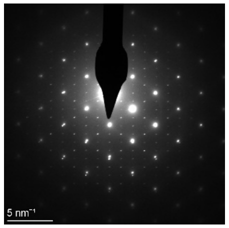
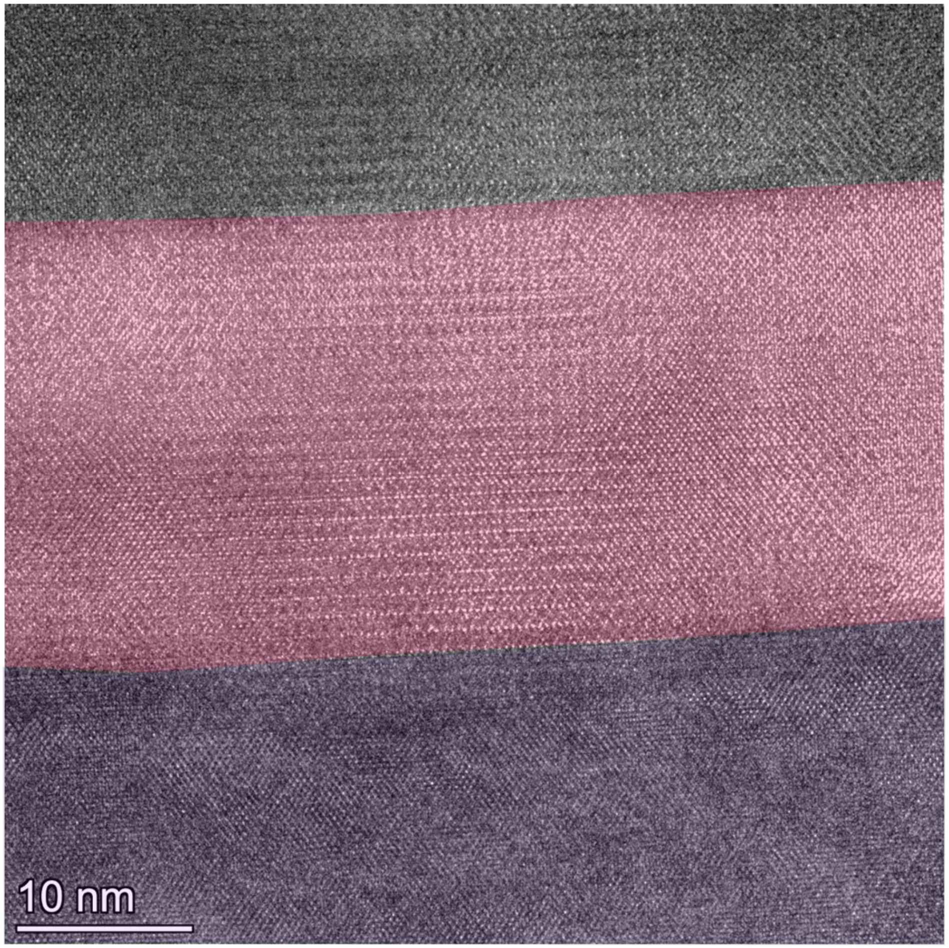




Crysal growth by epitaxy MSE-649

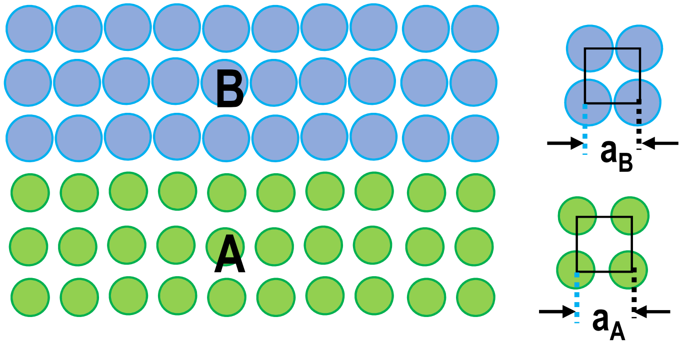
Anna Fontcuberta i Morral
Laboratory of Semiconductor Materials

Image & material credits: S. Escobar-Steinvall

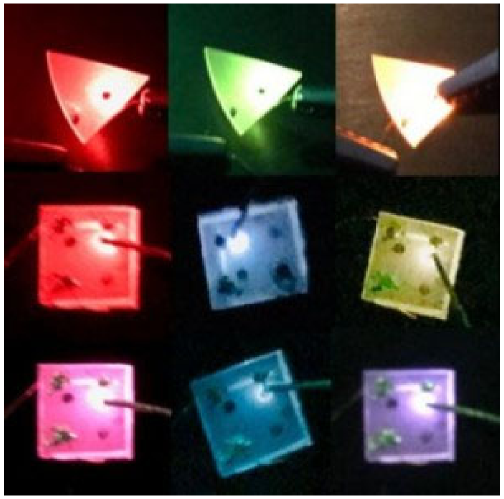
Epitaxy?

From the greek: **Epi:** above
Taxos: an ordered manner

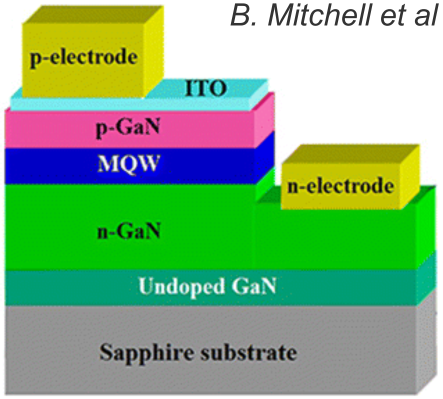
Epitaxy: deposition of a crystalline overlayer on a crystalline substrate



Color engineered LEDs based on GaN

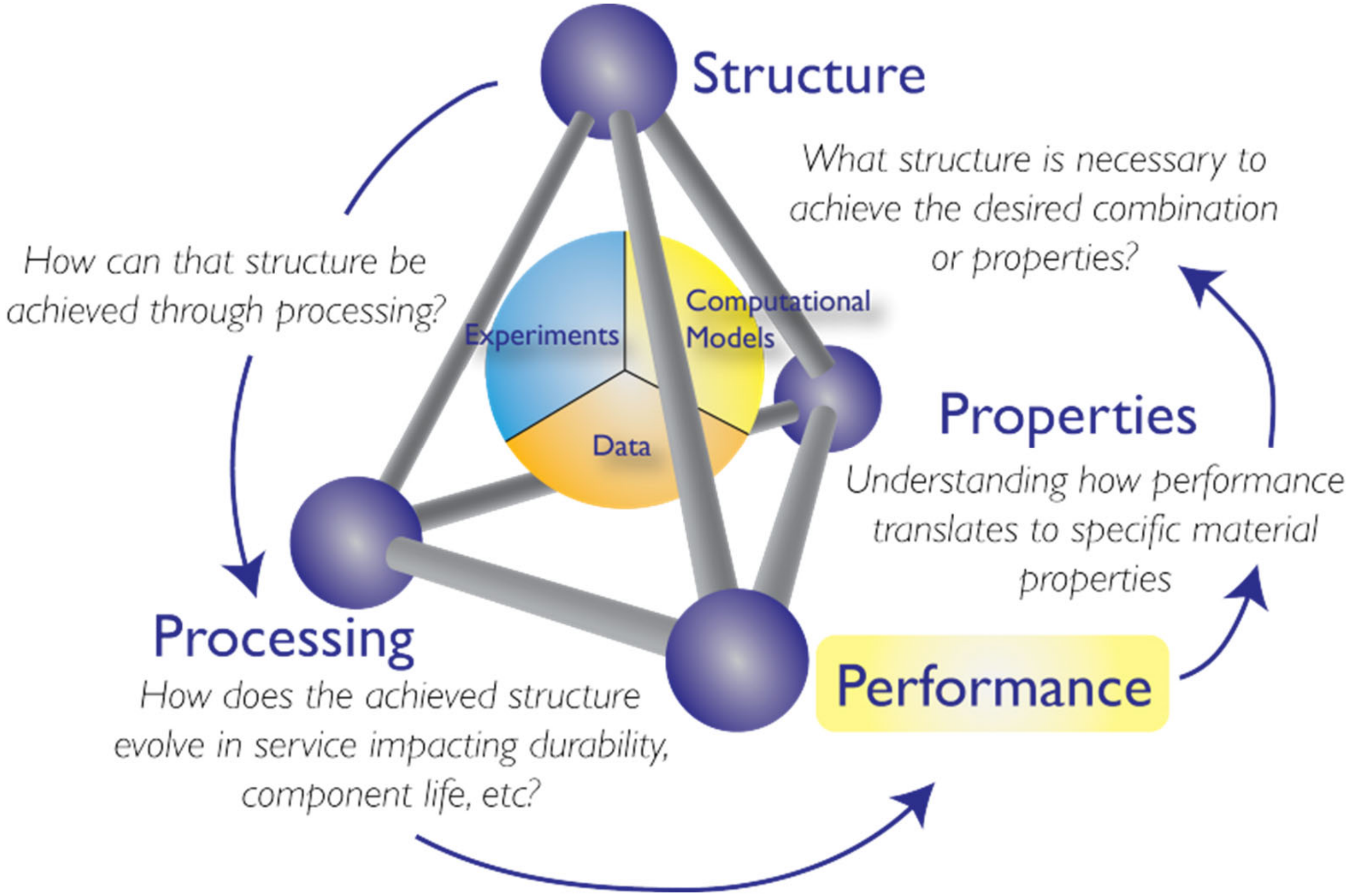


B. Mitchell et al ACS Photonics, 2019



DOI: 10.1007/s10853-018-2177-8

What makes a good material?



Structure

What structure is necessary to achieve the desired combination or properties?

How can that structure be achieved through processing?

Experiments

Computational Models

Data

Properties

Understanding how performance translates to specific material properties

Processing

How does the achieved structure evolve in service impacting durability, component life, etc?

Performance

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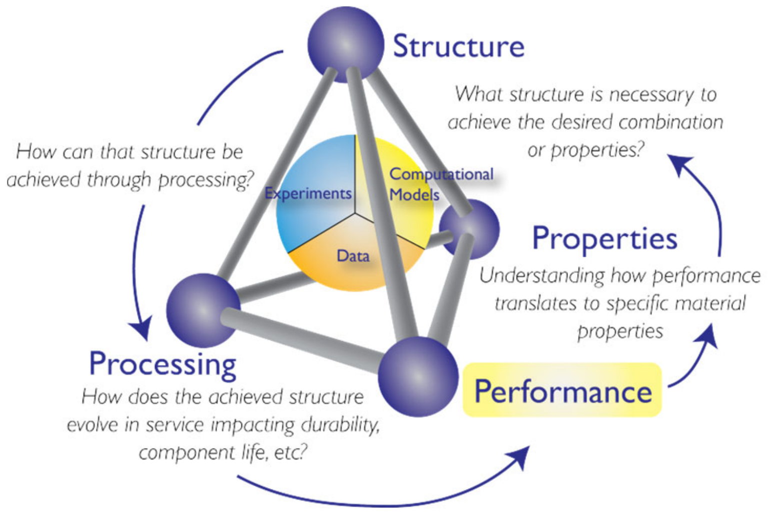
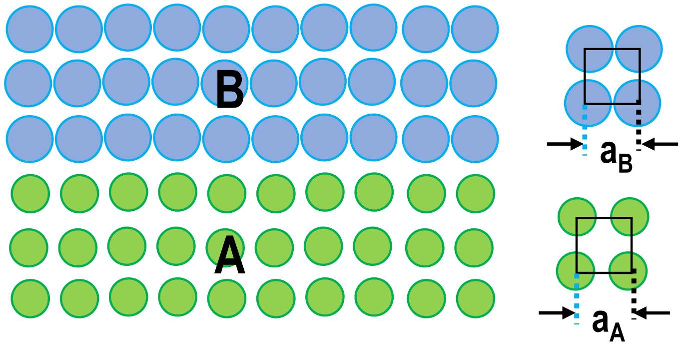
What makes a good material?



