Lecture 22 –
Thin Film Deposition

EECS 598-002 Winter 2006
Nanophotonics and Nano-scale Fabrication
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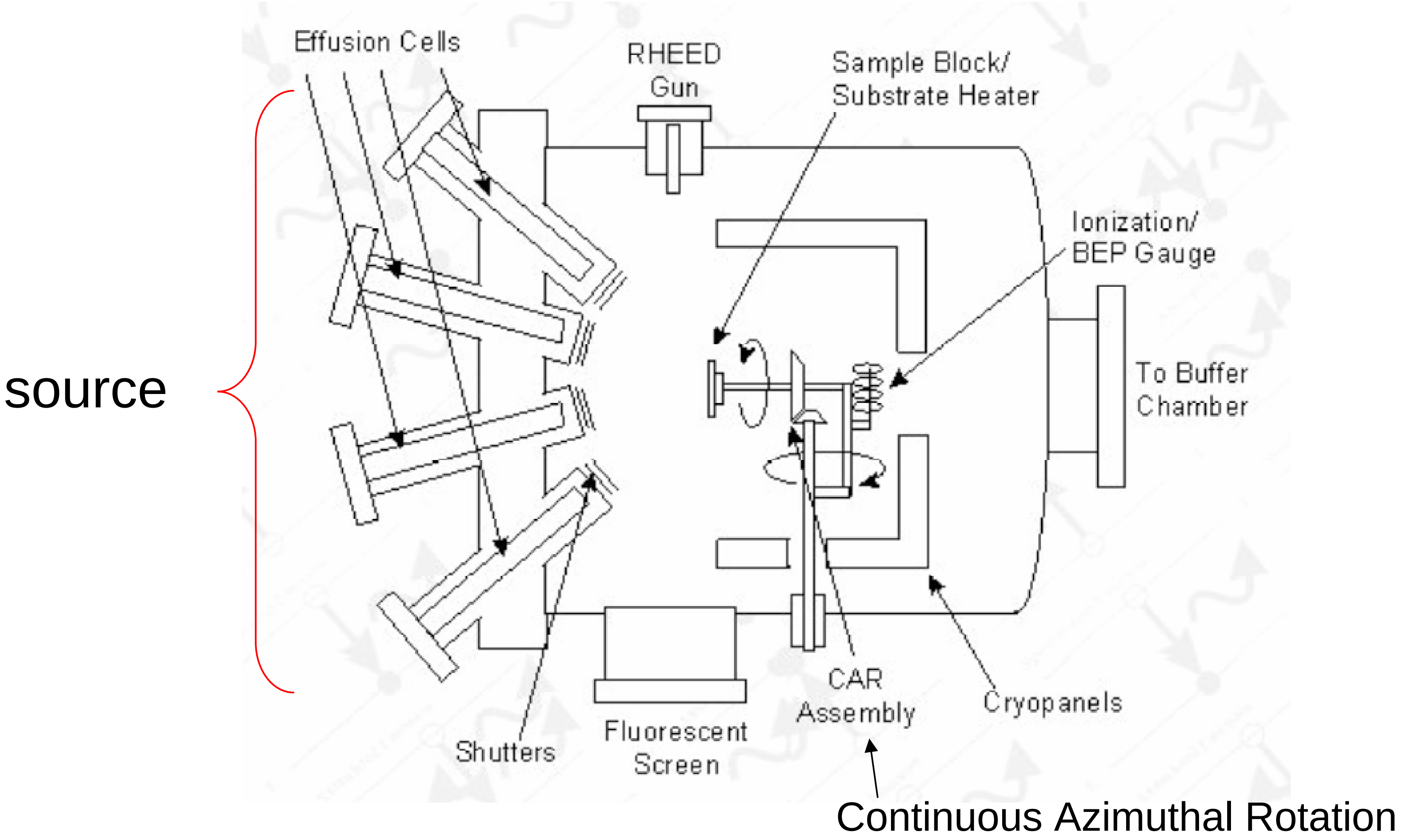
Overview

- MBE (molecular beam epitaxy)
- MOCVD (metal-organic chemical vapor deposition)
- ALE (atomic layer epitaxy)

- All of the above techniques provide single crystalline epitaxy with atomic layer precision.

MBE schematic

From UCSB course materials:
http://www.ece.ucsb.edu/courses/ECE594/594F_F05Gossard/September 27b.pdf

