Epitaxial Growth
FYS4310

Outline

What is it? Homo-epitaxy, Hetero-epitaxy

Why Epi/What is it used for?

Techniques for epitaxi-overview ,classification

VPE : Vapor Phase Epi

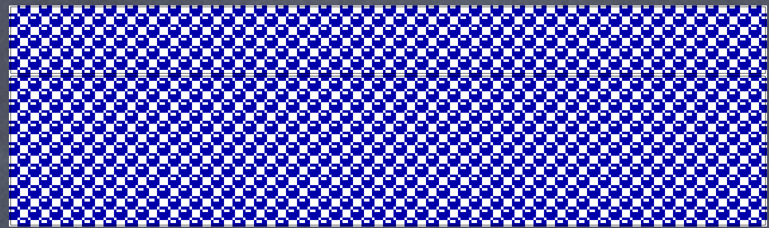
CVD, LPCVD, MOCVD, Rapid Thermal Epi,
Laser Assisted Epi, Ion Beam Assisted Epi,
Cluster beam Epitaxi, MBE, ALE

LPE

SPE (speg)

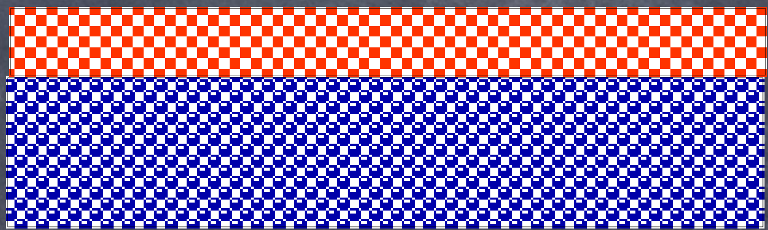
What is it?

Homo-epitaxy,



Example : Si on Si, GaAs on GaAs

Hetero-epitaxy

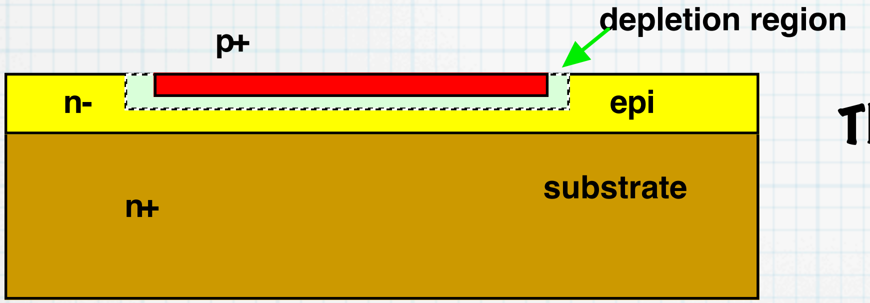


Example: $Ga_xAl_{(1-x)}As$ on GaAs, GaAs on Si,
$Si_xGe_{(1-x)}$ on Si, Si on Al_2O_3 (SOS)
$Ga_xIn_{(1-x)}As$ on InP, $Cd_xHg_{(1-x)}Te$
ZnO on Al_2O_3, GaN on Si

Why epi, What is it used for?

1. Control of doping

For example low doping towards the surface, High doping deeper in Diodes (Signal diodes, power diodes, detectors(not totally depleted)

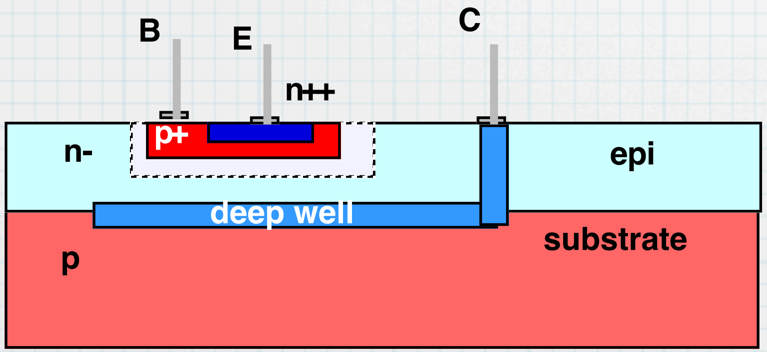


This can not be achieved by diffusion from the surface

Abrupt Doping Concentration changes

If the growth can be done at low enough temperature that there are little diffusion.

Used For Base and Emitter in BiPolars.



0.27

Why epi, What is it used for?2

2. Improve Xtal Quality

3. Three dimentional structures

Quantum dots

4 Quantum Wells, Superlattices, Heterojunctions

Lasers, HEMT, Strain relieve for lattice match, mismatch

5. Graded compositional structures

Base grading, Strain engeneering Si-SiGe transistors

CVD deposition -typical Si system

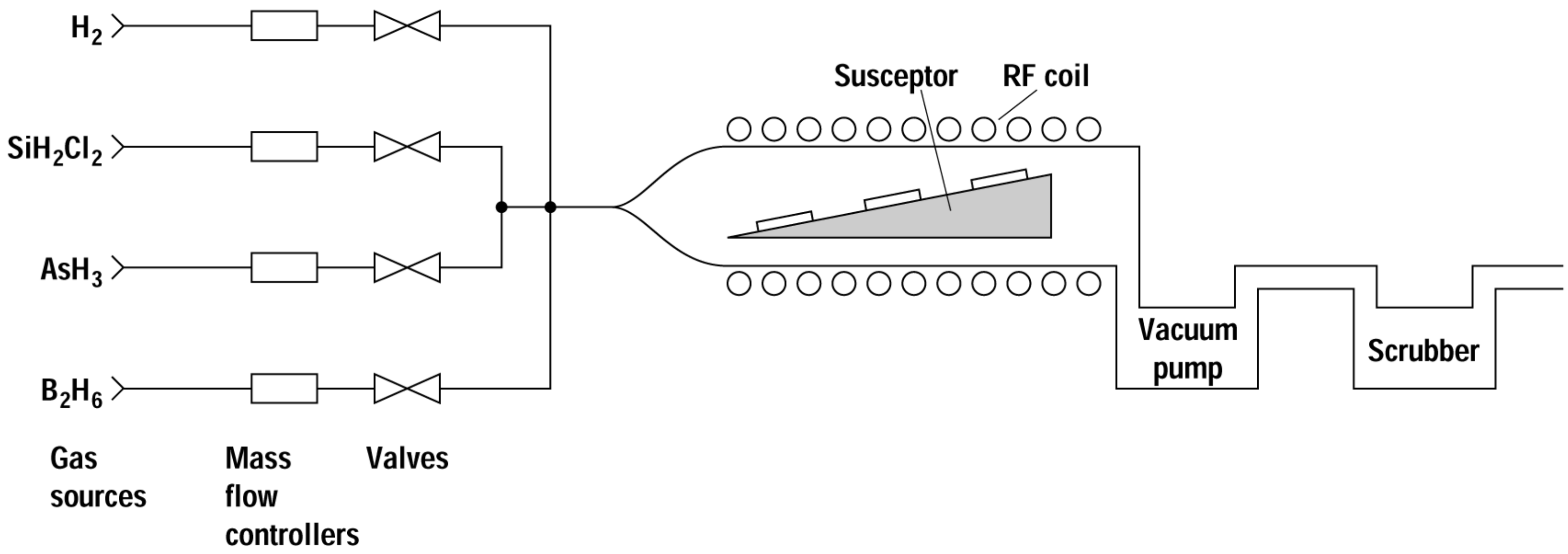
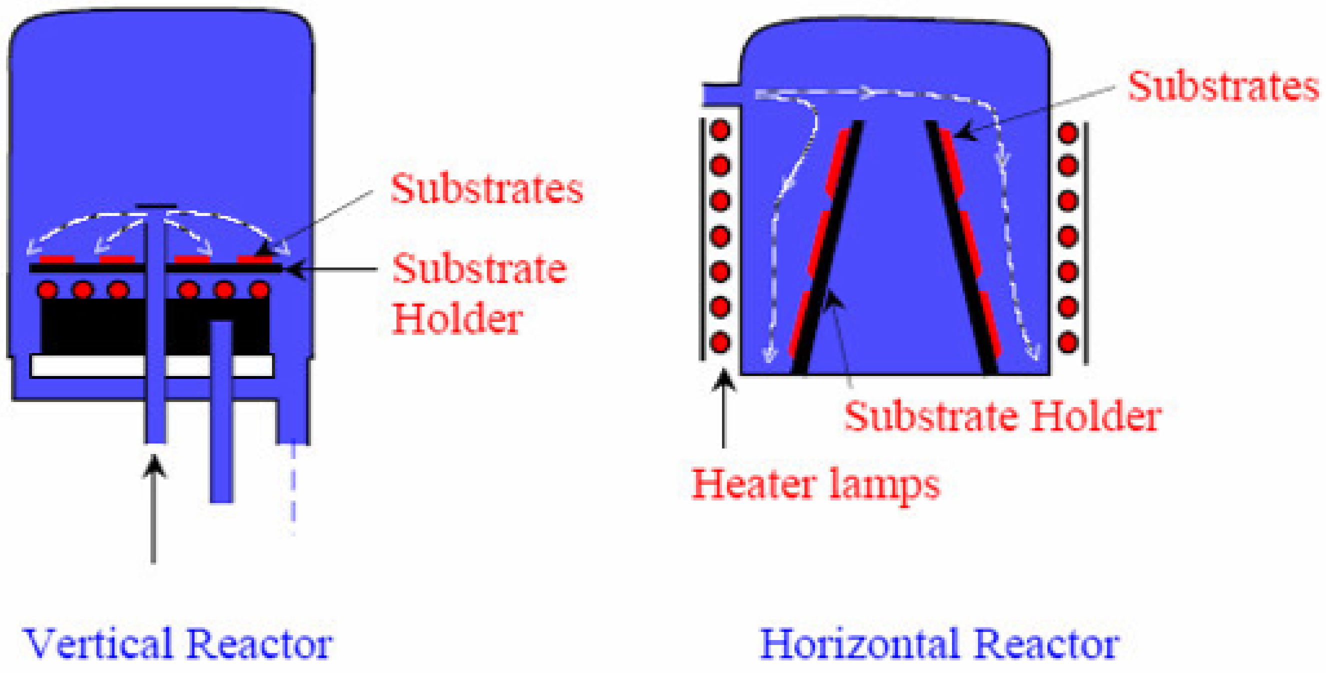