Factors affecting the properties/performance:

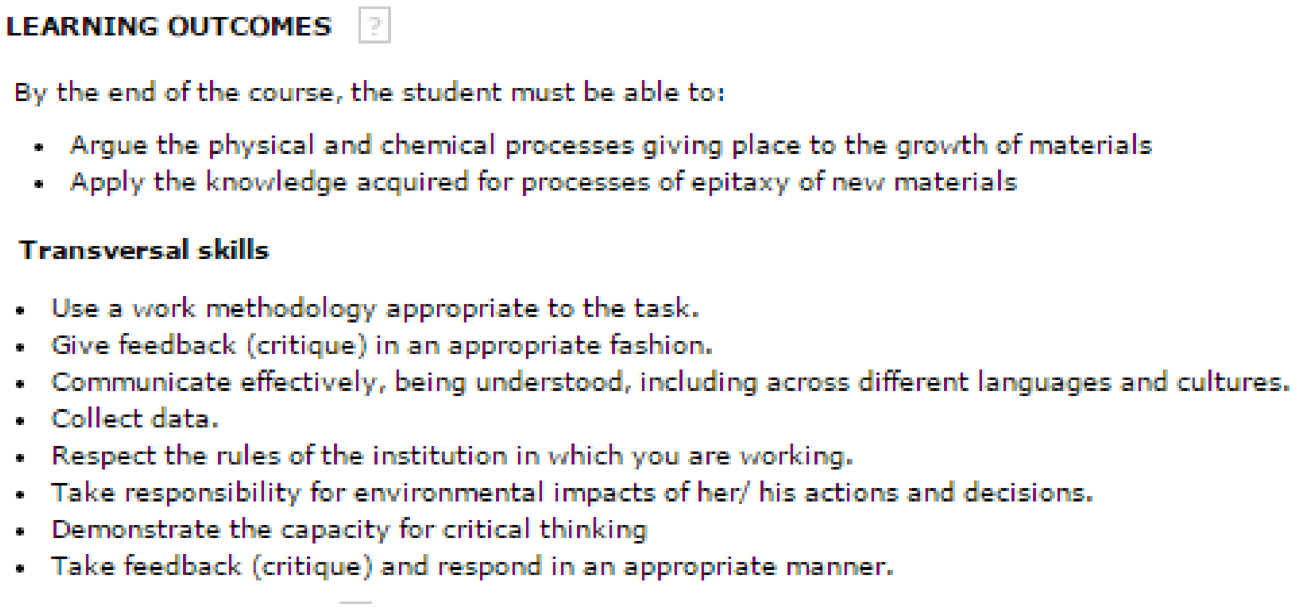
- Defects: grain boundaries, dislocations, crystal phase
- Impurities in bulk and/or at interfaces

What makes epitaxy challenging?



As materials scientists we know that the properties of materials depend on the microstructure, which at the same time depends on the fabrication process.

While the proportion of atoms in a material that lie on the surface is extremely small, the fabrication process is very often critically dependent on processes occurring at the surface (both for bulk and thin films). A better understanding of these results in a better control of the properties.



LEARNING OUTCOMES

By the end of the course, the student must be able to:

- Argue the physical and chemical processes giving place to the growth of materials
- Apply the knowledge acquired for processes of epitaxy of new materials

Transversal skills

- Use a work methodology appropriate to the task.
- Give feedback (critique) in an appropriate fashion.
- Communicate effectively, being understood, including across different languages and cultures.
- Collect data.
- Respect the rules of the institution in which you are working.
- Take responsibility for environmental impacts of her/ his actions and decisions.
- Demonstrate the capacity for critical thinking
- Take feedback (critique) and respond in an appropriate manner.

Evaluation:

1. Group seminar 70%
2. Report on seminars (max 1 page per seminar) 30%
3. Participation in class discussions

Structure of the course

1. Epitaxy in general, reminder of thermodynamics
2. SiGe, alloy phases (SiGe)
3. Phase diagram GaAs, ordering and clustering: microscopic strain
4. Kinetics in spinodal decomposition, coherency and semicoherency
5. Microscopic surface morphology (roughening and kinks), Wulff
6. Thin film growth modes, epitaxy of nanostructures
7. Epitaxy of less standard materials
8. Seminars
9. Sept: visit to two epitaxy facilities: MBE and MOCVD

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Structure of the course

August 19	**August 20**	**August 21**
Introduction, basics Team constitution	Application to two materials systems: SiGe & GaAs	Spinodal decomposition, coherency Microscopic surface morphology Thin film growth modes
August 26	**August 27**	**August 28**
Nanostructures Less standard materials	MOCVD	1-3pm Seminars & discussion

Morning:
9:15 am
Lectures and interaction (Q&A)
Afternoon:
Reading, watching
Seminar preparation

August 21: additional lecture at 4pm (public thesis defense)

September: visit to experimental facilities (on site & via zoom, voluntary)

Discussion groups: for the daily activities and the seminar

Aqeel, Ahmed
Babashah, Hossein
Balgarkashi, Akshay

Dede, Didem
Huang, Haonan
Kukolova, Anna

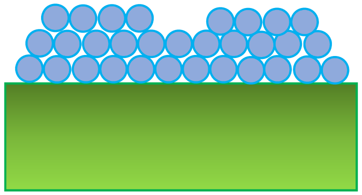
Paul, Rajrupa
Ryu, Jeheyeok
Shirzad, Hoda
Stutz, Elias

1. Stability and instability of a highly strained system: GeSi
2. Epitaxy of two-dimensional materials
3. Spinodal decomposition in ternary and quaternary alloys in core-shell nanowires
4. Understanding crystal shape in the growth of nanostructures

Epitaxy

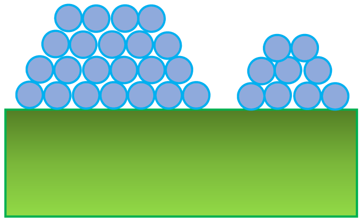
Surface Energy considerations

Frank-van der Merwe



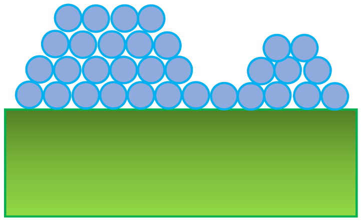
$\gamma_m+\gamma_i<\gamma_s$

Volmer-Weber



$\gamma_m+\gamma_i>\gamma_s$

Stranski-Krastanov



$\gamma_m+\gamma_i\sim\gamma_s$ + strain

γ_m: surface free energy of the material

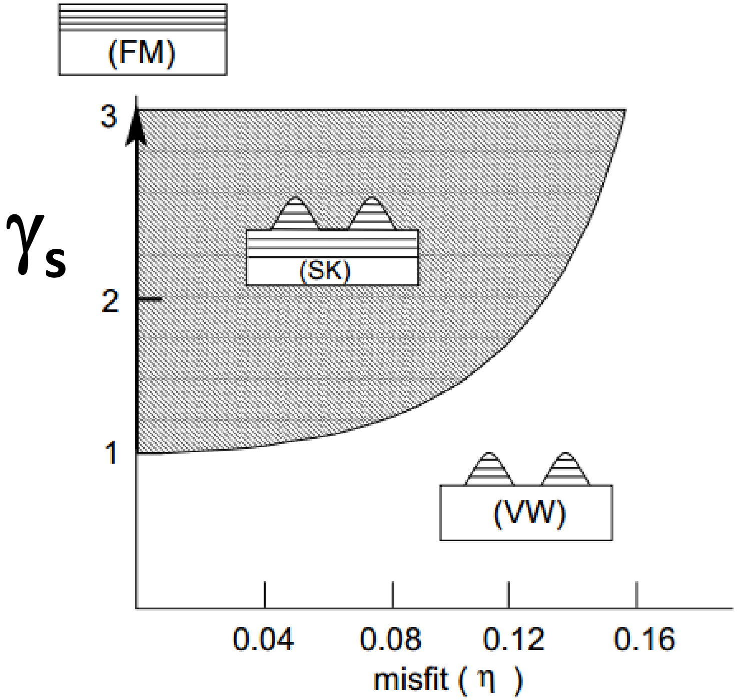
γ_i: surface free energy of the interface

γ_s: surface free energy of the substrate

The surface energy is the excess energy at the surface of a material compared to the bulk