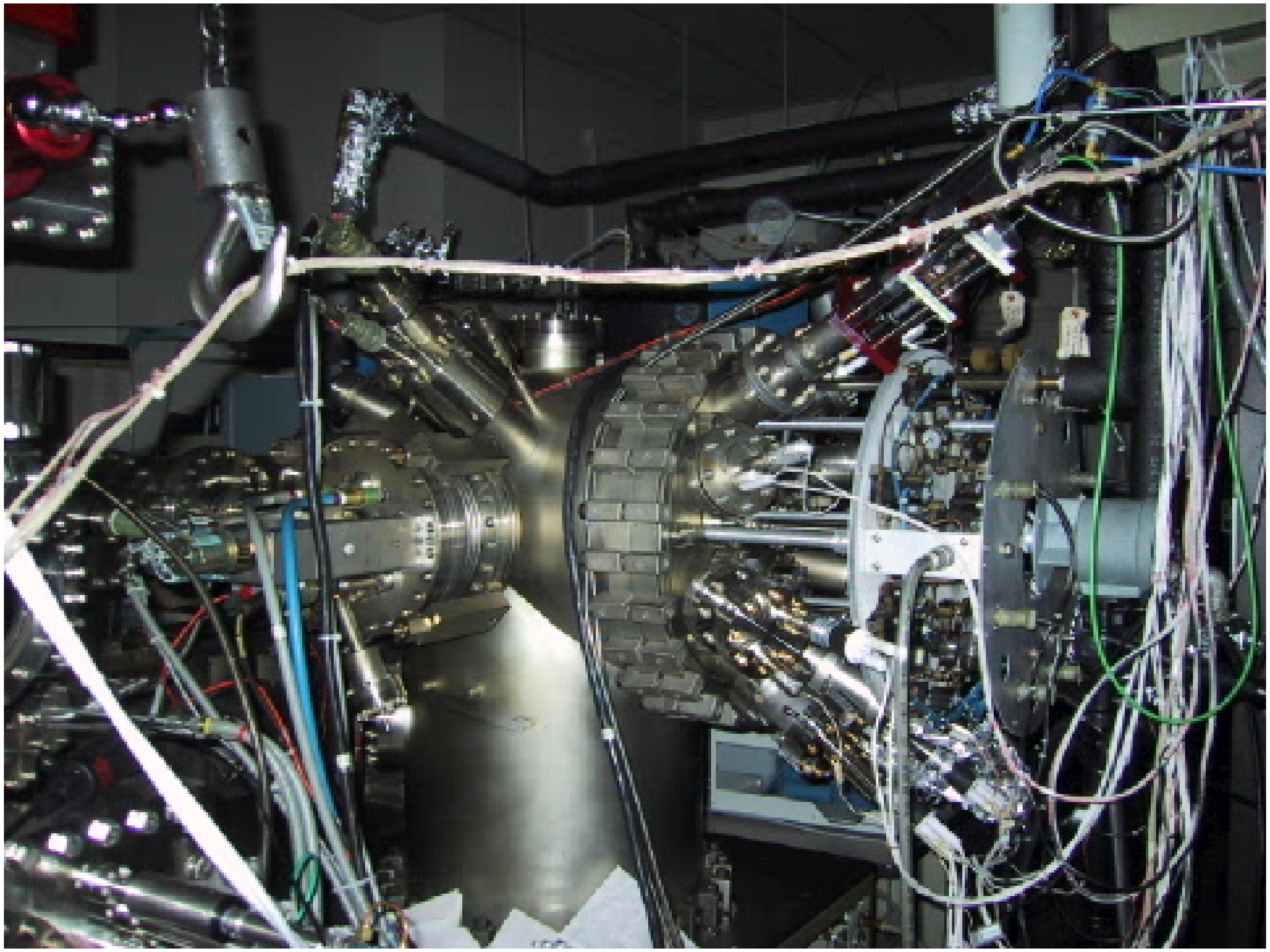


MBE operation

- MBE operates under an ultra-high vacuum ($< 10^{-10}$ torr) environment. That means during growth, the background residual gas such as H_2O, CO_2, and etc have negligible partial pressures compared to the sources.

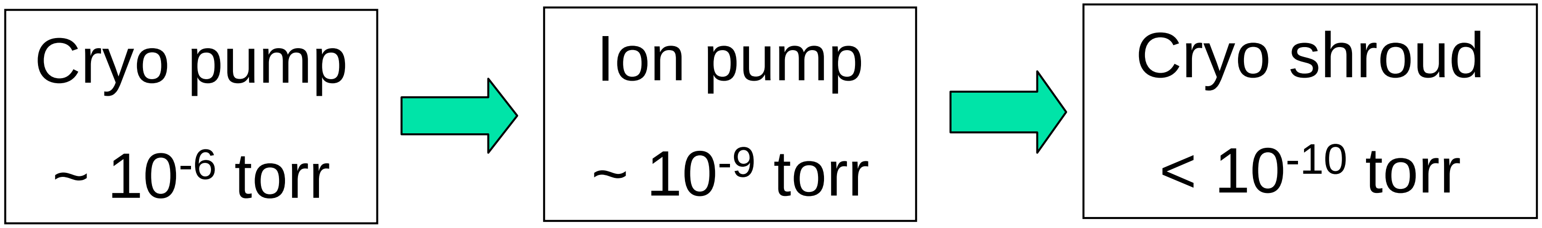
- The source either evaporates at ~ 600 ° C (solid-source MBE) or cracks into elemental form (gas-source MBE) and deposits onto a heated substrate (~ 400 ° C).

MBE system



Vacuum pumps

- MBE is mostly about vacuum. It is crucial to maintain a good vacuum environment to ensure the quality of the epitaxial layers.
- But it is also the UHV environment that makes a lot of insitu monitoring techniques applicable (e.g. RHEED).



