

Principles of Epitaxial Growth and Epitaxy from Molecular Beams (MBE)

Eduard Hulicius,

Semiconductor dep., FZÚ AV ČR, v.v.i.

Preparation and properties of the bulk crystals:

(Not only for semiconductor)

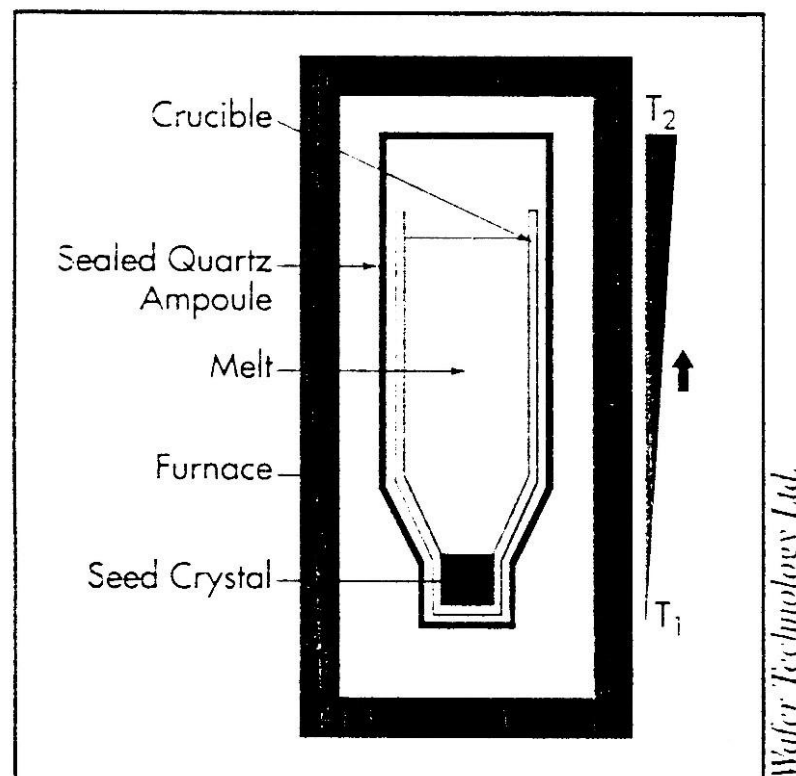


Figure 2. Vertical gradient freeze (VGF). The thermal gradient is moved upwards from the seed crystal.

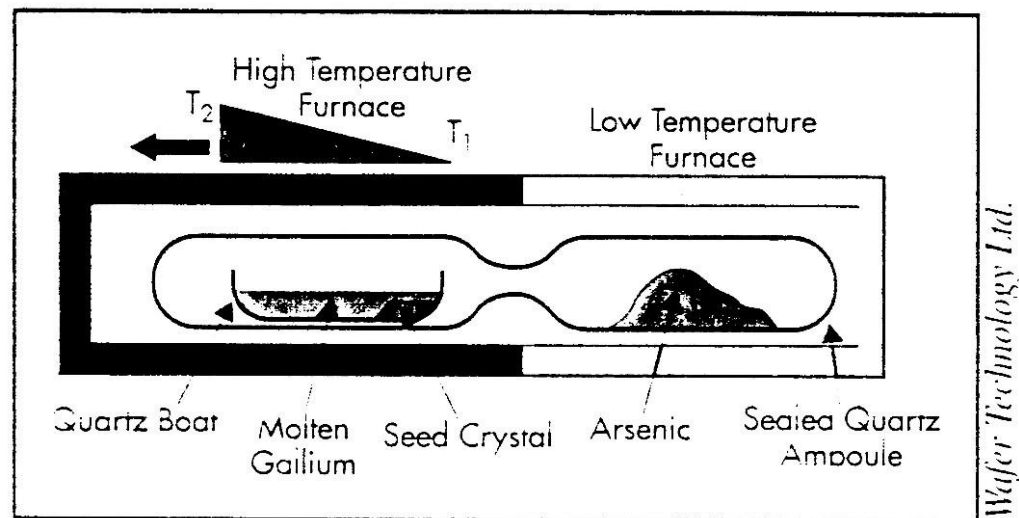


Figure 1. Horizontal gradient freeze. The thermal gradient ($T_2 > T_1$) is moved along the boat from right to left by changing furnace settings.

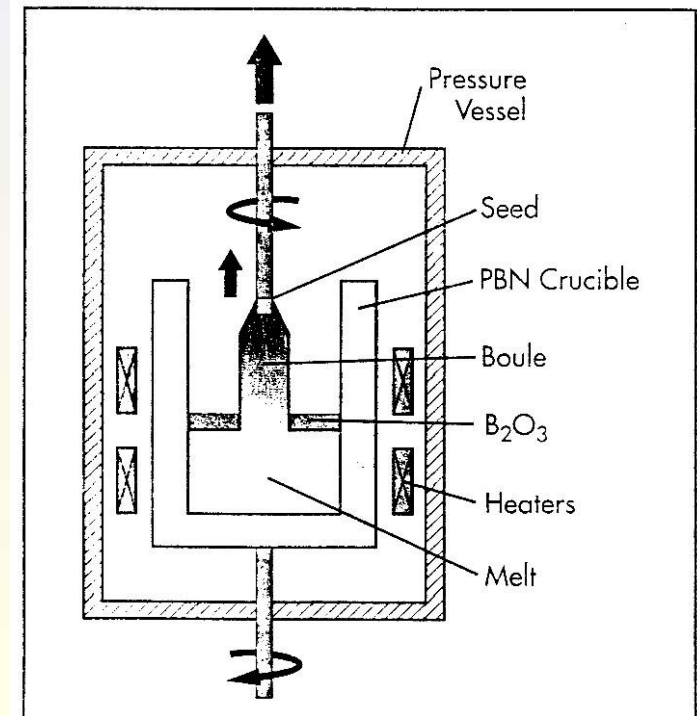
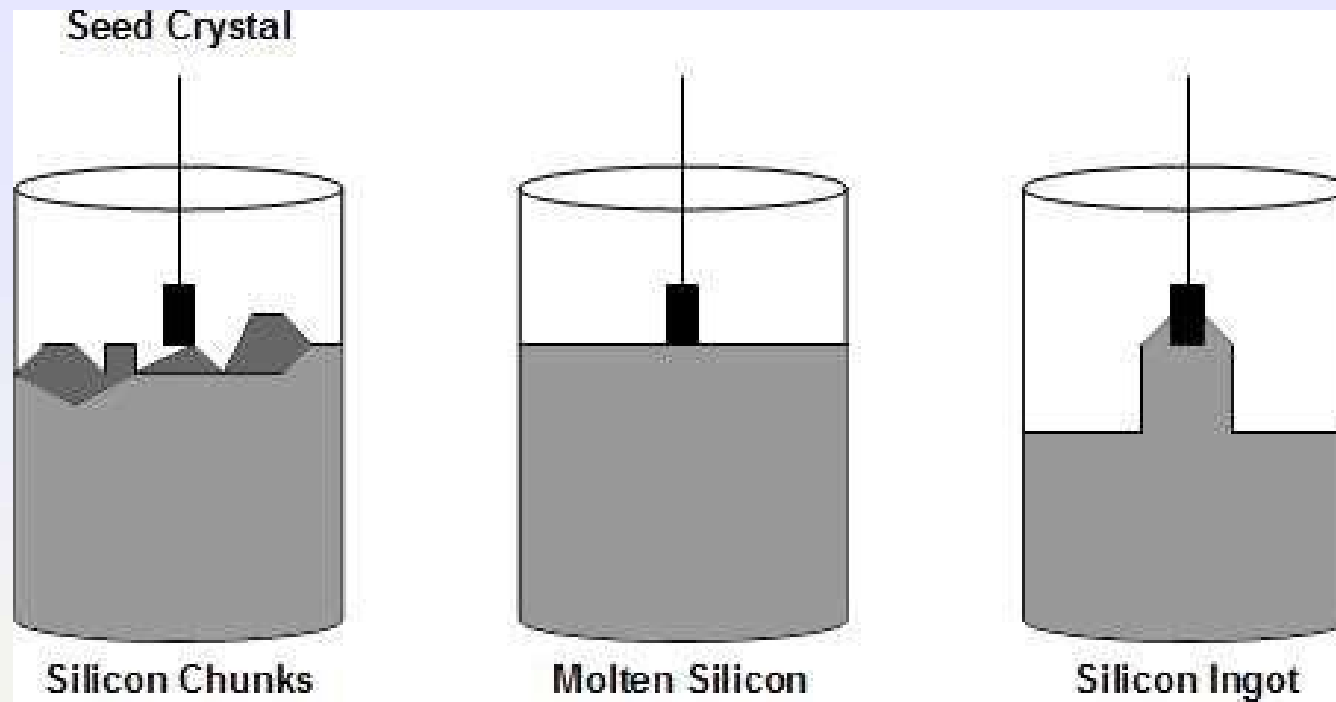
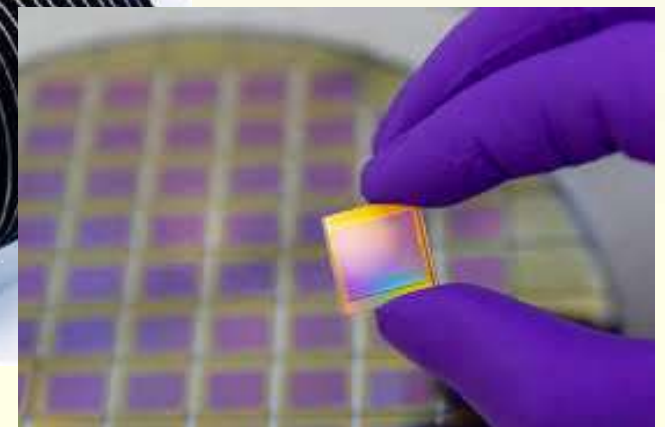
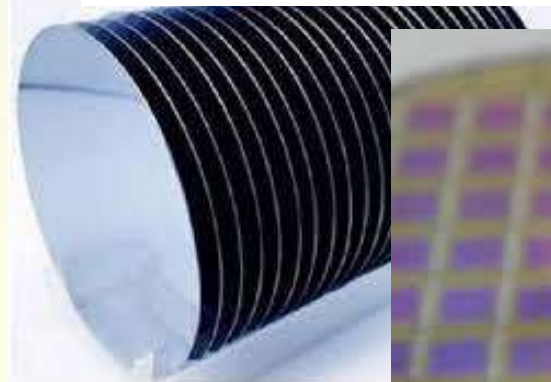
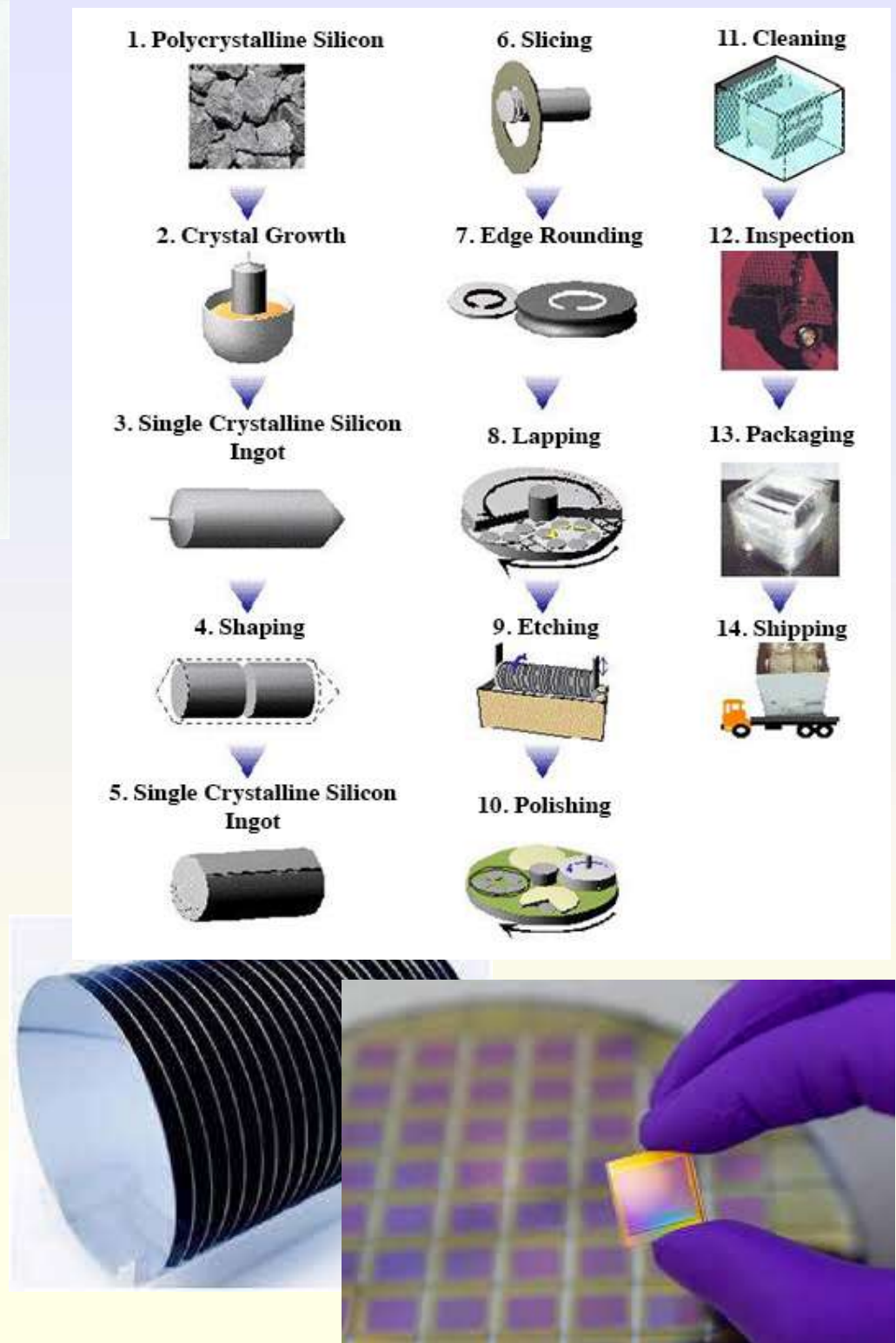


Figure 3. Liquid-encapsulated Czochralski (LEC). The seed crystal is dipped through the liquid boric oxide into the melt and slowly removed while being rotated.