NOTE: surface free energy of a monolayer may differ from the bulk values

Surface energy and misfit

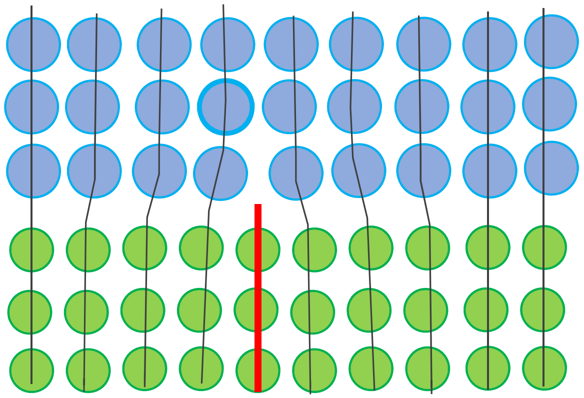


Misfit might be useful for the creation of nanoscale islands

$$\eta = \frac{a_A - a_B}{a_A}$$

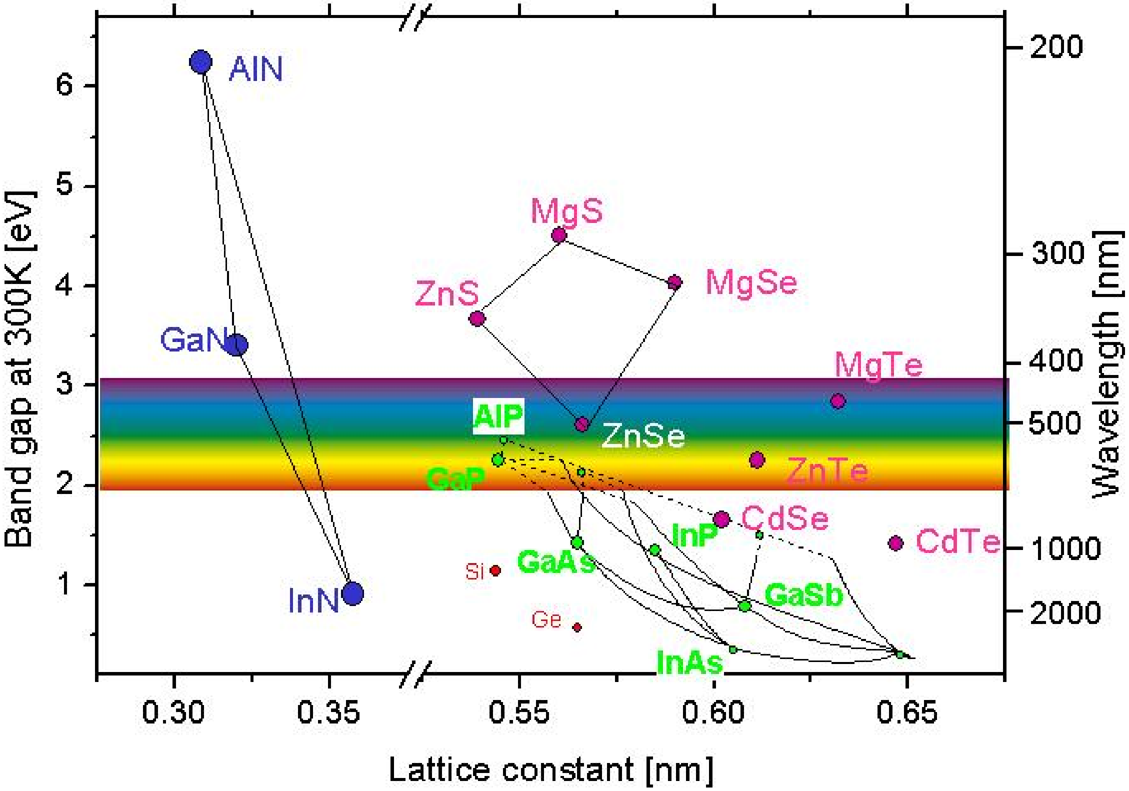
Source: DK Goswami PhD thesis, 2004

Lattice Mismatch: appearance of defects



www.tf.uni-kiel.de

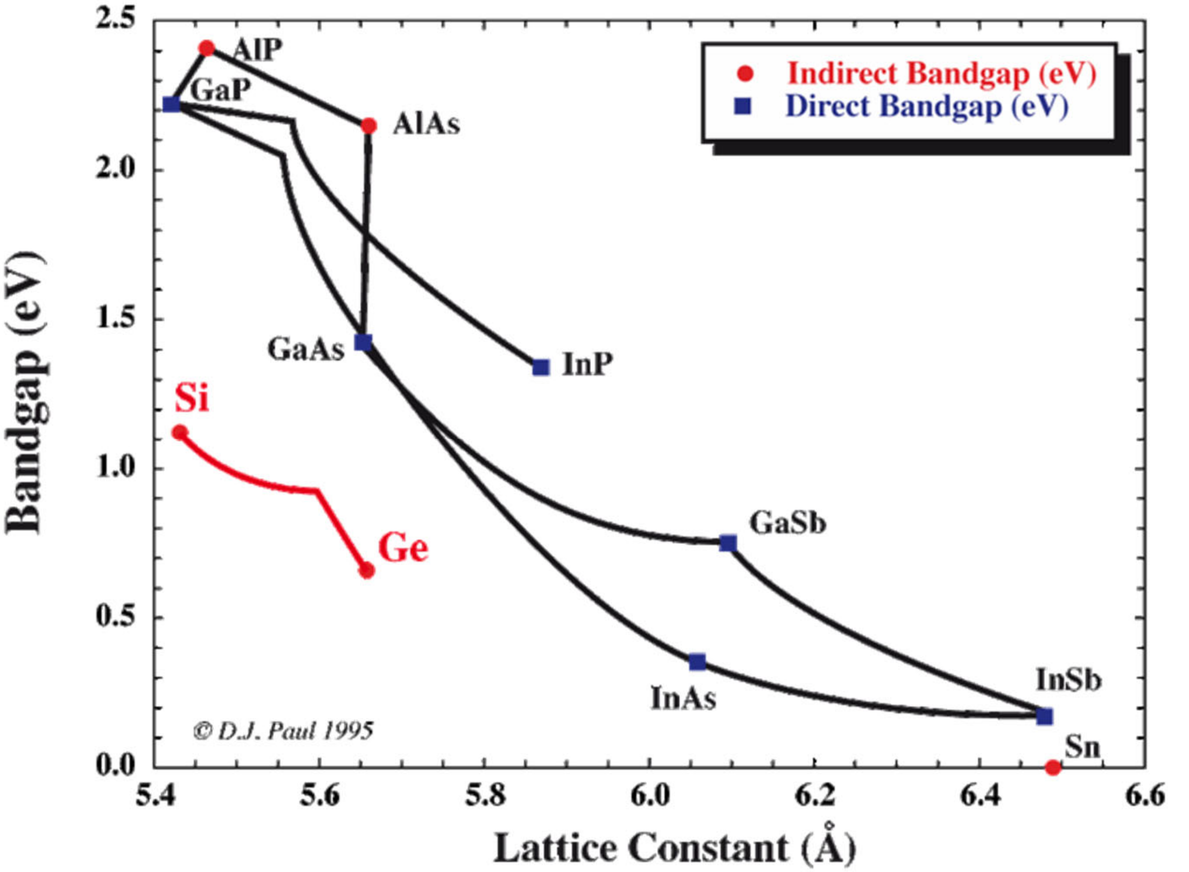
Epitaxial systems



www.seas.ucla.edu

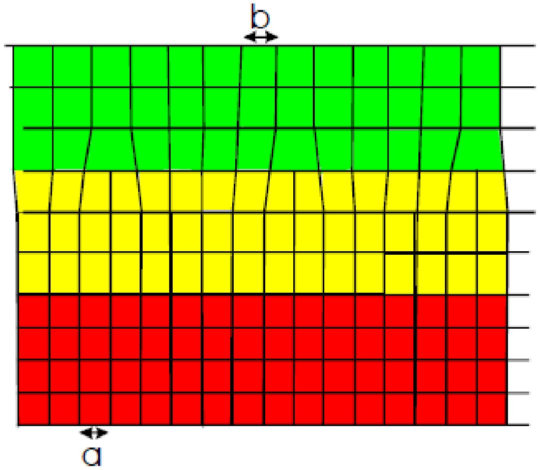
Epitaxial systems

- The lattice constant of the two materials should be similar.



userweb.eng.gla.ac.uk

How much misfit can we afford?

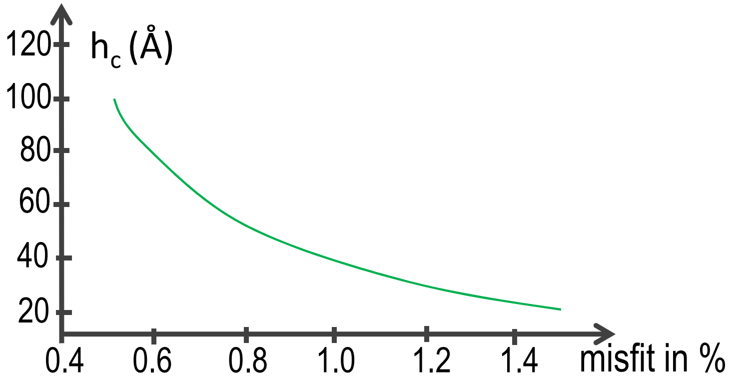


Film, lattice constant b

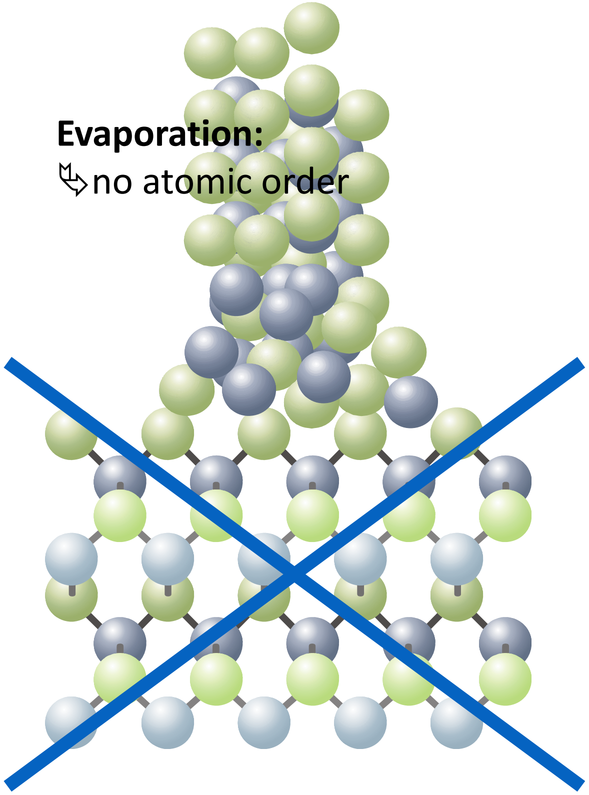
Pseudomorphic transition zone

Substrate, lattice constant a

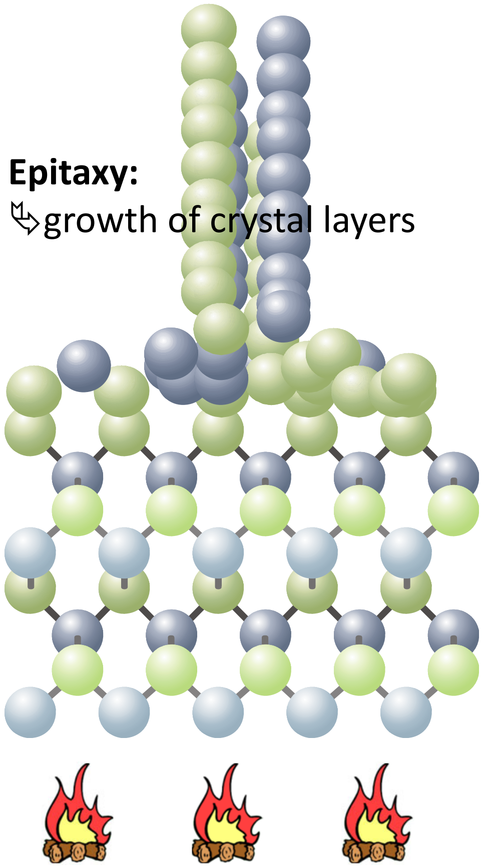
$$h_c = \frac{a_B}{8\pi\eta(1+\nu)} \ln \frac{h_c e}{r_o}$$



What else is required for epitaxy?

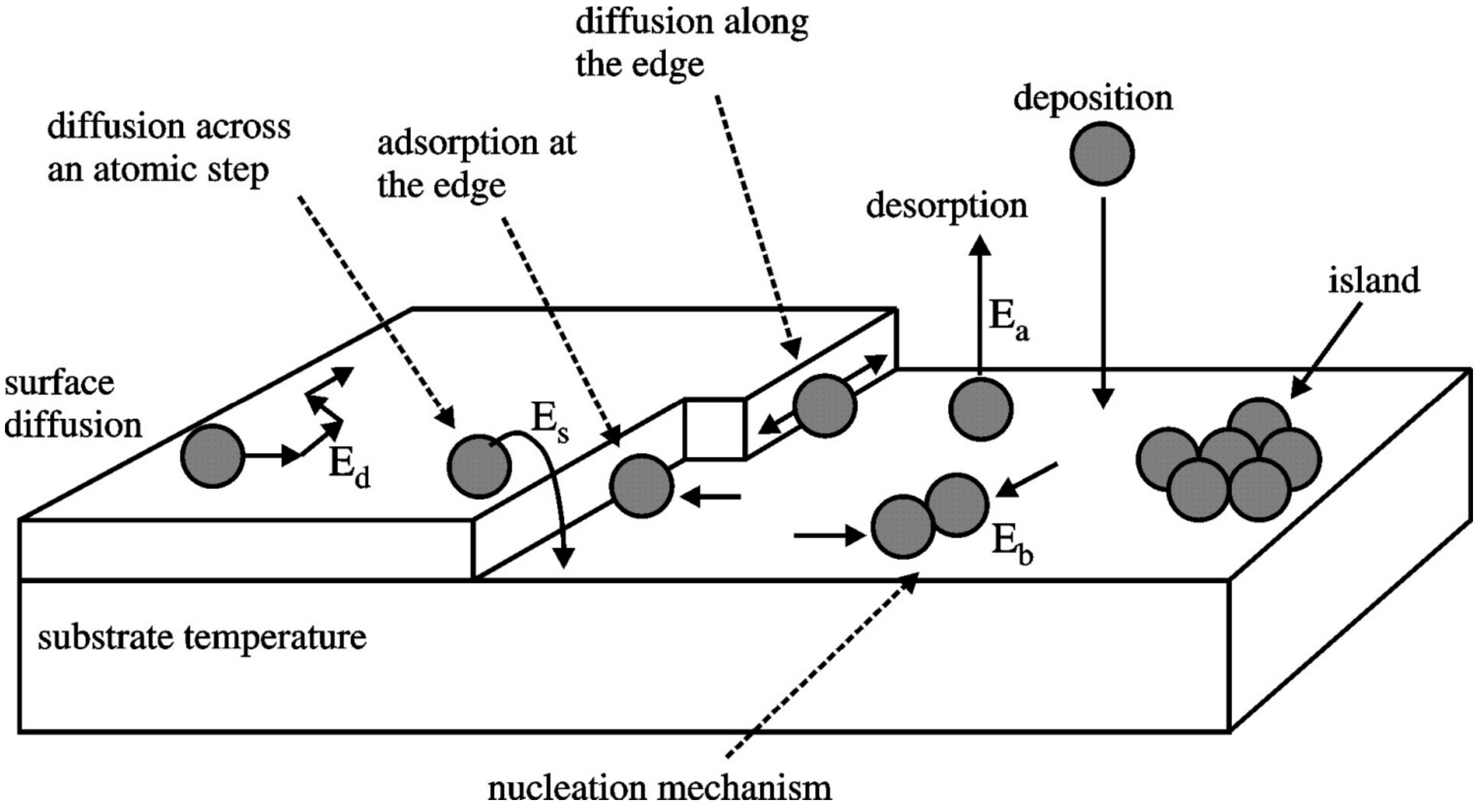


Evaporation:
↳no atomic order



Epitaxy:
↳growth of crystal layers

Processes during epitaxial growth



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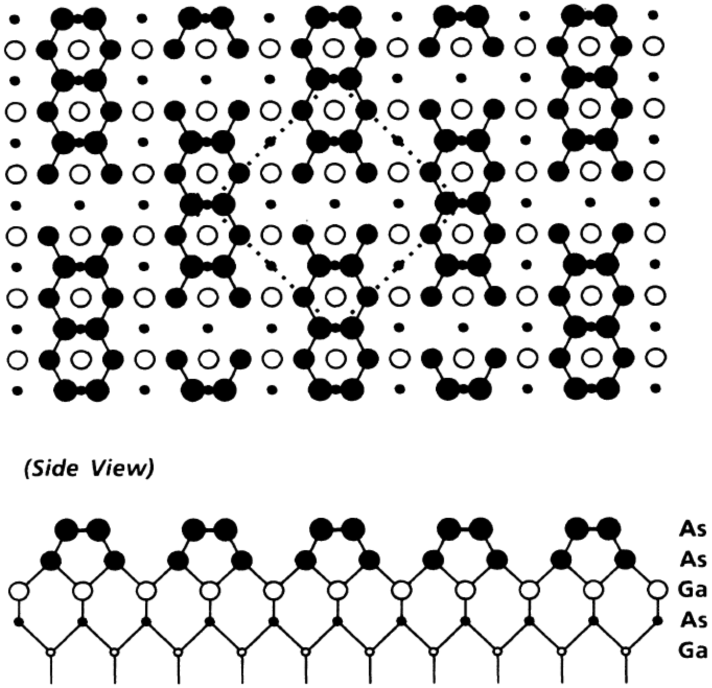
Surface reconstruction

In epitaxial growth the proper surface is prepared by adjusting the chemical potential of the surface via the flux of the sources

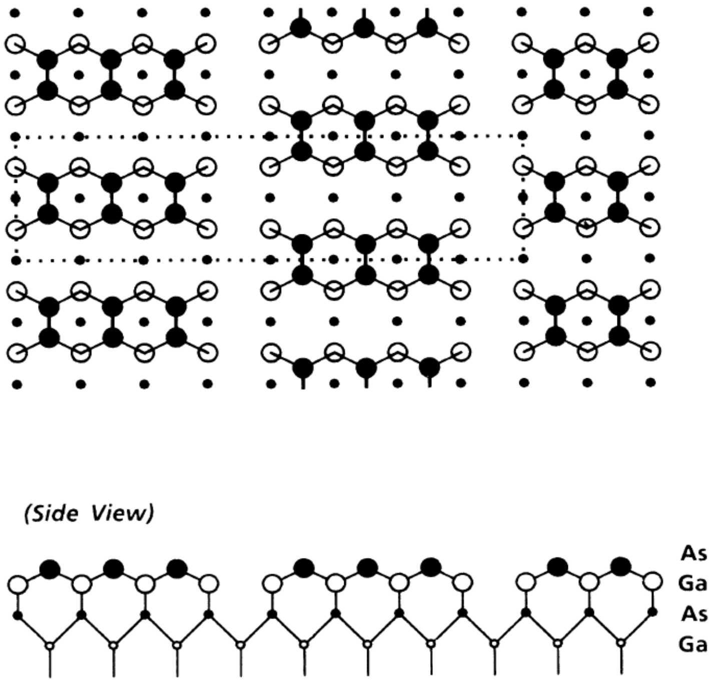
Decreasing arsenic pressure on GaAs (001),

