Molecular Beam Epitaxy
Presentation and issues related to UHV

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Outlook

1. Introduction
    - 1.1. What's and why epitaxy?
    - 1.2. Main application areas

2. III-V semiconductor epitaxy

3. III-V Molecular Beam Epitaxy (MBE)
    - 3.1. Why ultra high vacuum (UHV)?
    - 3.2. Core element : the effusion cell
    - 3.3. Other cells

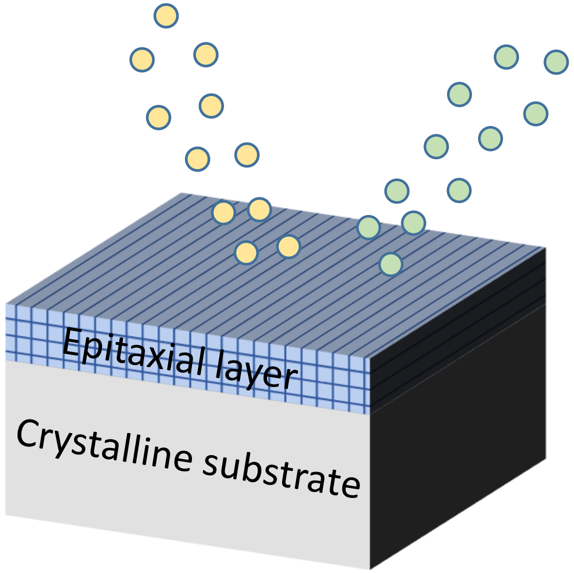
4. 2D material epitaxy

What's and Why Epitaxy?

- ❖ Epitaxy or epitaxial growth

Growth of material B on crystalline material A (substrate) keeping crystalline order

≠ material deposition ⇨ amorphous or polycrystalline material



- ❖ Interest
  - monocrystalline layers, high quality materials
  - interface and thickness precise control ⇨ quantum structures

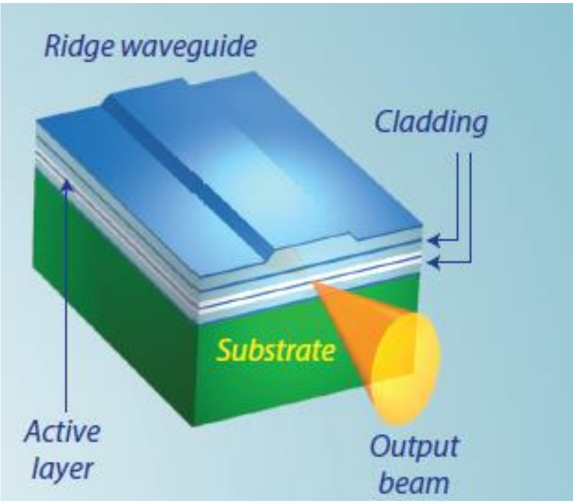
- ❖ Main concerned materials and some related applications

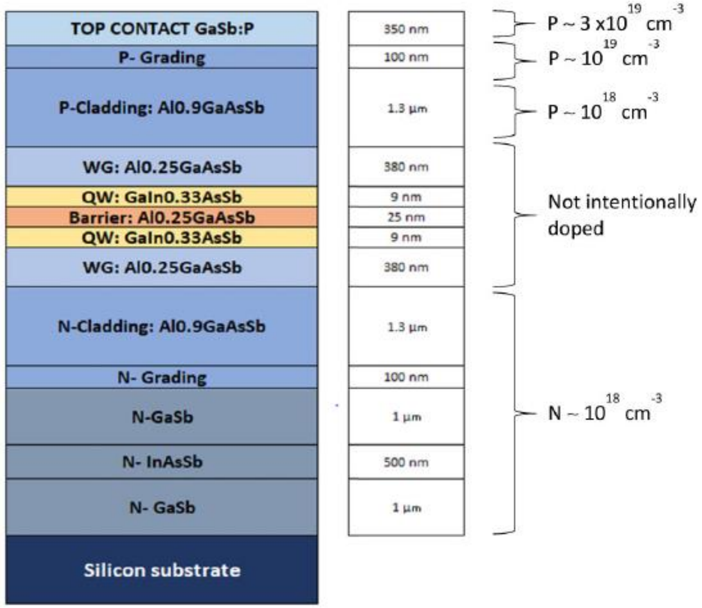
Semiconductors	⇨ photonics (lasers, detectors, lighting), THz
	⇨ high frequency microelectronics (µwave circuits for telecoms, radars,…)
Metals	⇨ spintronics, Giant magnetoresistance, memories
Oxides	⇨ functional materials, energy harvesting, photonics
2D materials	⇨ graphene, TMDs

- ❖ Besides : at the heart of numerous main discoveries and Nobel prizes

Applications : photonics

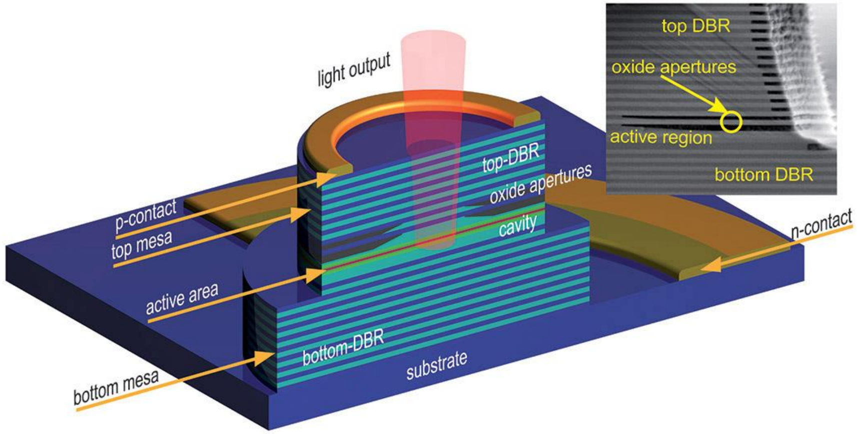
Lasers





Mid-infrared laser diodes epitaxially grown on (001) silicon

M. Rio Calvo et al., Optica 7, 263 (2020)



Vertical-cavity surface-emitting lasers (VCSEL) with InGaAs based active region and AlGaAs/GaAs bragg reflectors

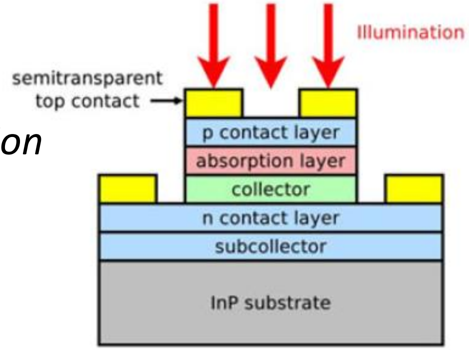
Si Zhu et al, Optics express 26, 14514 (2018)

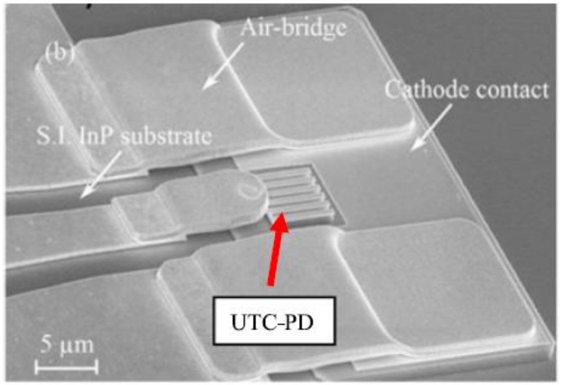
- Fiber optics communications
- Sensing
- Lighting

THz

Uni-travelling carrier photodiode for THz generation

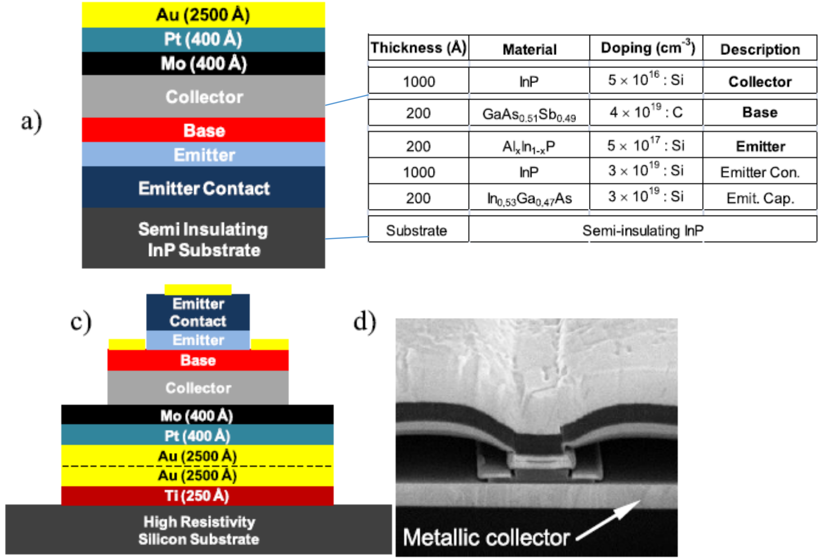
P. Latzel et al., IEEE Trans. THz Sci. and Technol. 7, 800 (2017)





Applications : high frequency electronics

Heterojunction bipolar transistor (HBT)