Cryo pump

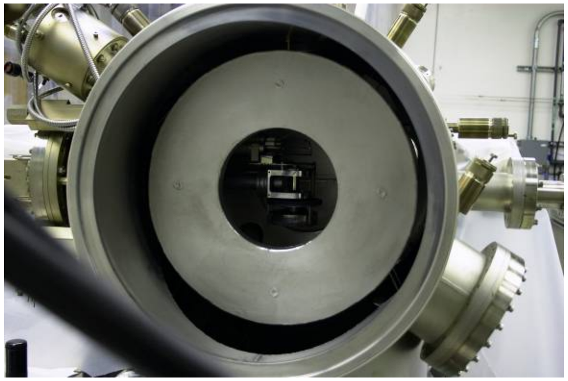
~ 10^{-6} torr

Ion pump

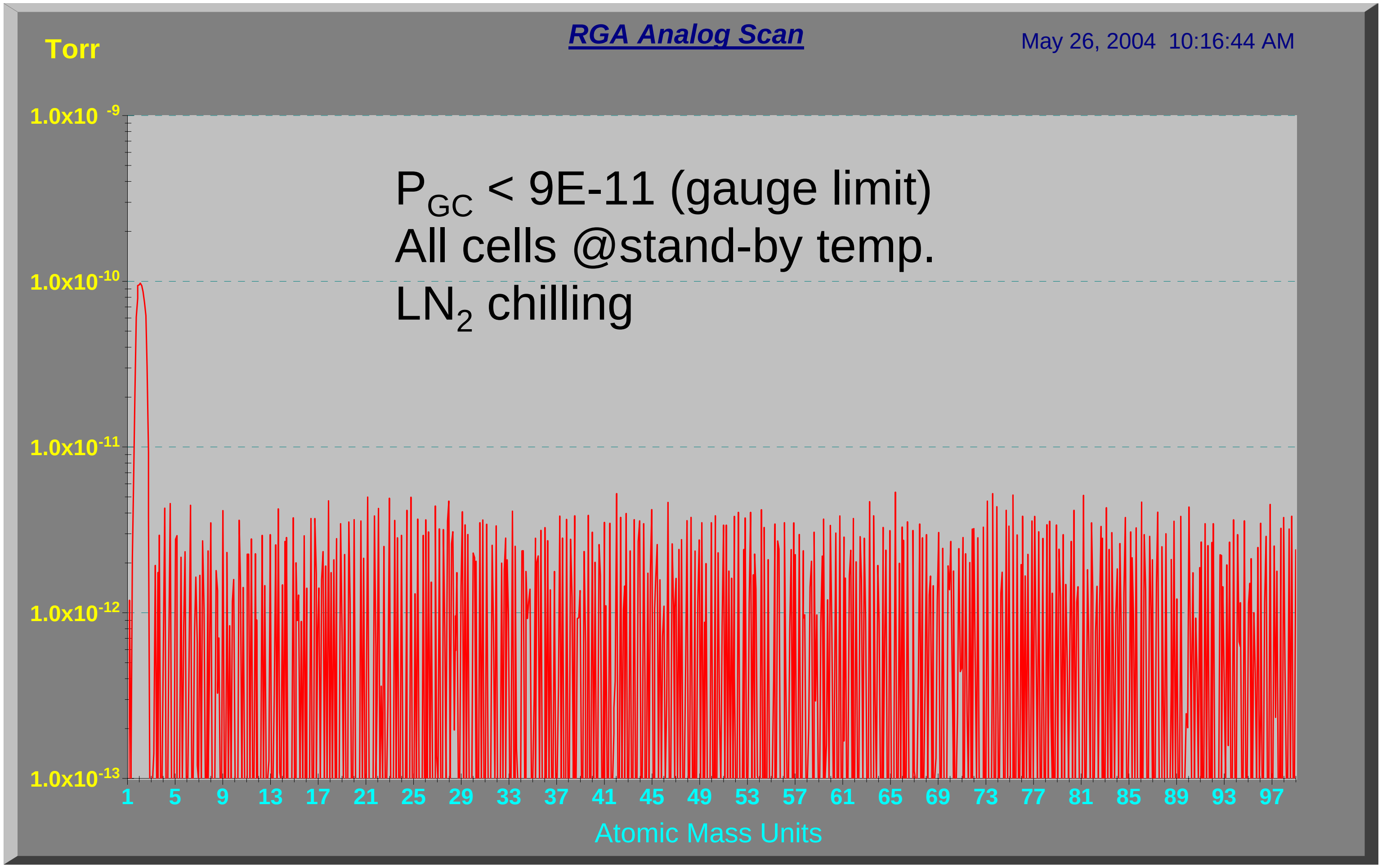
~ 10^{-9} torr

Cryo shroud

< 10^{-10} torr

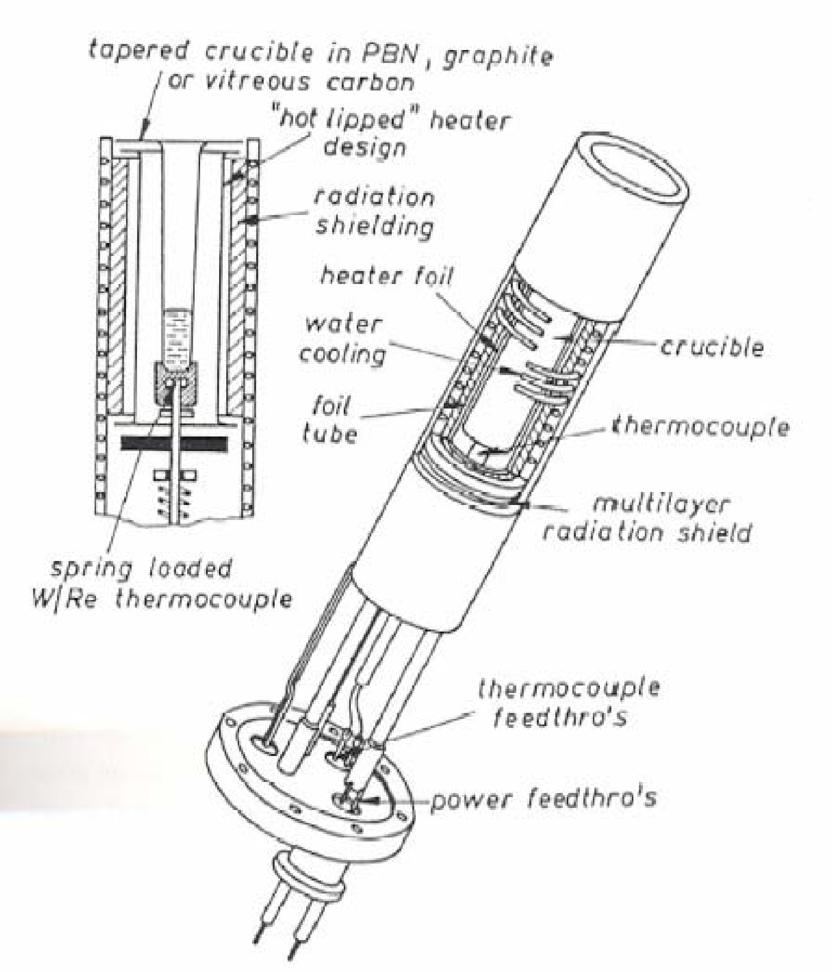


RGA (residual gas analyzer)



P_{GC} < 9E-11 (gauge limit)
All cells @stand-by temp.
LN_2 chilling

Effusion cell (Knudsen cell)



PBN = pyrolytic boron nitride

- The mean free path of the evaporated source element is long enough (if pressure is < 10^{-5} torr during growth) to allow the element to travel to the substrate surface along a straight path.