GaAs(100)-c(4x4)



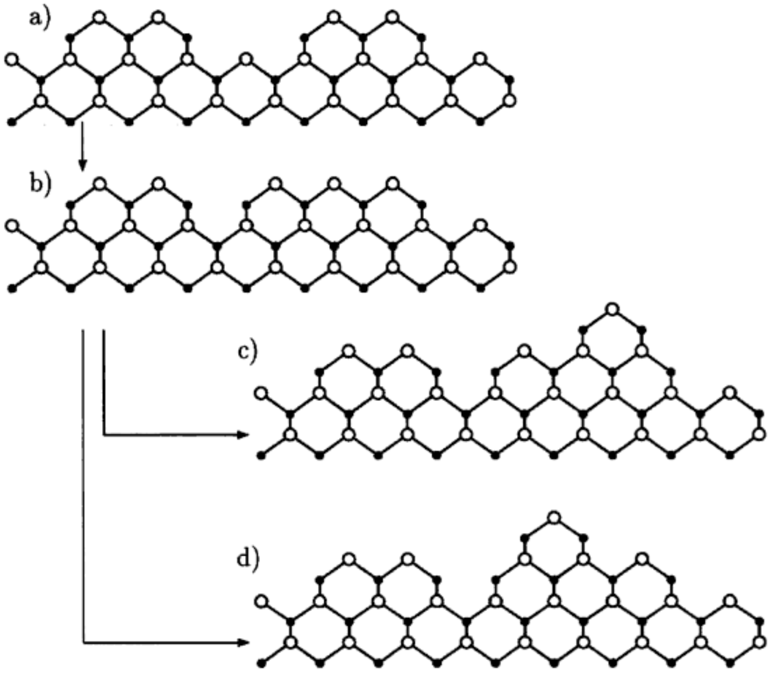
C.K. Biegelsen et al PRB 41, 5701 (1990)

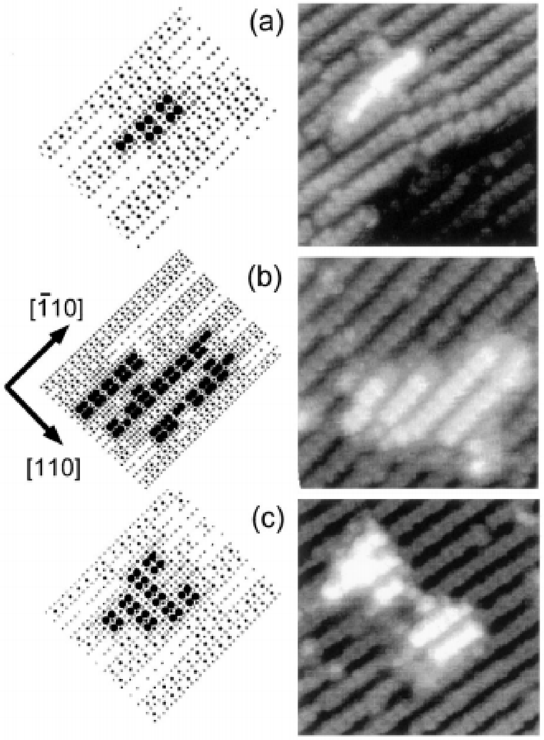
GaAs(100)-(2x4)



Surface reconstruction

In epitaxial growth the proper surface is prepared by adjusting the chemical potential of the surface via the flux of the sources

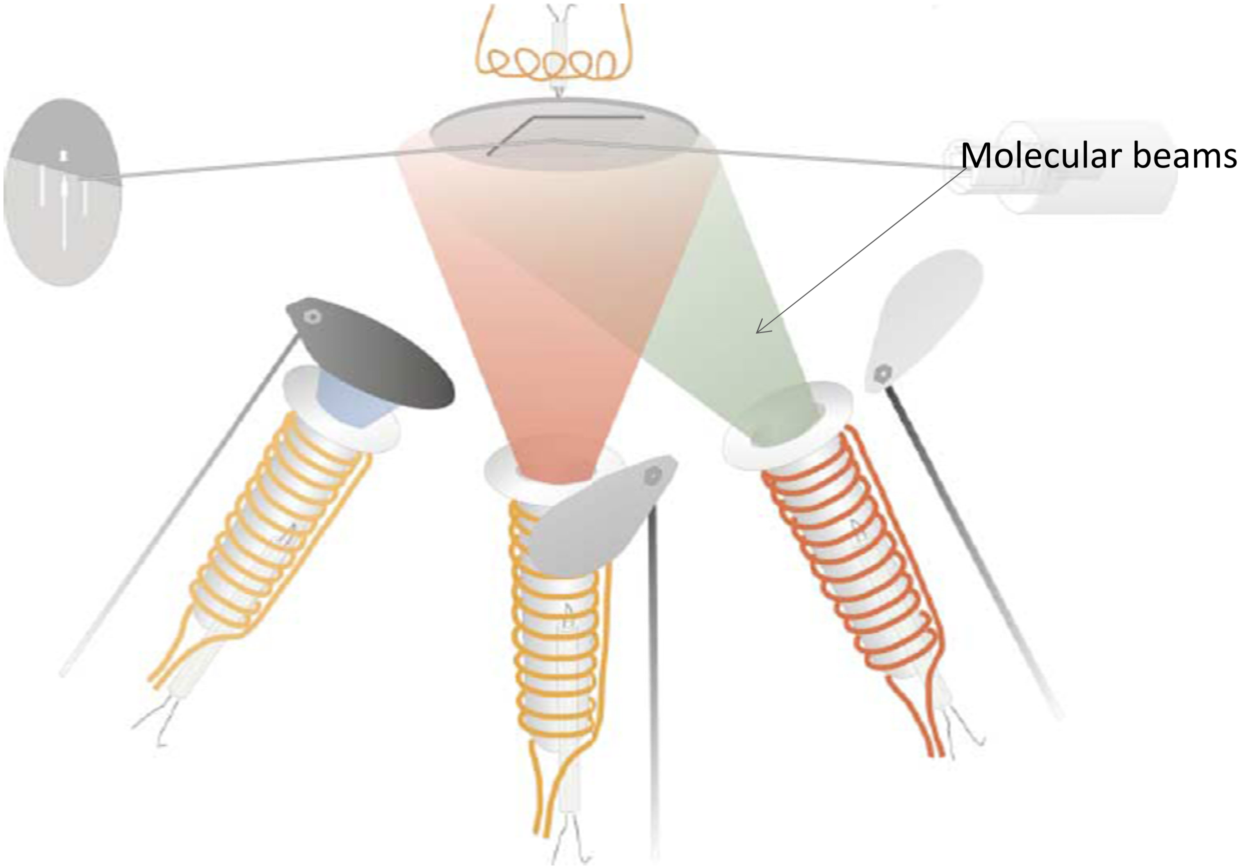




M. Itoh et al PRL (1998)

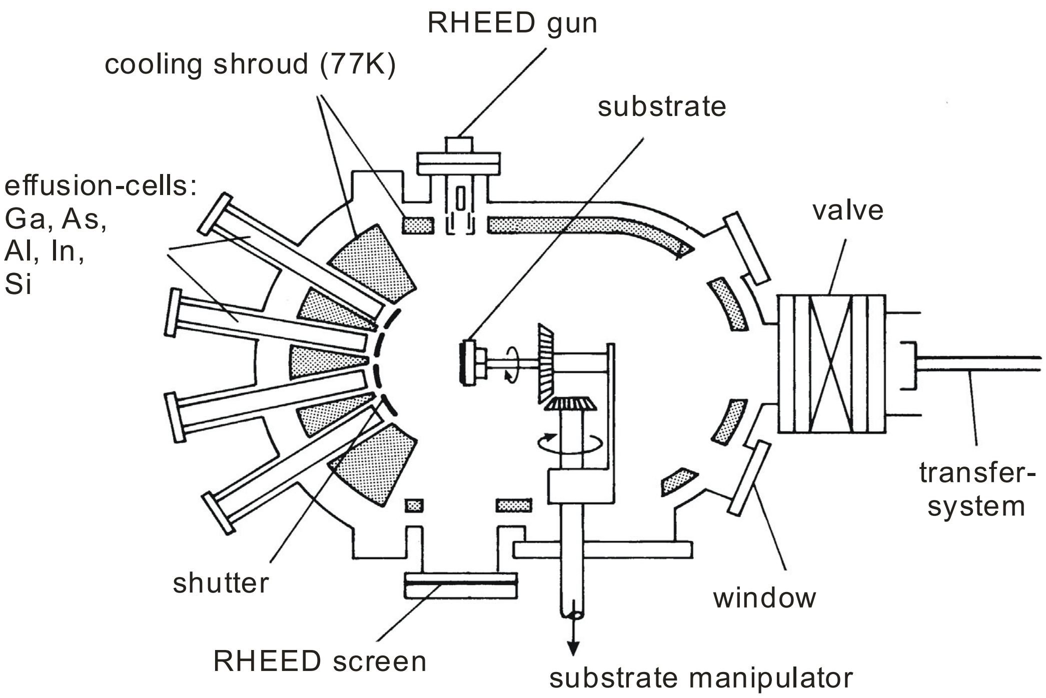
Molecular Beam Epitaxy (MBE)

What is molecular beam epitaxy?



Molecular beams

Schematics



Schematics of a Gen-II machine

- Epitaxy: homo-epitaxy hetero-epitaxy
- Very slow: 1µm/hr
- Very low pressure: 10^{-11} Tor

Up to now, they are not used in the Si IC technology

Some numbers about the vacuum

The number n of gas atoms impinging of a unit area of surface in unit time is:

$$\frac{dn}{dt} = \frac{P}{\sqrt{2\pi mkT}} cm^{-2}s^{-1}$$

P is the gas pressure, m the atomic mass, k is the Boltzmann constant, T temperature

T=25C, residual gas (m=40), P=10^{-6}Torr
→ dn/dt~3.2×10^{14} $cm^{-2}s^{-1}$ (~1ML/s)

⇓

To guarantee purity at one part per million, a vacuum of 10^{-12} torr is necessary!

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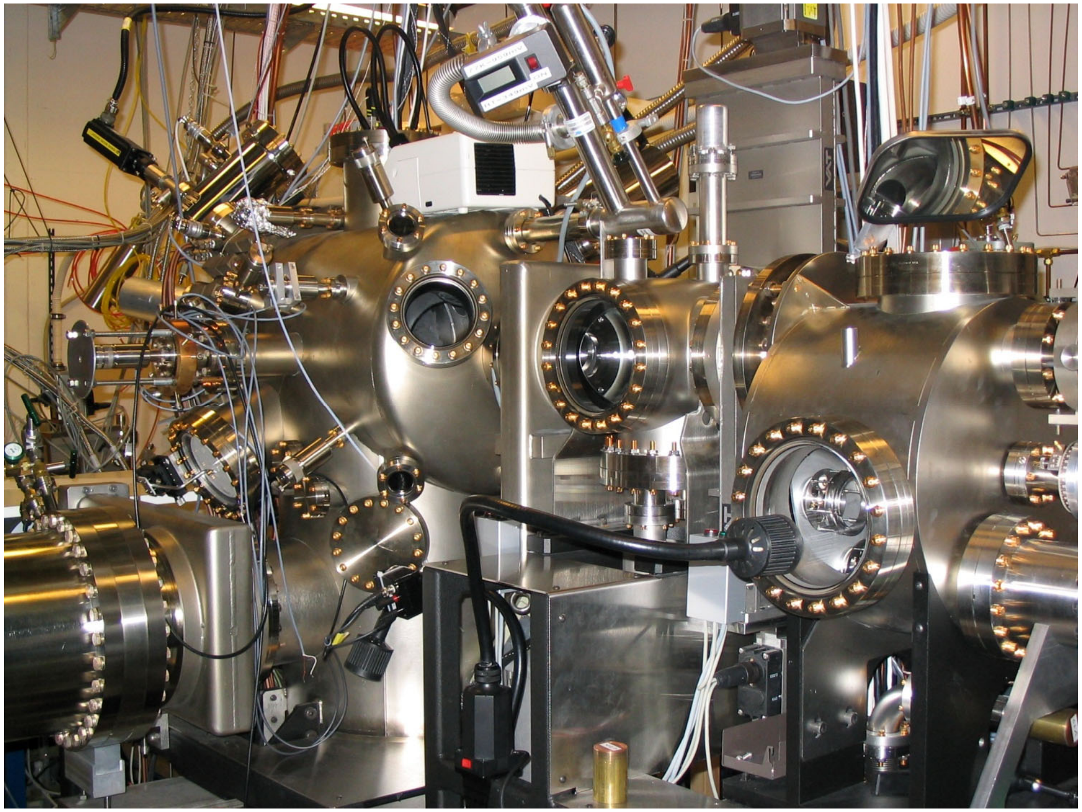
One example of MBE system: Gen II (Veeco)

EPI GEN II system

- ultra-clean vacuum (p ≤ 5×10^{-12}mbar)
- long-term closed growth chamber
- source materials: Ga, Al, In, As
- Valved cracking cell provides As_4 *or* As_2
- *only* Si as dopant