Figure 14.1 A simple VPE system. The susceptor in this chamber is inductively heated using RF power in the external coil.

CVD deposition -various common systems

VPE Growth



Reactors for VPE growth. The substrate temperature must be maintained uniformly over the area. This is achieved better by lamp heating.

Ref: Singh

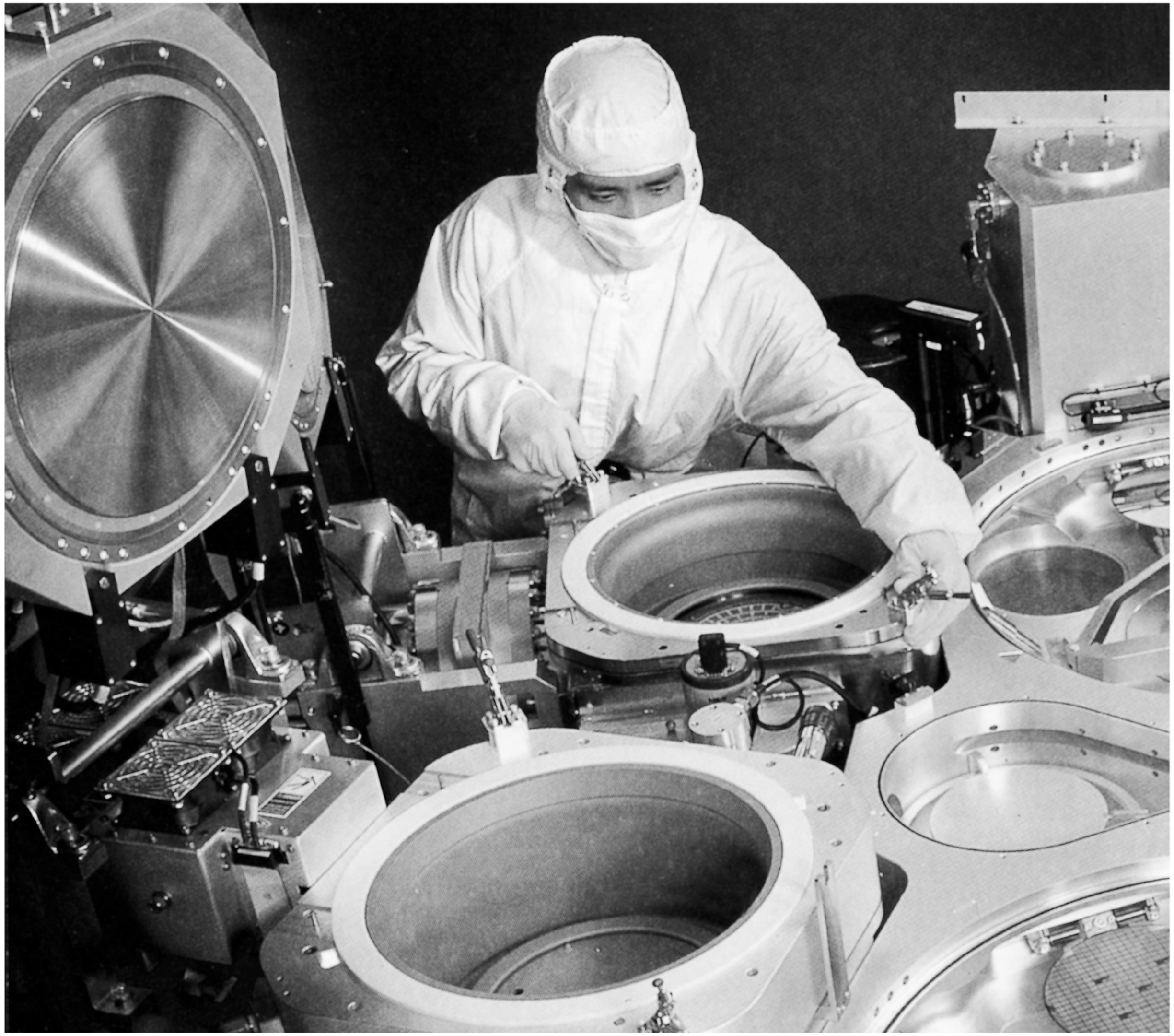
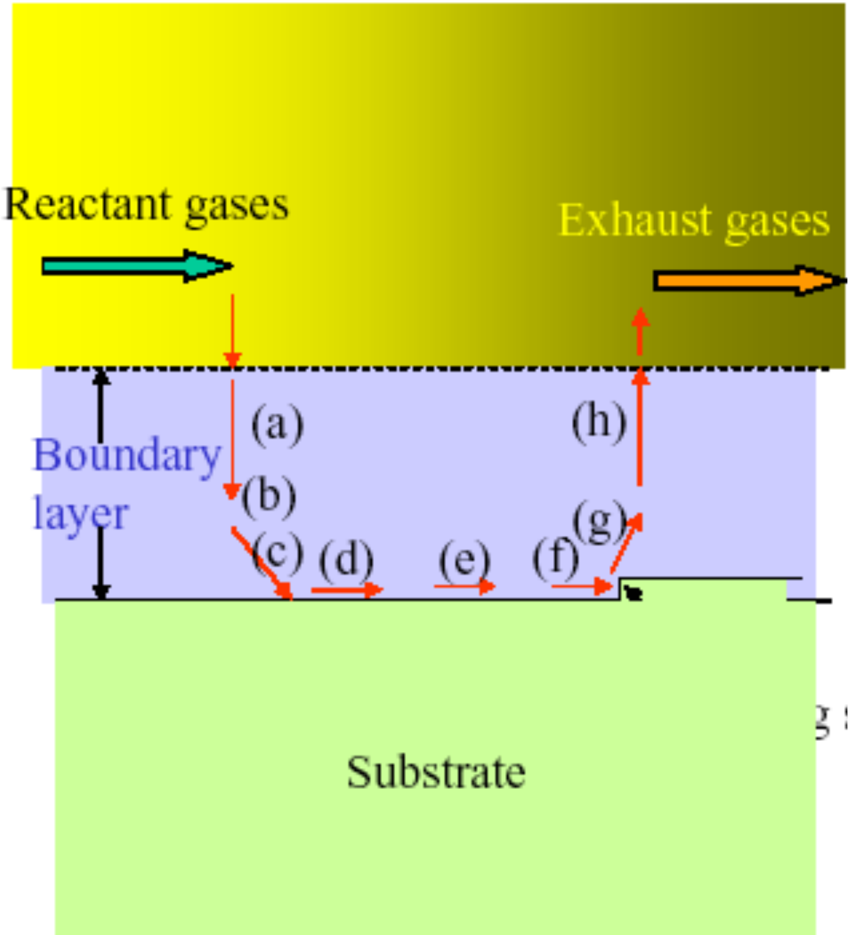


