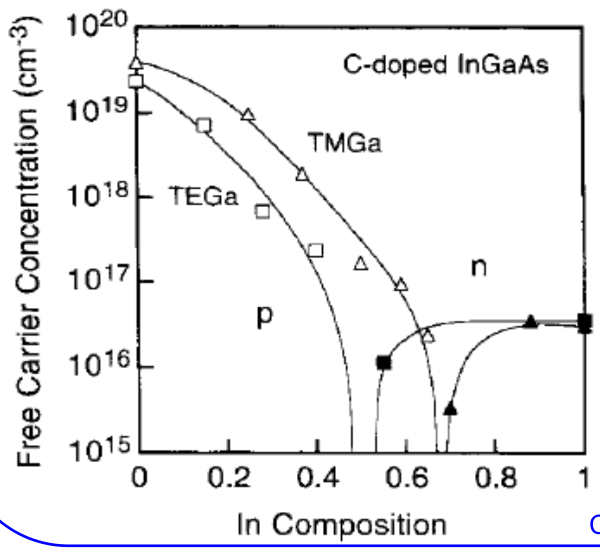
Influence of gallium sources on carbon incorporation efficiency into InGaAs grown by metalorganic chemical vapor deposition

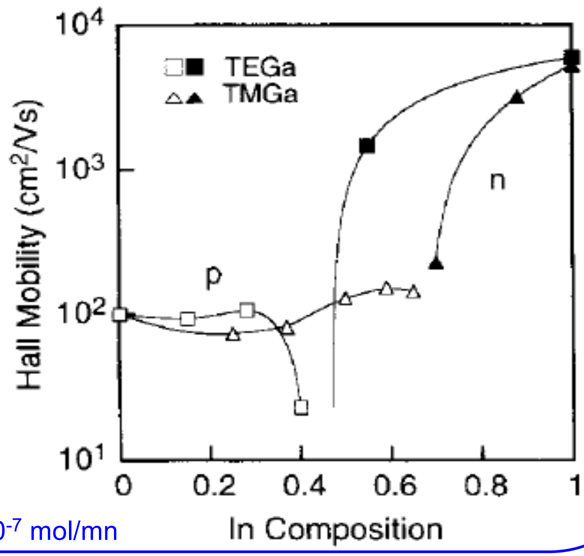
Hiroshi Ito *, Kenji Kurishima

NTT LSI Laboratories, 3-1, Morinosato Wakamiya, Atsugi-shi, Kanagawa 243-01, Japan

- H_2 ambient
- 500° C
- 0.9µm/h
- CBr_4, AsH_3
- TMGa/TEGa
- V/III = 4
- GaAs/InP
- substrates

InGaAs:C free carrier concentration and Hall mobilities



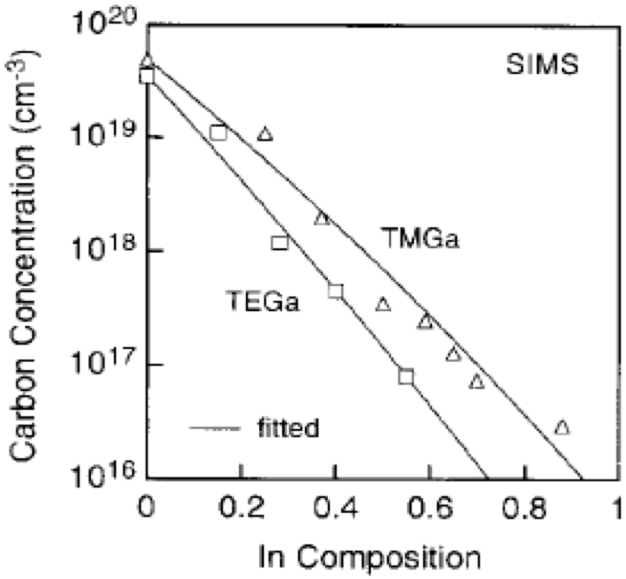


CBr_4: 4 10^{-7} mol/mn

With TEGa:
- Lower free carrier concentration
- p- to n-type transition shifted to higher In%
- Higher electron Hall mobility