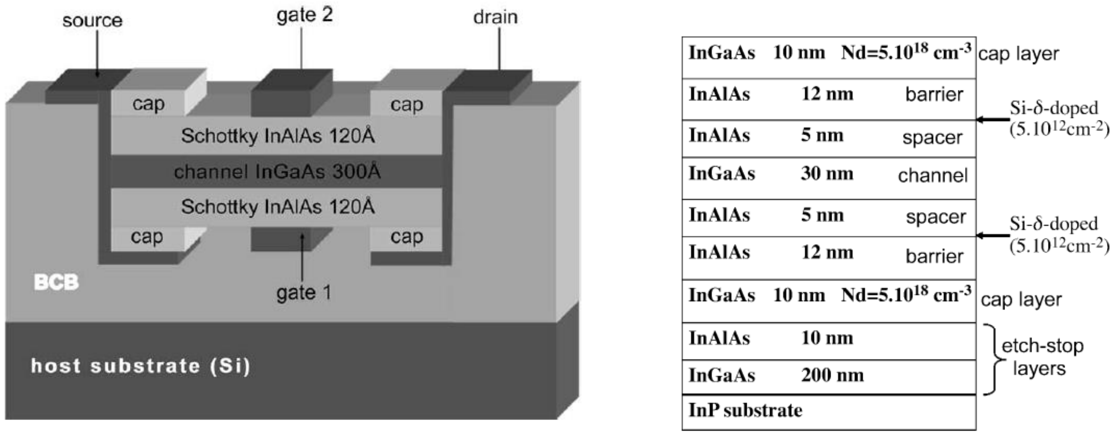


Thickness (Å)	Material	Doping (cm^{-3})	Description
1000	InP	5×10^{16} : Si	Collector
200	$GaAs_{0.51}Sb_{0.49}$	4×10^{19} : C	Base
200	$Al_xIn_{1-x}P$	5×10^{17} : Si	Emitter
1000	InP	3×10^{19} : Si	Emitter Con.
200	$In_{0.53}Ga_{0.47}As$	3×10^{19} : Si	Emit. Cap.
Substrate	Semi-insulating InP		

AlInP/GaAsSb DHBT transferred on a silicon substrate

A. Thiam et al., IEEE El. Dev. Lett. 35, 1010 (2014)

High electron mobility transistor (HEMT)



InGaAs	10 nm	Nd=5.10^{18} cm^{-3}	cap layer
InAlAs	12 nm	barrier	
InAlAs	5 nm	spacer	Si-δ-doped ($5.10^{12}cm^{-2}$)
InGaAs	30 nm	channel	
InAlAs	5 nm	spacer	Si-δ-doped ($5.10^{12}cm^{-2}$)
InAlAs	12 nm	barrier	
InGaAs	10 nm	Nd=5.10^{18} cm^{-3}	cap layer
InAlAs	10 nm		etch-stop layers
InGaAs	200 nm		
InP substrate			

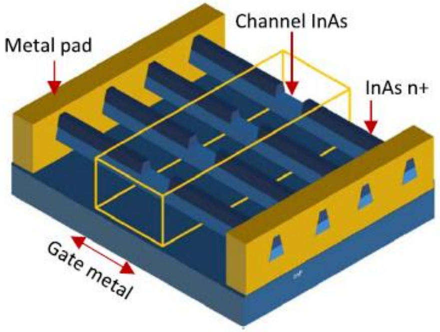
InAlAs–InGaAs Double-Gate HEMTs transferred on a silicon substrate

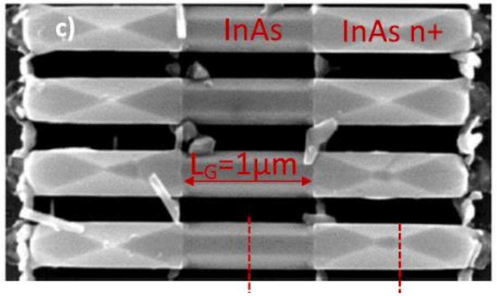
N. Wichmann et al., IEEE El. Dev. Lett. 25, 354 (2004)

Quantum structures

Suspended InAs nanowire-based transistors

M. Pastorek et al., Nanotechnology 30, 035301 (2019)



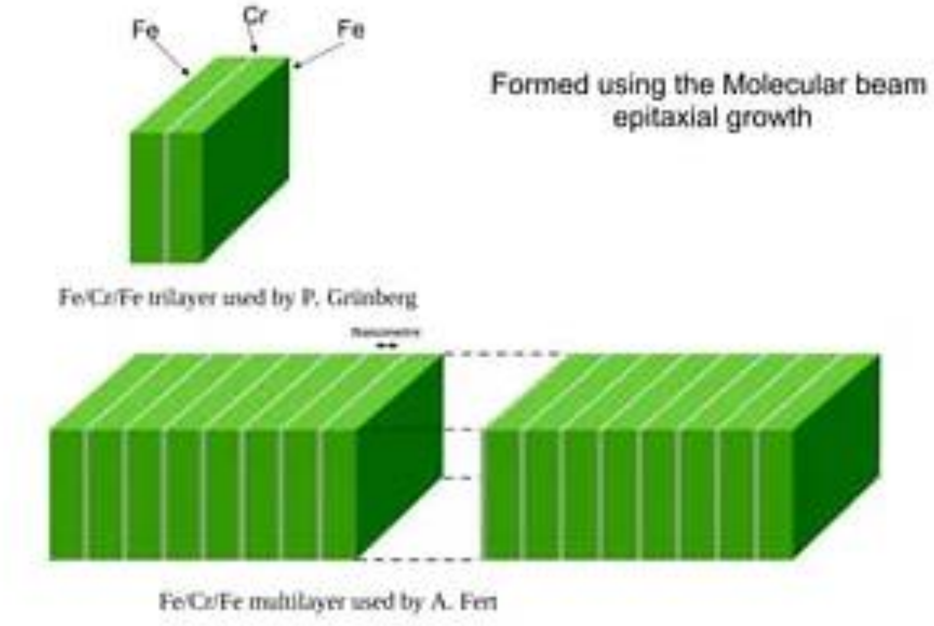


- High frequency electronics and communications
- Radar
- Aerospace and military systems
- Quantum electronics

Other applications

Giant magnetoresistance in metallic heterostructures

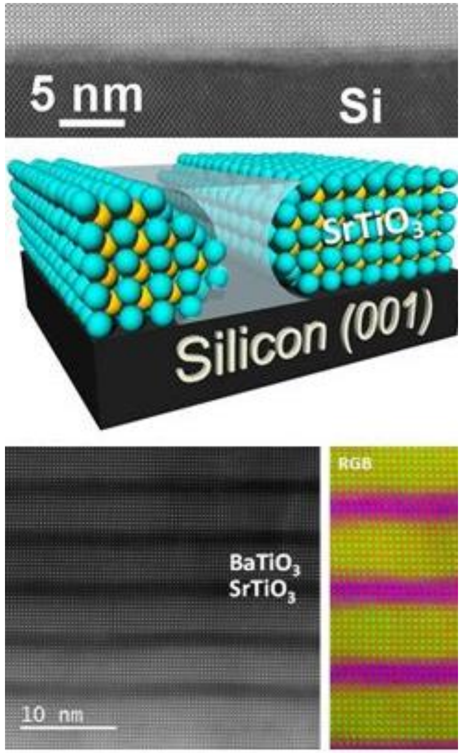
A. Fert, P. Grunberg, Nobel Prize 2007



- Sensors
- Memories

Oxide heterostructures for functional materials

(piezoelectrics, ferroelectrics,…)



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⇨In all examples, stacking of several layers a few nm or 10 nm thick with high crystalline quality

Requirements for applications

- **Pure single crystal layers**
  - Minimum structural defect density
  - Low impurity concentrations

  Why ?

  Defects and impurities ⬂ electron transport and optoelectronic properties

- **Precise thickness control**

  Why?

  Variation of thickness ⇨ change in laser wavelength emission/transport properties

- **Doped layers with** controlled impurities to increase layer conductivity

  Why?

  Formation of p-n junctions for lasers/increase current in transistors

- **Precise control of strain**

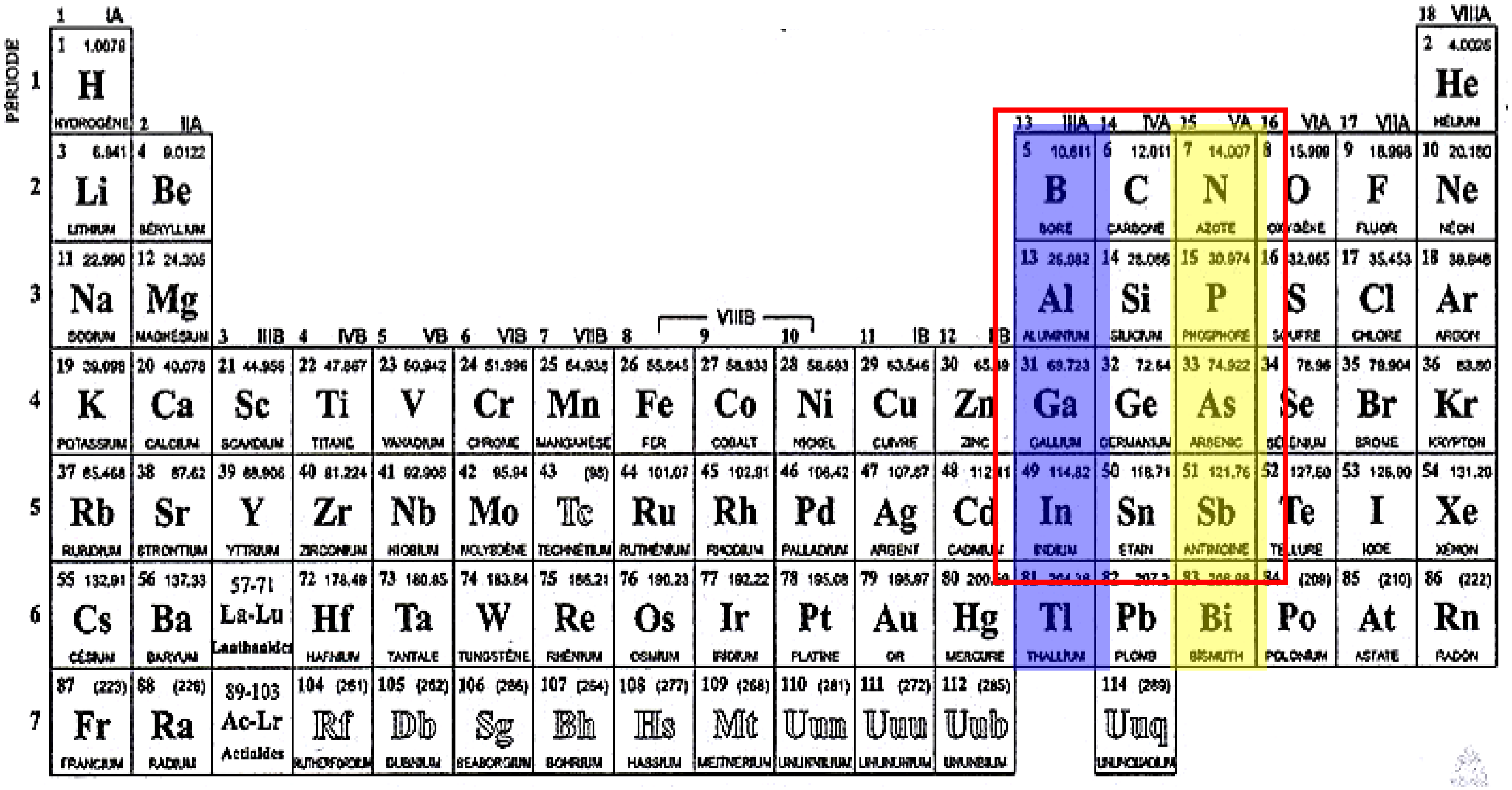
  Why?