Figure 12.24 The Endura system by Applied Materials uses a number of PVD or CVD chambers fed by a central robot. For conventional and IMP sputtering, targets are hinged to open upward. Two open chambers are shown in this photograph along with the load lock *(from Applied Materials).*

CVD Growing steps



Growing steps in CVD

(a) Gas phase diffusion
(b) Gas phase reaction
(c) Adsorption
(d) Surface reaction
(e) Surface diffusion
(f) Incorporation into the crystal lattice
(g) Desorption
(h) Gas phase diffusion

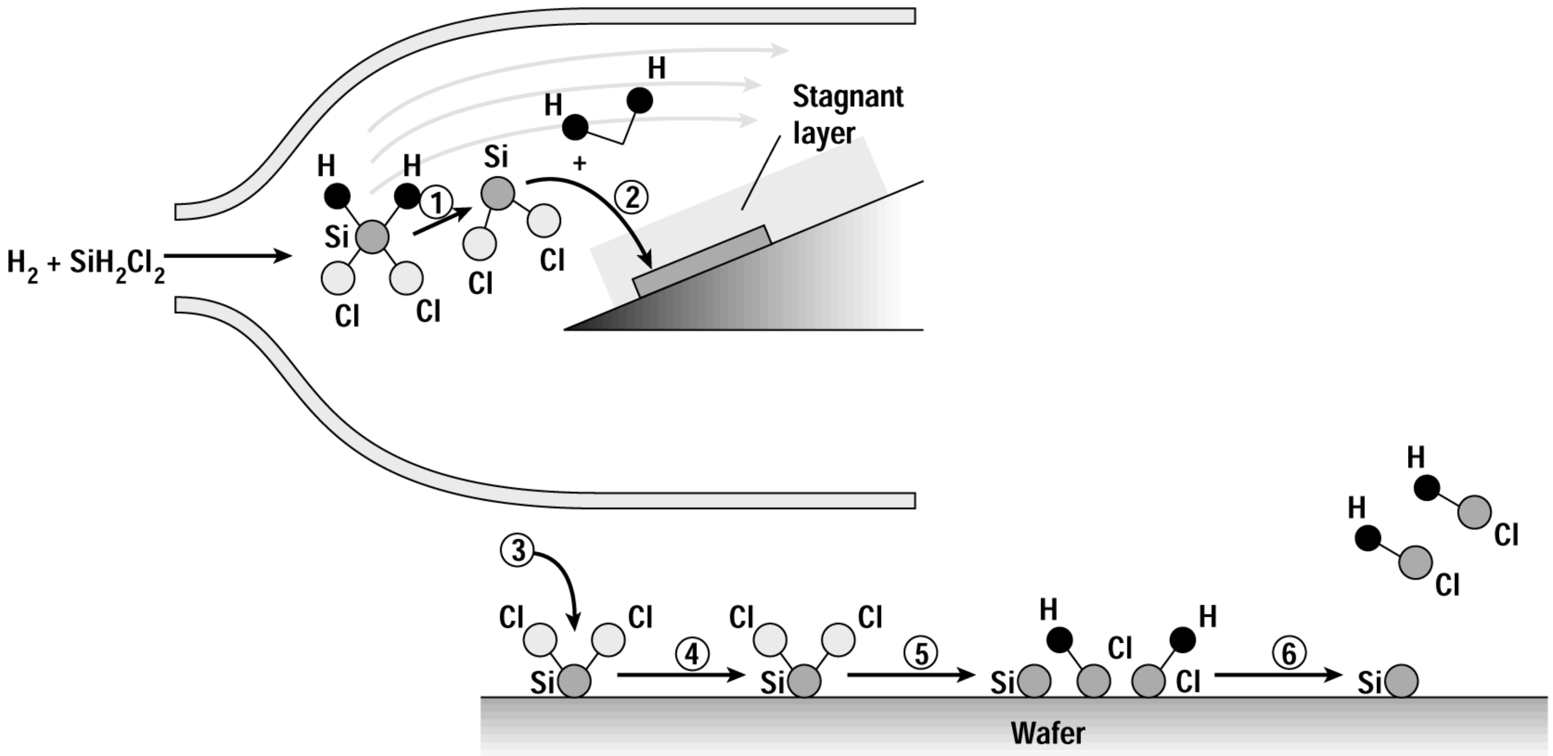
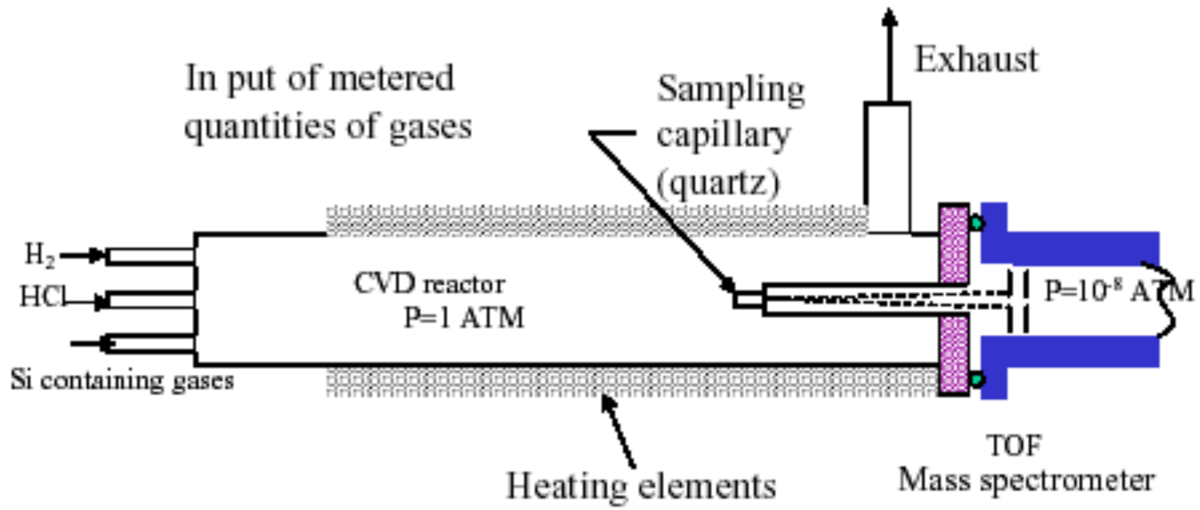


Figure 14.4 VPE steps include (1) gas-phase decomposition and (2) transport to the surface of the wafer. At the surface the growth species must (3) adsorb, (4) diffuse, and (5) decompose, and (6) the reaction by-products desorb.

CVD Chemical reactions for many systems



CVD products	Chemical system	Input reactants	Vapor species
GaN	Ga-Cl-H-N	HCl, NH_3, Ga, H_2	H_2, HCl, GaCl, NH_3,$GaCl_3$, NH_3, N_2
GaP	Ga-Cl-H-P	HCl, PH_3, Ga, H_2	H_2, HCl, GaCl, PH_3,P_2, P_4
GaAs	Ga-Cl-H-As	HCl, AsH_3, Ga, H_2	H_2, HCl, GaCl, AsH_3,As_2, As_4
InP	In-Cl-H-P	HCl, PH_3, In, H_2	H_2, HCl, InCl, PH_3, P_2, P_4
InAs	In-Cl-H-As	HCl, AsH_3, In, H_2	H_2, HCl, InCl, AsH_3, As_2, As_4
Si	Si-Cl-H	$SiCl_2H_2$, H	H_2, HCl, $SiCl_2$, $SiCl_2H_2$, $SiCl_4$, $SiCl_6$
Si	Si-Cl-H	$SiCl_3H$, H_2	H_2, HCl, $SiCl_2$, $SiCl_2H_2$, $SiCl_4$, $SiCl_6$
Si	Si-Cl-H	$SiCl_4$, H_2	H_2, HCl, $SiCl_2$, $SiCl_2H_2$, $SiCl_4$, $SiCl_6$
Si	Si-Cl-He	$SiCl_4$, He	H_2, $SiCl_2$, $SiCl_4$