Growth of monocrystals by the Czochralski method



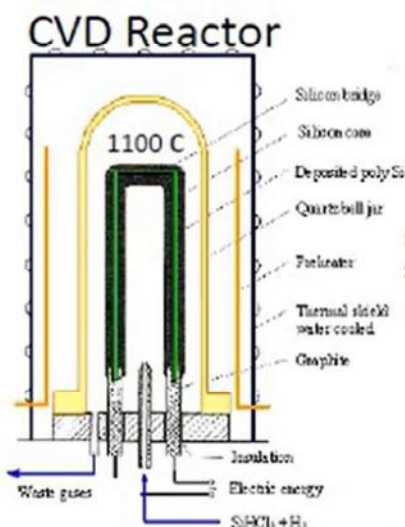
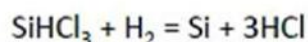
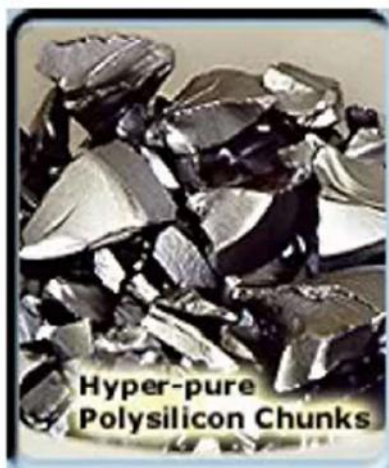
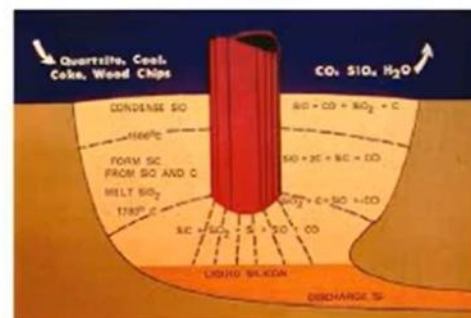


Production of Silicon from Sand



1800 C
Arc Furnace

$\text{SiO}_2 + 2\text{C} = \text{Si} + 2\text{CO}_2$

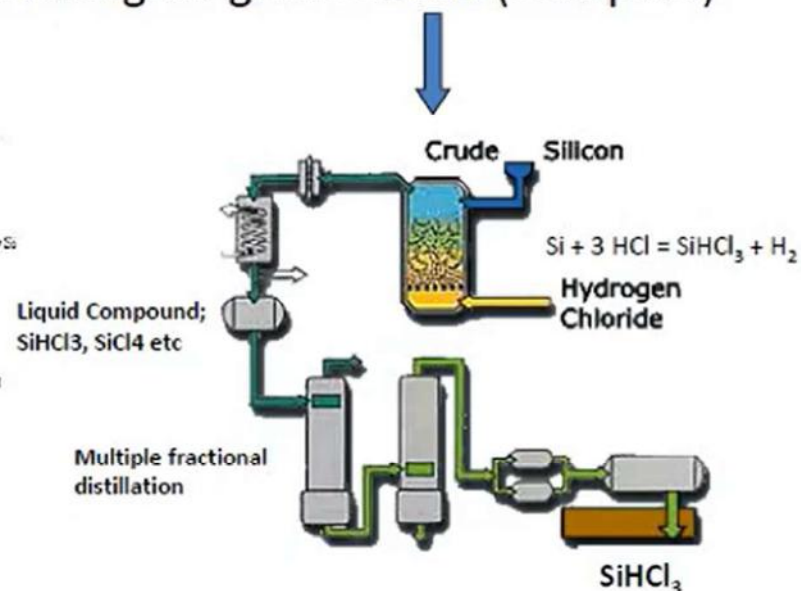


Semiconductor-grade poly Si

From the rods

(99.999999999 % pure)

Siemens reactor
Polysilicon rod



Fine MG Si particles are fudilized with HCl in presence of Cu catalyst and the emitted gases are passed through a condenser and the resulting liquid is subjected to multiple fractional distillation to produce SEG SiHCl3

Písečný vrch, Bečov, České středohoří, Sandy Hill near Bečov

Ditches/furrows after quartzite surface mining for Si semiconductor production, quarried until 1993.



Usually this procedure starts with sand (SiO_2), but:

In the 1960s, industrial mining of **quartzite** began, which covered the hill in the form of thousands of large, light-coloured boulders, creating a picturesque scenery visible from afar on the grassy hill. Quartzite mining, used in the production of semiconductors and laboratory glass, continued until 1993, when the quartzite on Sand Hill was virtually quarried.

Písečný vrch (Bečov, České středohoří)

*Quartzite (also „křemenec“, metaquartzite) is a metamorphosed rock of regional origin characterized by fine to medium grain size. It has the granoblastic texture of metamorphosed rocks. At first glance, quartzite can be mistaken for marble. On the other hand, sedimentary orthoquartzites are mature sediments with very well worked grain sizes ranging from 2 to 0.05 mm. They contain up to **95% quartz grains**. The colour ranges from white and grey to yellowish to reddish. The texture tends to be tooth-like to mosaic. The cement is usually quartz-like. Due to its composition, quartzite is a resistant rock. It may also contain impurities such as pyrite, mica, feldspar, magnetite, cinnabarite – **but during the formation, most of these undesirable impurities were washed away.***

Leading Quartzite Mining Regions for Semiconductors:

United States (North Carolina, Arkansas), Brazil, Norway, China, India



Photograph of a long Cz ingot taken at the SNEC Exhibition in 2018.

In 2019, the largest mono-Si silicon wafer manufacturer was Xi'an Longi Silicon Materials Corp.

<https://pv-manufacturing.org/silicon-production/cz-monocrystalline-silicon-production/>

World silicon production 2025:

- 10,000,000 tonnes of Si (mainly) for metallurgy. (3N = 99,9)*
- 330,000 tonnes of monocrystalline Si for PV. (6N)*
- 50,000 tonnes of monocrystalline Si for electronics. (9-11N)*

**Not only semiconductor
(mono/single)crystals are created**



i jiné:



Semiconductor (mono/single)crystals

and their structure – crystallin, electron, optical, ...

Defects of crystal lattice and their influence on band structure

Grains, microcrystals, inclusions *no in semiconductor material!*

Plane defects (grain boundaries, ...) *also not too much.*

Line defects (dislocations,...) *mainly harmful*

Point defects *majority applications are*
(intrinsic, impurities, dopants) *based on them, but they are*
also undesired nonradiative recombination
centres, electron diffraction, ...

All can be harmful or useful!

Why bulk momocrystals are not sufficient

Single crystals exist because atoms take positions that give a (local) minimum of energy = no defects? No.

Equation of **minimum of energy**:

$$\mu = \Delta G = \Delta H - T\Delta S$$

The chemical state of a given system is described by the chemical potential μ . For a given phase, it is defined as the increase in Gibbs free energy δG when one mole of a substance is added at constant temperature and pressure.

Chemical potential $\mu = \delta G / \delta n_{T,p}$

Gibbs free energy G

Enthalpy - H

Entropy - S

Temperature - T

Boltzman entropy $S = \log n$

(Mind you, this is not nano or quantum physic, it's a chapter in thermodynamics or statistical physics - more than a hundred years old.)

Name „**epitaxy**“ origins from Greek words „**epi-taxis**“, which means „arranged on" was introduced by L. Royer in 1928.

French mineralogist Louis Royer (1895-1980) in "Recherches expérimentales sur l'épitaxie ou orientation mutuelle de cristaux d'espèces différentes," Bulletin de la Société française de minéralogie, tome 51 (1928), p. 8.

It is monocrystalline growth on the (usually) monocrystalline substrate (wafer).

Growth is not (usually) epitaxial when lattice constant difference is bigger than 15%.

The tech community uses the term "growth" instead of the more accurate crystallization.

Explanation of importance and principles and comparison with other monocrystal preparation methods

Why so monstrous, expensive, dangerous and demanding technology equipment?

Principle of the epitaxial growth.

Atoms or molecules of the compound, which we would like to deposit on suitable substrate, are transported to its surface, which have to be atomically clean – cleaned from oxides and sorbents - and atomically smooth (only with atomic steps due to disorientation of the monocrystal substrate). On the surface the atoms will be physisorbed, and after that chemisorbed to the crystal structure. By this way atomic layers and all structure are grown.

Epitaxy

is the orderly growth/deposition at temperatures much below the melting point - it allows the preparation of

- **crystallographically more perfect and cleaner layers,**

but also, using different sources and slow growth preparation of:

- **hetero-structures** (heteroepitaxy) and also
- **nano-structures** preparation.

You mind, it is not vaporization or sputtering; it is preparing a single crystal on a single crystal!

Epitaxy technologies

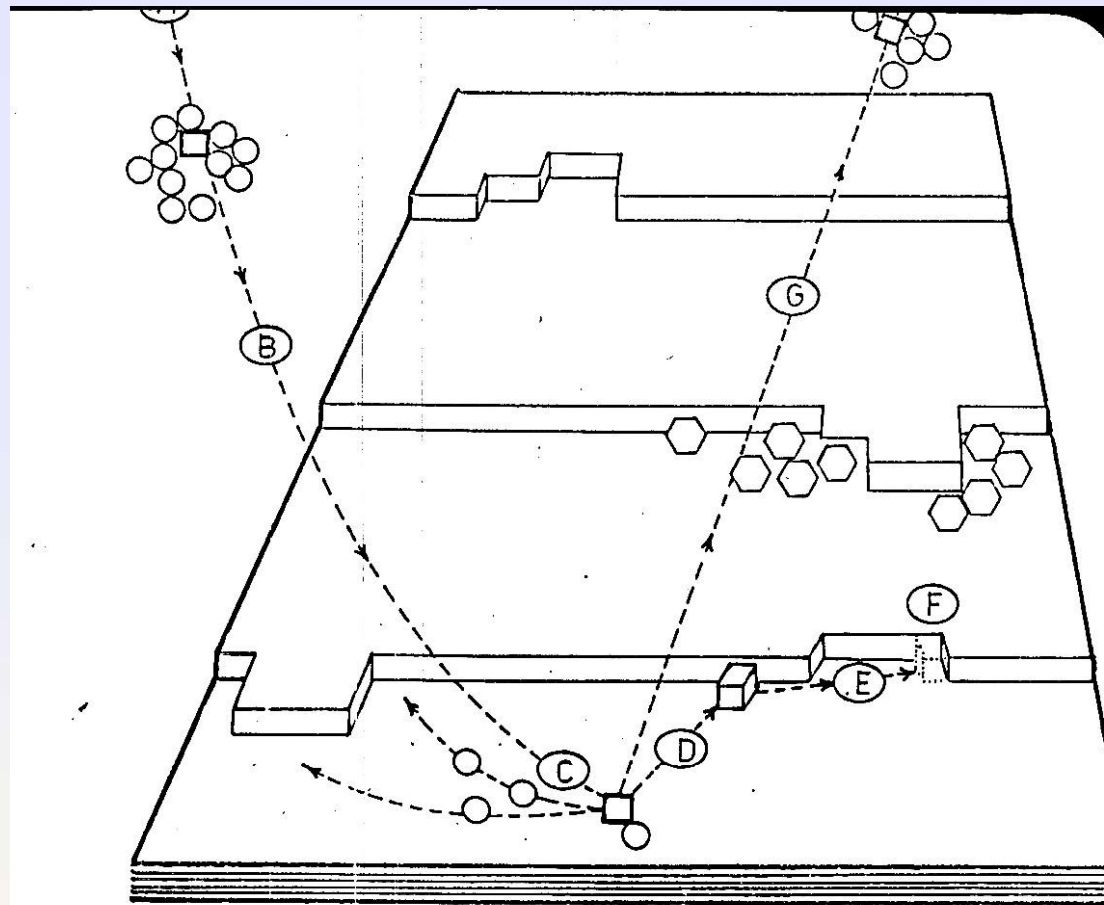
Epitaxial growth of monocrystal layers (on the bulk monocrystal wafers = substrates) is realised at lower temperature than growth of monocrystals from melted material, which is substantial for:

Influence of the **entropy** (native **defects**), lower solubility of the **unintentional impurities** into the prepared layers.

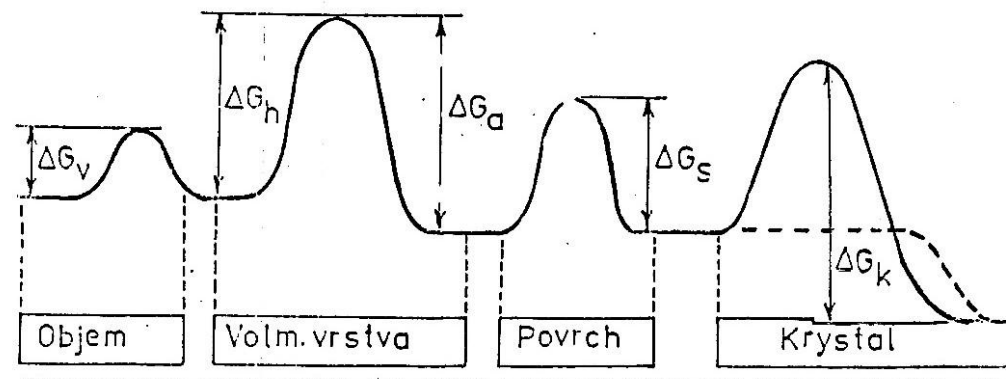
Nevertheless, this lower temperature (usually 500 - 800°C) is high enough for creation of atomically **clean and flat surface** and enable atoms jump over the energy barriers for **physisorption** and **chemisorption**.

Principle of epitaxial growth

(This is MOVPE, but MBE is similar, but simpler.)



Obr. 17. Schéma elementárních růstových dějů u povrchu tvořící se krystalové plochy.



Obr. 18. Energetické schéma přestupu růstové jednotky z objemu roztoku do krystalické mřížky.

Types of epitaxial growths

explanation of used abbreviations:

SPE (Solid Phase Epitaxy)

LPE (Liquid Phase Epitaxy)

LPEE (Liquid Phase Electroepitaxy)

VPE (Vapour (Vapor) Phase Epitaxy)

CVD (Chemical Vapour Deposition)

PVD (Physical Vapour Deposition)

Steps of the Solid State Epitaxy:

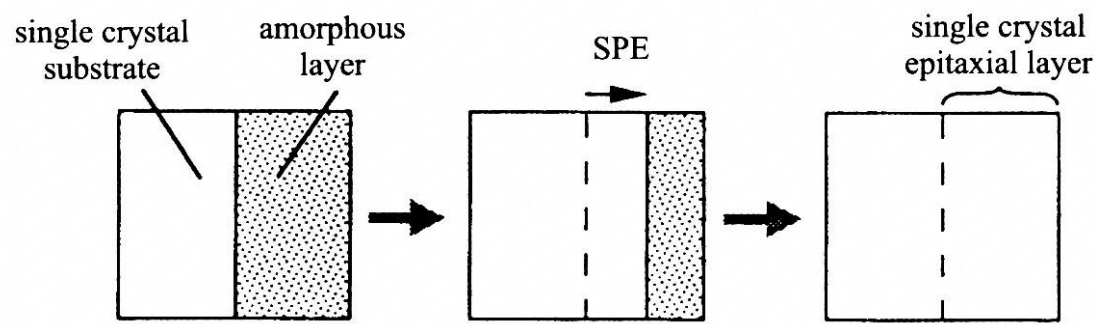


Fig. 4.1. Solid phase epitaxy of an amorphous thin layer on a single crystal substrate (taken from [4.2])

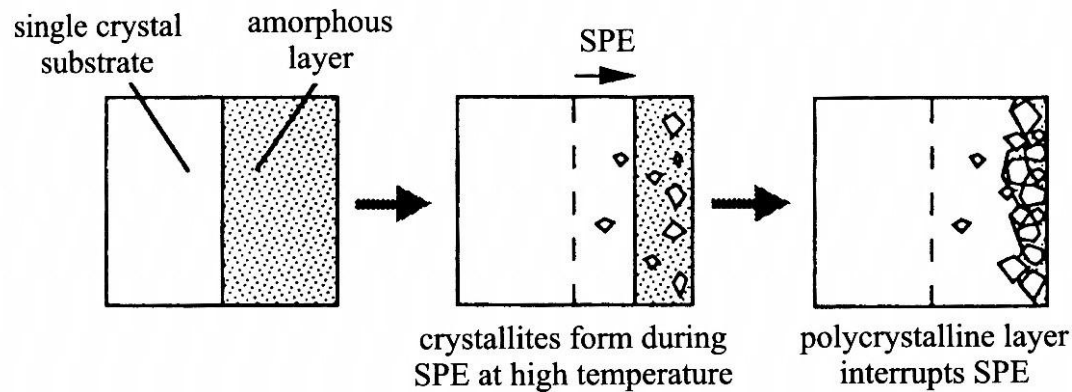


Fig. 4.2. Random nucleation and growth can interfere with SPE at high temper-

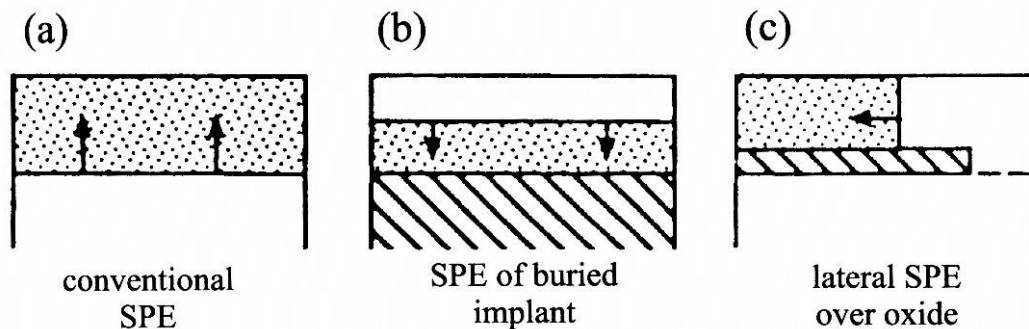


Fig. 4.3. Typical sample configurations employed for studies of solid phase epitaxy. (a) Amorphous film in direct contact with crystalline substrate – SPE growth toward surface; (b) buried amorphous layer formed by channeled ion implantation – SPE growth downward toward heterointerface; (c) amorphous layer deposited on patterned substrate – vertical SPE in seeded region followed by lateral SPE over insulator (taken from [4.2])

Liquid Phase Epitaxy - LPE

The most important epitaxial method during seventies and eighties of the last century.