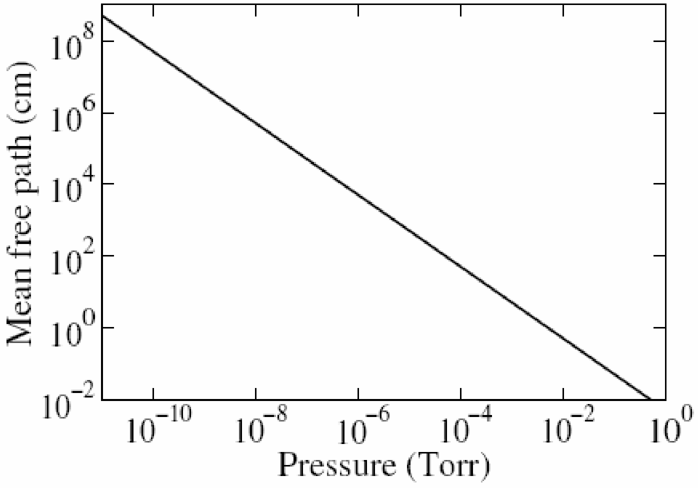
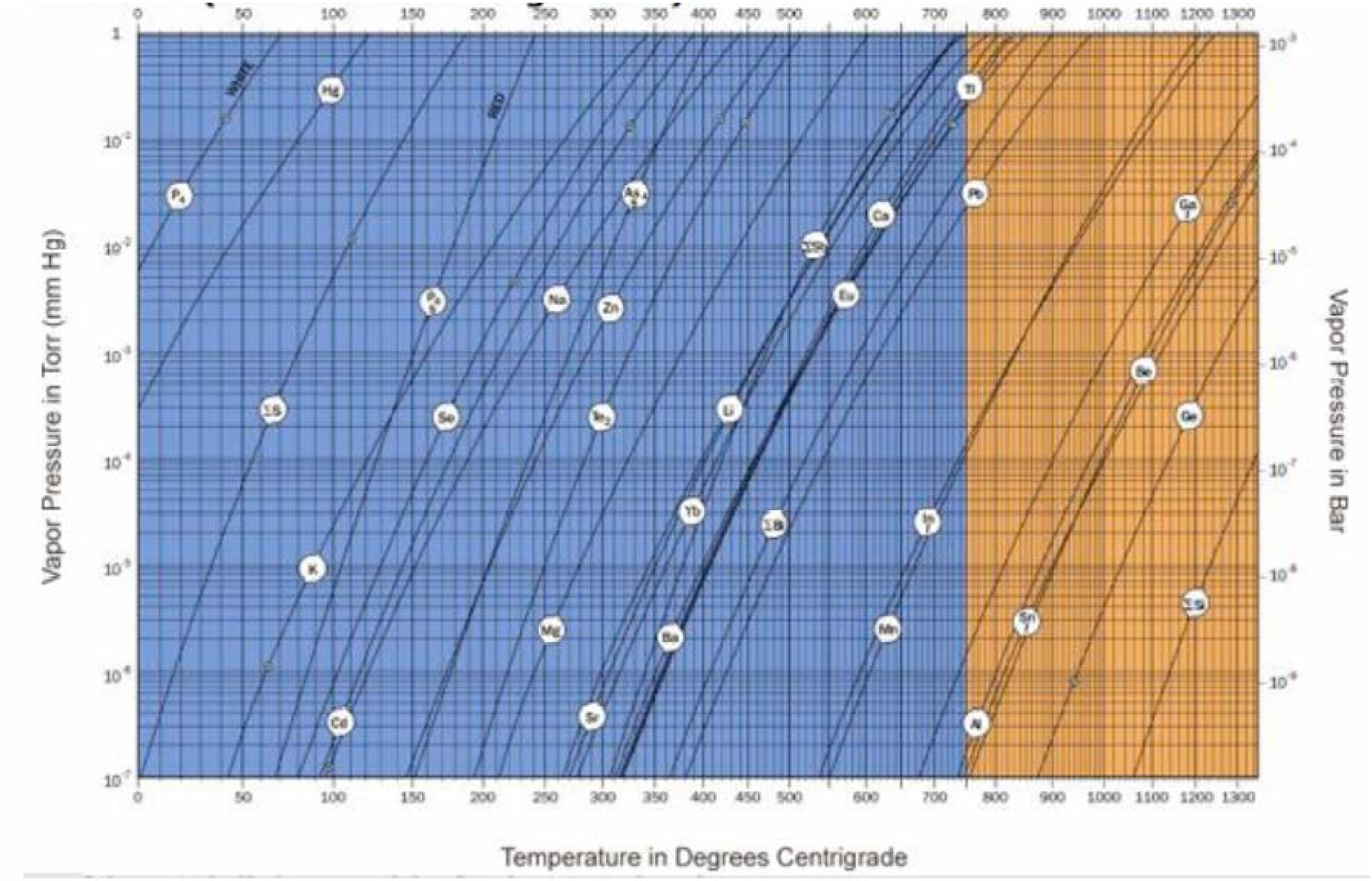


Fig. 2: Mean free path for nitrogen molecules at 300K.


Vapor Pressure in Torr (mm Hg)
Vapor Pressure in Bar
Temperature in Degrees Centrigrade
1
10^{-1}
10^{-2}
10^{-3}
10^{-4}
10^{-5}
10^{-6}
10^{-7}
10^{-3}
10^{-4}
10^{-5}
10^{-6}
10^{-7}
10^{-8}
10^{-9}
0
50
100
150
200
250
300
350
400
450
500
600
700
800
900
1000
1100
1200
1300
WHITE
RED
Hg
P_4
As
Na
Zn
Se
Te
Li
Yb
In
K
Mg
Ba
Mn
Cd
Sr
Tl
Pb
Ca
Eu
Al
Sn
Ga
Be
Ge

RHEED

- RHEED = reflection high energy (5-100 keV) electron diffraction
- One RHEED oscillation corresponds to one monolayer growth

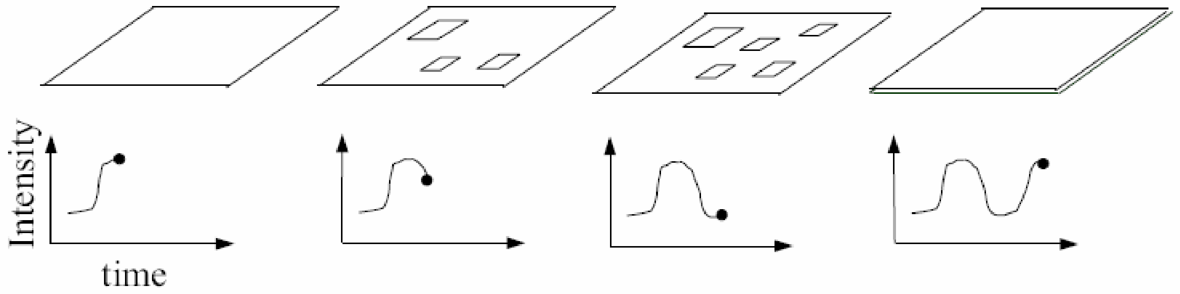
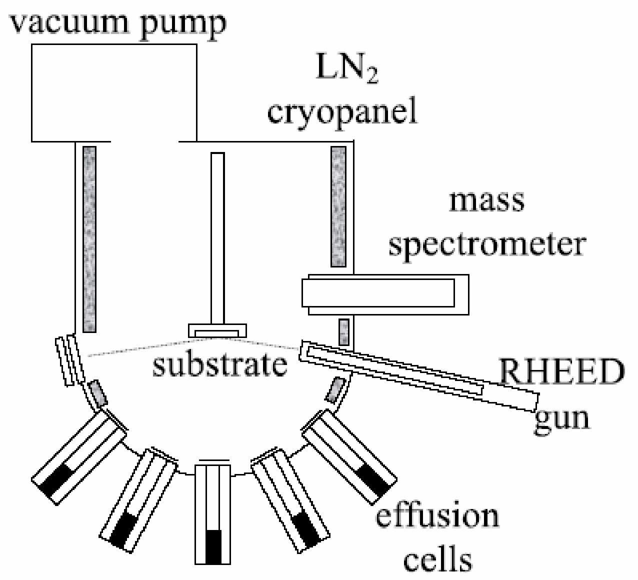


Fig. 3: RHEED oscillations.