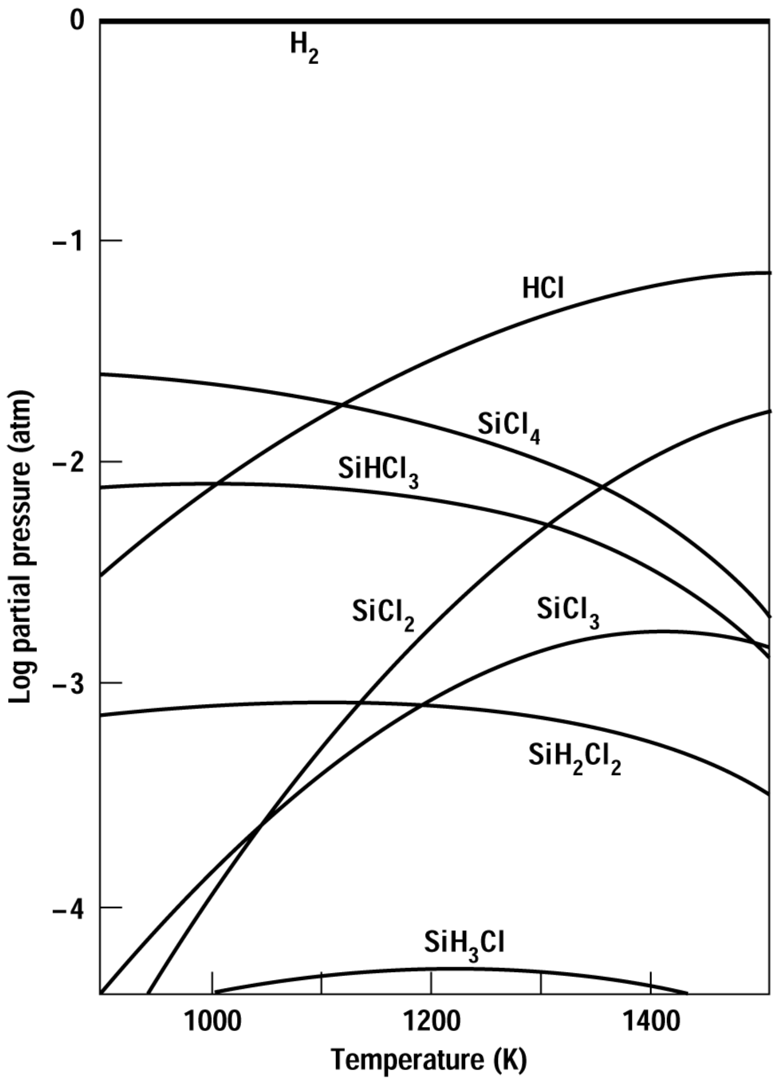


Figure 14.5 Equilibrium partial pressures in the Si–Cl–H system at 1 atm and a Cl to H ratio of 0.06 *(after Bloem and Claasen, reprinted by permission, Philips).*

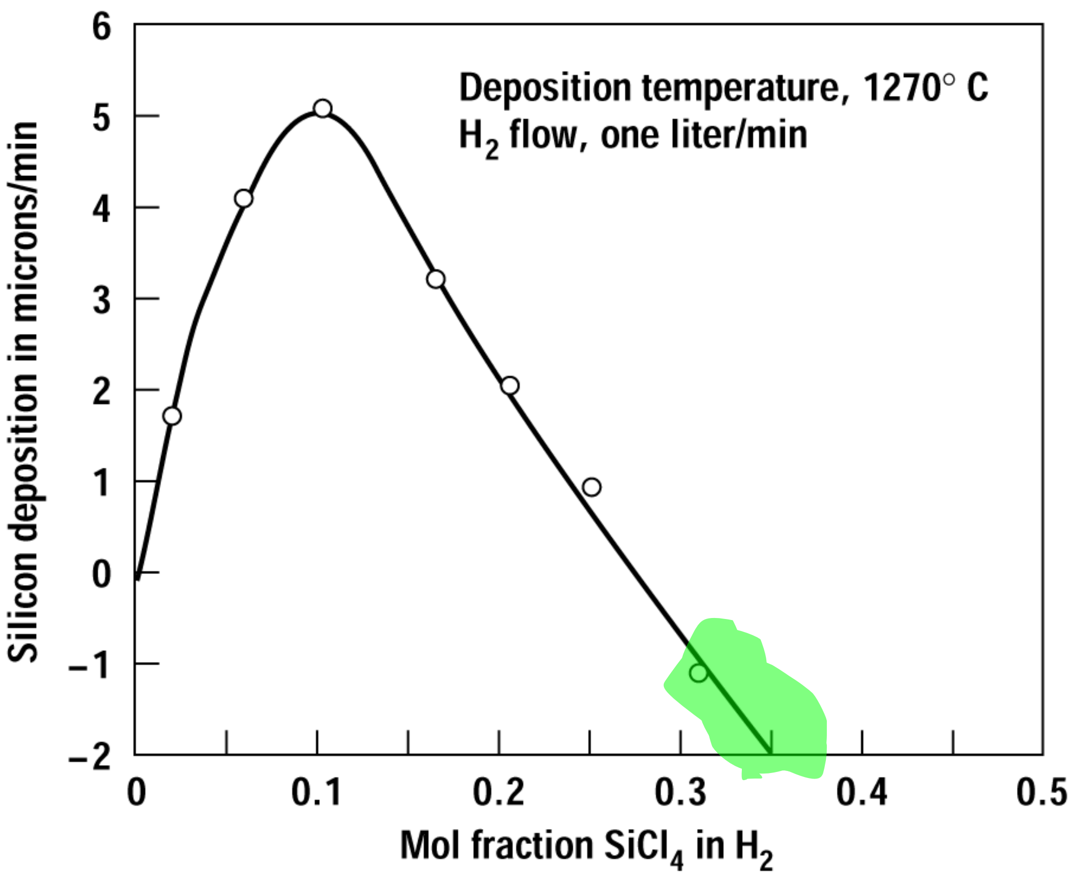


Figure 14.6 Growth rate as a function of the $SiCl_4$ flow. At high concentrations, the chlorine in the chamber leads to etching *(after Theuerer, reprinted by permission of the publisher, The Electrochemical Society).*