Still using in the industry (cheap LEDs and when tens of microns are necessary).

Important for thermodynamical equilibrium grown structures.

Principle of the LPE:

Saturated solution of suitable materials (e.g. As in Ga) is cooling (or the liquid part is evaporated – this is not realistic for Ga (it has low vapour pressure)) and thus starts to be oversaturated, thus As is going out from solution and created GaAs on the reasonable bulk or epitaxial substrate.

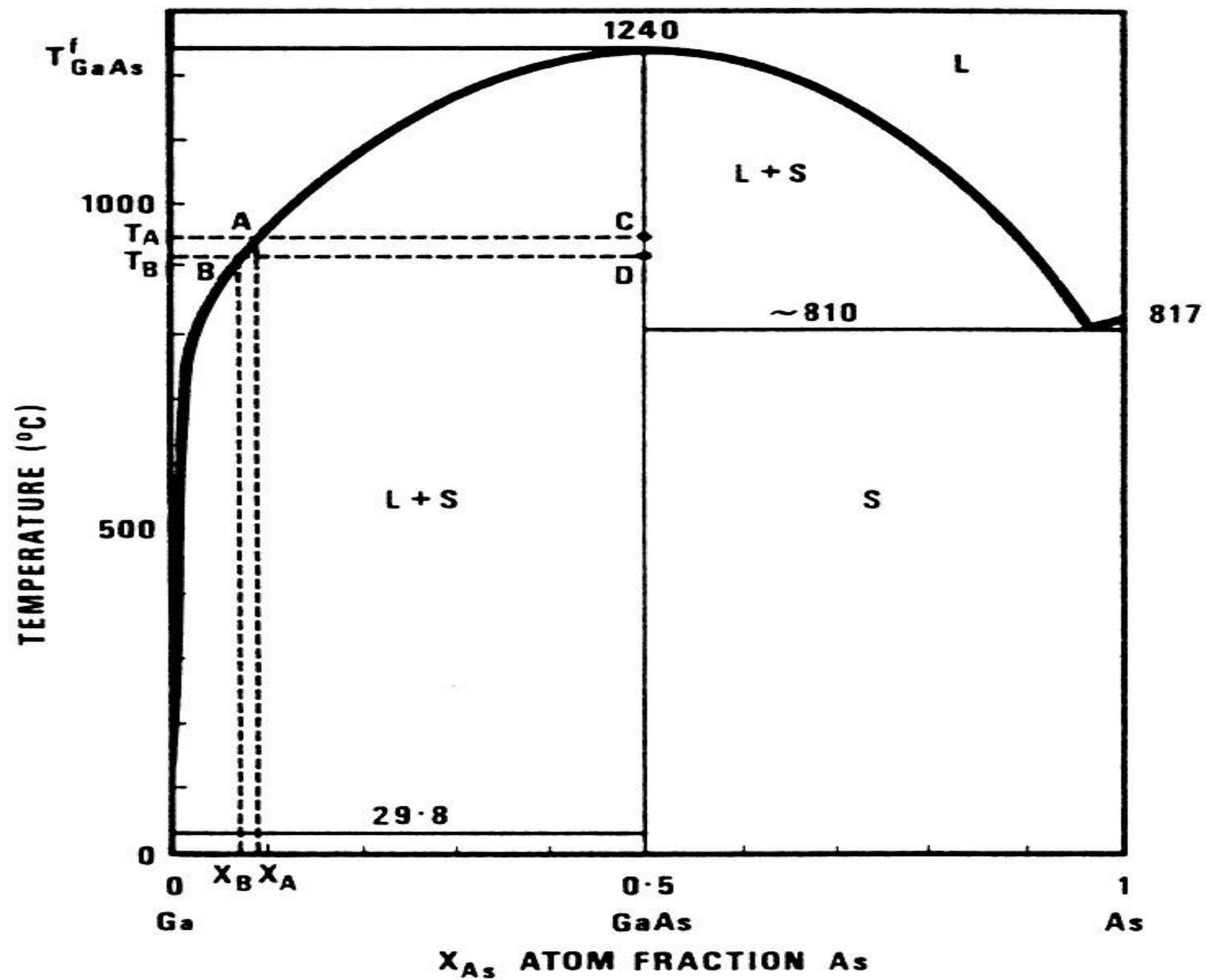


Figure 1.1 Liquid–solid phase diagram for the binary Ga–As system (after Hall [3])

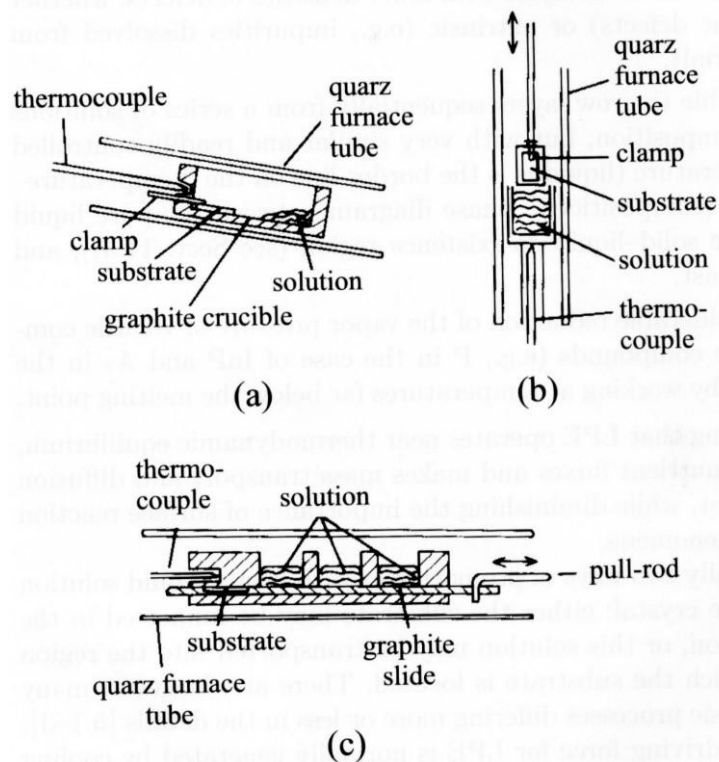


Fig. 5.1. Schematic illustrations of the basic LPE growth systems: (a) tipping furnace system [5.4], (b) vertical dipping system [5.5], (c) multicompartment slider boat system [5.6] (taken from [5.3])

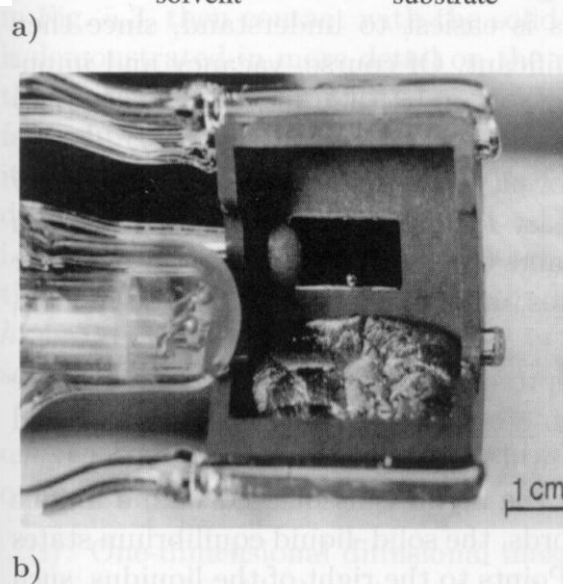
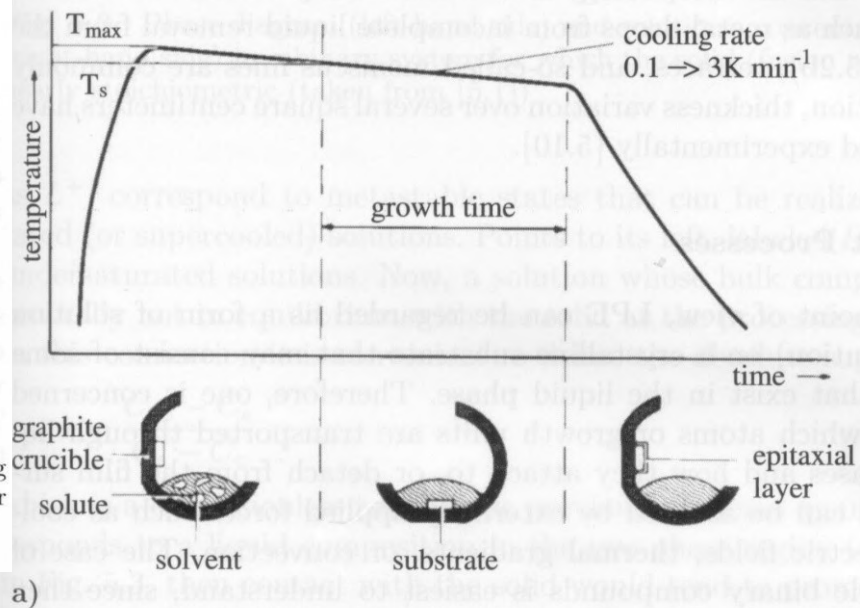


Fig. 5.2. (a) Temperature changes during one growth cycle in a tipping furnace (higher part); the substrate is exposed to the solution at temperature T_s . A schematic illustration of the rotated tipping crucible positions in the cycle is shown in the lower part. (b) Photograph of the rotated tipping crucible, supported by elastic quartz rods in the position when layer growth was terminated. A small droplet of solution residue is visible at the lower edge of the substrate (taken from [5.3])

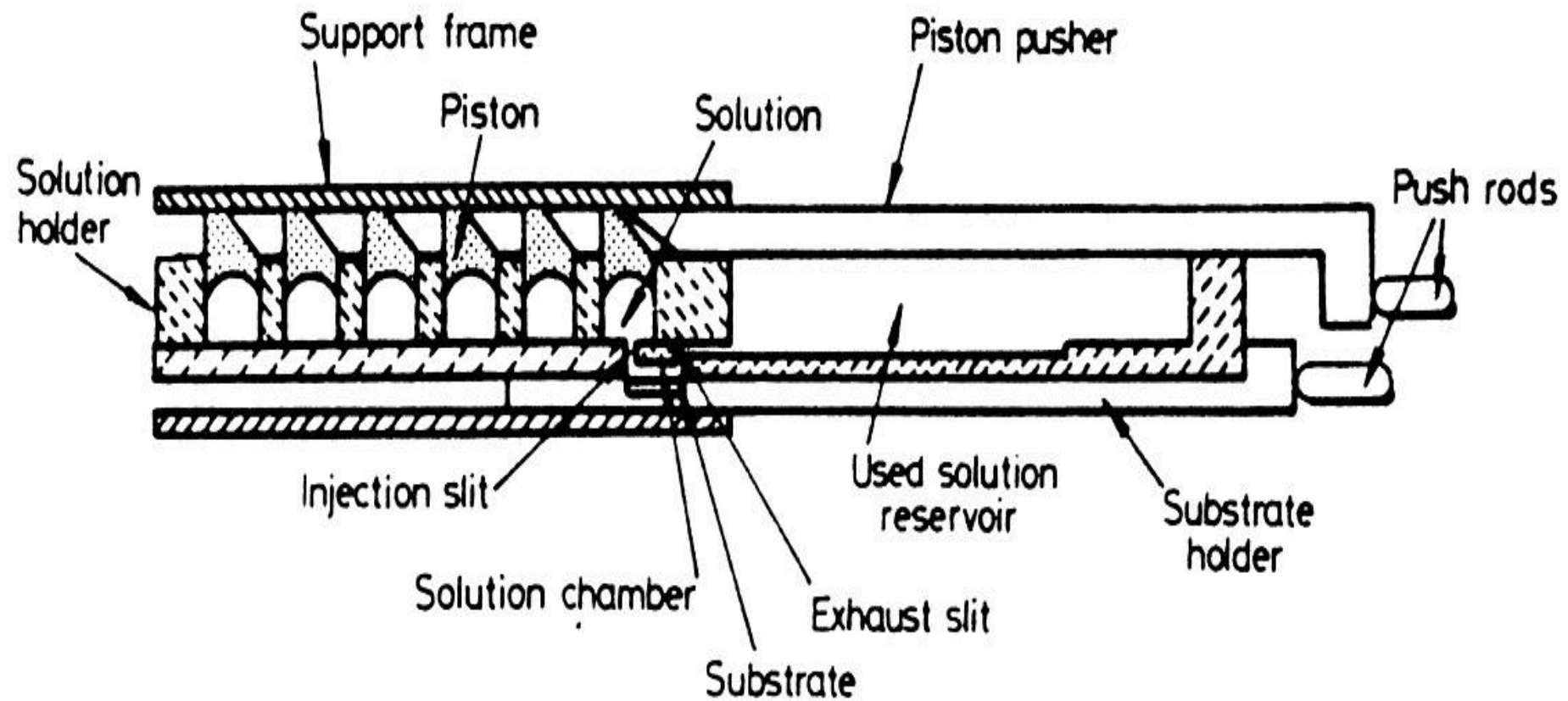


Figure 2.8 'Wipingless' horizontal sliding boat system (after Hori-koshi [72]).

LPE

Thin layers under 100 nm are possible by LPE, but contact of substrate and solution have to be shorter than ms. Problems with reproducibility homogeneity etc.

Liquid Electroepitaxy

Modification of LPE, which is controlled by current, which flow through boundary solution-substrate. Peltier effect and electro migration are created.

It is used for several mm thick homogenous (better than 1%) ternary layers. E.g.: InGaAs on InP or GaAs; AlGaSb on GaSb, ...