From http://www-opto.e-technik.uni-ulm.de/forschung/jahresbericht/2002/ar2002_fr.pdf

Surface reconstruction

- RHEED can also be used to monitor the surface reconstruction because of its shallow incidence angle (< 5 °)



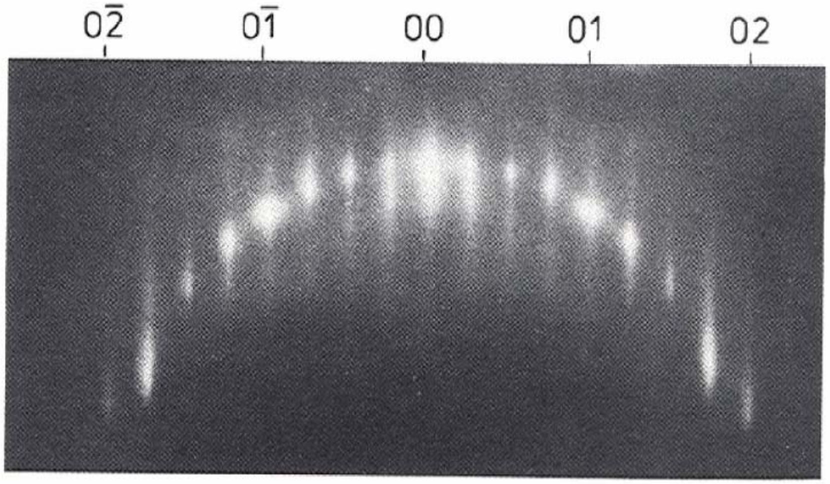


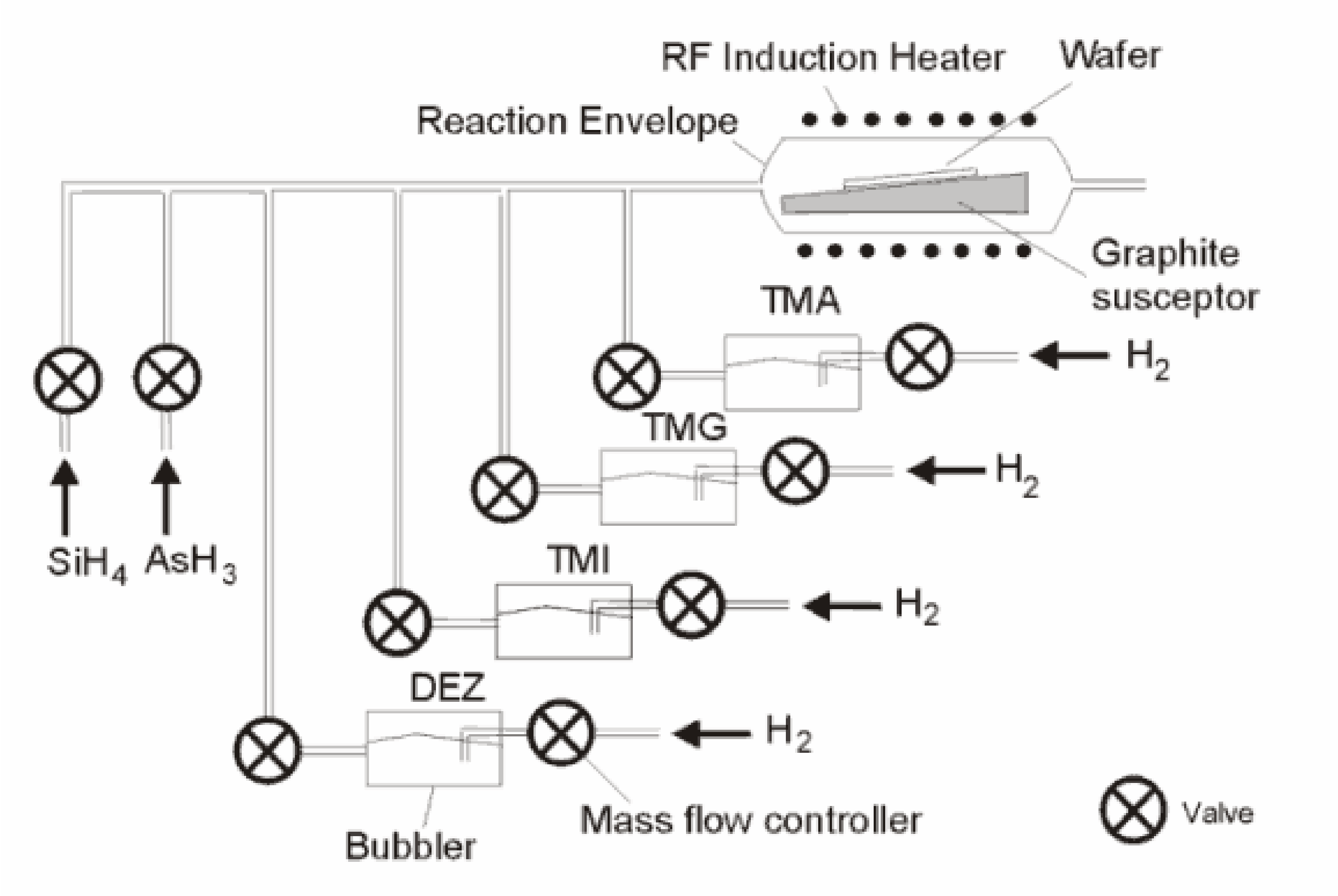
Fig. 3.30. Diffraction pattern from the GaAs(001)-(2 × 4) surface, in the [$\bar{1}10$] azimuth, taken at an electron energy of 12.5 keV and an incident angle of 3.1° [3.22]

From http://www.courses.vcu.edu/PHYS550/presentations2000/rheed.pdf

Free MBE simulator

- http://uberfast.ece.ucsb.edu/~mgrund/kmcinteractive/kmcinteractive.html
  - Runs only on Mac OS

MOCVD


RF Induction Heater
Wafer
Reaction Envelope
Graphite susceptor
TMA
H_2
TMG
H_2
SiH_4
AsH_3
TMI
H_2
DEZ
H_2
Bubbler
Mass flow controller
Valve

Hydrogen purification

- Using palladium cell, the hydrogen can be purified to > 99.9999999% purity.