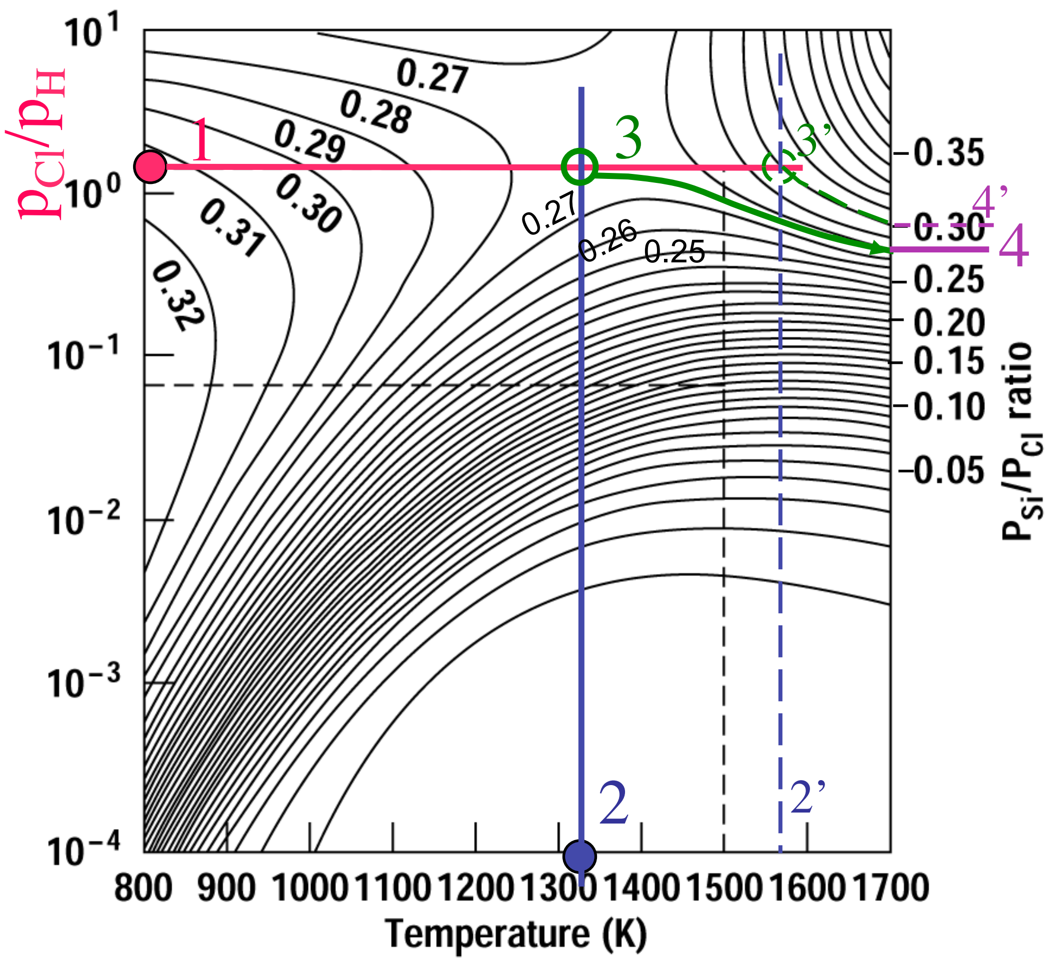


Figure 14.7 The equilibrium ratio of silicon to chlorine at 1 atm *(after Arizumi, reprinted by permission, Elsevier Science).*

imp

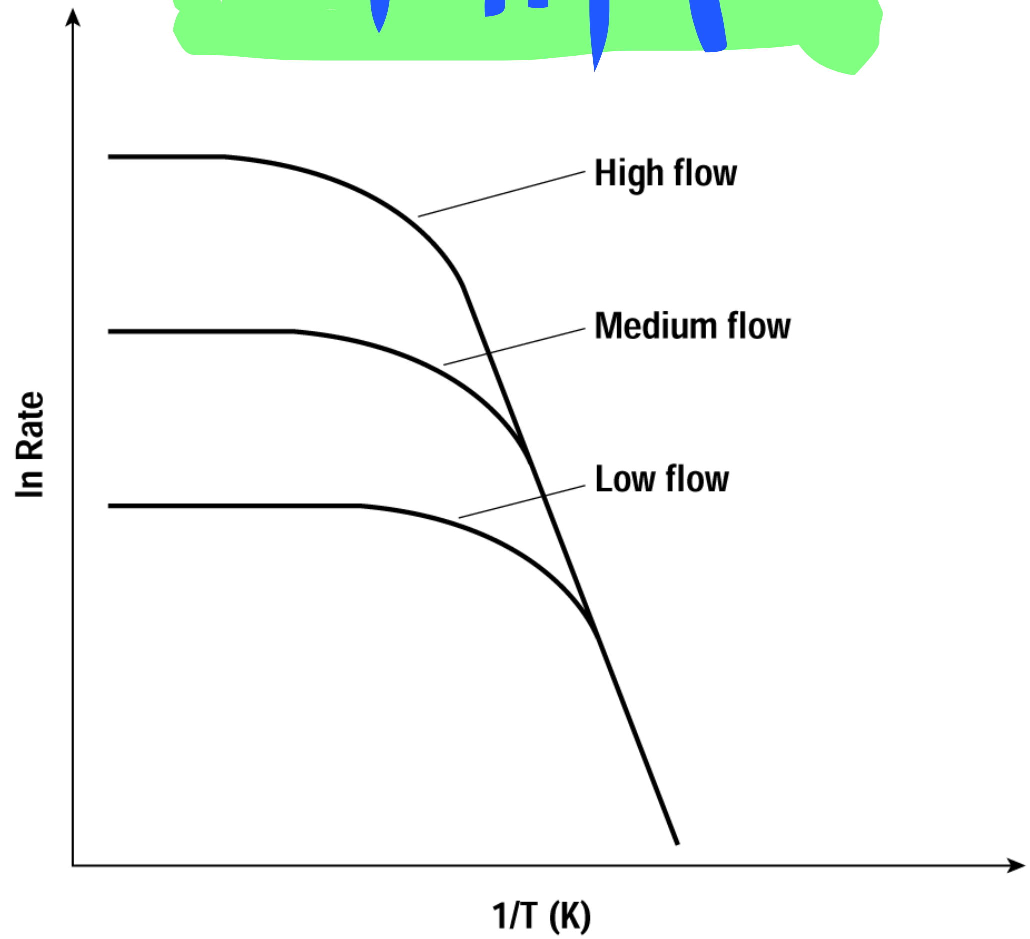


Figure 13.8 Typical deposition rates for CVD as a function of the temperature with flow rate as a parameter.

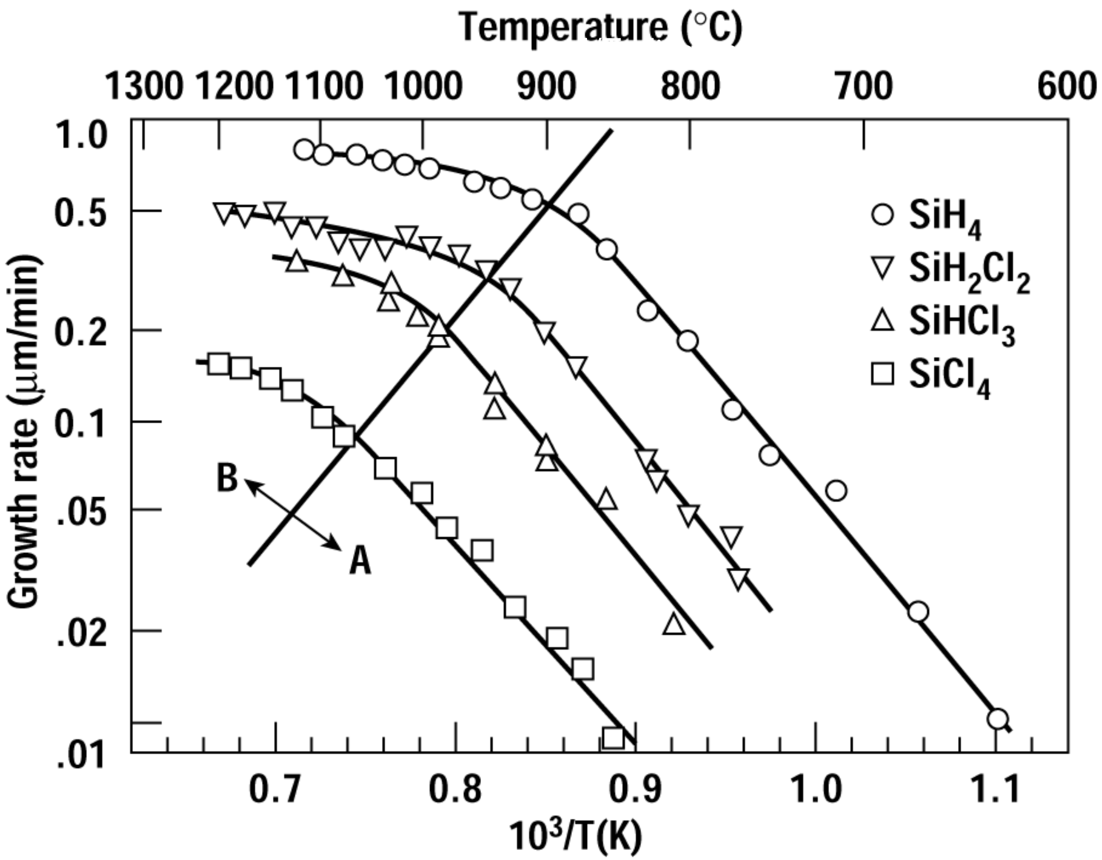
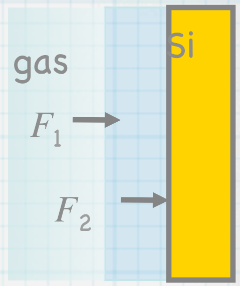


Figure 14.8 Arrhenius behavior of a variety of silicon-containing growth species *(after Eversteyn, reprinted by permission, Philips).*

CVD Kinetics



Diffusion

Flux of one particular specie from the bulk of the gas to the surface

$$F_1 = h_g\left(C_g - C_s\right)$$

C_g Concentration in gas bulk
C_s Concentration on surface
h_g transport coefficient
D_g Diffusivity