Vapour Phase Epitaxy - VPE

The most important VPE growths are

Molecular Beam Epitaxy -

MBE (Molecular beam epitaxy)

SSMBE = Solid Source MBE,

CBE = Chemical Beam Epitaxy,

GSMBE = Gas Source MBE (Hydride Source MOMBE or Metal Organic MBE),

UHV ALE = Ultra High Vacuum Atomic Layer Epitaxy

Vapour Phase Epitaxy from organometallic compounds and hydrides

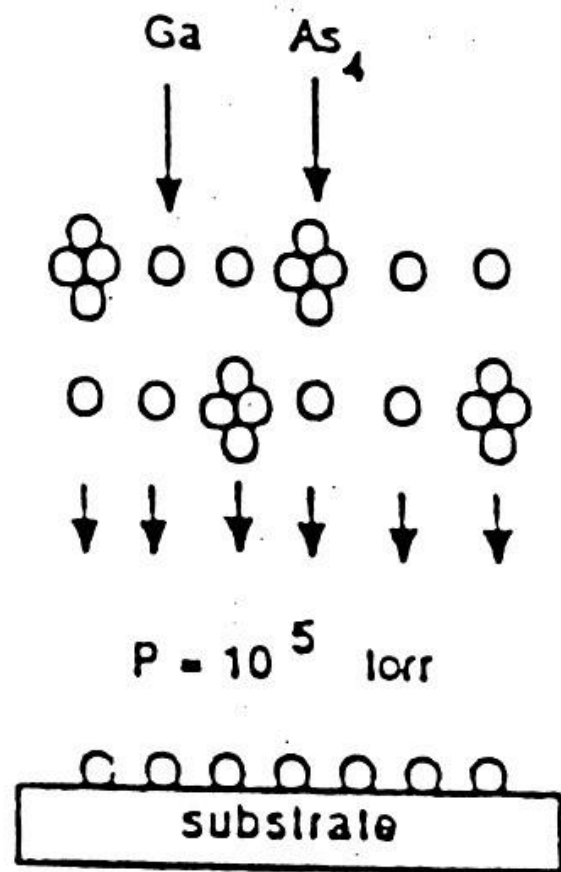
MOVPE (MetalOrganic Vapour Phase Epitaxy)

MOCVD (MetalOrganic Chemical Vapour Deposition) – *it is synonym.*

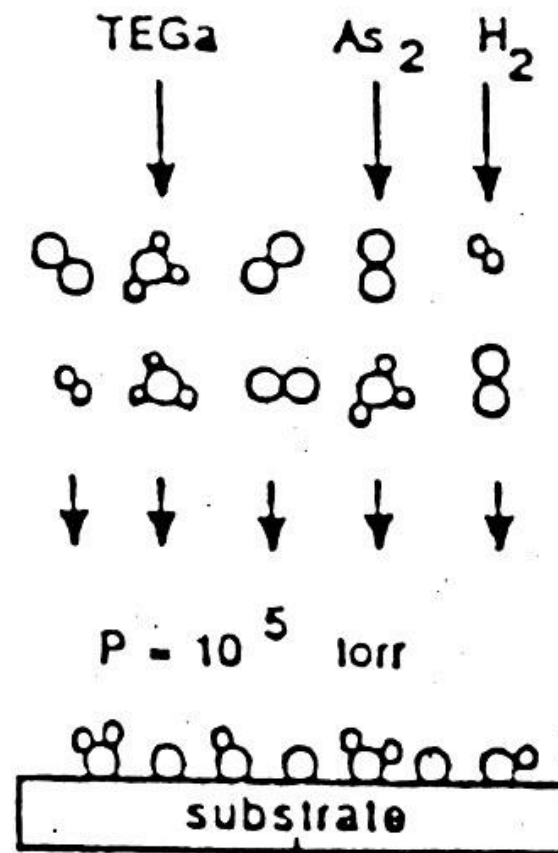
Photo-MOVPE (Nonthermal, light activated)

Plasma-MOVPE (Nonthermal, plasma activated)

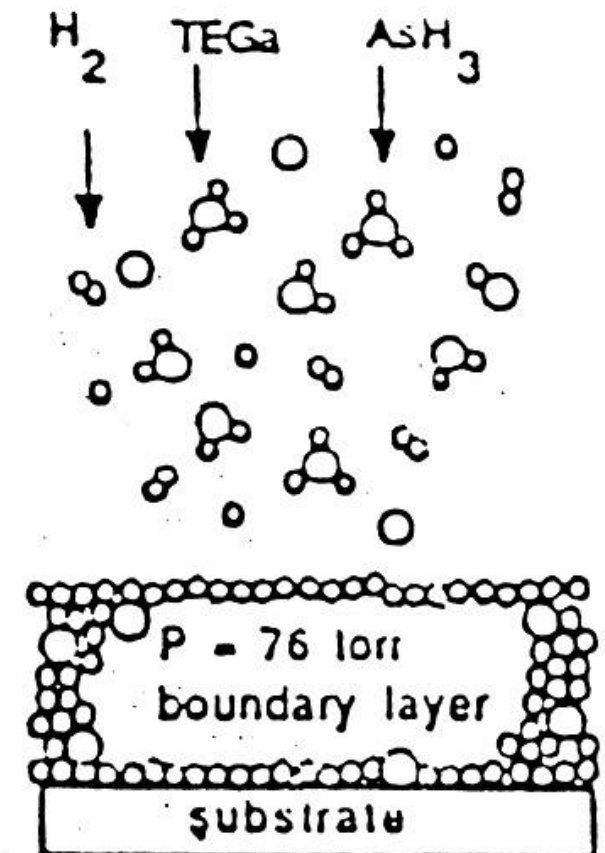
MBE



CBE

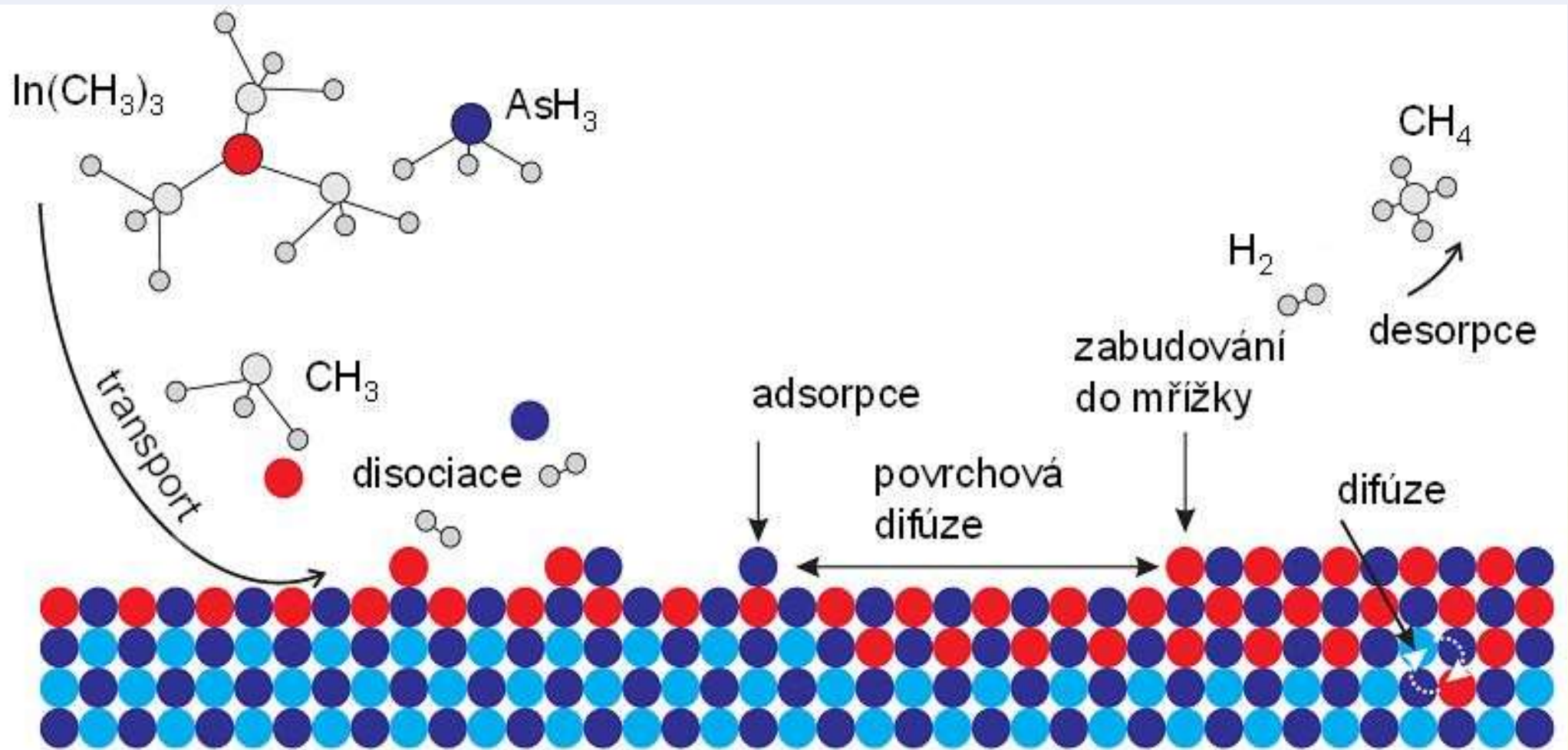


MOCVD



Principle of epitaxial growth

(This is MOVPE, but MBE is similar, simpler)



Vapour phase Epitaxy - VPE

Today and at least next ten years it will be the most important semiconductor preparation technology not only for industry but also for research!

In principle it is possible to describe it as physical (**PVD** - Physical Vapour Deposition) and chemical (**CVD** - Chemical Vapour Deposition), according the transport of material from the source to the substrate.

At first –PVD – it is evaporation of atoms or molecules (using heat, sputtering, ablation, discharge, etc.) without their chemical changes.

At second – CVD – it is transport of volatile chemical compounds (precursors) using some transport gases (H_2 , N_2) to the heated substrate near of its surface their are decomposed.

Epitaxial growth on atomically clean and flat surface of usually monocrystal substrate (wafer) is then similar. Also parameters of prepared layers are similar.

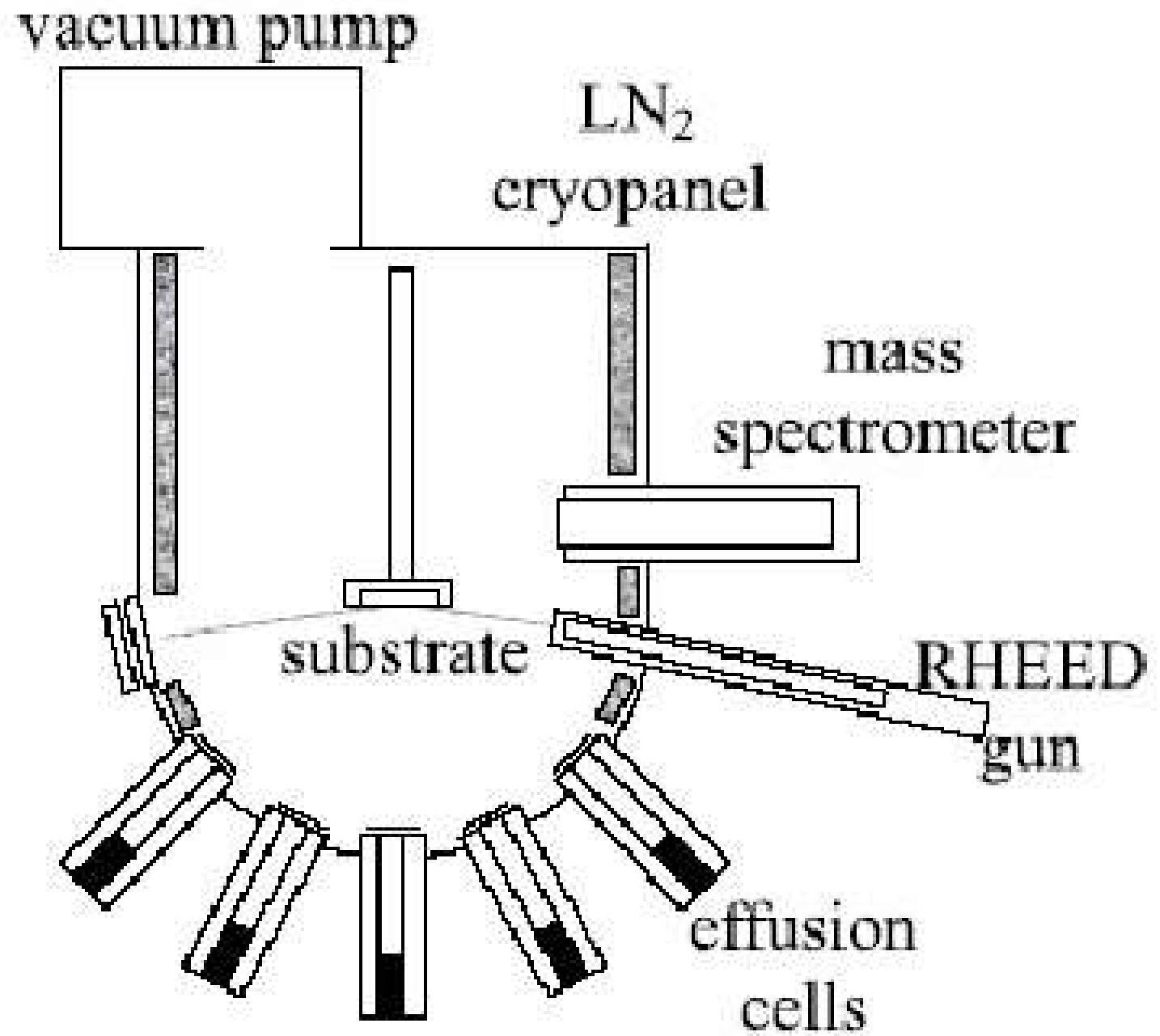
In both cases we need extreme „semiconductor“ cleanness – vacuum (10^{-10} torr) or transport gas H_2 či N_2 (at the level of fractions of ppb).