Gen-II machine

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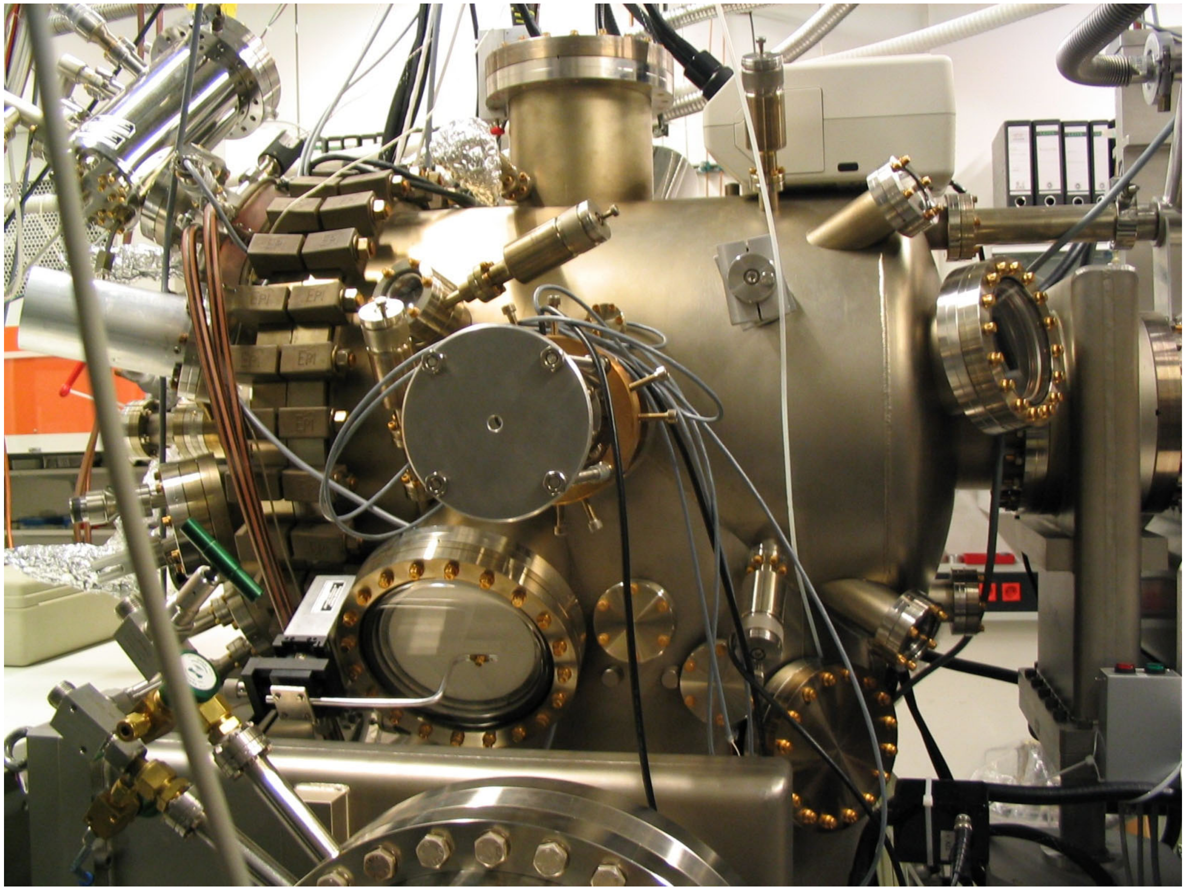
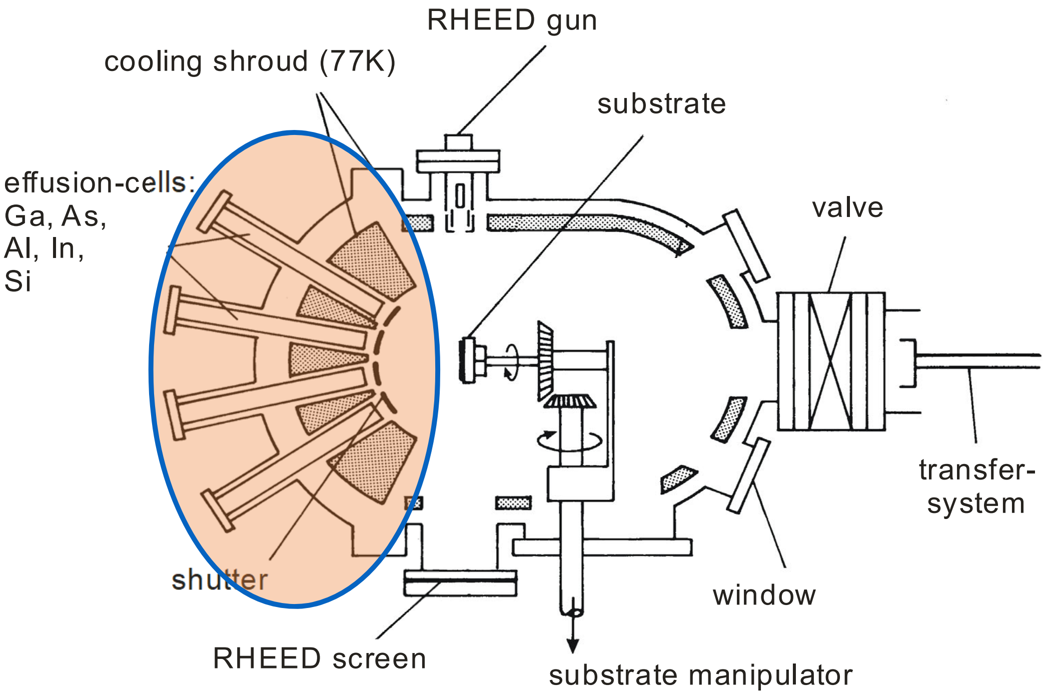
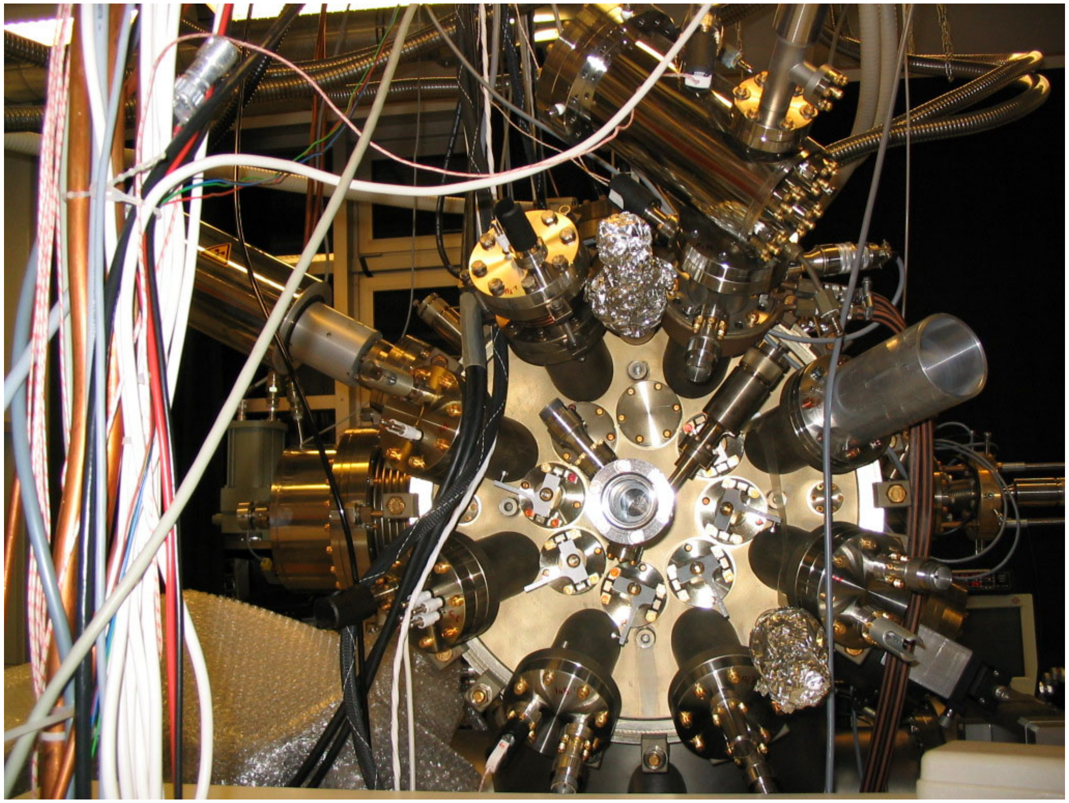


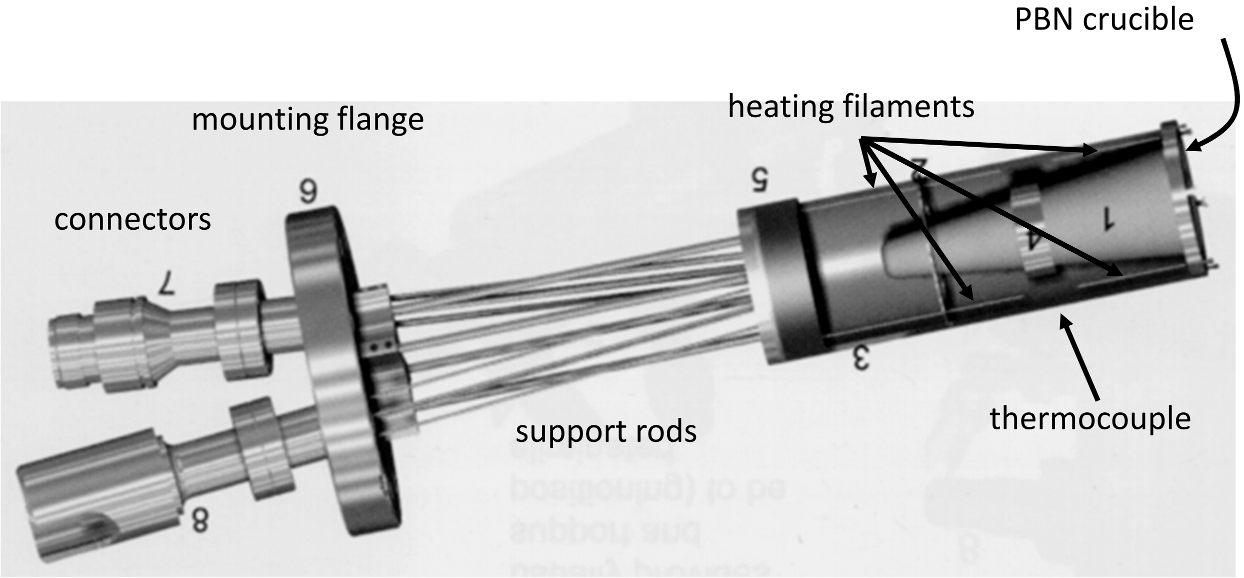
Effusion cells



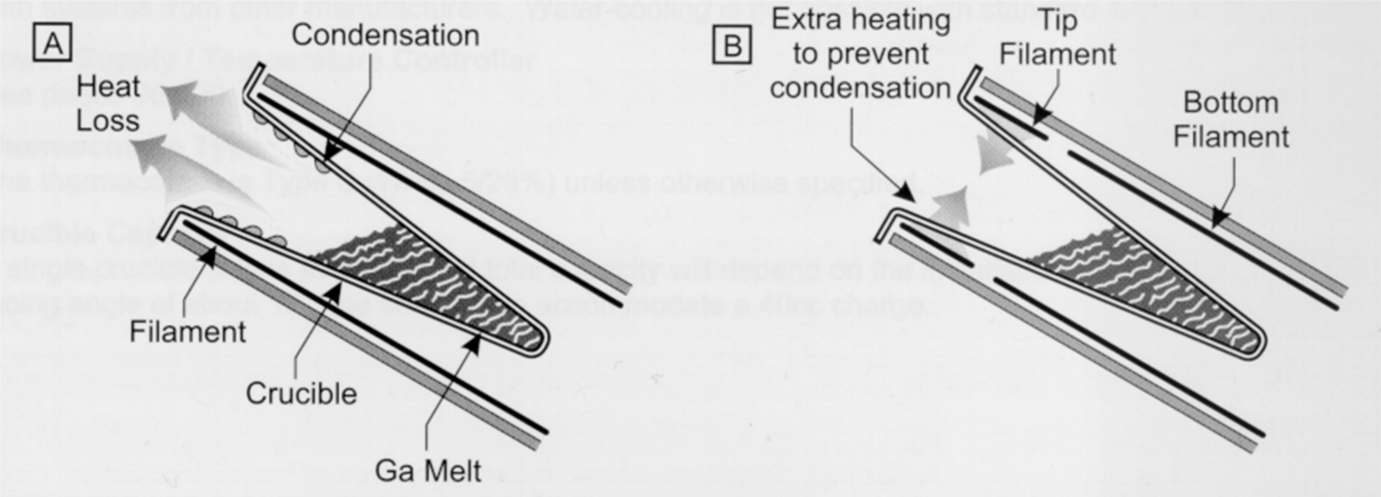


Close-up to the effusion cells

‚typical‘ evaporation cell (Knudsen cell):