For a simple stagnant gas model

$$F_1 = -D_g \frac{\partial C}{\partial y} \approx D_g \frac{C_g - C_s}{\delta}$$

δ boundary layer thickness

Surface reaction

$$F_2 = k_s C_s = k_o C_s \exp\left(-\frac{E_a}{kT}\right)$$

k_s reaction koeff
E_a Activation energy
T temperature

Growth rate

under steady flow conditions

$$F_1 = F_2 \Rightarrow k_s C_s + h_g C_s = h_g C_g \Rightarrow C_s = h_g \frac{C_g}{k_s + h_g}$$

$$F_{Si} = n \cdot F_2$$

$$R = F_{Si} \cdot \frac{1}{N_{Si}} = F_2 \cdot n \cdot \frac{1}{N_{Si}} = \frac{k_s h_g}{k_s + h_g} \cdot \frac{C_g}{N_{Si}}$$

n number of Si atoms per molecule reactant
R Growth rate
N_{Si} at/cm^3 in Si Xtal

Regarding Stagnant model

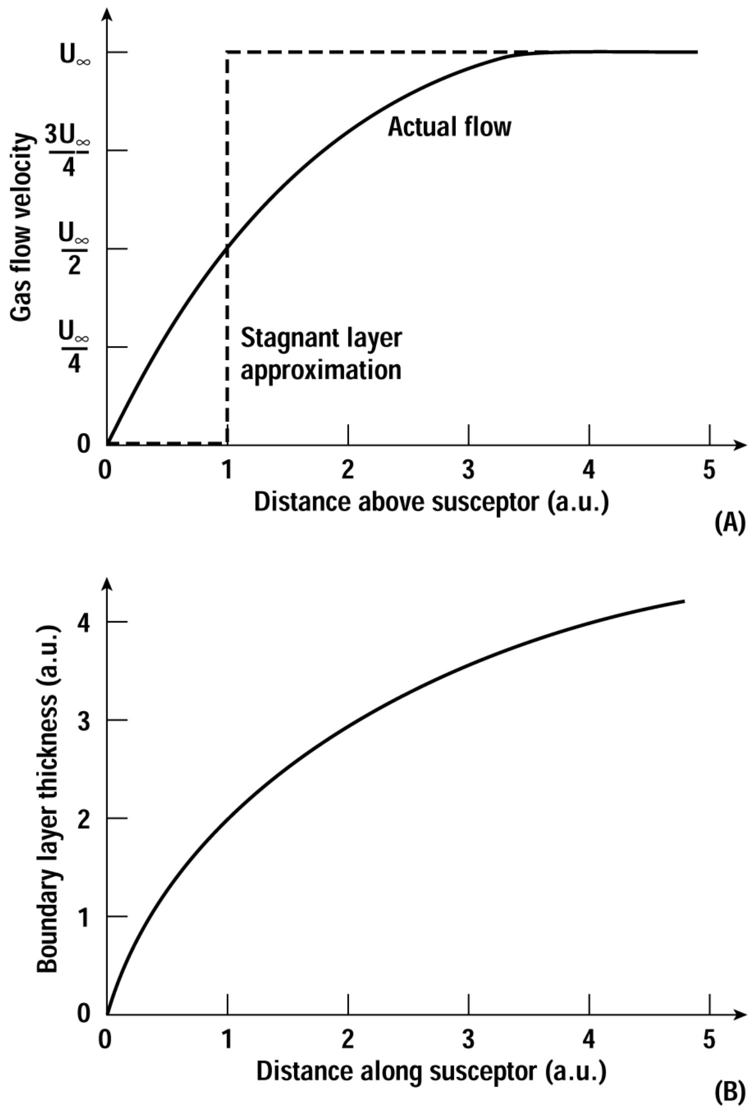


Figure 13.5 (A) Gas flow as predicted by a parabolic flow model and in the stagnant layer approximation. (B) Stagnant layer thickness versus position assuming a plug flow inlet.

Flow tubular CVD reactor

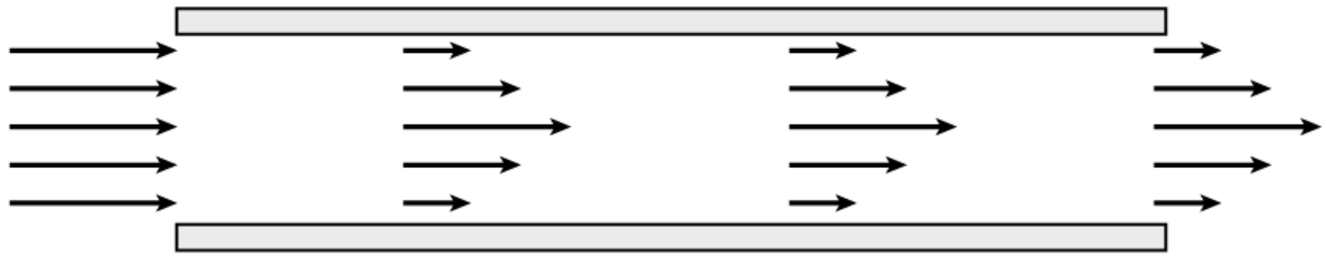


Figure 13.4 Flow development in a tubular reactor. The gas enters with a simple plug flow on the left and exits with a fully developed parabolic flow.

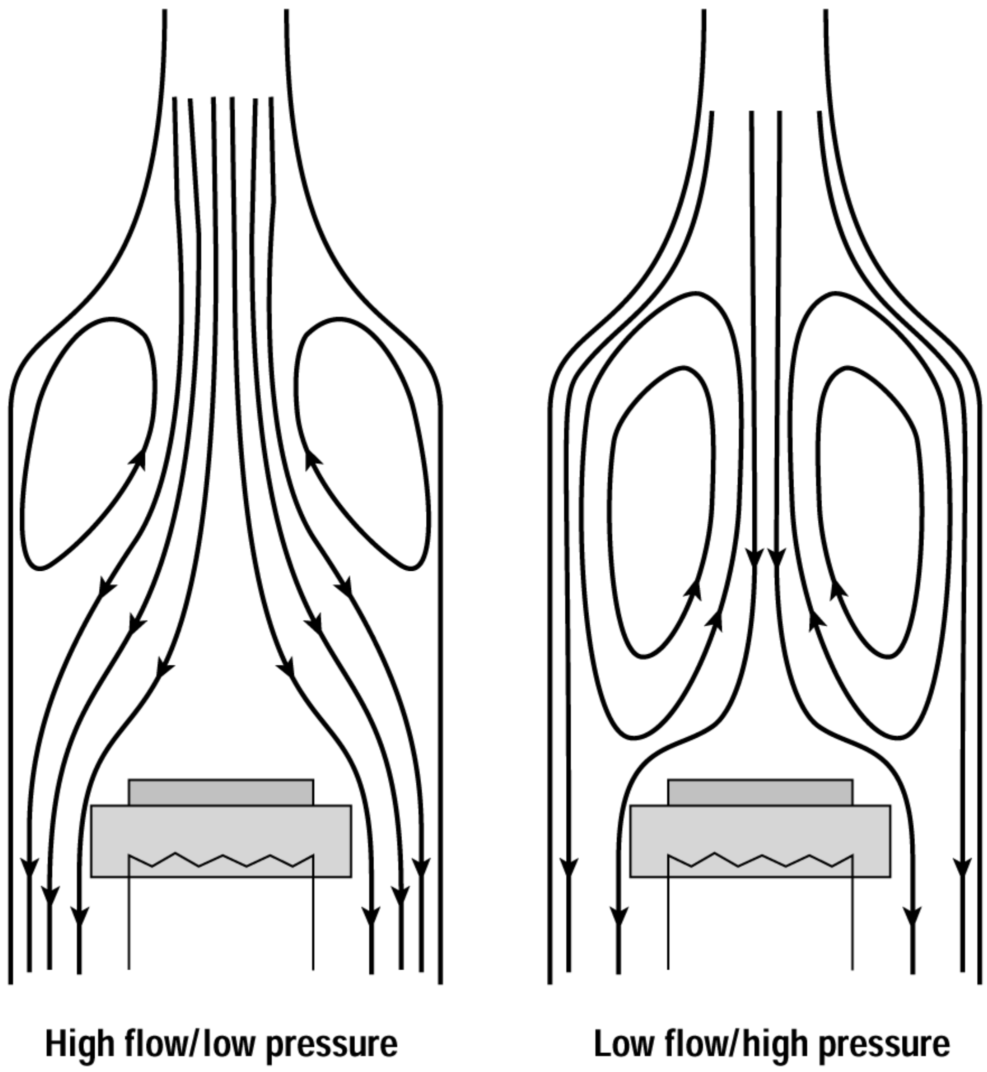


Figure 13.7 Buoyancy-driven recirculation cells.