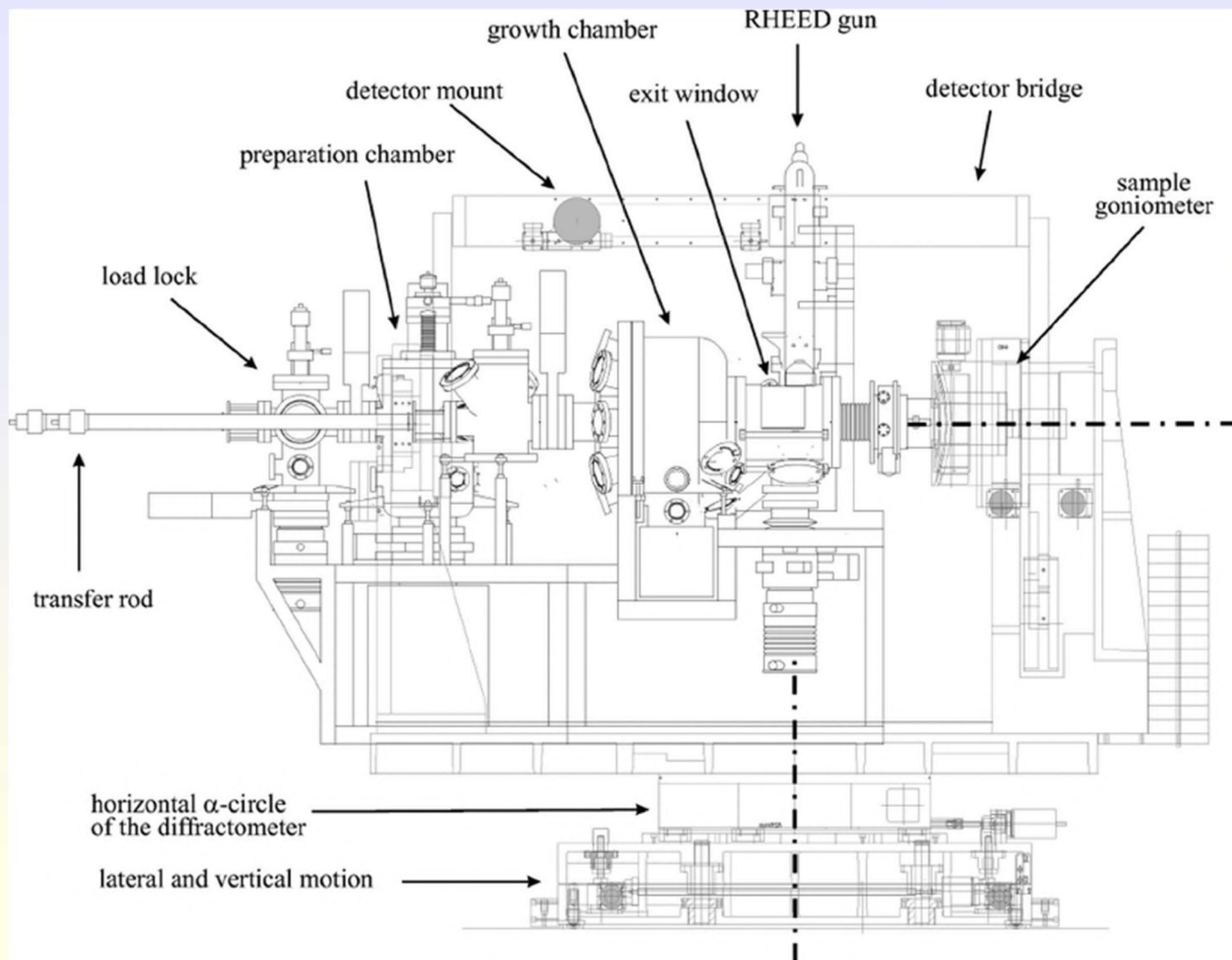
Molecular Beam Epitaxy (MBE)

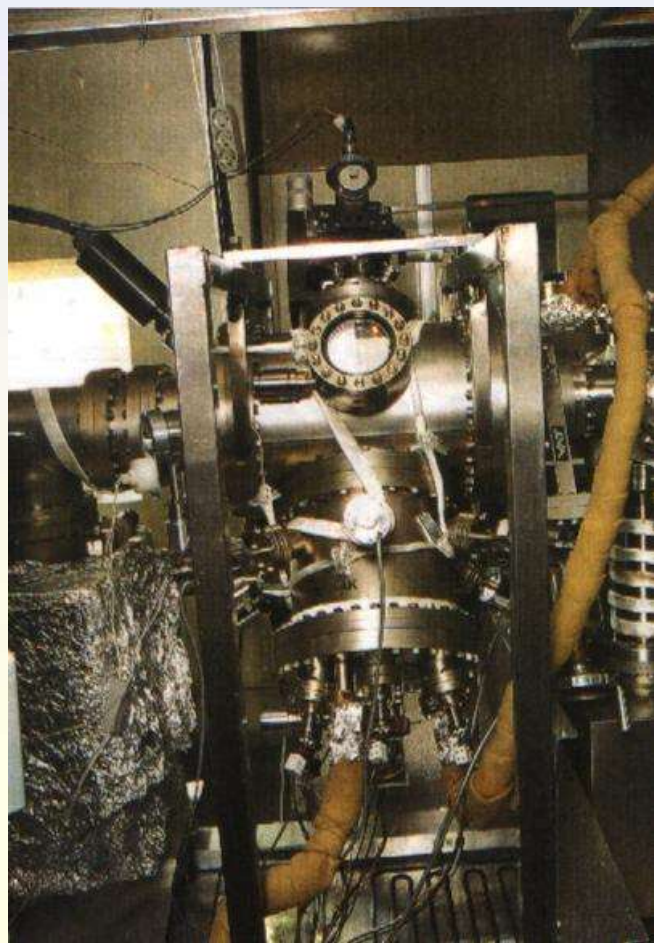
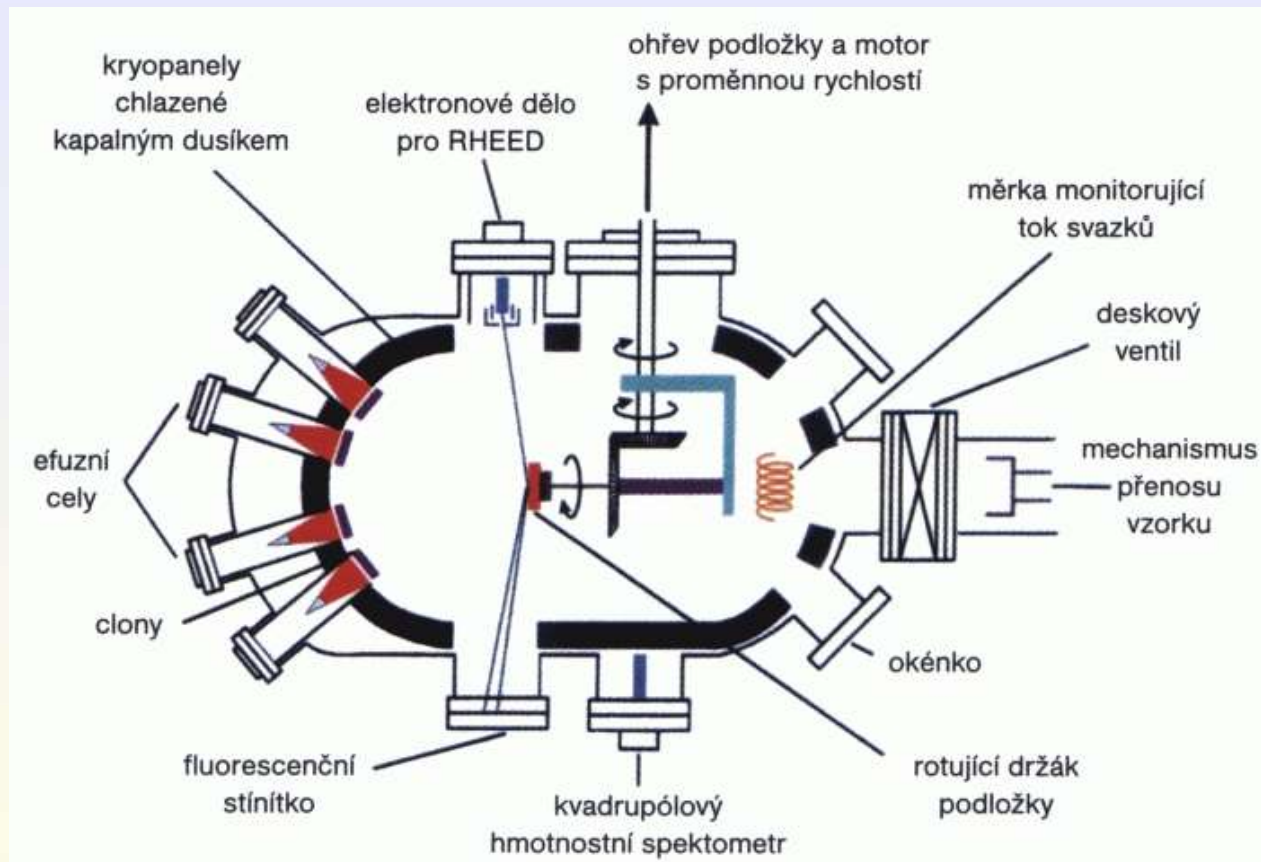
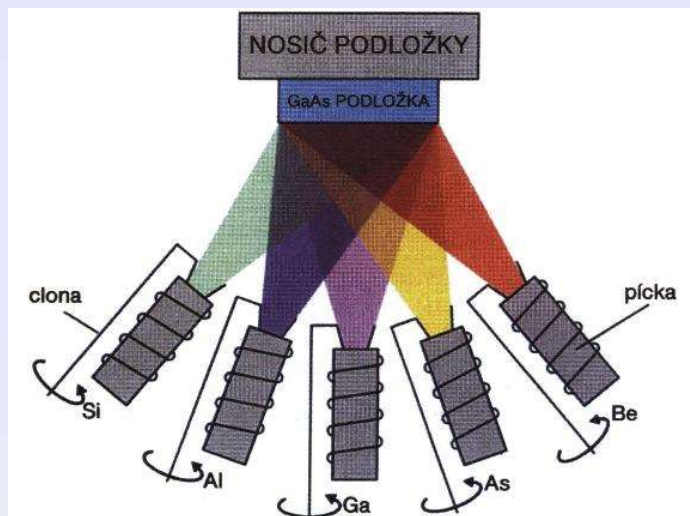
*Explanation of basic principles of technology.
MBE technology parameters, properties and
reasons of its limits.*

*This chapter is also fundamental. Description and
scheme of MBE or MOVPE will be in each set of
questions.*

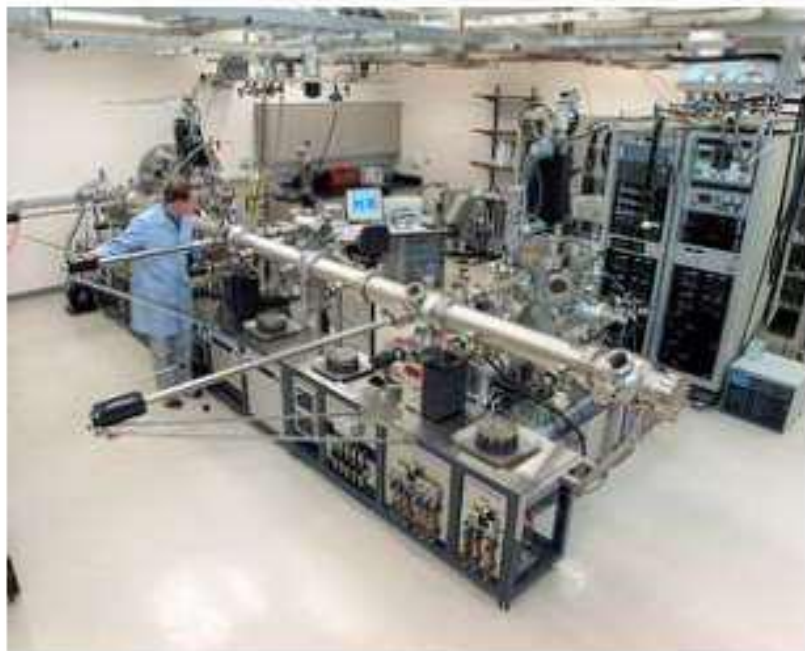
**Scheme of a
typical growth
chamber in
MBE system.**





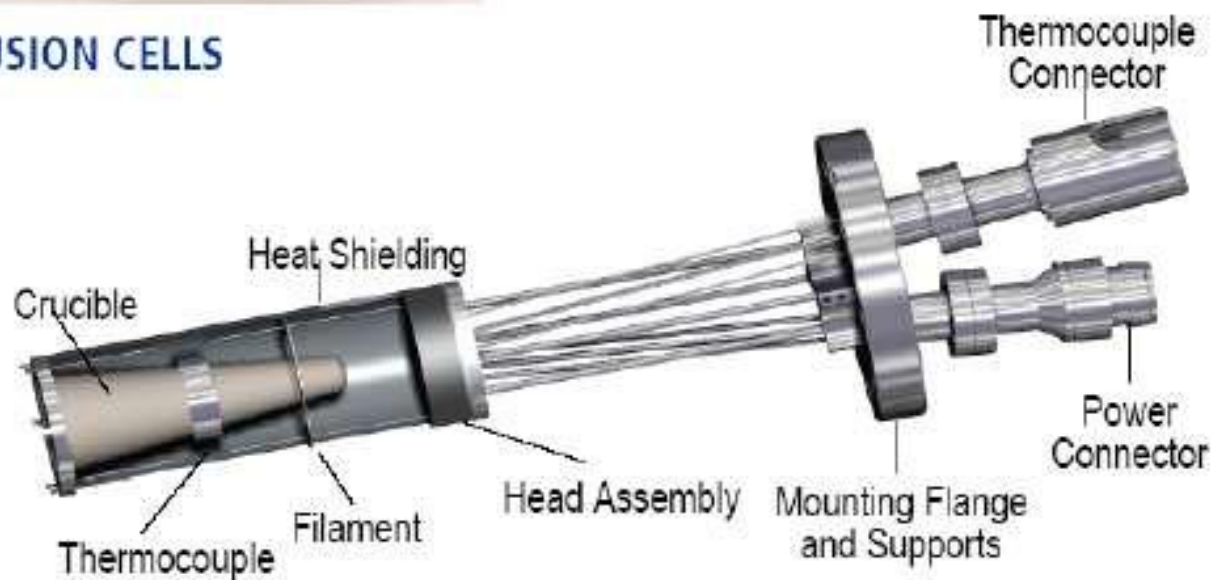


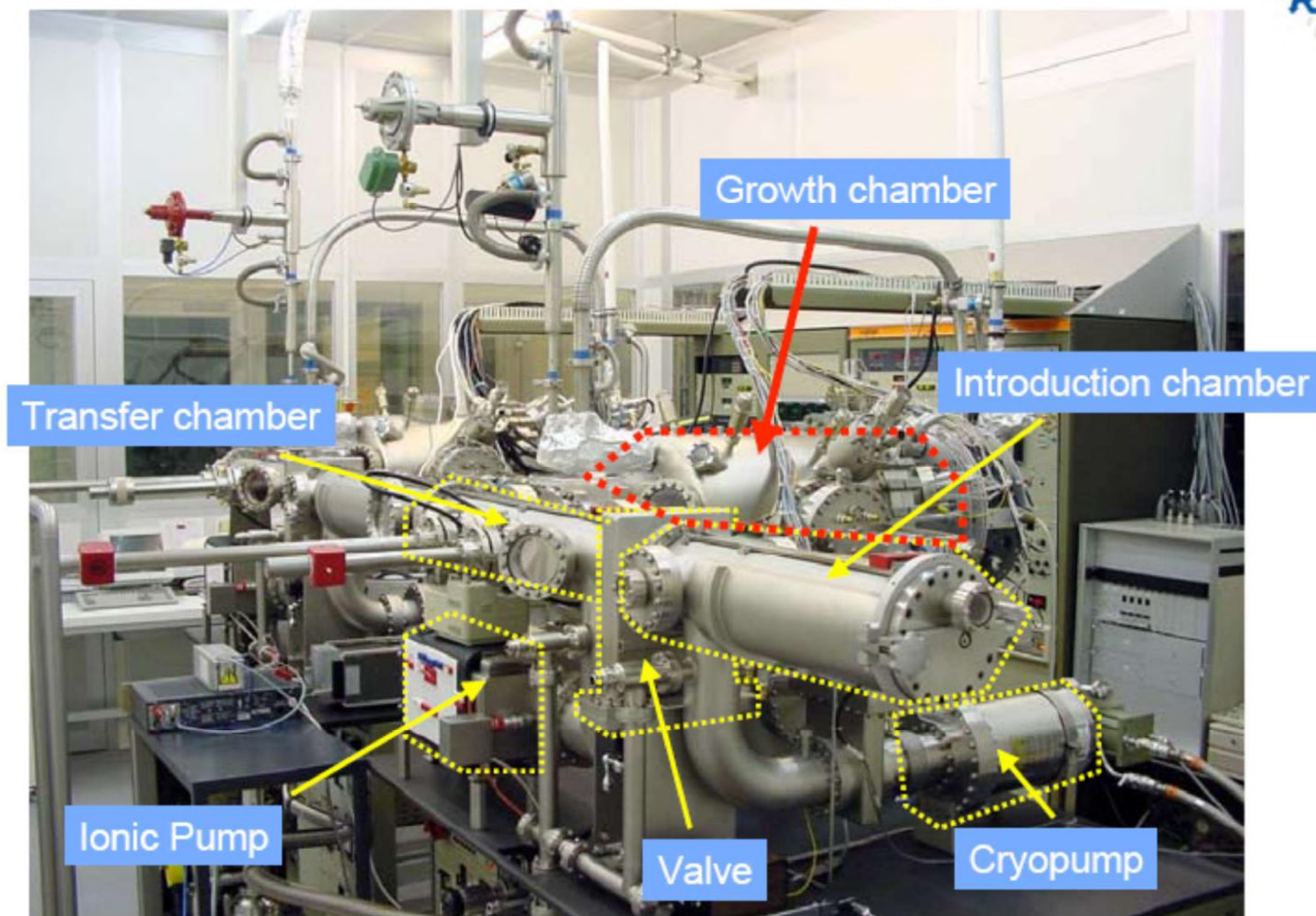
Molecular beam Epitaxy (MBE)