  Strain ⇨ change in electronic/optical properties

  ⇨ can induce structural defects

In the following, mainly III-V semiconductor and 2D material epitaxy

III-V semiconductors

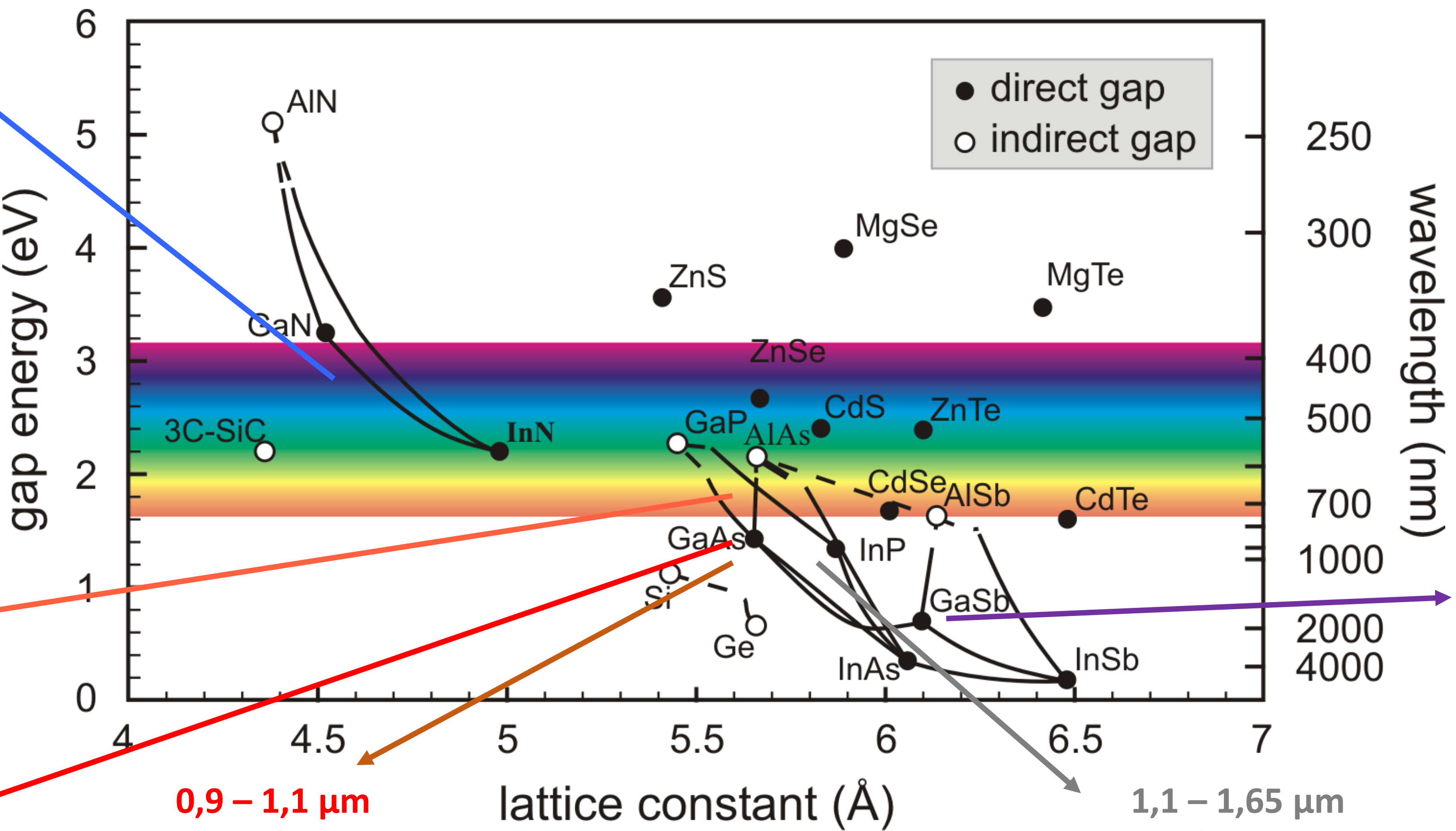


GaN, GaAs, InP, GaSb, InAs…. and associated alloys

III-Vs : a whole family - bandgaps and applications

0,35 – 0,5 µm
GaN/InGaN
Blue-ray discs, HD DVD,
Lighthing, high power HF
electronics
No substrate available yet
SiC, sapphire

0,6 – 0,8 µm
AlGaInP/GaInP
opt. ROM
GaAs substrate



0,7-0,9 µm
AlGaAs/GaAs
Aerospace, military
systems
GaAs substrate

0,9 – 1,1 µm
AlGaAs/InGaAs
HF electronics,
Telecommunications,
GaAs substrate

1,1 – 1,65 µm
InP/InGaAsP
Fiber optics communications
[silica fiber low dispersion (loss)
at 1.3 (1.55) µm], transceivers
InP substrate

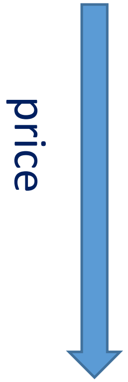
1,7 – 4,4 µm
AlGaAsSb/InGaAsSb
Spectroscopic
sensing of humidity,
gas impurities, drugs
GaSb or InAs
substrate

Starting point : crystalline substrate

❖ Growth of a high quality heterostructure

⇨ grown materials and substrate with very close crystallographic structure and lattice parameters

❖ Main substrates :



- Si : 12-inch wafers currently used in µelectronics but not directly suitable for III-V growth
- Sapphire : up to 8-inch available substrates : not lattice matched but used for nitrides (GaN)
- GaAs : up to 8-inch available substrates – 6 inch currently used
- InP : up to 6-inch available substrates – 3 or 4 inch currently used
- GaSb/InAs : up to 4-inch available substrates – 2 inch currently used
- SiC : up to 8- inch available substrates – 2 or 3 inch currently used

⇨ Availability of the substrate conditions the materials that can be grown epitaxially

❖ 2 main epitaxial approaches

- Based on chemical processes : Metal Organic Vapor Phase Epitaxy (MOVPE)
- Based on physical processes : **Molecular beam Epitaxy (MBE)**

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III-V Molecular Beam Epitaxy : general features

- Ultra-high vaccum chamber :base pressure : 10^{-10} Torr

  Cryo panels (Liquid N_2) ⇨ improved vacuum around the sample and cooling around the cells

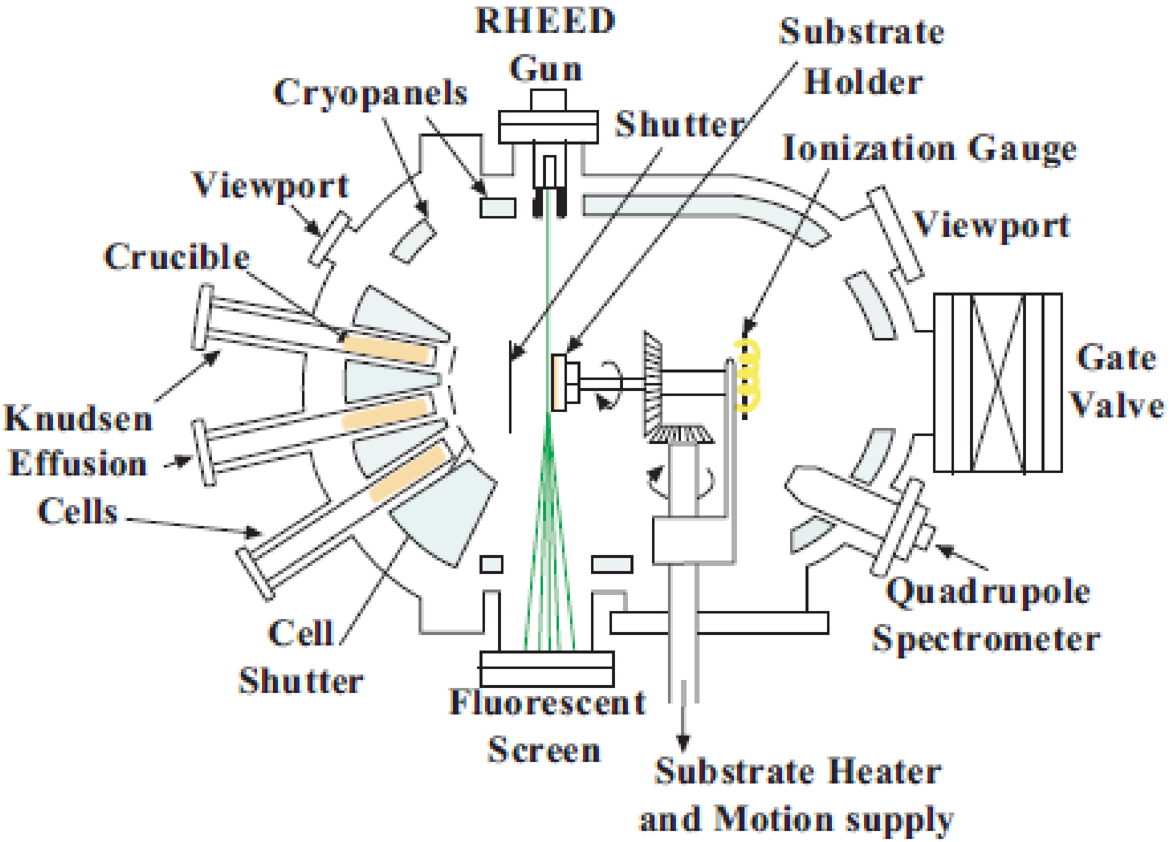
- Effusion cells (ovens) for elements III and V with shutters

  Elemental fluxes condensate on the surface

- Typical growth rate : 1 µm/h or 1 atomic layer/s

- Advantages
  - High purity materials
  - in-situ control during growth (RHEED)
  - thickness defined within 1 ML

- Drawbacks
  - no selectivity
  - complex technology



What does it look like?