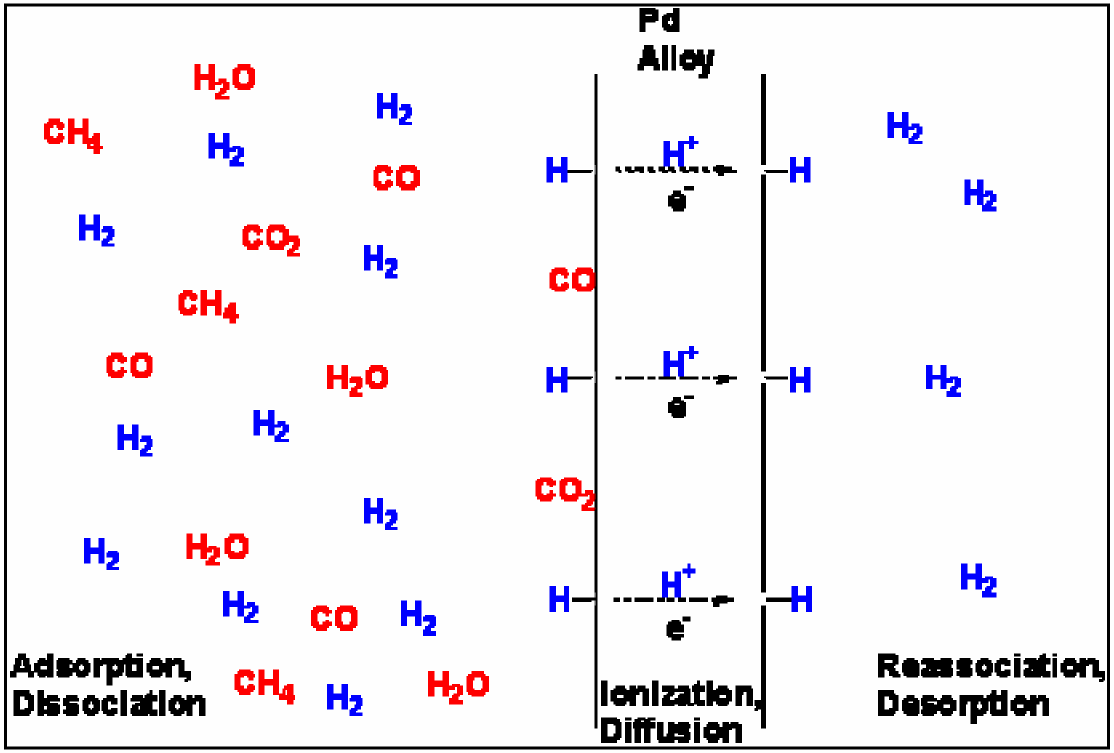


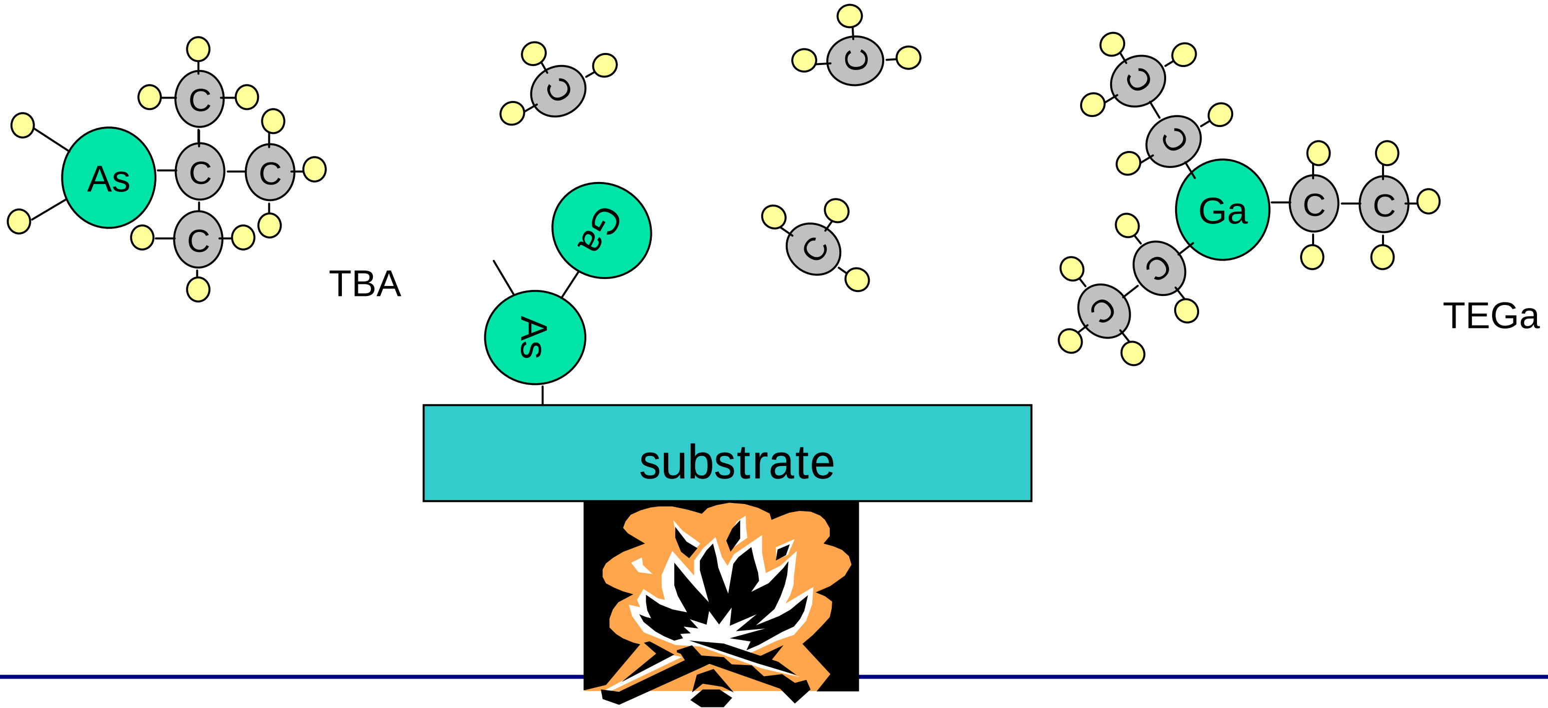
Figure 1. Mechanism of hydrogen diffusion through Pd alloy