Heating of the cells



<u>Ga and In cells</u>: Heating realized with two filaments in order to avoid condensation of the liquid on the upper walls of the crucible

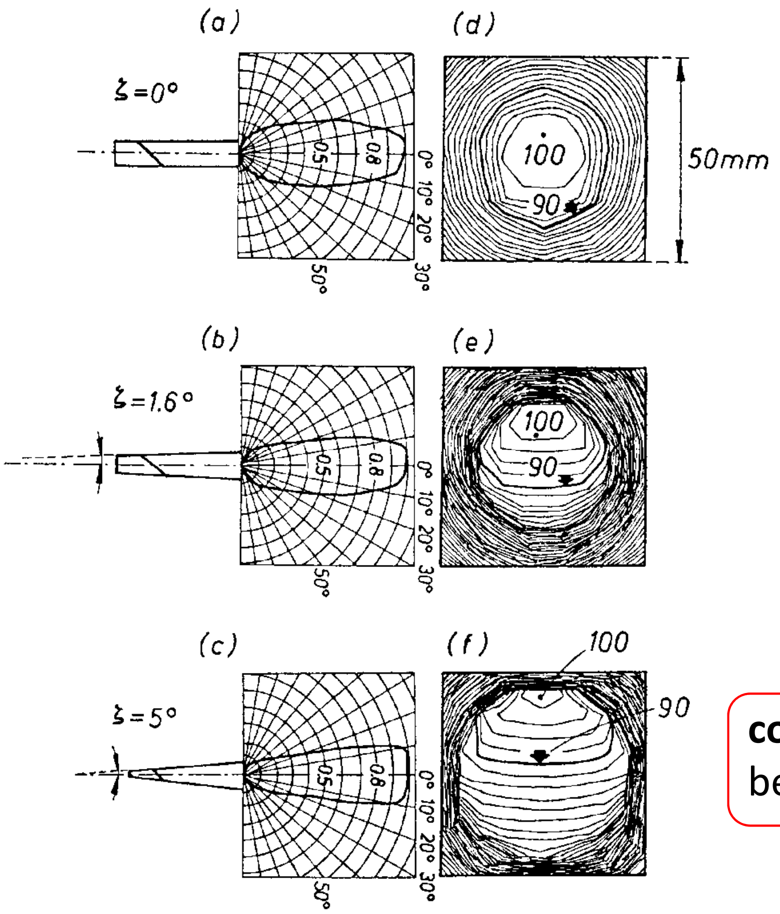
<u>Al cells</u>: Aluminium tends to creep out of the cell. To avoid this, the upper part of the crucible has to be cold. This is called cold-lip.

Geometry of the fluxes

cylindrical

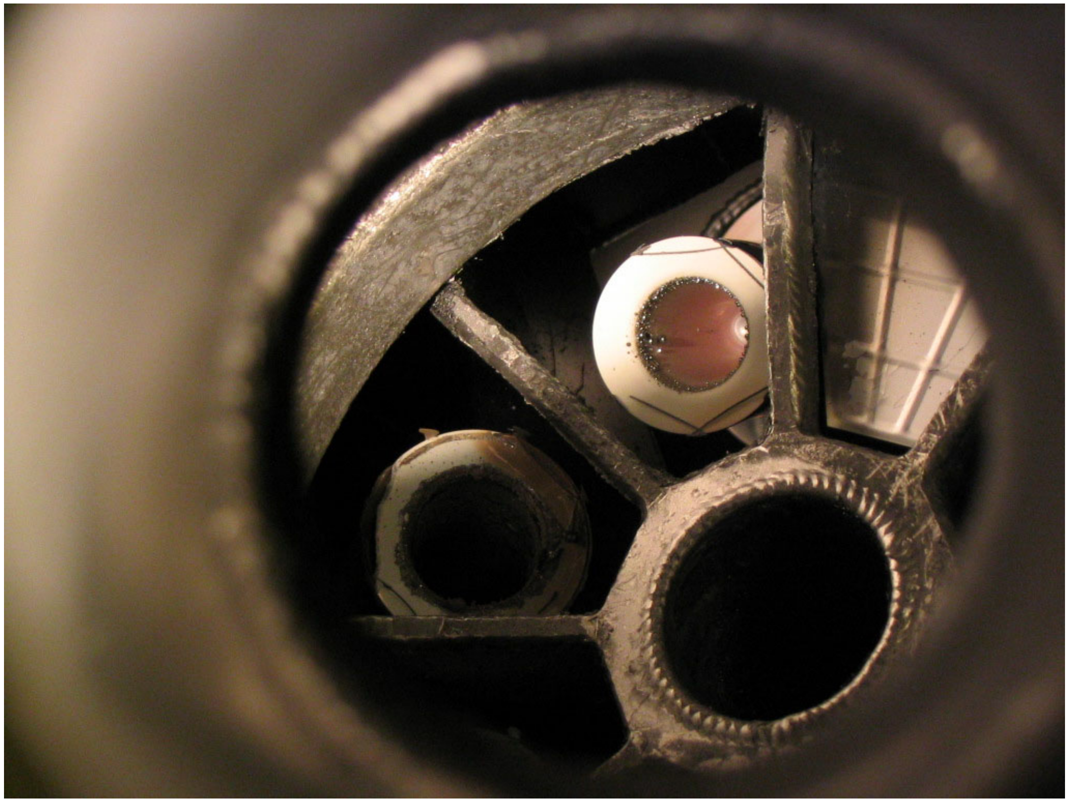
tapered cylindrical

conical

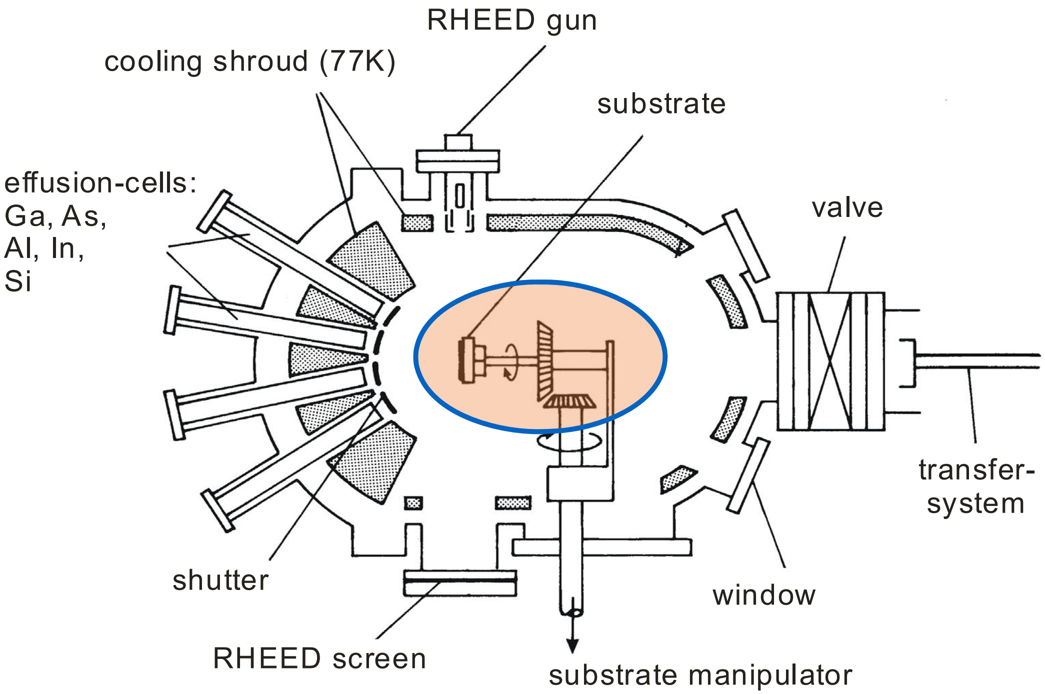


wafer diameter: 2“

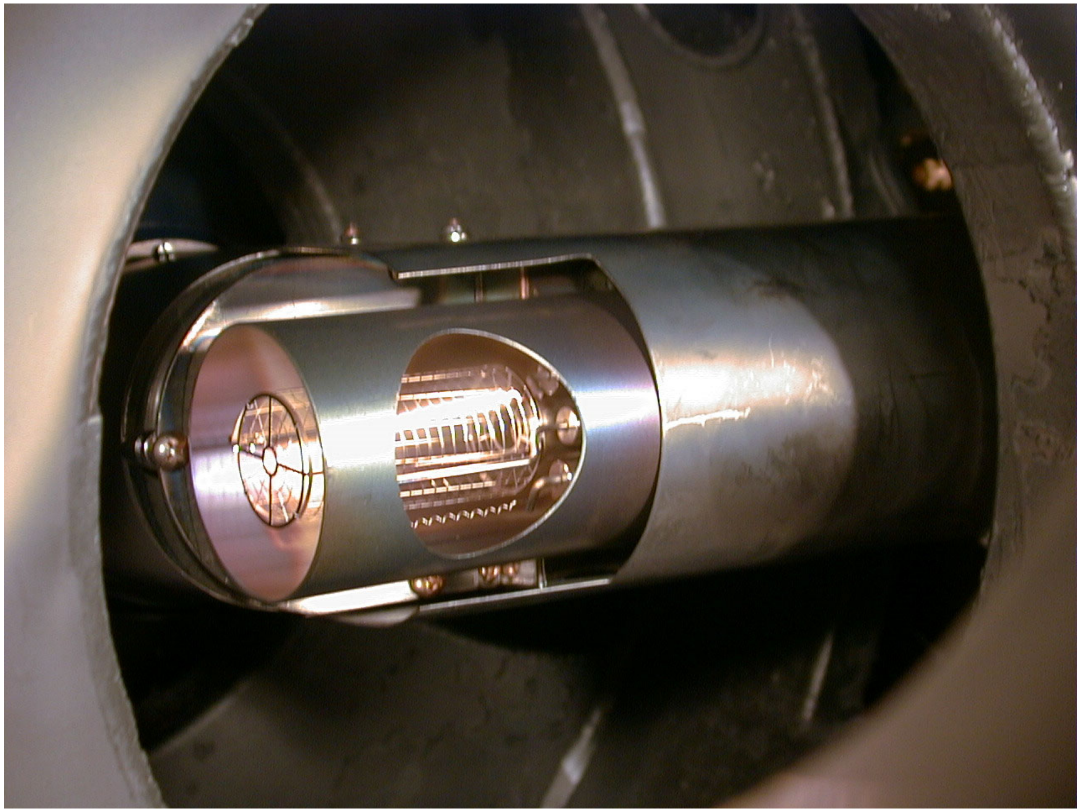
conical crucibles:
better beam homogeneity