Cryo panel

Chamber with integrated cryo panel

Reactor fitted with equipment

Why UHV?

- 2 main reasons for UHV
  - Molecular regime
  - Contamination/doping

- Vacuum regimes
  - Description within the kinetic theory of gases
    - ⇨ interactions molecules-molecules and molecules-reactor
  - Atom or molecule mean free path λ_m : mean distance between 2 successive collisions

$$\lambda_m = \frac{1}{\sqrt{2}\,\pi \circled{n} d^2}$$

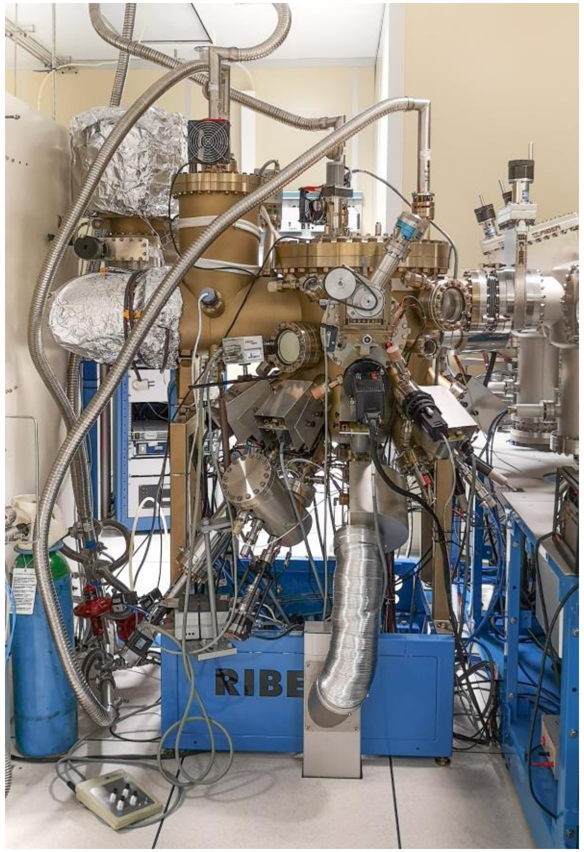
with *n* : number of molecules/m^3

d : molecule diameter

  - Ideal gas law

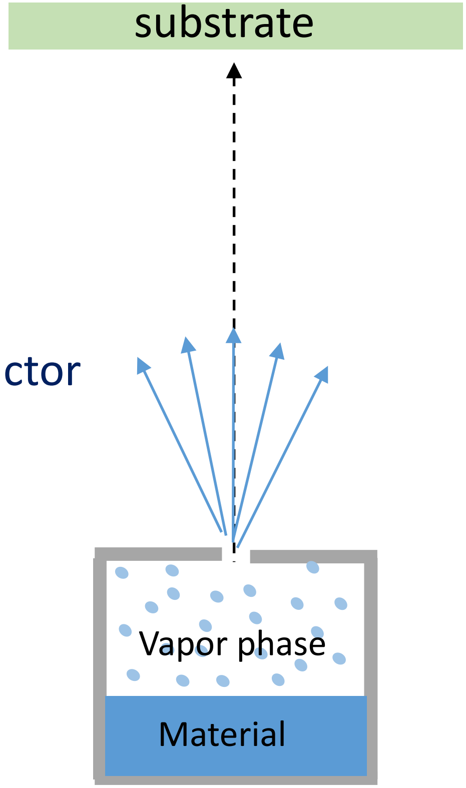
$pV = NkT$, then $p = nkT$ with *k* : Boltzmann constant

⇨ λ_m depends only on *n* and on the type of molecules



Molecular regime

$$\lambda_m = \frac{1}{\sqrt{2}\,\pi n d^2}$$



❖ Vacuum regimes

- λ_m << reactor dimensions ⇨ laminar regime : numerous collisions between molecules
- λ_m ~ reactor dimensions ⇨ intermediate regime
- λ_m >> reactor dimensions ⇨ molecular regime : mainly collisions between molecules and reactor

❖ MBE

- No collisions between molecules from the cell to the substrate

⇨ $\lambda_m \geq$ reactor dimensions (~ 1m)

$$n \leq \frac{1}{\sqrt{2}\,\pi \lambda_m n d^2}$$ ~ 9.10^{17} molecules/m^3 with λ_m = 1m and d = 5Å

$p = nkT \leq 4.10^{-3}$ Pa (~3.10^{-5} Torr)

⇨ Not ultra high vacuum

Contamination

- ❖ Reactor at a pressure *p* (residual gases)

  ⇨ impurity flux F_i on the growing surface

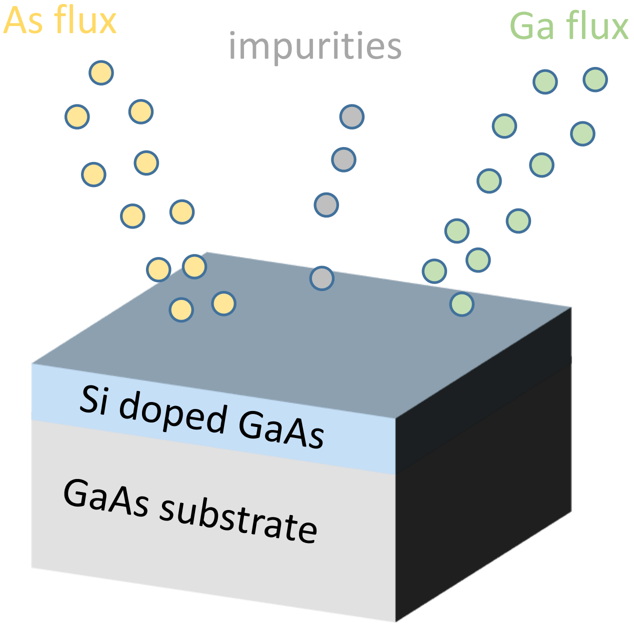
- ❖ Kinetic theory of gases ⇨ $F_i = \frac{p}{\sqrt{2\pi mkT}}$

- ❖ Conditions on F_i

  $F_i \ll F_0$ with F_0 growth flux : typically 10^{15} at./cm^2.s or 1 atomic layer/s

- ❖ What does $F_i \ll F_0$ mean exactly?

  ⇨2 concerns : doping and material purity



Contamination

- For semiconductor, importance of doping
  - Common situation

    ~ 10^{16}/cm^3 < dopant concentration < ~ 10^{19}/cm^3

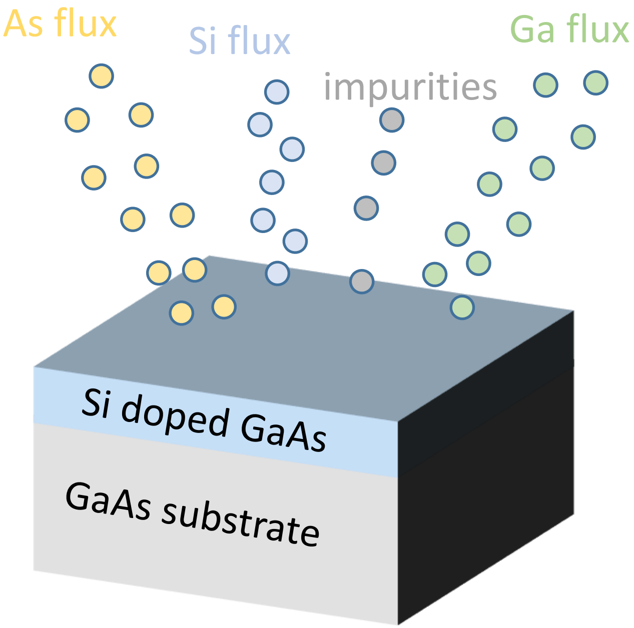
    To be compared with ~ 5.10^{22} at./cm^3 in the semiconductor crystal

    ⇨ $10^{-6} F_0 < F_{doping} < 10^{-3} F_0$ with F_0 : growth flux
  - Controlled doping and pure material

    ⇨ $F_i << F_{doping}$

$$F_i < 10^{-6} F_0 \Rightarrow p < 10^{-6} F_0 \sqrt{2\pi mkT} \approx 10^{-11} - 10^{-12} \text{ Torr}$$

↳ Ultra-high vacuum domain



$F_i < F_{doping}$ ⇨ F_i gives the lowest controlled doping level /residual impurity concentration for undoped material

- Remarks
  - Sticking coefficient for impurities assumed to be 1 ☹ but dependence on surface and gas reactivity
  - Best MBE material : 10^{13}-10^{14} impurities/cm^3