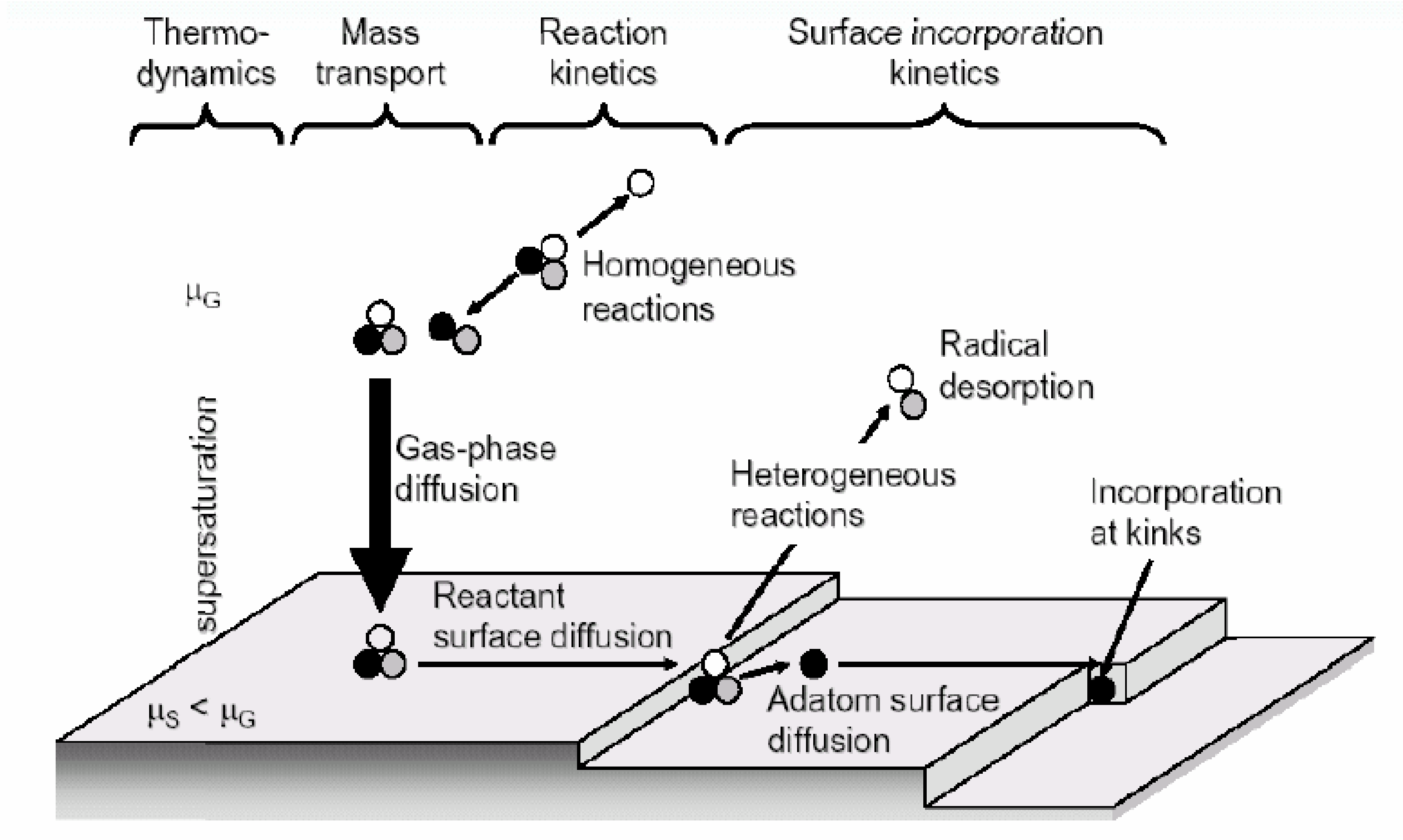
MOCVD vs MBE

- Advantages
  - Faster growth rate (favored by industry)
  - Wide temperature control range. Better film quality.
  - Shorter system downtime
- Disadvantages
  - Toxic sources
  - Huge set of parameters. Hard to control.
  - Not UHV environment. Some insitu monitoring techniques are not applicable.

MOCVD operation

- Precursors (e.g. TEGa for Ga and TBA for As) carried by hydrogen gas to the reactor.
- Precursors transported from reactor top to the heated substrate surface with a flux rate determined by flow pattern.
- Precursors crack due to high temperature on top of the wafer surface.
- Ga+As (gas phase) → GaAs (stable solid compound)



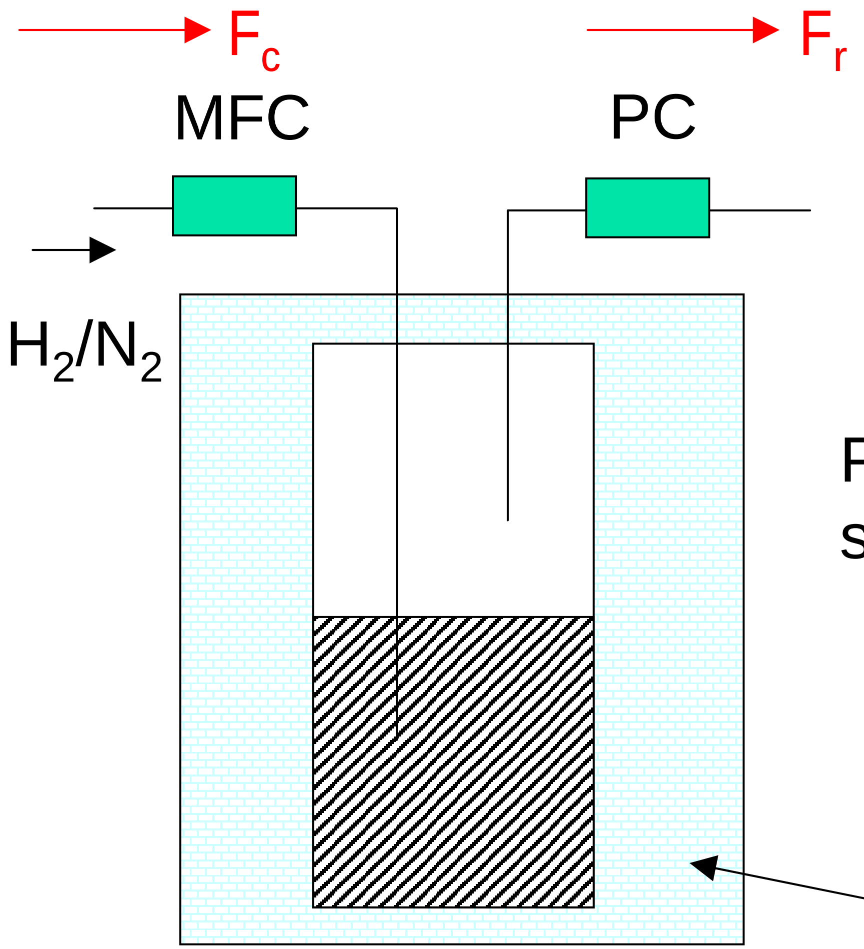

Thermo-
dynamics
Mass
transport
Reaction
kinetics
Surface *incorporation*
kinetics
Homogeneous
reactions
μ_G
Radical
desorption
supersaturation
Gas-phase
diffusion
Heterogeneous
reactions
Incorporation
at kinks
Reactant
surface diffusion
Adatom surface
diffusion
$\mu_S < \mu_G$

Growth regimes

- Reaction limited regime:
  - At low temperature (e.g. < 500 ° C for GaAs growth), the diffusion process is faster than the surface process. The growth rate increases with temperature.

- Diffusion limited regime:
  - At higher temperature (e.g. 600 ° C for GaAs growth), the diffusion process is slower than the surface process. The growth rate is limited by the diffusion process and therefore controlled only by the mass flow. It is the normal growth regime.