CVD Transport

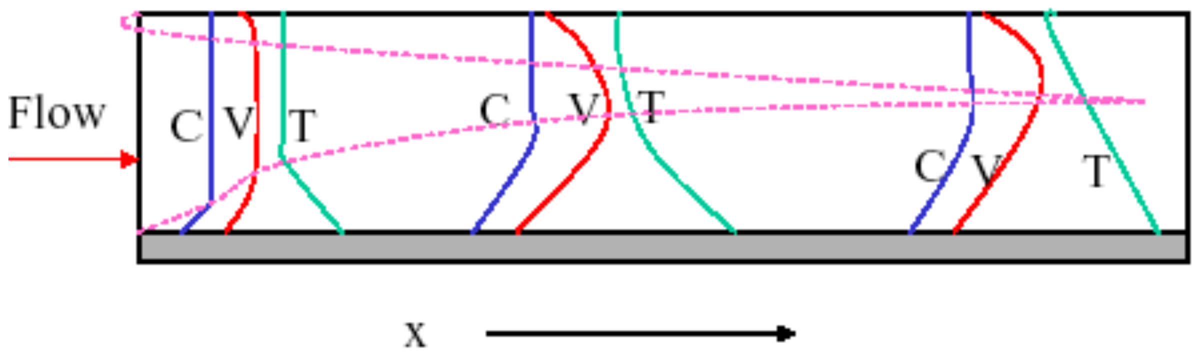
Heat, mass, and momentum transport in CVD reactors

1) Requirement of thickness and doping uniformity

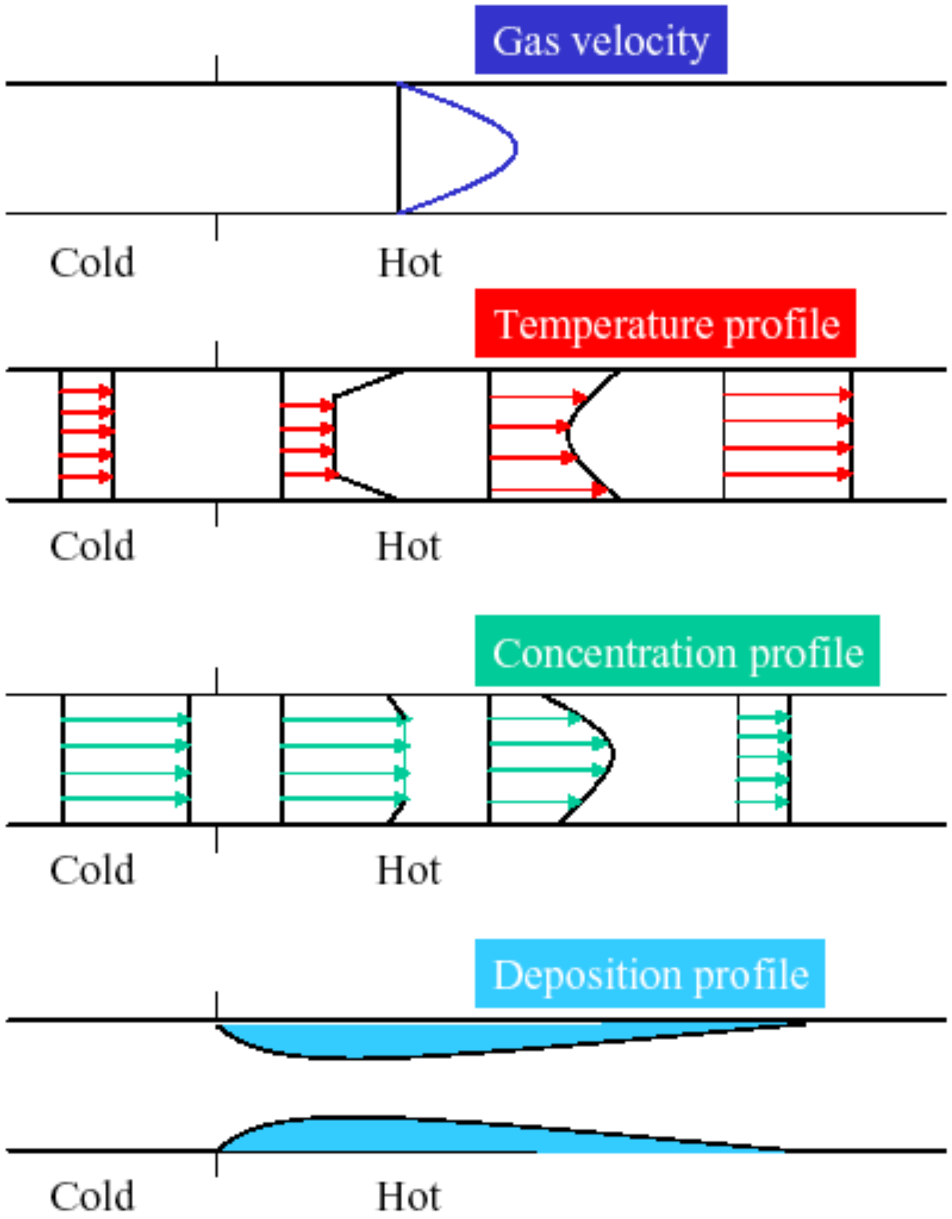
2) Requirement of high chemical efficiency

Parameters affecting the nature of gas flow in reactors:

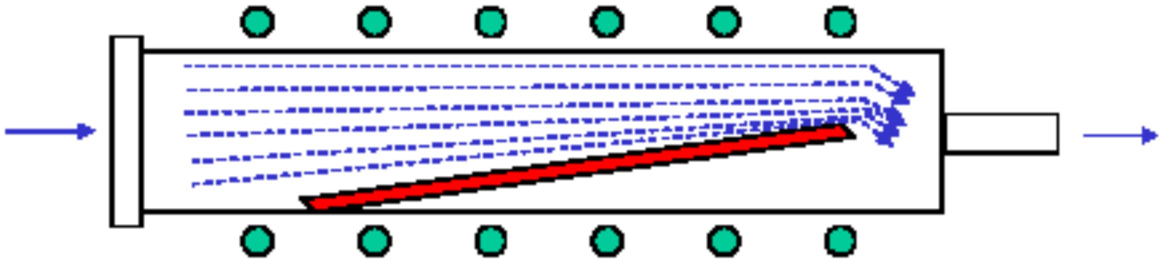
1) Velocity of flow
2) Temperature
3) Pressure
4) Geometry of the reactor
5) Gas or vapor characteristics