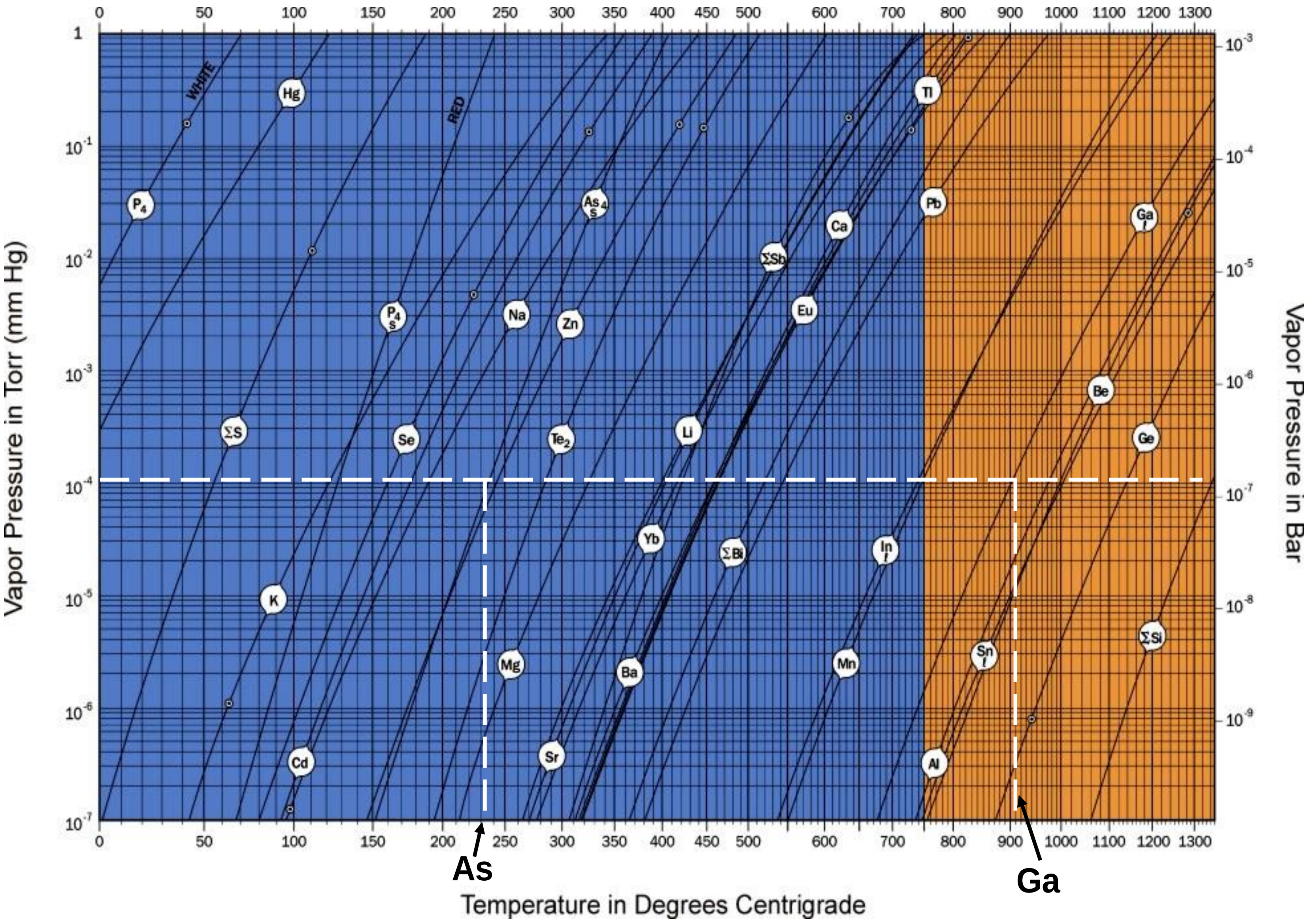
III-V MBE : How does it work?

❖ Key point : Thermodynamics

Large vapor pressure difference between elements III and V at a given temperature T

Or

Large temperature difference between elements III and V to get the same vapor pressure



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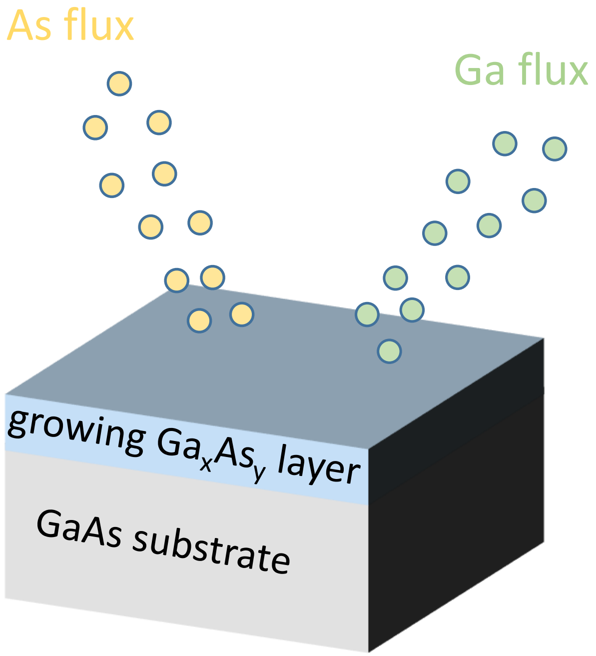
3 temperature rule

- Vapor pressure difference between element III and V
  - $P_{III} << P_V$ at a given T
  - or $P_{III} = P_V$ if $T_{III} >> T_V$

⇨ $T_V < T_{substrate} < T_{III}$

(T_V ~200°C, $T_{III} \geq 750$°C, $T_{substrate}$ ~ 500-600°C)



x = *y* thanks to thermodynamics!😊

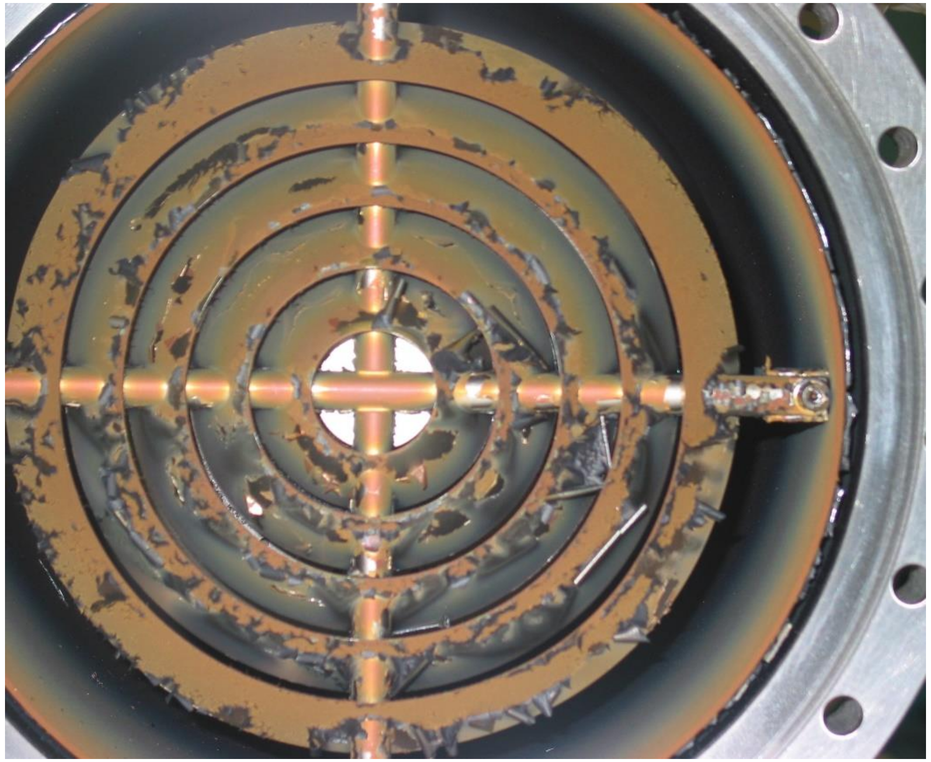
- At T_V, evaporation of element V → element V flux (As) on the substrate
- At T_{III}, evaporation of element III → element III flux (Ga) on the substrate
- At $T_{substrate}$
  - $T_{substrate} < T_{III}$ → element III condensates : sticking coefficient ~ 1
  - $T_{substrate} > T_V$ → element V reevaporates unless element III on the surface

- In excess of element V, growth of a stoichiometric compound
- Growth rate V_g determined by element III flux
- During growth overpressure of group-V element (As, P, Sb)

⇨ no more UHV ($10^{-8} – 10^{-7}$T)

MBE under operation

Cell cryopanel with material residues



Cryo pump shroud with material residues

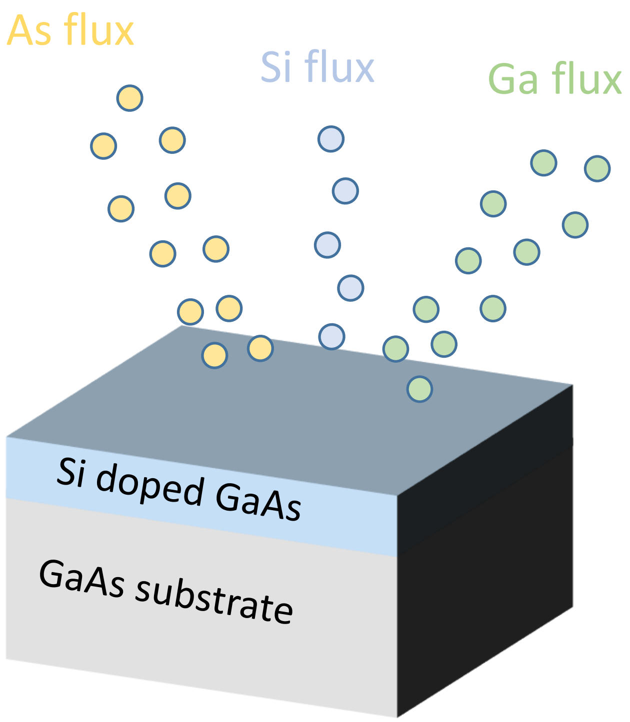
Doping

- Doping atoms incorporated during growth (specific cells)

- Candidates
  - n-type
    - Group IV : Si, Ge, Sn in an element III site
    - Group VI : Te, S, Se in an element V site
  - p-type
    - Group II : Be, Mg, Mn, Zn in an element III site
    - Group IV : C in an element V site

- Which is the best?
  - Precise control of the doping profile

⇨ mainly Si and Te for n-type / Be and C for p-type



Not so easy!