Ethyl- vs methyl- sources and doping: InGaAs:C

C concentration in InGaAs:C



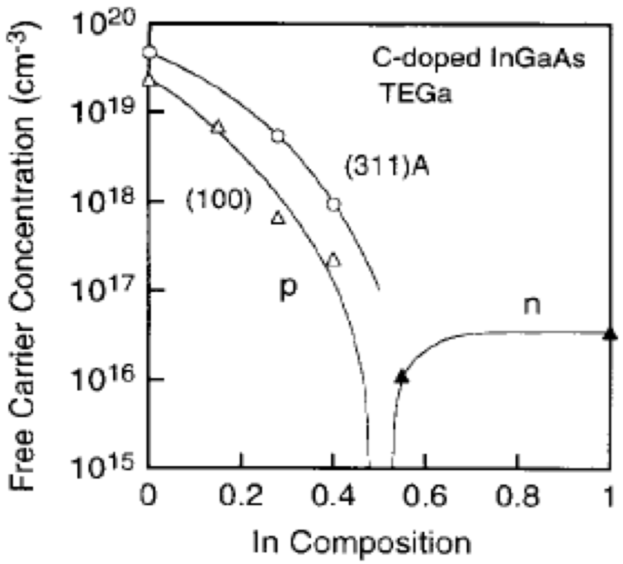
- ✓ [C] decreases with [In]
- ✓ Higher [C] with TMGa vs TEGa

- C-Ga bond stronger than C-In bond
- CBr_4 dissociates at step edges
- C « lost » in presence of In

Ito *et al*., J. Crystal growth (1996)

Ethyl- vs methyl- sources and doping: InGaAs:C

Surface orientation dependence of free carriers concentration in InGaAs:C



- ✓ More free carriers with (311)A vs (100) surfaces
- ✓ More [C] with (311)A vs (100) surfaces

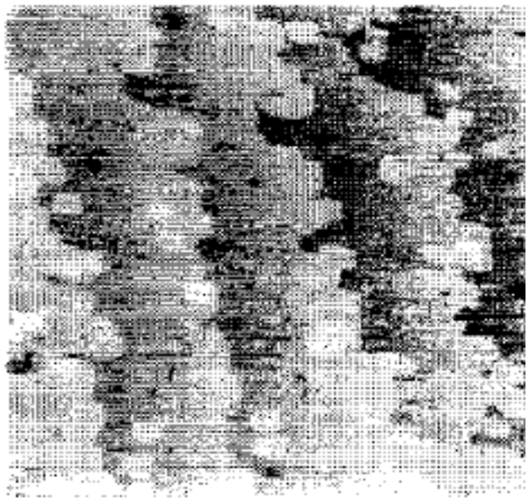
- CBr_4 dissociates at step edges
- Higher step density on (311)A
- Higher C uptake on (311)A

Ito *et al.*, J. Crystal growth (1996)

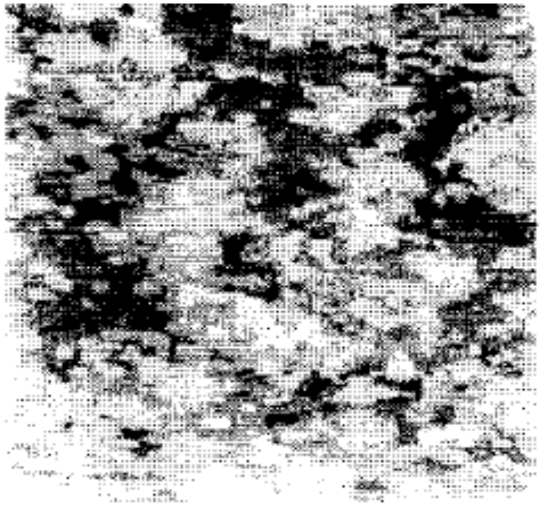
From growth *regimes* to growth *modes*

AFM of GaAs: C surfaces

TEGa



TMGa



Monolayer stepped terraces

↓

Mass transport limited

2D islands

- ✓ Higher step density
- ✓ Enhanced CBr_4 dissociation
- ✓ Increased C incorporation

↓

Kinetically limited

2D growth mode

- Adatoms do not reach a specific site within their lifetime
- Are incorporated at random locations on the surface
- Have several dangling bonds available for binding with other adatoms.
- Conglomerate and form islands randomly on the surface.

Ito *et al.*, J. Crystal growth (1996)