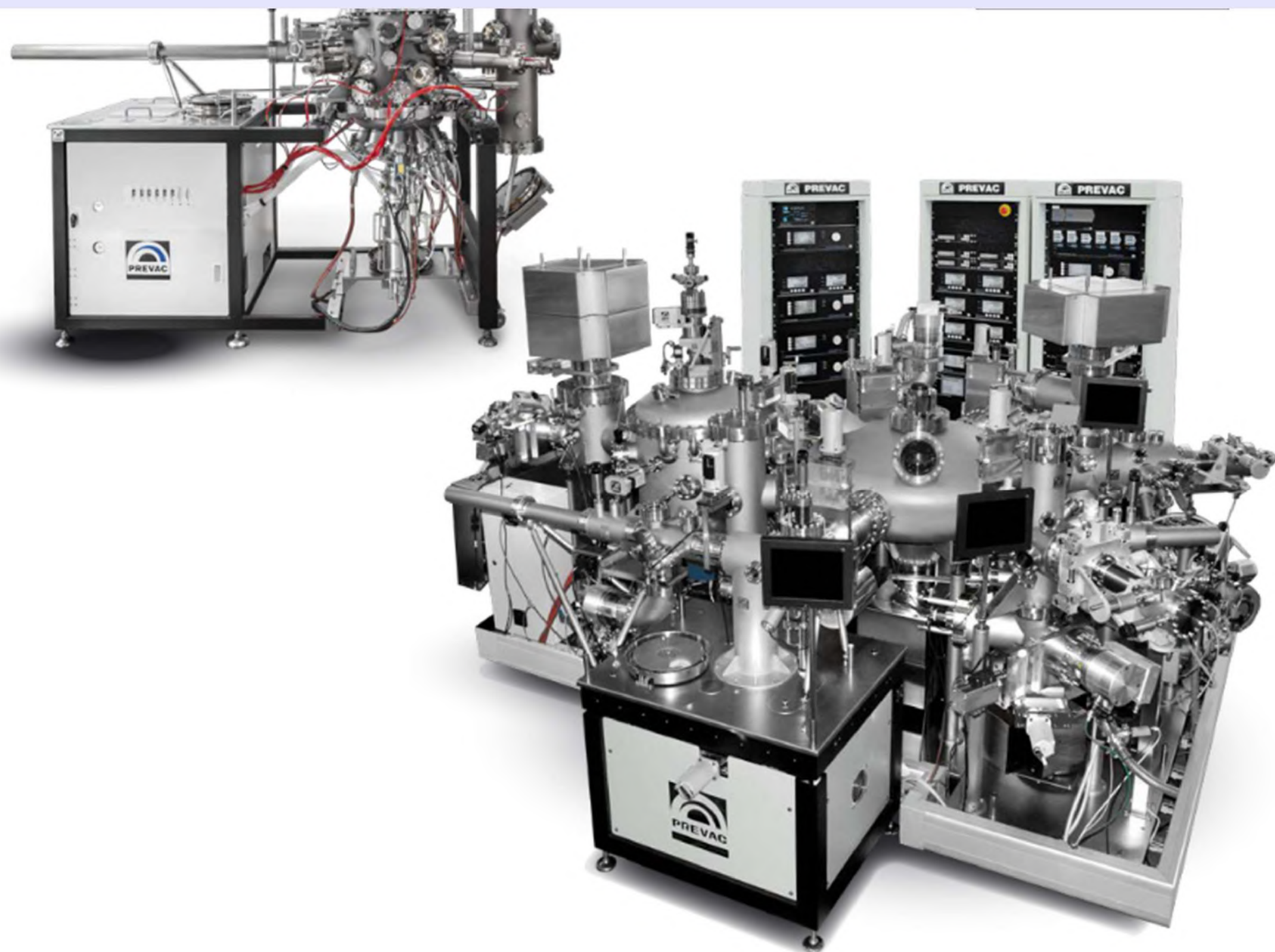


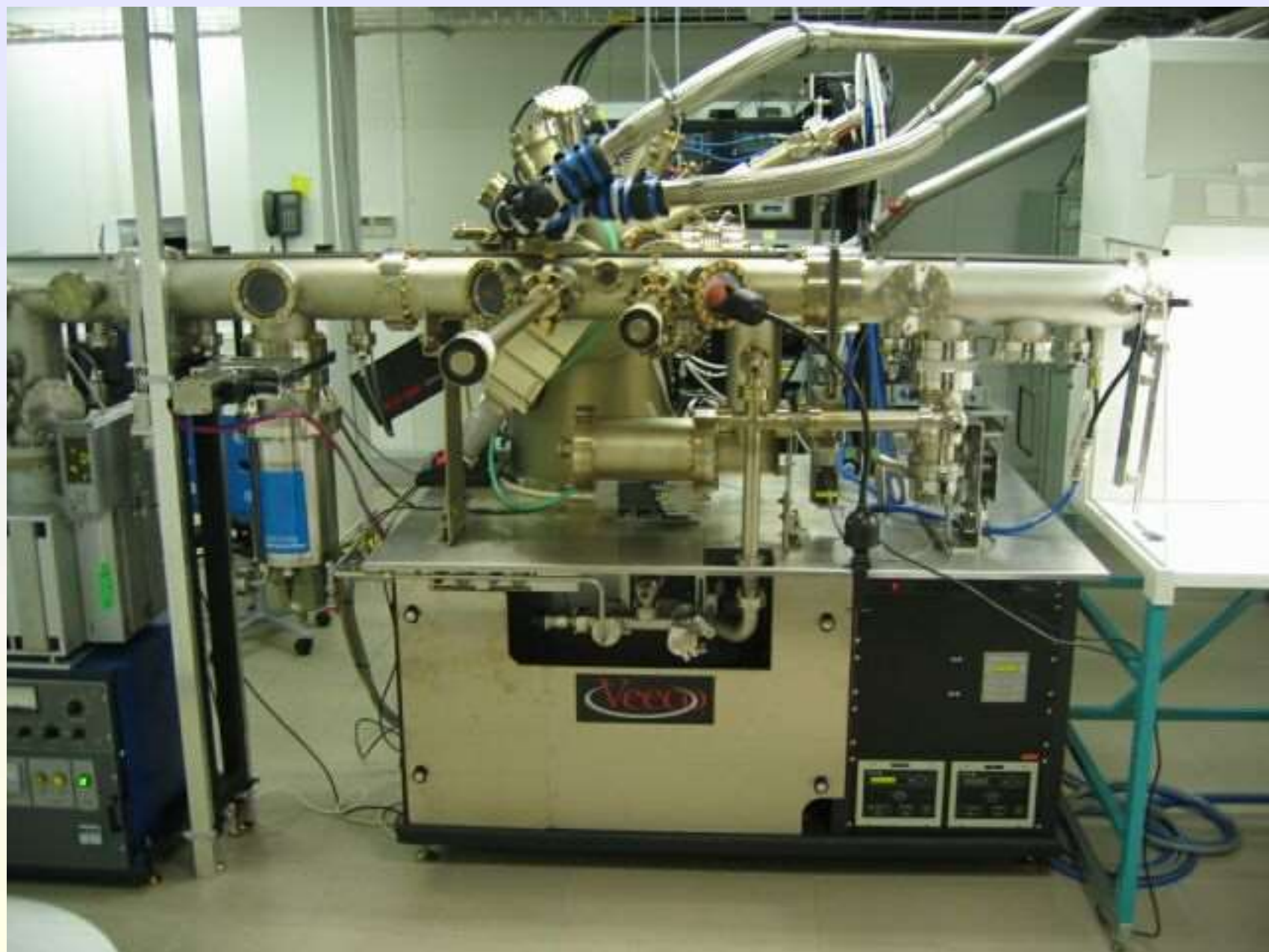
EFFUSION CELLS

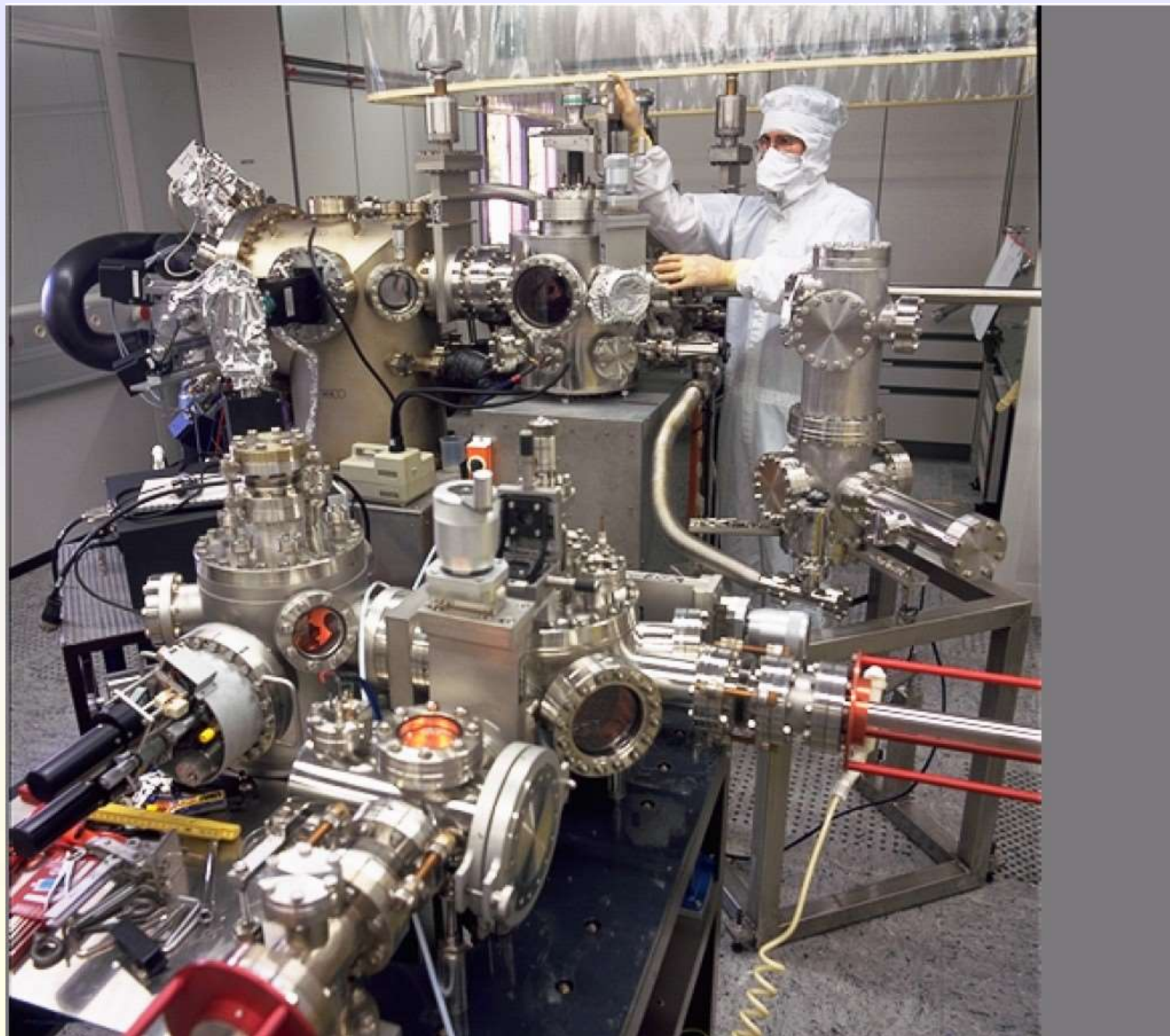
Vacuum Kf Metal Flexible Bellow











40 years old Riber MBE machine

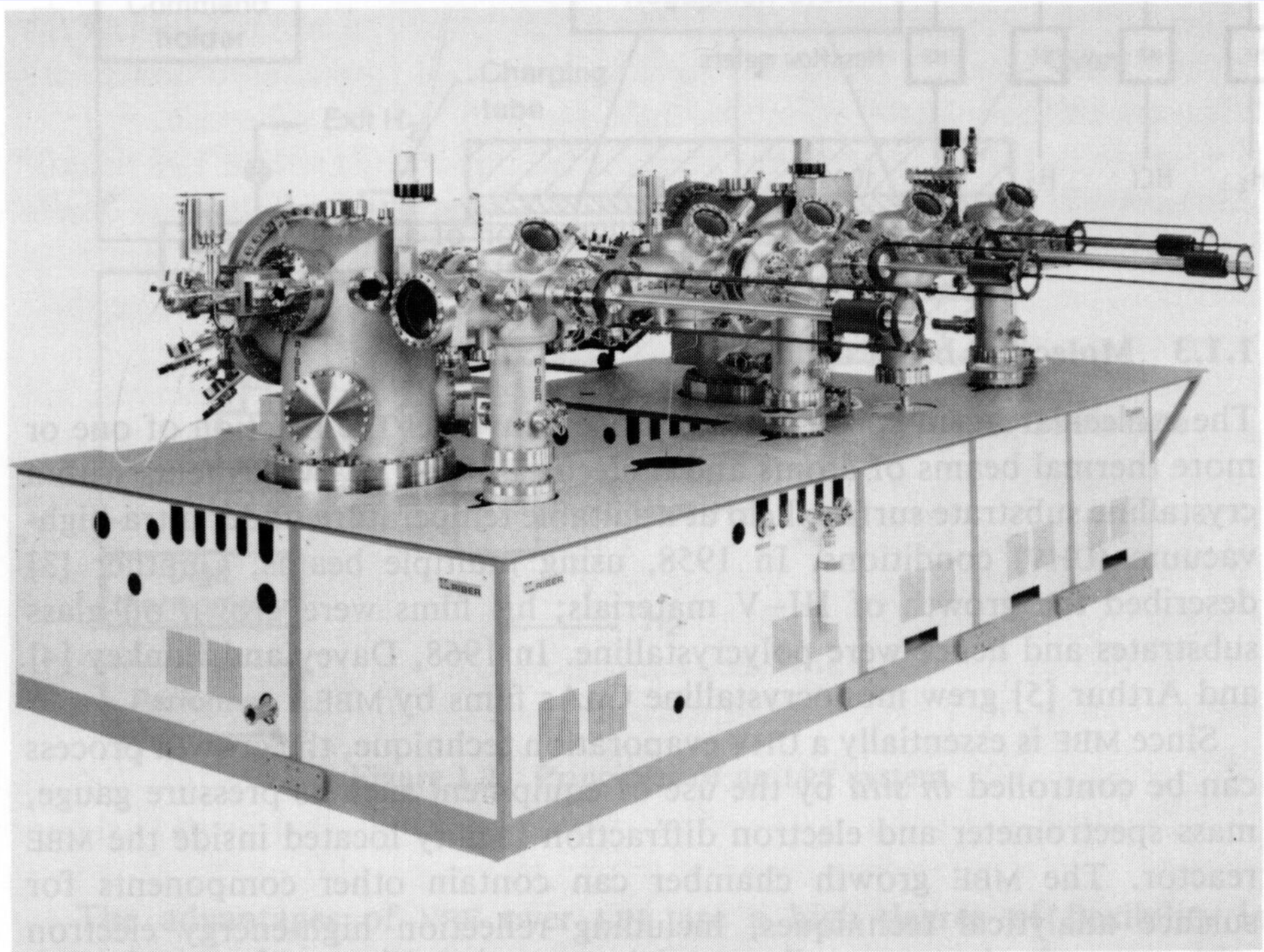
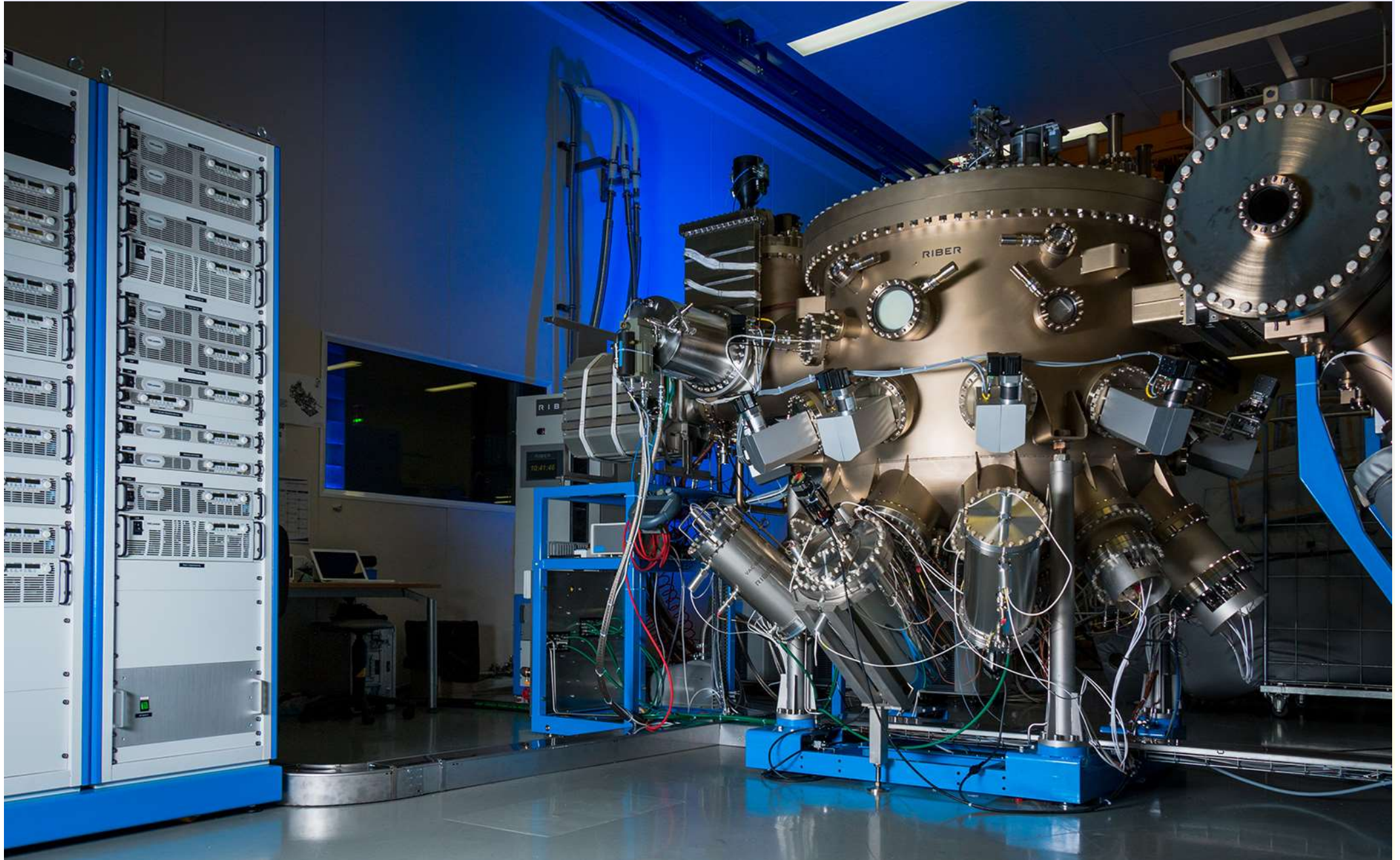


Figure 1.4 Photograph of an MBE reactor.

Riber MBE 6000 - Multi 3", 4", 6", 200mm



Molecular beam epitaxy

Principle of method:

The **substrate(s) is heated** in a **high vacuum** (about 10^{-10} torr) to such a high temperature that the **native oxides and surface impurities are desorbed** and the **substrate surface is atomically clean**. The preheated Knudsen (effusion) cells are then opened (by shutters/ screens) and the atoms or molecules fly tens of centimetres through the growth chamber onto the substrate without collisions (*they also settled non epitaxially near the substrate*). The atoms of the future epitaxial layer sit on the surface of the single crystal (**physisorption**) and move to the corresponding crystallographic sites where they are bounded (**chemisorption**). This is how the epitaxial layer is formed.

Substrate is monocrystalline semiconductor wafer with diameter from 2 to 8 inches, which is 300 – 500 μm thick.

Questions?

Expected questions:

Why this substrate size? How input and take out substrate? What is maximal size of substrate(s)?

The substrate(s) is heated in a high vacuum (about 10^{-10} torr) to such a high temperature that the native oxides and surface impurities are desorbed and the substrate surface is atomically clean. The preheated Knudsen (effusion) cells are then opened (by shutters/ screens) and the atoms or molecules fly tens of centimetres through the growth chamber onto the substrate without collisions (they also settled non epitaxially near the substrate). The atoms of the future epitaxial layer sit on the surface of the single crystal (physisorption) and move to the corresponding crystallographic sites where they are bounded (chemisorption). This is how the epitaxial layer is formed.

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How open and close effusion cells? Influence on vacuum?

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Expected questions:

Why this substrate size? How input and take out substrate? What is maximal size of substrate(s)?

Why substrate rotates?

Why so high vacuum is necessary?

How high substrate temperature is necessary?

How recharge, heat, open and close effusion cells? Influence on vacuum?

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Are there difference between atomic and molecular beam?