Doping levels in the 10^{16}-10^{19}/cm^3 ⇨ dopant flux ~ 10^{-6}-10^{-3} growth fluxes!😰

Core element : effusion or Knudsen cells

- Cell filled with a material at thermodynamical equilibrium with its vapor : $T_{cell} \Rightarrow P_{cell}$
- Kinetic theory of gases
  - Effusion rate for a cell with an orifice of area A (A<< and orifice thickness ~0)

$$\Gamma_e = F_e . A = \frac{P_{cell} A}{\sqrt{2\pi m k T_{cell}}}$$

in atoms (molecules)/unit time

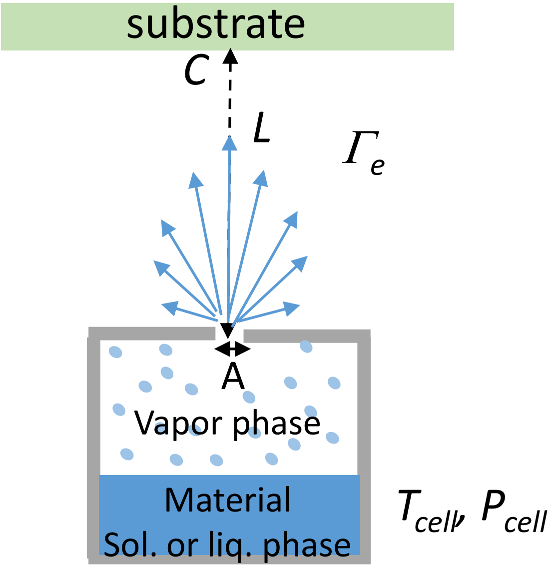
Knudsen equation

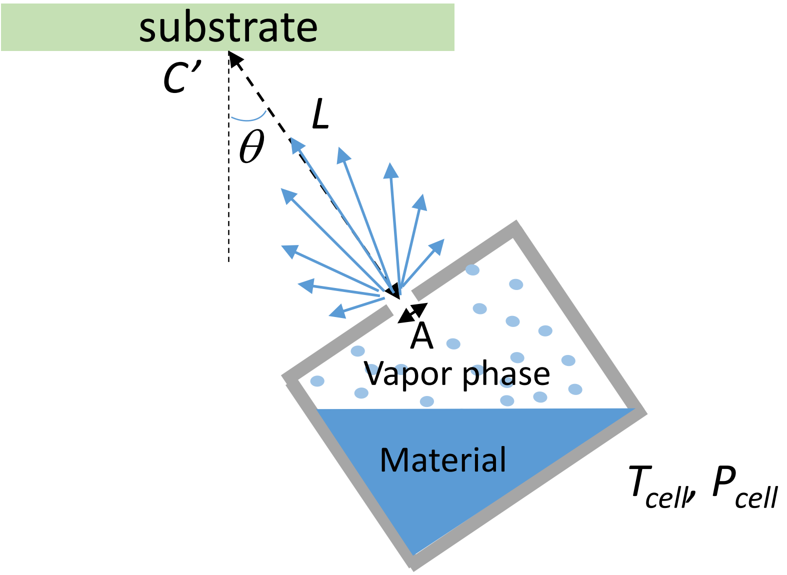
  - Flux of atoms or molecules at the center *C* of the substrate at a distance *L*

$$F_C = \frac{\Gamma_e}{\pi L^2} = \frac{P_{cell} A}{\pi L^2 \sqrt{2\pi m k T_{cell}}}$$

  - With an angle θ between the cell axis and the substrate normal

$$F_{C'} = F_C \cos\theta$$





Core element : effusion or Knudsen cells

$$F_C = \frac{\Gamma_e}{\pi L^2} = \frac{P_{cell} A}{\pi L^2 \sqrt{2\pi m k T_{cell}}}$$

P_{cell} is only dependent on T_{cell} and on the material

⇨ for a given geometry and material, the flux *F* only depends on T_{cell}

⇨ For III-V MBE, the growth rate only depends on the temperature of the group-III element cells

- Expression above derived for ideal case of very small aperture A
- In practice, cylindrical of conical shape for the cell to increase the flux homogeneity (growth rate) across the substrate

  ⇨ corrections to be applied for specific cell design but the flux remains controlled by the cell temperature

- Typical cell temperatures

  Ga : 900-1000°C Al : 1000-1150°C In : 750-850°C Si : 900-1250°C

  ⇨ Usefulness of the cryo panels at 77K (!!!) to avoid excessive outgassing of the cell surrounding

  ⇨ Specific water-cooled integrated panel for large cells

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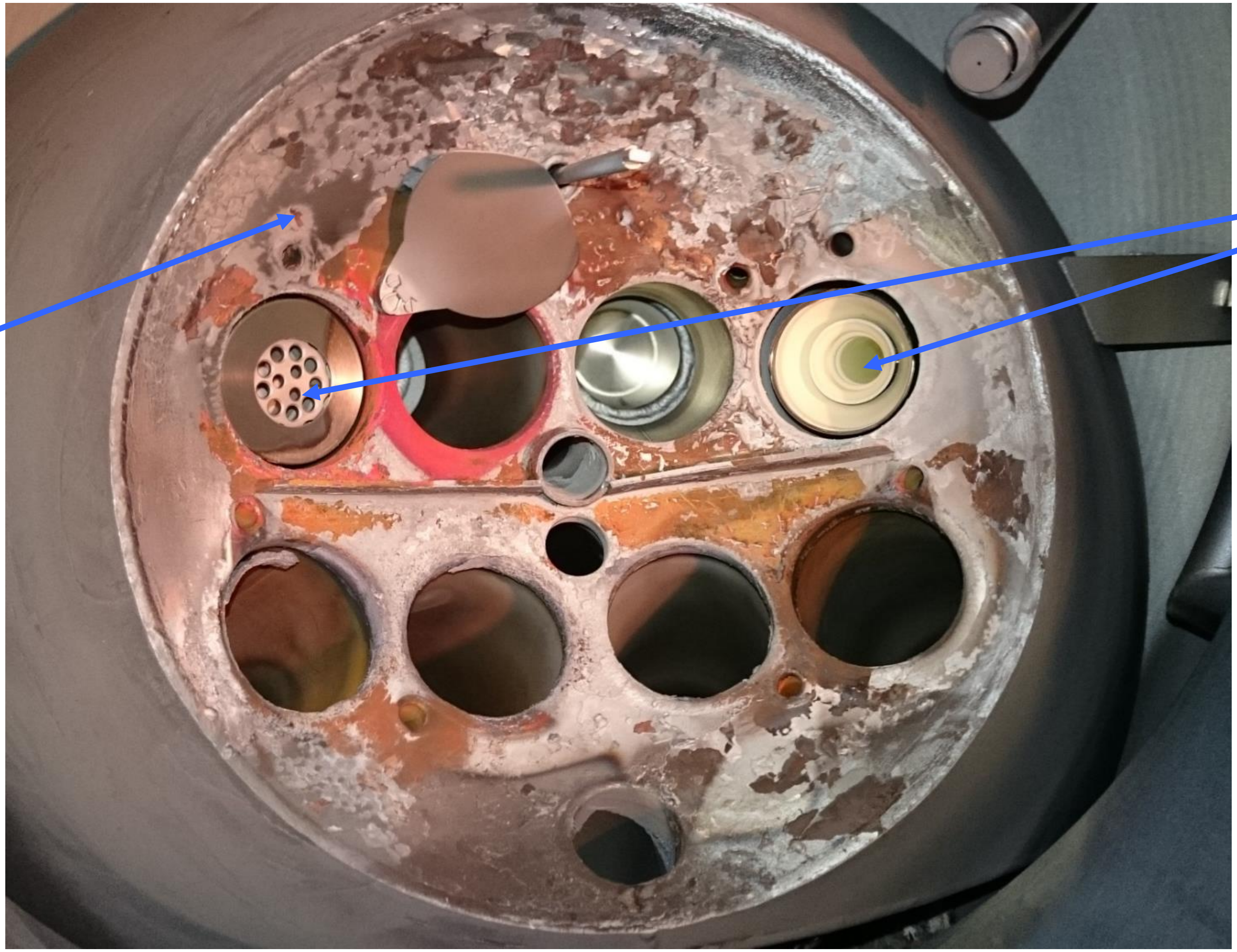
Thermal strain within the system