Bubbler theory



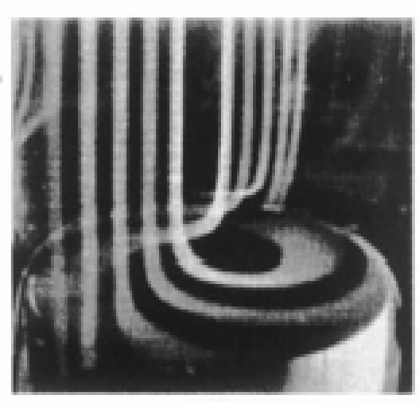
$$F_r = F_c \frac{P_r}{P_i} = F_c \frac{P_r}{P_o - P_r}$$

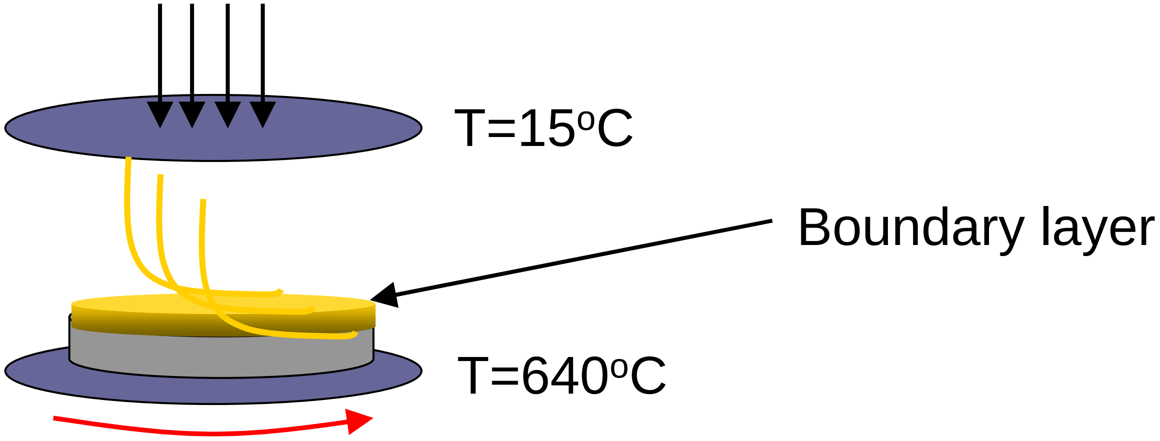
Pr = vapor pressure of the MO source = *f*(T)

Water bath

Rotating disk reactor

- Rotating-disk reactor schematics and fluid flow pattern as follows*





- Metal-organic precursors decompose into reactant adatoms near the wafer surface in the boundary layer.

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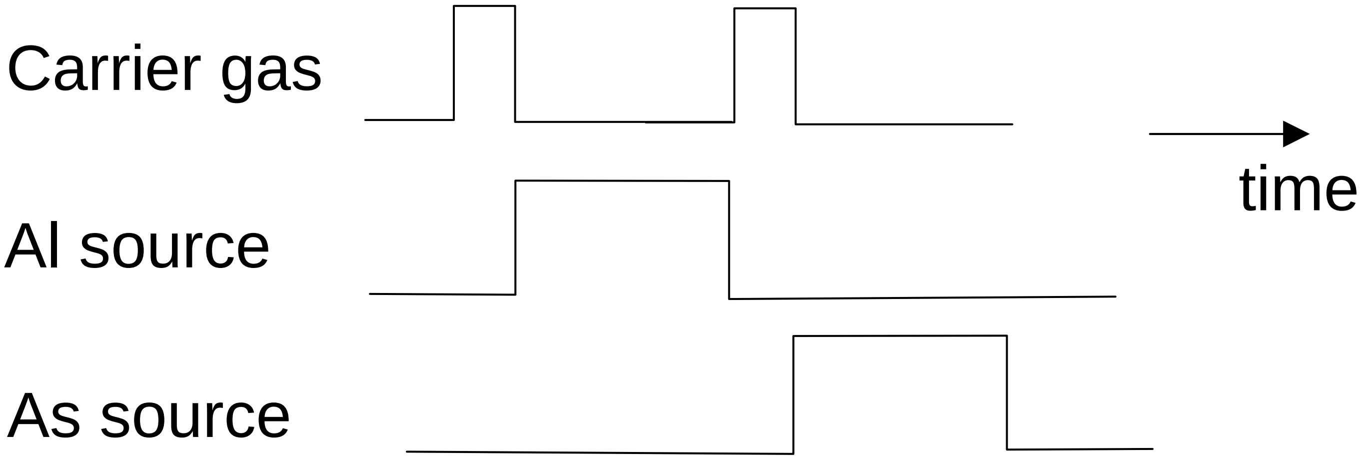
* W. G. Breiland et al, Material Science and Engineering, R24 (1999) p.241

Atomic layer epitaxy

- Similar to MOCVD but instead of flowing all source species at the same time, each source species of the compound reaches the substrate surface in an alternating fashion.

e.g. AlAs growth



Carrier gas

Al source

As source

time

ALE operation

- Since the ALE growth is a self-limiting process, one monolayer is deposited during each cycle.

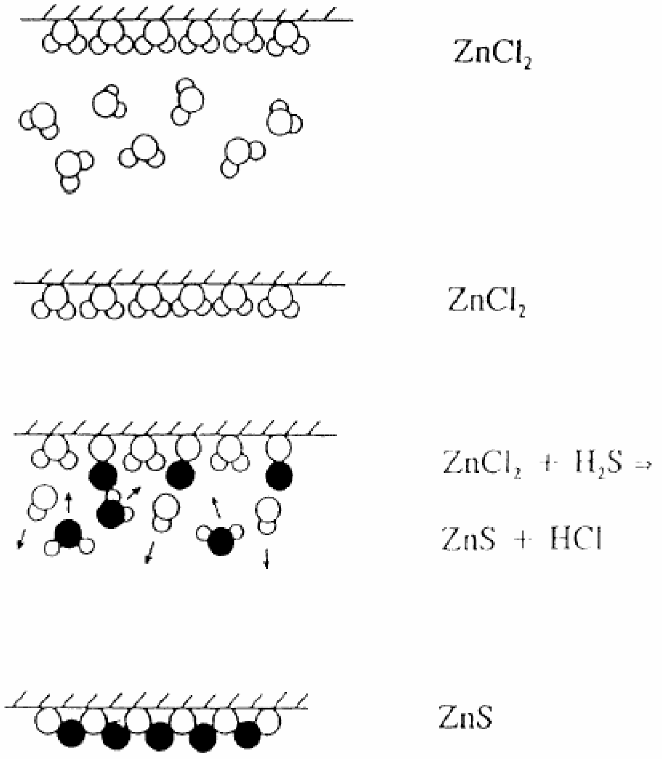


Figure 1. A schematic representation of the basic principle of the ALE process showing the growth of ZnS film from $ZnCl_2$ and H_2S.

From Nanotechnology **10** (1999) 19.