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Are there difference between atomic and molecular beam?

How is MBE influence by growth chamber size?

The substrate(s) is heated in a high vacuum (about 10^{-10} torr) to such a high temperature that the native oxides and surface impurities are desorbed and the substrate surface is atomically clean. The preheated Knudsen (effusion) cells are then opened (by shutters/ screens) and the atoms or molecules fly tens of centimetres through the growth chamber onto the substrate without collisions (they also settled non epitaxially near the substrate). The atoms of the future epitaxial layer sit on the surface of the single crystal (physisorption) and move to the corresponding crystallographic sites where they are bounded (chemisorption). This is how the epitaxial layer is formed.

Expected questions:

Why this substrate size? How input and take out substrate? What is maximal size of substrate(s)?

Why substrate rotates?

Why so high vacuum is necessary?

How high substrate temperature is necessary?

How recharge, heat, open and close effusion cells? Influence on vacuum?

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In-situ diagnostics?

In-situ characterisation

The most important for nanotechnology are **MBE and MOVPE**
Molecular beam epitaxy - MBE

MBE is vacuum (exactly “high vacuum”) method, so we can use majority of the electron characterisation techniques.

Scheme of in-situ measuring technique
RHEED, picture on the screen is created by
electron reflected by the crystal surface.
Dependence of signal on the growth time is
shown.

“Size” of electrons (probability of their position in the space = de Broglie wavelength) is comparable with the crystal (= with size of atoms).

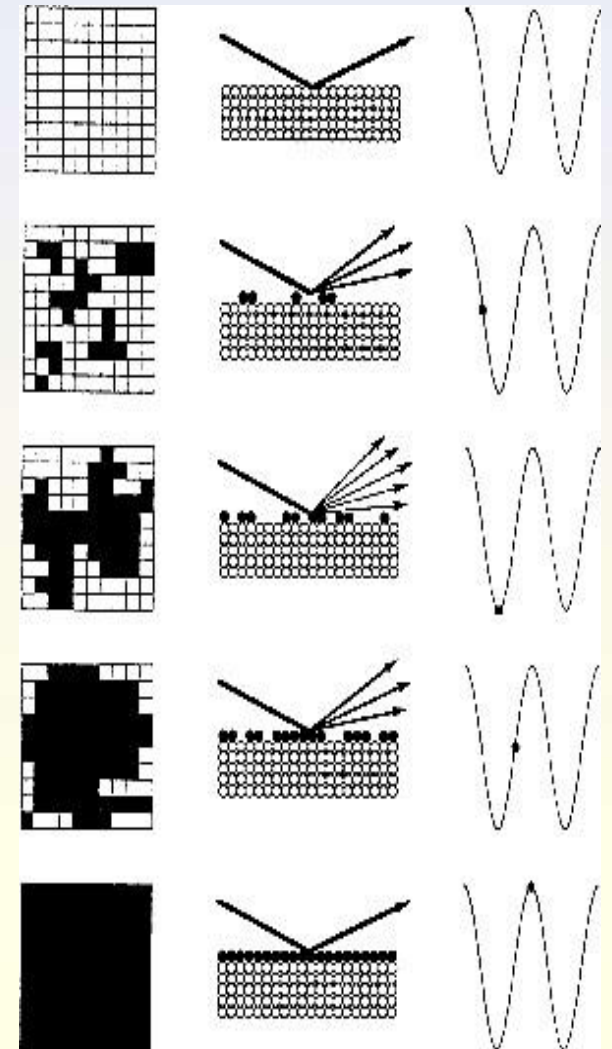
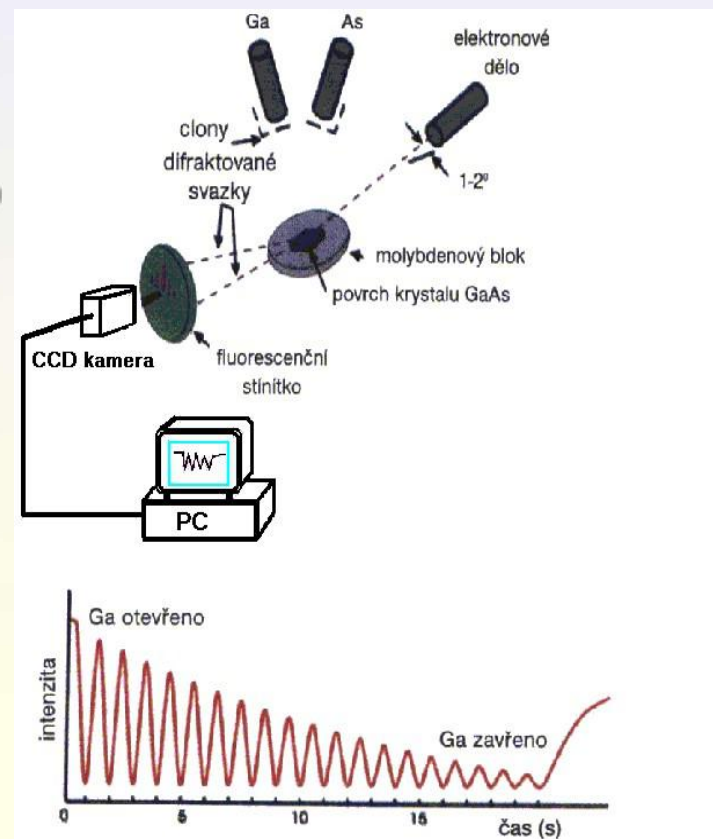
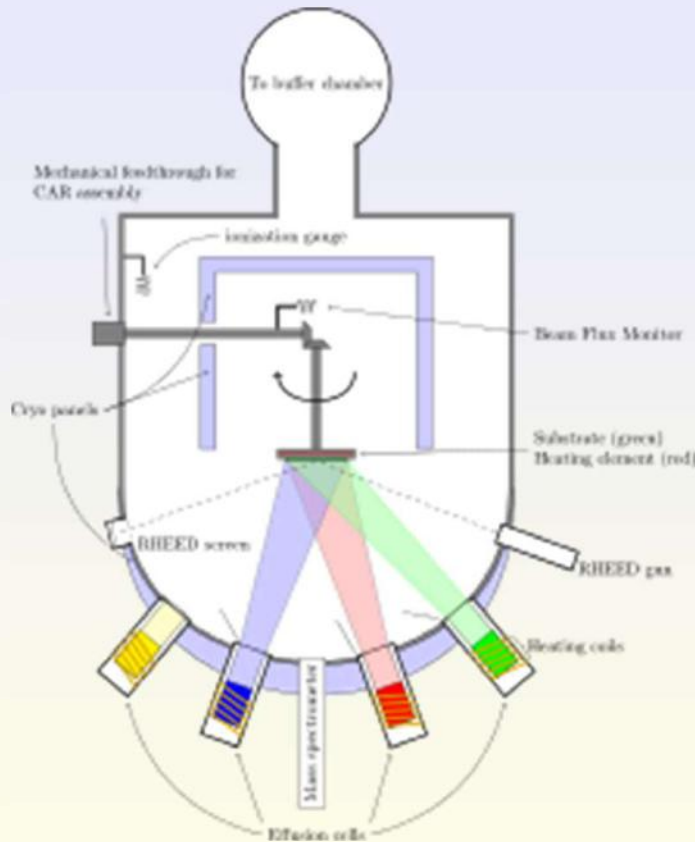
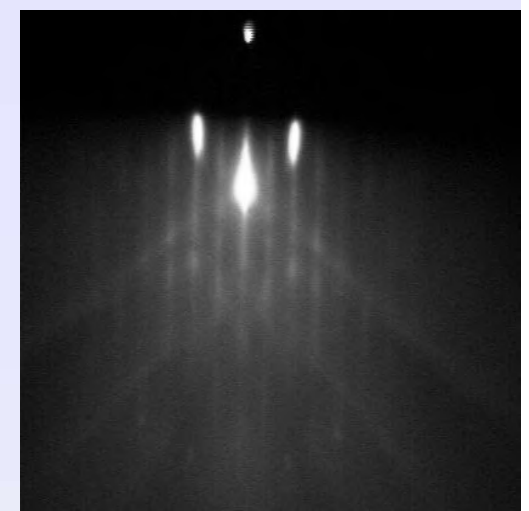
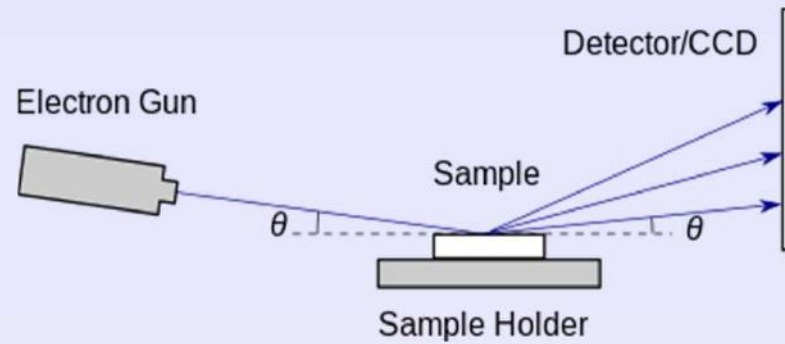
Advanced characterization technologies, such as X-ray diffraction (XRD), Raman spectroscopy (RS), and photoelectron spectroscopy (PES), have been incorporated into MBE to gain insight into material growth mechanisms and optimizing growth parameters.

In-situ **RHEED (Reflection High-Energy Electron Diffraction)** measurements provide real-time information about the surface structure and morphology of materials, particularly during growth processes like thin film deposition. This technique allows researchers to monitor the growth process, identify crystal structure and epitaxy, and understand growth mechanisms, all while the sample is undergoing changes.