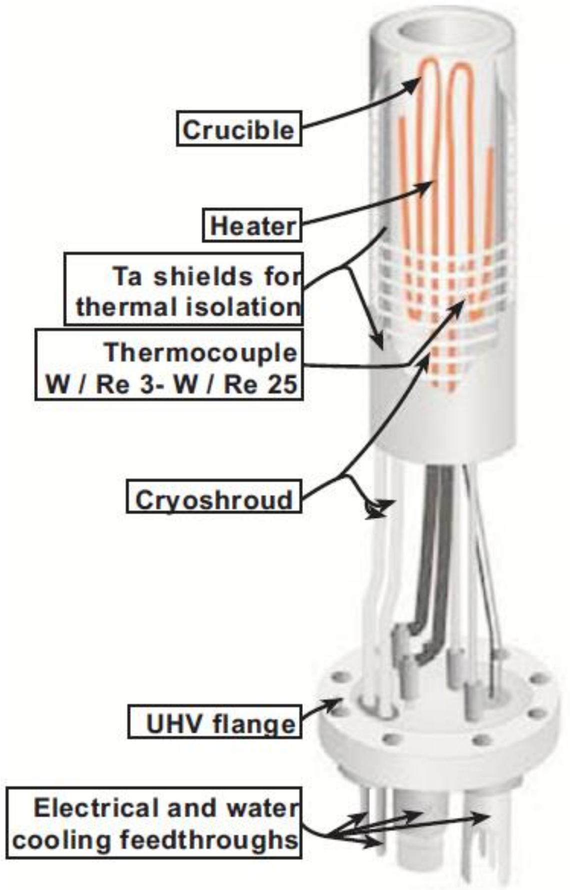


Cryo panel at 77K

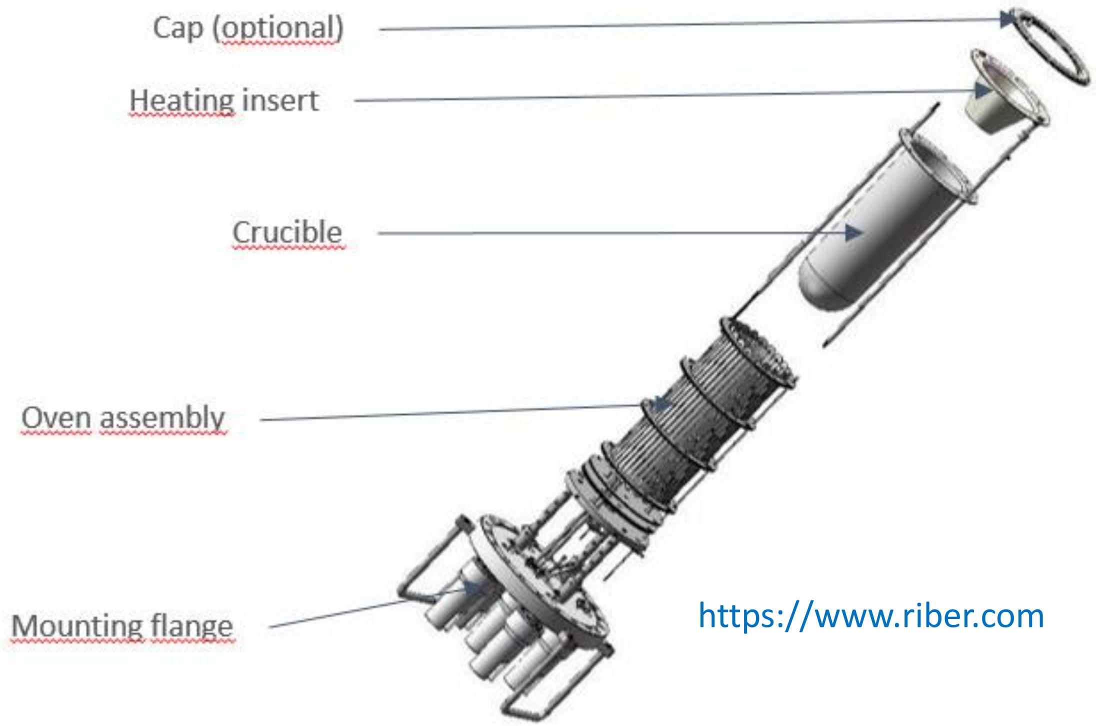
Cells at 1000 - 1300 K

❖ Issues with
  - the large temperature gradient between cells and cryo panel
  - the periodic thermal cycling of the cryo panel

Effusion or Knudsen cells : real cells



Roberto Murri , " Silicon Based Thin Film Solar Cells ", Bentham Science Publishers (2013)
https://doi.org/10.2174/97816080551801130101

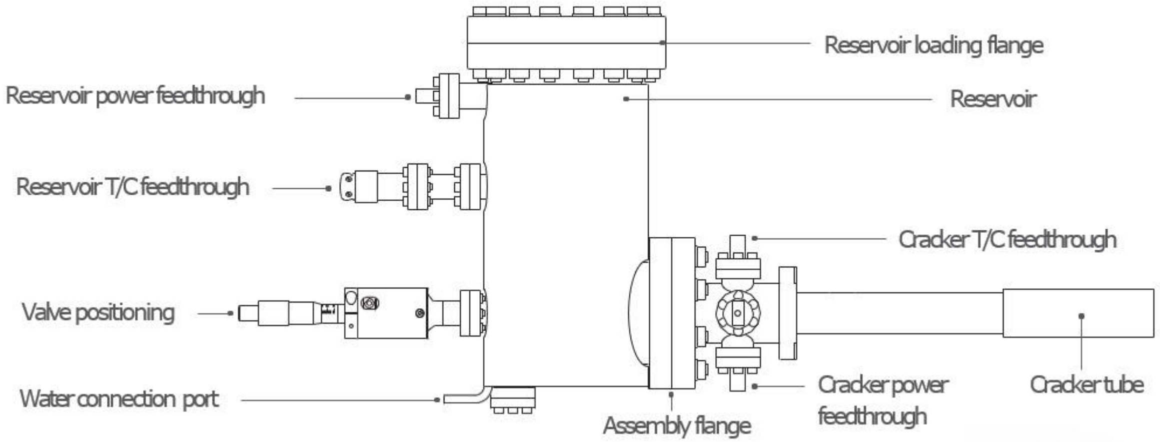


https://www.riber.com

- ❖ Effusion cells mainly used for element III (Ga, In, Al) and dopants (Si, Be, Te)
- ❖ Materials used : Ta, Mo, pBN or graphite for crucible

Other cells for group-V elements

- Group-V elements : As, P, Sb
  - High vapor pressure ⇨ valve to avoid excess group-V element in the MBE chamber
  - Rather large molecules produced by evaporation : As_4, Sb_4, P_4 ⇨ thermal cracker ⇨ $As_4 \xrightarrow{950^\circ C} 2\ As_2$



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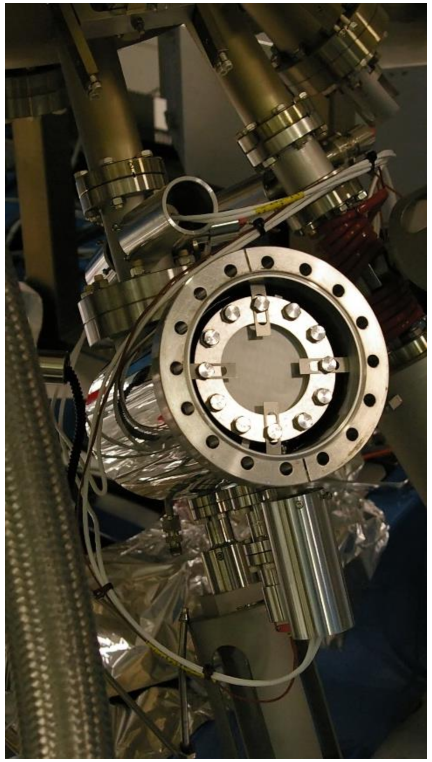
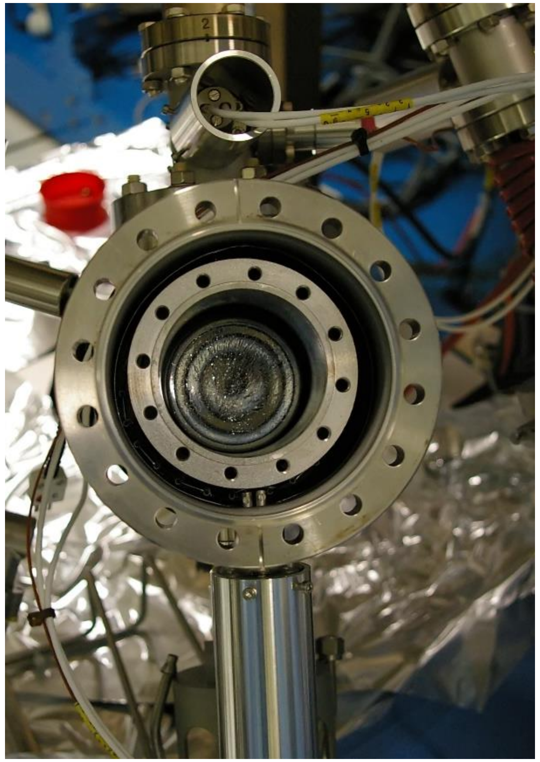
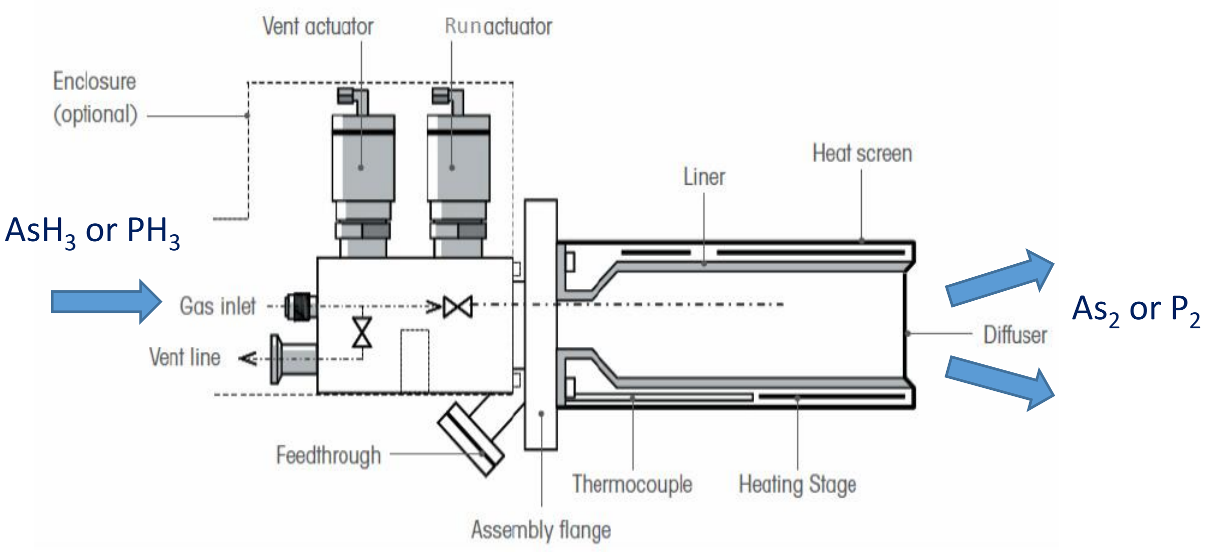




Other cells for gases

- High temperature gas injector for gas thermal cracking

AsH_3 (PH_3) can be used after thermal cracking to get As_2 or P_2 : $2\,AsH_{3(g)} \xrightarrow{950°C} As_{2(g)} + 3\,H_{2(g)}$