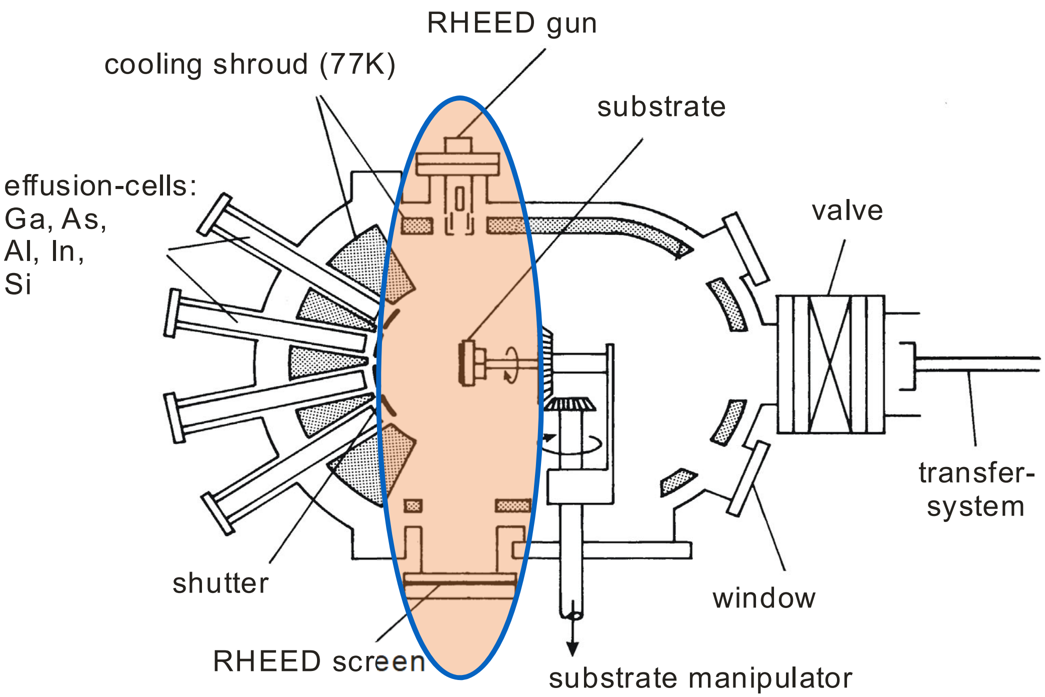
Substrate and manipulator



Beam flux monitor

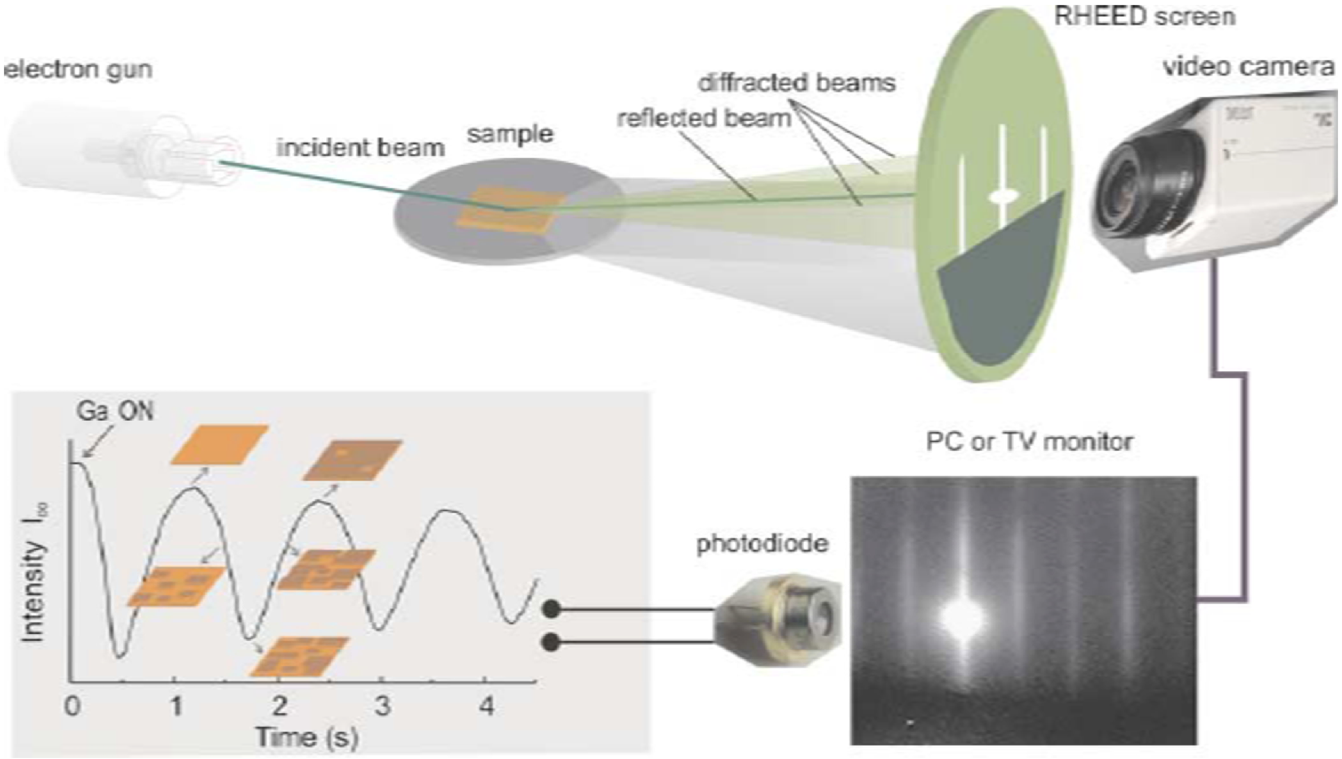


In situ monitoring



The strength of MBE is the purity of materials but also control of growth conditions and in situ monitoring.

Surface analysis: RHEED



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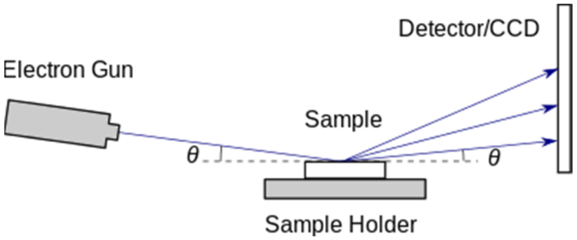
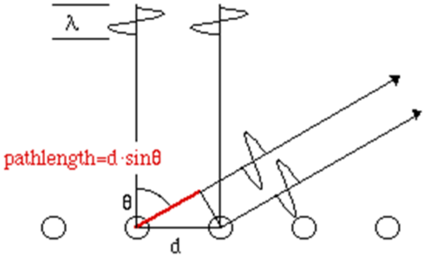
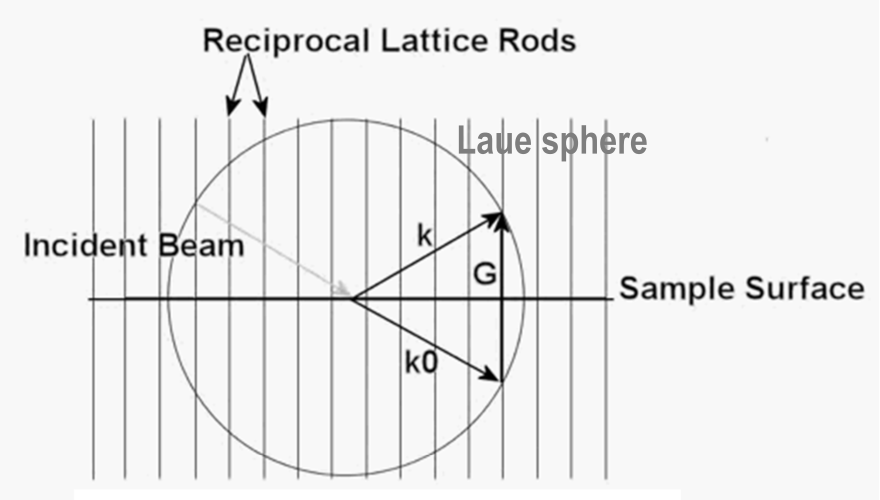
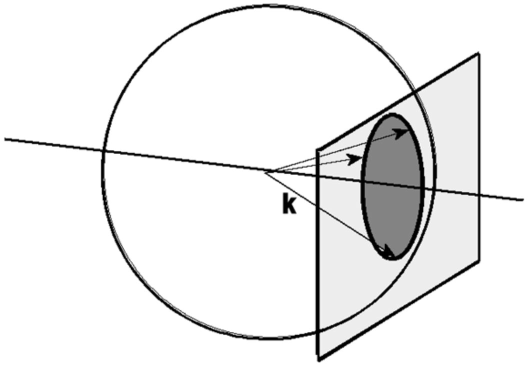
Surface analysis: RHEED

Surface diffraction

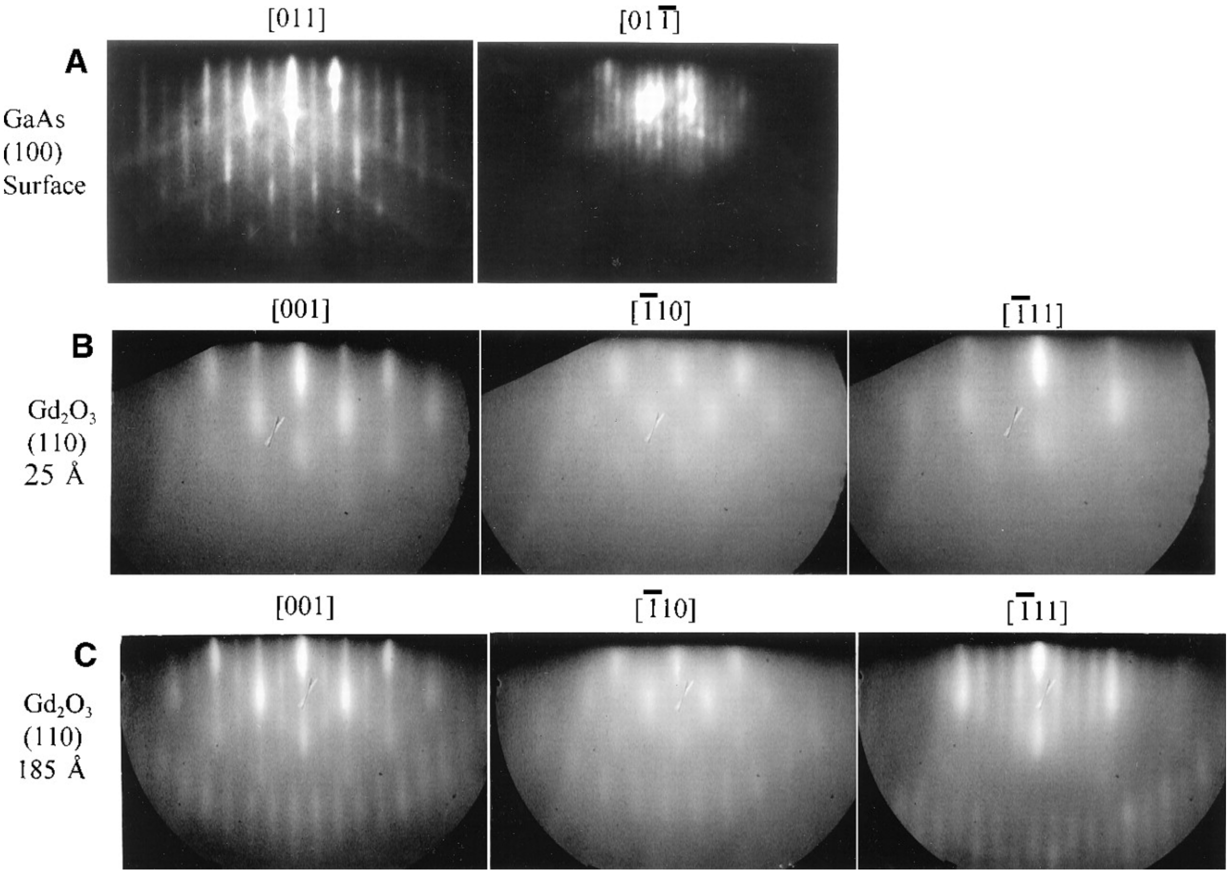






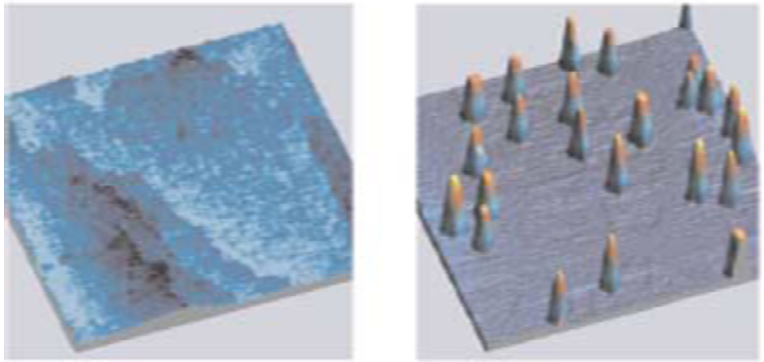


Surface analysis: RHEED

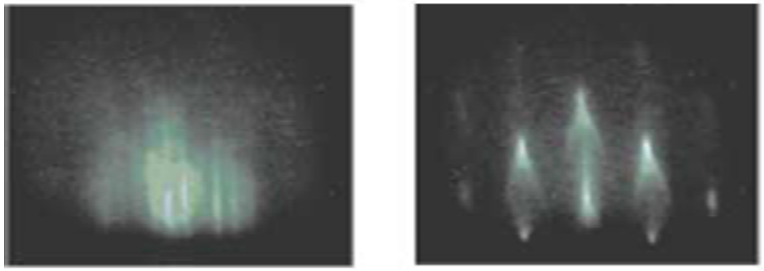


Science. 283, 1897-900 (1999)