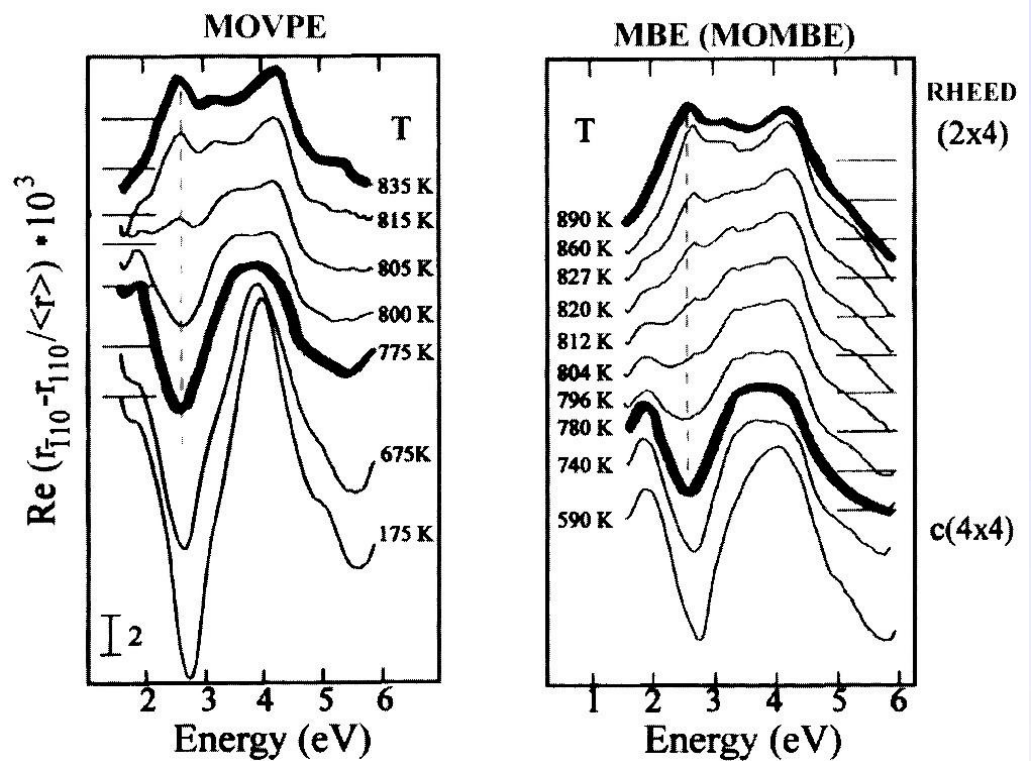
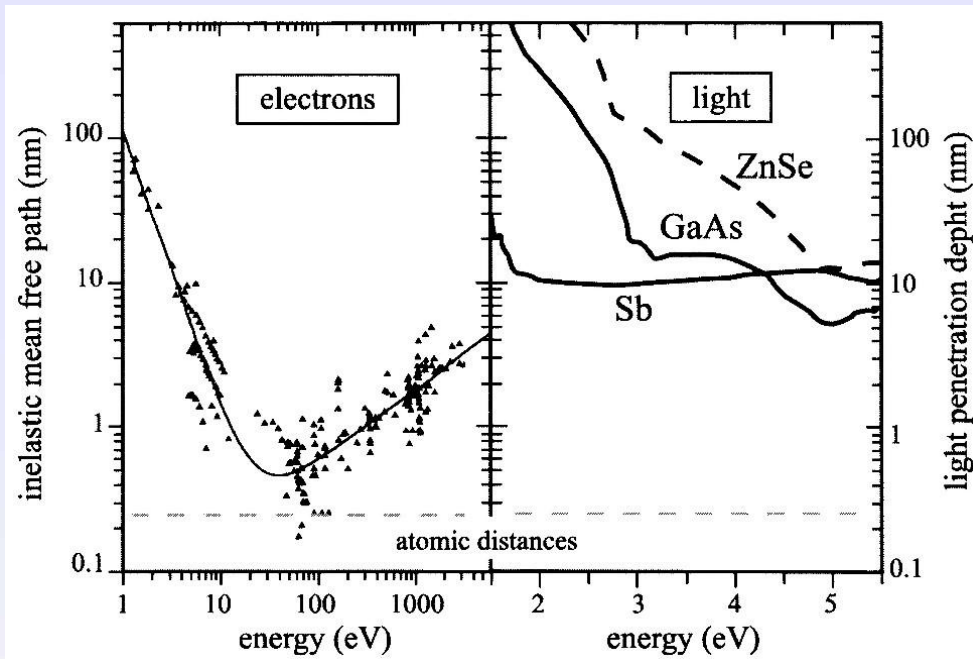
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RHEED →

(Reflection High-Energy Electron Diffraction)



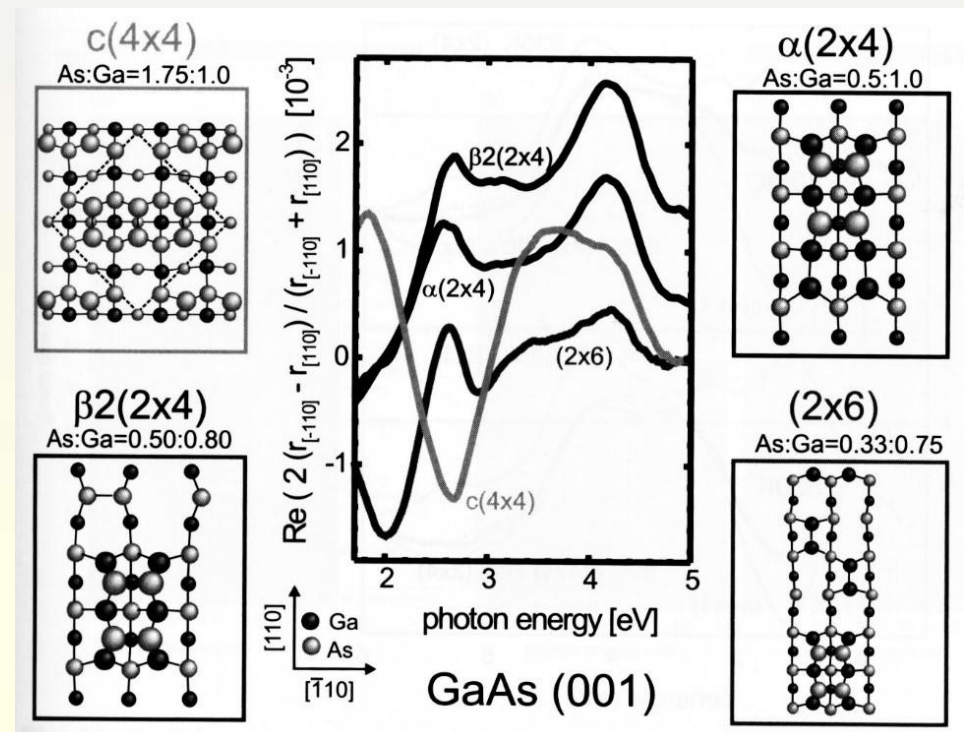
Principle of MBE



MOVPE, which is not a vacuum technology, cannot use electrons for in-situ characterization.

Photons are too large, but there are still possibilities for in-situ characterization using photons.

MBE measurement can be used for calibration.



The most important for nanotechnology are **MBE** and **MOVPE**:

Organometallic Vapour Phase Epitaxy

MOVPE (Metal-Organic Vapour Phase Epitaxy) **Europe**

MOCVD (Metal-Organic Chemical Vapour Deposition), **USA, Asia**

MOVPE technology is not so controllable and „exact“ for research as MBE, (which has better control of growth driving, it is able to prepare sharper hetero-boundaries and lower growth temperatures), but it is fundamental for industry, mainly for optoelectronic devices. MOVPE structures (= chips) are cheaper, with higher productivity. It is more suitable for nitrides.

Comparison of devices prepared by MBE and MOVPE

MetalOrganic Vapour Phase Epitaxy/Chemical Vapour Deposition, MOVPE/ MOCVD is the most important industrial technology for the preparation of various devices such as:

MOVPE

LEDs, (blue!)

Semiconductor lasers (opt. com.)

Semiconductor detectors,

Semiconductor scintillators,

Record efficient solar cells,

High frequency transistors – HEMTS

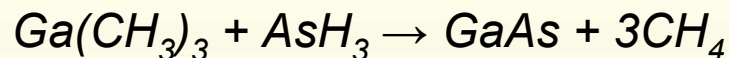
...

MBE

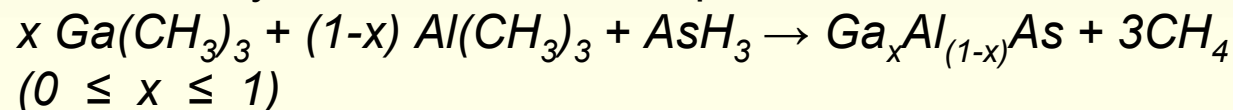
Quantum cascade lasers

Quantum Hall effect (Ω)

QDot based devices



and similar for ternary semiconductor compounds



History of MBE in the CR, mainly in FZÚ

In the 1980s, a "homemade" MBE was built at the FZU apparatus, which but it never really worked. (Kejř, Láznicka)

At the end of the 1980s, the small but expensive Finnish research apparatus, without original Knudsen's cells, which were not subject to the export due to embargo from the West. This equipment worked for about 30 years. (Láznicka, Cukr, V. Novák)

At the end of the 1980s, a large apparatus from the French company Riber was cunningly transported to the then USSR, probably for military research. It was in the FZÚ only briefly, and the test runs and deceived workers (Šimeček, Hulicius, Melichar) then were told it would go away.

In the 1990s, it was removed from the MBB company, homemade "embryonic" MBE equipment was imported, apparently from seventies Just a vacuum chamber, no insertable chamber and diagnostics (only vacuum measurement), effusion cells and non-rotating substrate inside, powerful ion and titanium pump. It served us as a fine evaporator (Melichar, Šimeček, Hulicius)

Modern apparatus of the American comp. Veeco, was launched in 2003. (V. Novák). Apparatus of the company MBE Komponenten is launched in 2019/20 (V. Novák).

Other commercial, well-equipped apparatus at CEITEC in Brno, is operating in CR.

Question to AI (chatGPT free) about epitaxy

1. Why is epitaxial growth being introduced?

Summary: Epitaxial growth is introduced to enable advanced material engineering and device fabrication at the atomic scale. Its precision and flexibility are key to modern electronics, photonics, and quantum technologies.

1. High-Quality Crystal Growth

Epitaxy enables the growth of a crystalline layer on a crystalline substrate with minimal defects. The atomic arrangement of the layer closely matches that of the substrate, resulting in better structural quality compared to other deposition techniques.

2. Tailored Electronic Properties

Epitaxial layers can be engineered with **specific doping levels, bandgaps, and compositions**, making them ideal for advanced electronic and optoelectronic devices (e.g., transistors, lasers, LEDs, and solar cells).

6. Material Combinations Not Possible by Bulk Growth

Some compound semiconductors (e.g., GaN, InP) can't be grown in bulk easily, but can be deposited as epitaxial layers on compatible substrates.

3. Heterostructures and Quantum Devices

Epitaxy makes it possible to grow **heterostructures**—layers of different materials with atomically sharp interfaces—which are essential in:

- High-electron-mobility transistors (HEMTs)
- Quantum wells, dots, and superlattices
- Tunnel diodes and photodetectors

4. Improved Device Performance

Because epitaxial layers are more uniform and can be grown to atomic-level precision, devices made with them typically have **better performance**, such as:

- Higher speed
- Lower power consumption
- Greater efficiency and reliability

5. Integration and Scaling

Epitaxial growth supports:

- **Vertical stacking** of different materials (3D integration)
 - **Monolithic integration** of different functions (e.g., logic + photonics)
- This is critical for next-generation semiconductor technologies

2. How epitaxy enables the growth of a crystalline layer on a crystalline substrate with minimal defects.

1. Lattice Matching

The key to low-defect growth in epitaxy is **lattice matching**:

2. Controlled Nucleation and Growth

Growth begins with **nucleation sites** that replicate the atomic pattern of the substrate.

3. Types of Epitaxy That Minimize Defects

There are several types, but two key ones are:

Homoepitaxy: Same material (e.g., silicon on silicon) → virtually no lattice mismatch → very low defect density.

Heteroepitaxy: Different materials (e.g., GaAs on Si) → requires careful engineering (e.g., buffer layers) to reduce mismatch strain.

5. Interface Coherence

In epitaxy, the interface between substrate and layer is usually **coherent** (i.e., atoms line up at the boundary), which: Promotes structural continuity

Minimizes energy states that would otherwise lead to defects

4. Thermodynamic and Kinetic Control

The process is performed under **precisely controlled temperature and pressure**. These conditions let atoms move into their lowest-energy, most stable positions on the substrate. This further **reduces point defects and dislocations?**

3. How the low temperature of epitaxy enables the growth with minimal defects?

*Great question! The **low temperature** used in certain types of epitaxy (especially in **Low-Temperature Epitaxy**, such as **Low-Temperature Chemical Vapor Deposition – LT-CVD** or **Low-Temperature Molecular Beam Epitaxy – LT-MBE**) plays a crucial role in **reducing defects** during the growth of crystalline layers. Here's how:*

Why Use Low Temperatures in Epitaxy?

1. Suppresses Defect Formation

- **High temperatures** can lead to **excessive atom mobility**, which may cause atoms to move into incorrect positions, leading to:
 - Interstitials, Vacancies, Dislocations
- **Low temperatures** slow down atomic movement just enough to allow atoms to attach correctly to the crystal lattice without over-diffusing.

2. Reduces Interdiffusion

- At higher temperatures, **atoms from the substrate and the growing layer can interdiffuse**, leading to a **blurred interface** and unwanted impurities.
- **Low temperatures maintain sharp, well-defined interfaces**, which is crucial in: Heterostructures (e.g., GaAs/AlGaAs), Quantum wells, Superlattices

3. Strain Management

4. Improves Surface Smoothness

5. Compatible with Sensitive Materials

Summary of the 3. question:

Low-temperature epitaxy enables high-quality crystalline growth by:

- Suppressing defect formation
- Reducing interdiffusion and strain
- Maintaining smooth interfaces
- Allowing compatibility with sensitive layers

It's a **critical technique** in advanced semiconductor manufacturing, especially for finely scaled, defect-sensitive devices.

- Would you like a comparison chart of high- vs. low-temperature epitaxy effects?

4. Epitaxial crystal growth, defects, temperature and entropy?

Great—you're asking about how epitaxial crystal growth, defects, temperature, and entropy are interrelated,

4. Entropy's Role

Entropy (S) is a measure of disorder. In epitaxial growth:

- **Crystal formation = ordering** → $\Delta S < 0$ (entropy decreases)
- Nature opposes ordering unless there is enough **free energy driving force** (negative Gibbs free energy)

Gibbs Free Energy:

$\Delta G = \Delta H - T\Delta S$ To favor crystal growth:

- ΔG must be **negative**
- Lower T reduces the entropy penalty $T\Delta S$
- However, too low T → insufficient atomic mobility

This is why epitaxial growth must **balance entropy and temperature**:

- Low enough to favor ordering ($\Delta G < 0$)
- High enough to enable atomic rearrangement

5. Thermodynamic vs Kinetic Control

- **Thermodynamics** tells you **if** the growth will happen ($\Delta G < 0$)
- **Kinetics** (controlled by temperature) tells you **how fast and how well** it happens

You want: Low enough entropy (high order)

- Just enough temperature to overcome kinetic barriers without introducing defects