AsH_3 or PH_3

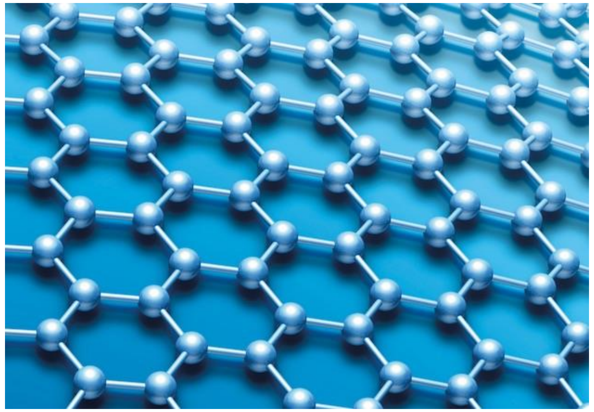
As_2 or P_2

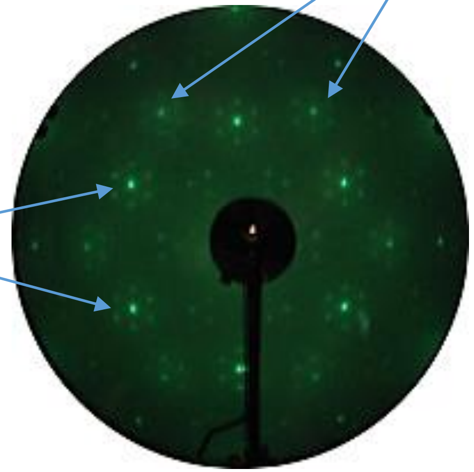
⇨ Pressure in the reactor in the 10^{-5} T range (H_2)

https://www.riber.com

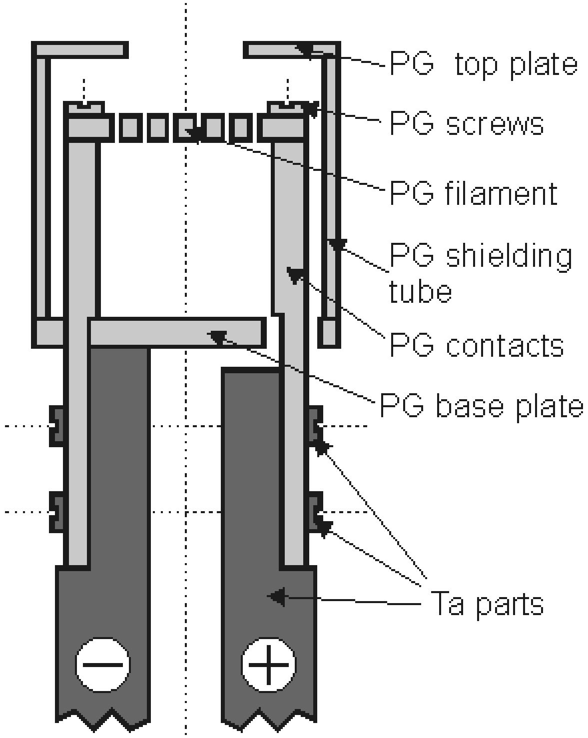
Graphene epitaxy : high T carbon cell

- MBE growth of graphene





LEED pattern of graphene on SiC Si face



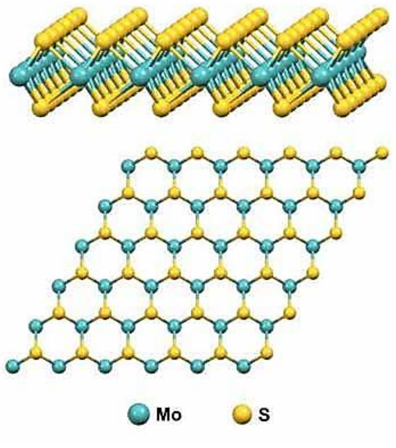
Main parts of a carbon cell assembly

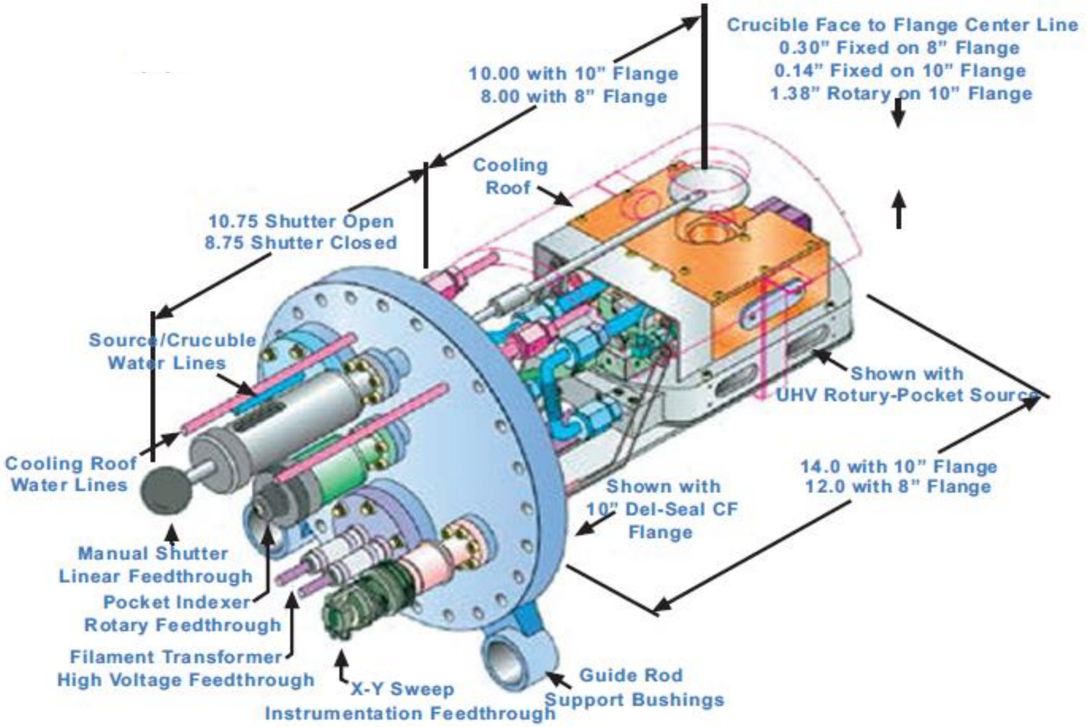
Hot graphite filament : up to 2300°C

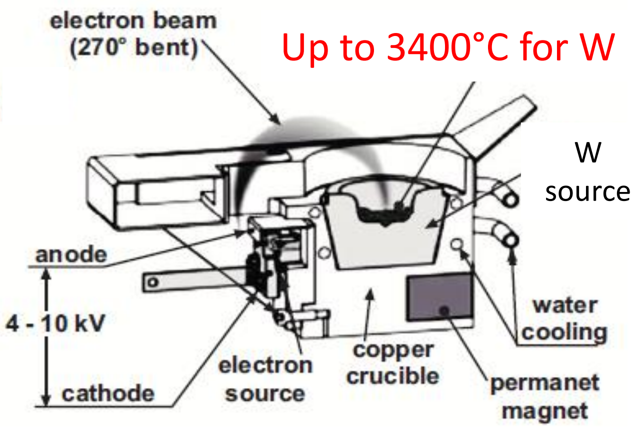
https://www.mbe-komponenten.de/

TMD epitaxy : electron beam evaporator

- ❖ Transition metal dichalcogenides (TMDs) MX_2
- ❖ Refractory materials Mo, W, Ta,…
  - Too high temperature needed to get Joule effect evaporation
  - Effusion cell not useful ⇨ electron beam evaporator







Up to 3400°C for W

Conclusion

- MBE requires UHV base pressure for material purity and doping control

  ….but the pressure during growth is not really UHV!!

- MBE is mainly a temperature story
  - Cell temperature determines the effusing flux, the growth rate and the alloy composition
  - Growth temperature allows stoichiometry for III-Vs
  - Cooling is mandatory to avoid excessive outgassing and allow high vacuum around the sample

- Large thermal stress during growth and the different cooling/warm up cycling of the cryo panel

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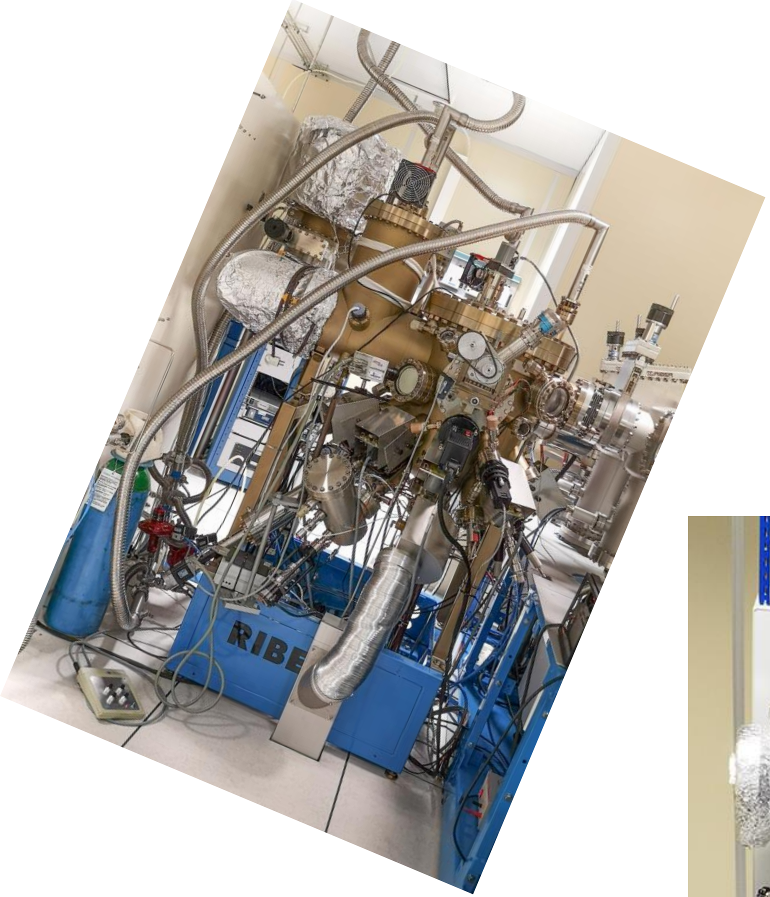

Thank you for your attention