RHEED patterns

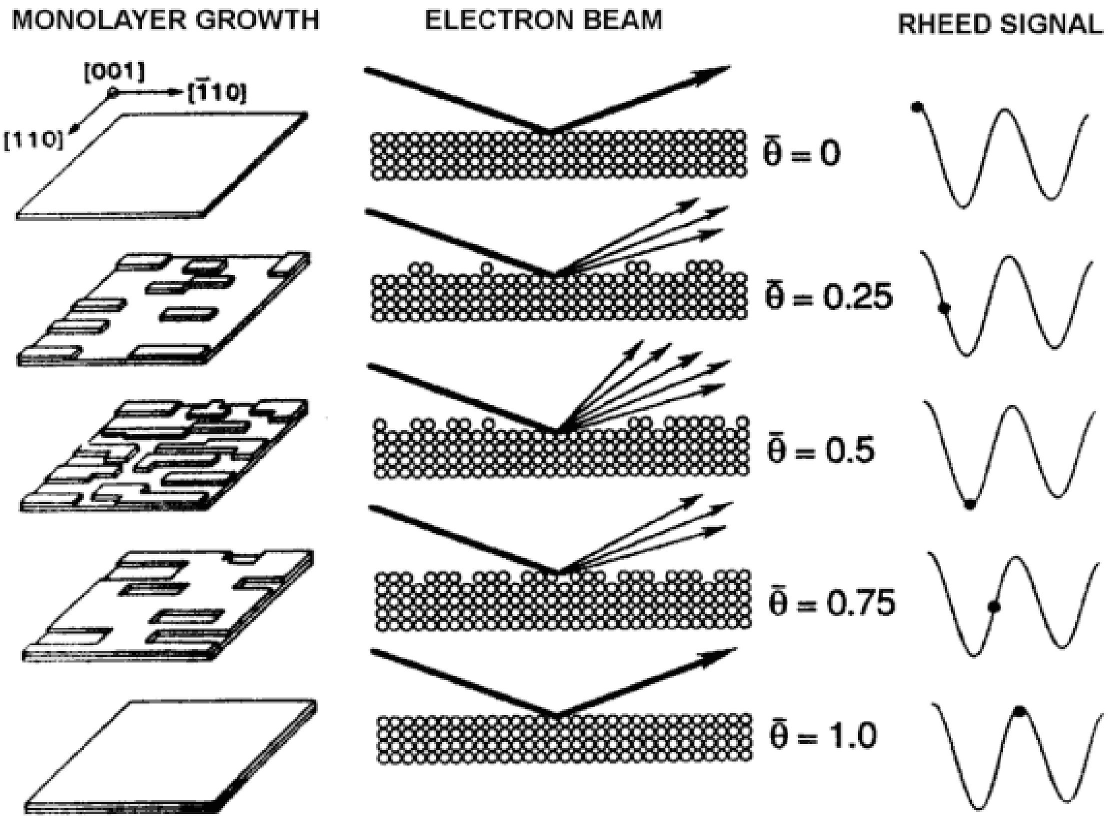


AFM



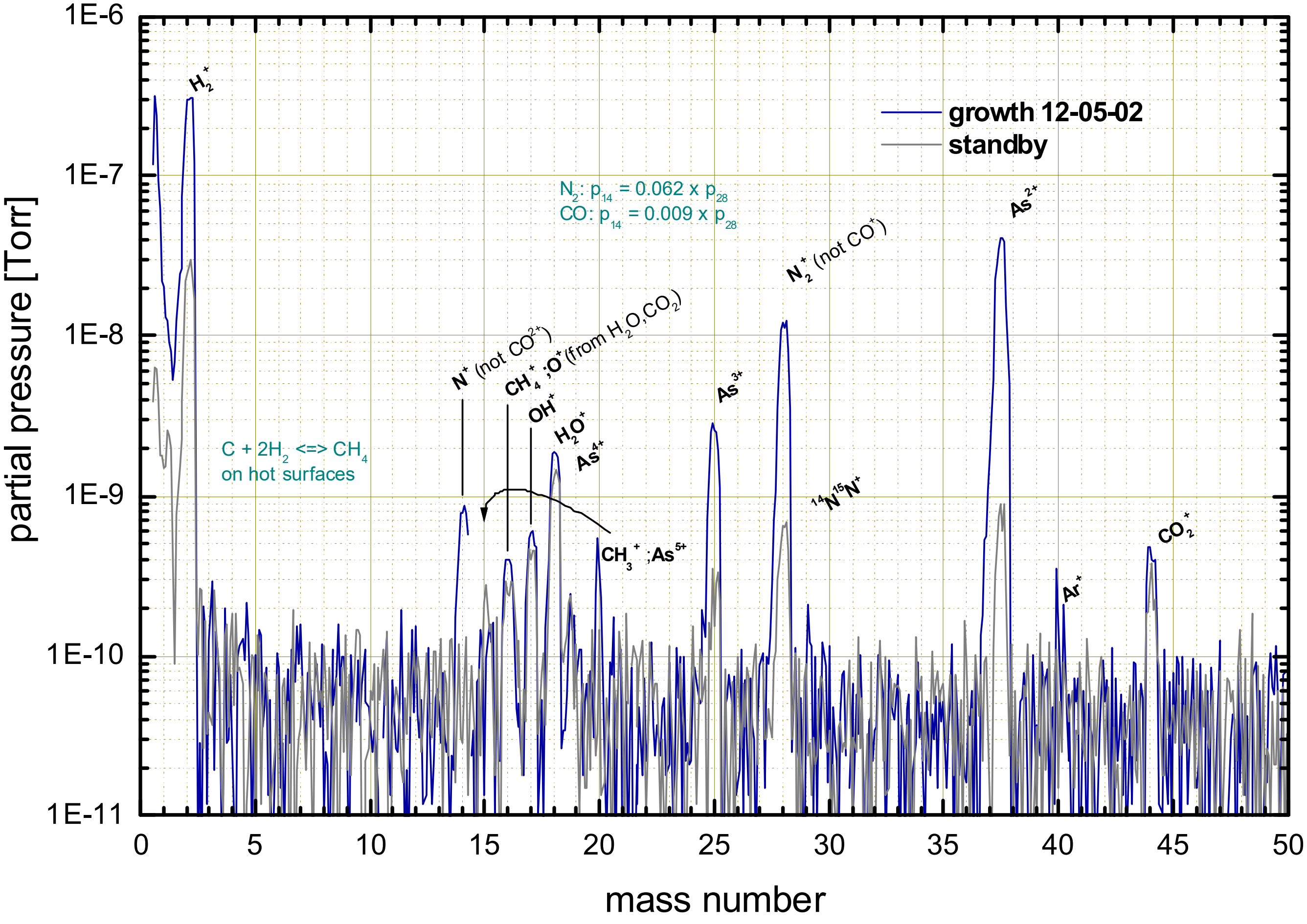
RHEED

Surface analysis: RHEED



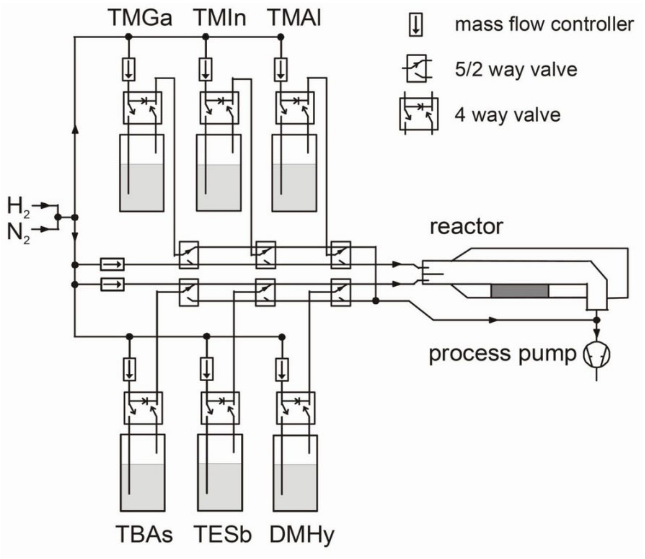
M. Ohring, The Material Science of Thin Films, Academic Press, New York, 1992

Analysis of the vacuum: mass spectrometry



MOCVD:
Metalorganic chemical vapor deposition
or MOVPE:
Metalorganic chemical vapor epitaxy

MOCVD



Main difference with MBE:
Precursors need to be decomposed at the surface.

MOCVD of III-Vs

Group III: organometallic or metal alkyl precursors

Trimethylgallium Ga/In/Al$(CH_3)_3$ TMGa TMAl ,TM In

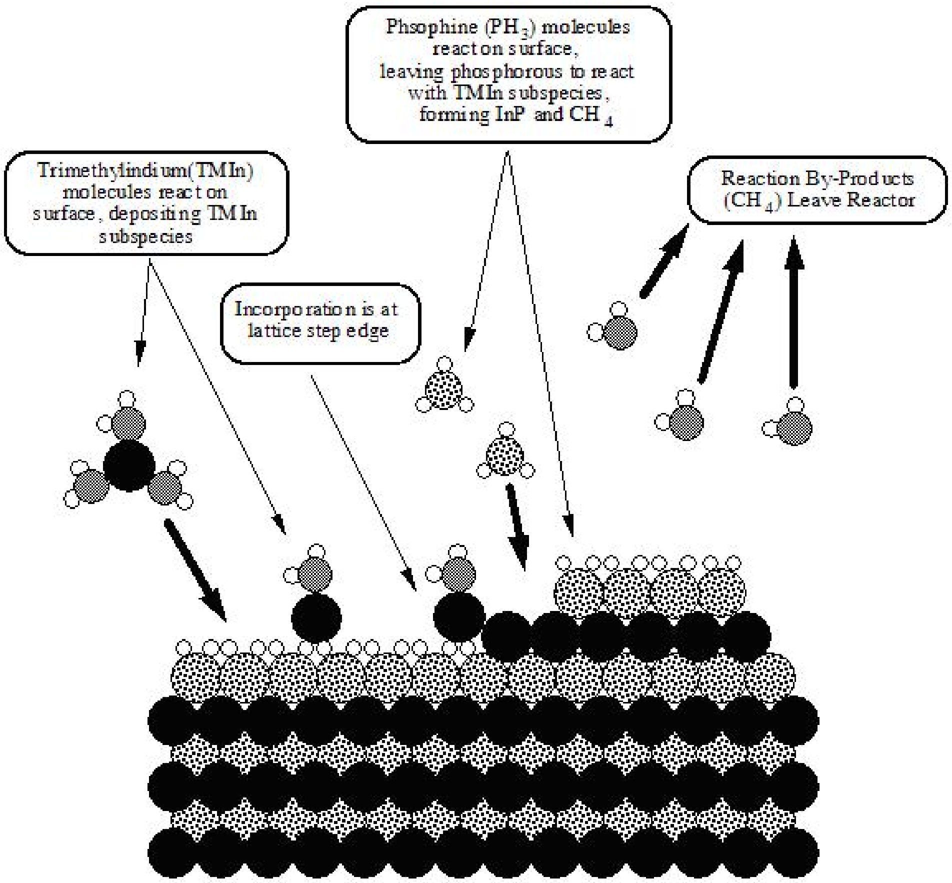
Group V:
hydride precursors AsH_3 and PH_3
Metalorganic for Sb: TMSb

H_2 carrier gas 5 000 -10 000 sccm, typical flows, e.g. 100 mbar

Growth occurs through pyrolytic reactions on the substrate or gas phase:

$$Ga(CH_3)_3 + AsH_3 \rightarrow GaAs + 3CH_4$$
$$Al(CH_3)_3 + AsH_3 \rightarrow AlAs + 3CH_4$$

Precursor decomposition and reaction kinetics

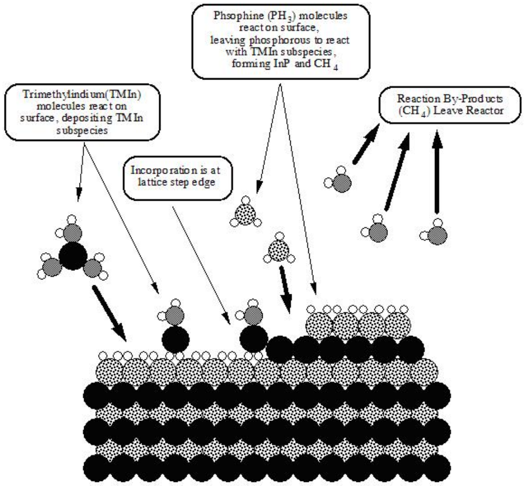


Phsophine (PH_3) molecules react on surface, leaving phosphorous to react with TMIn subspecies, forming InP and CH_4

Trimethylindium(TMIn) molecules react on surface, depositing TMIn subspecies

Reaction By-Products (CH_4) Leave Reactor

Incorporation is at lattice step edge



S.P. Den Baars et al JCrystGrowth 77, 188 (1986)
CA Larsen et al JCrystGrowth 102, 103 (1990)
M Wolf et al Surf Sci 275, 41 (1992)

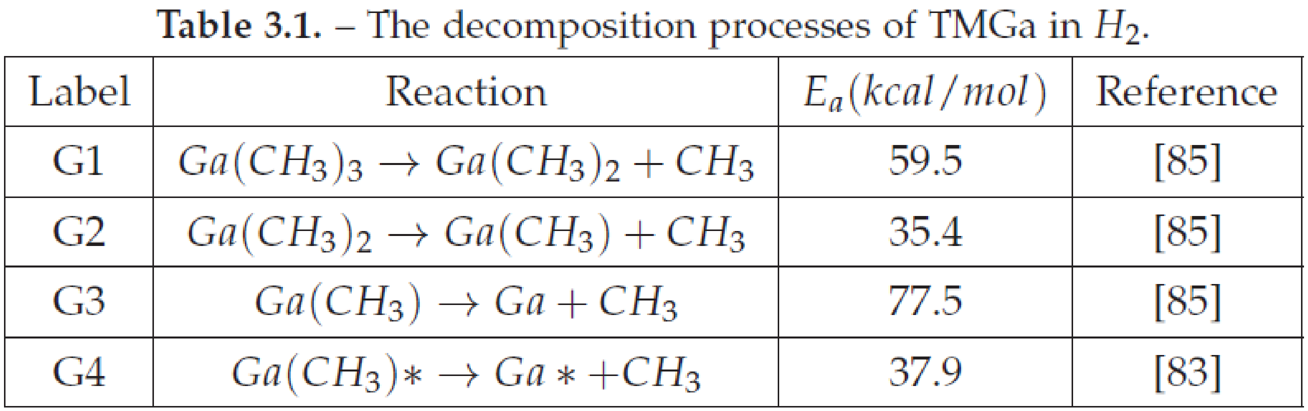


Table 3.1. – The decomposition processes of TMGa in H_2.

Label	Reaction	$E_a(kcal/mol)$	Reference
G1	$Ga(CH_3)_3 \rightarrow Ga(CH_3)_2 + CH_3$	59.5	[85]
G2	$Ga(CH_3)_2 \rightarrow Ga(CH_3) + CH_3$	35.4	[85]
G3	$Ga(CH_3) \rightarrow Ga + CH_3$	77.5	[85]
G4	$Ga(CH_3)* \rightarrow Ga * + CH_3$	37.9	[83]