CVD gas transport engineering



CVD reactor setups

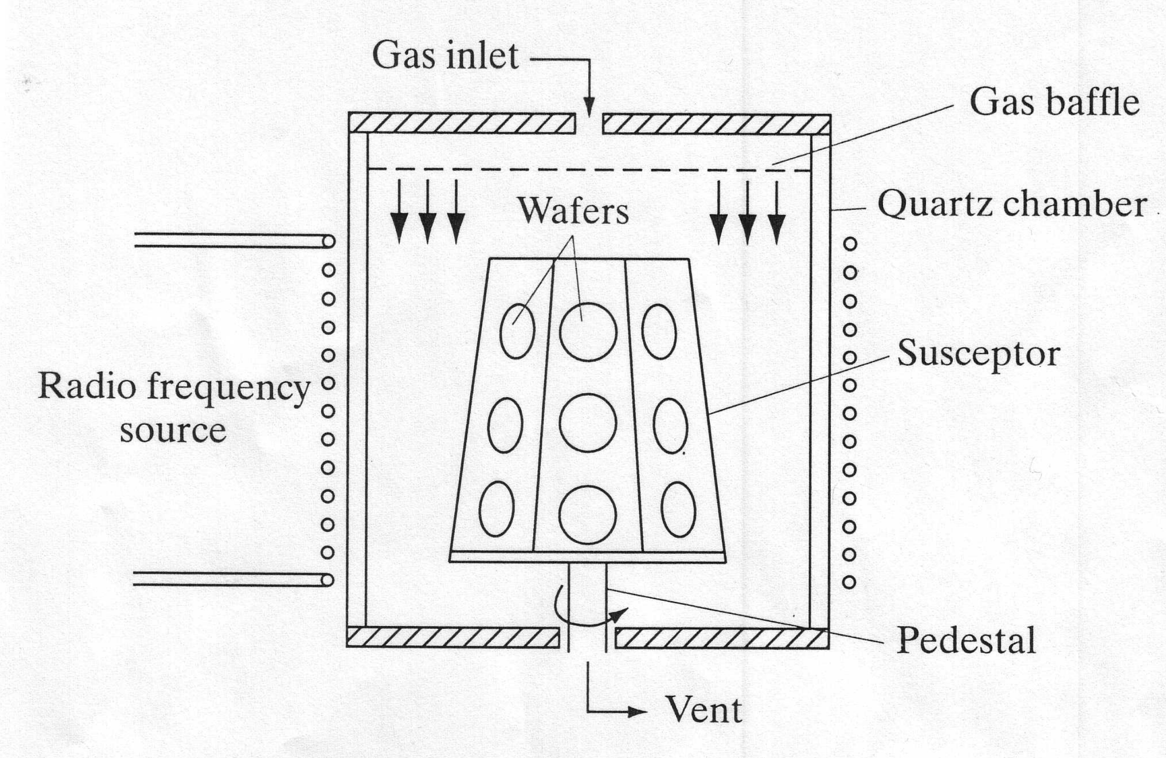


Horizontal reactor

Chemical Vapor Deposition (CVD)

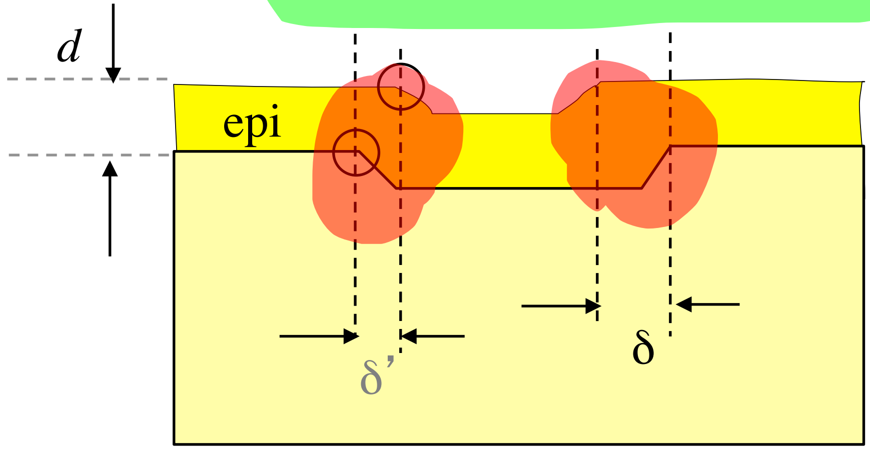
Sub Category: Vapor- Phase Epitaxy

Vapor-Phase Epitaxy: Expitaxial Growth that is achieved by crystallization from the vapor phase.



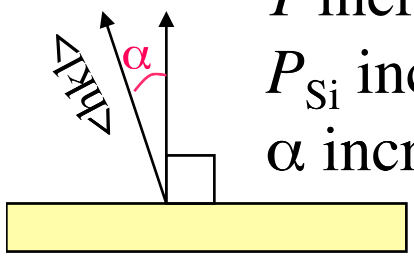
$$SiCl_4 + 2\,H_2 \longleftrightarrow Si + 4\,HCl$$

Pattern shift



Pattern shift δ
Distortion δ - δ'

Some observations



d increases -> δ increases
T increases -> δ decreases
P_{Si} increases -> δ increases
α increases -> δ decreases

Explain Why!

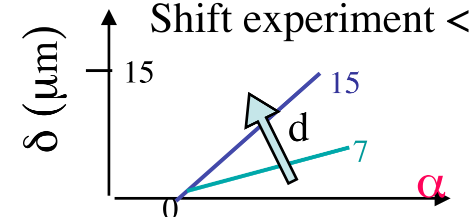
In which cases is it a problem?
What to do about it?

Typical data

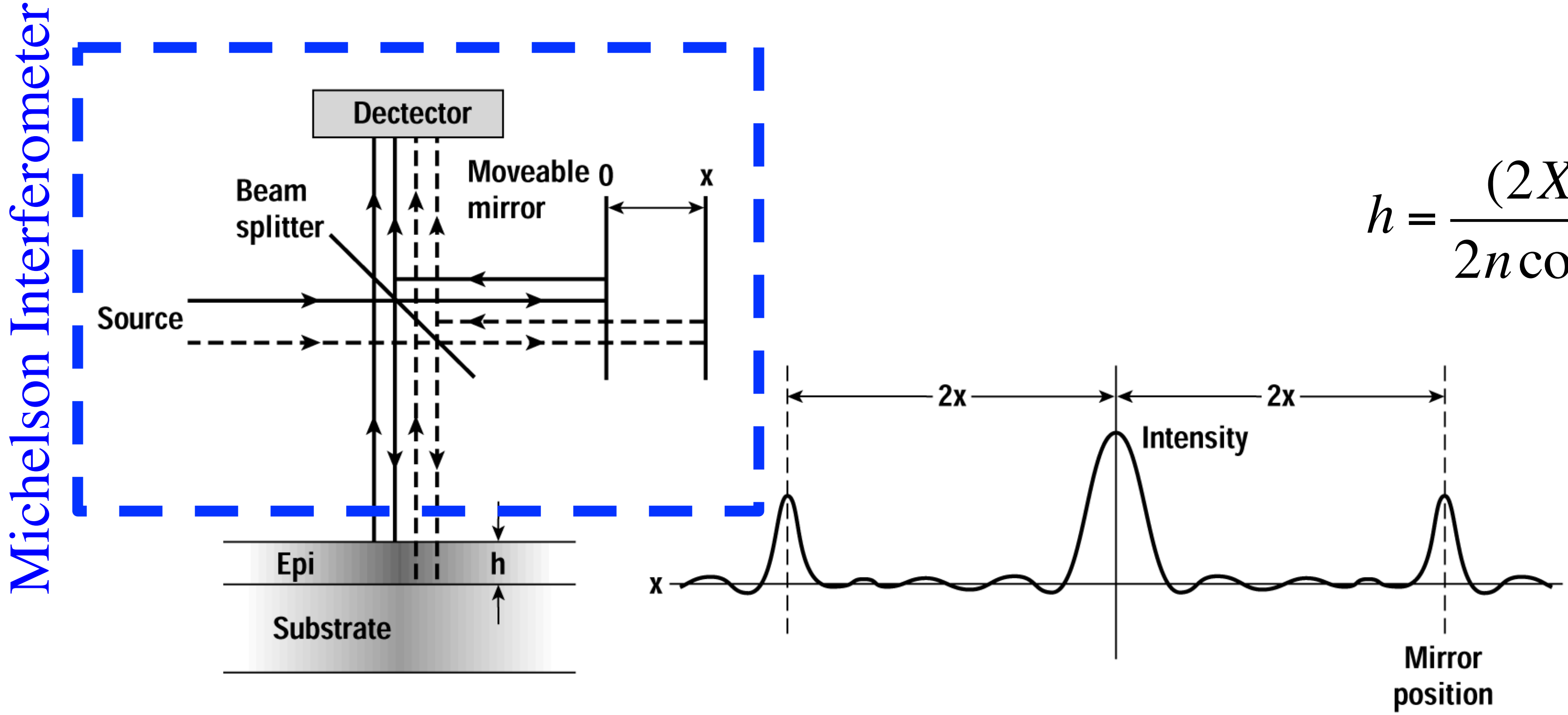
industry stad

Substrate thickness 500 μm
epi thickness 5 μm
<111> misorient 2-5 deg to <110>
<100> no misorient

Shift experiment <100> wafers



Thickness measurements Si epi FTIR



$$h = \frac{(2X)}{2n\cos\theta}$$

Figure 14.11 A Fourier transform infrared spectroscopy system. Infrared light is used since silicon is nearly transparent in this region.

Refractive index, n_e, of epi-layer must be different than that of the substrate, n_s

When ne-ns<<1, reflectance from interface weak;

Then a reference with same surface (i.e. a thicker film) is used to 'subtract' the surface

defect in epi (stacking fault)

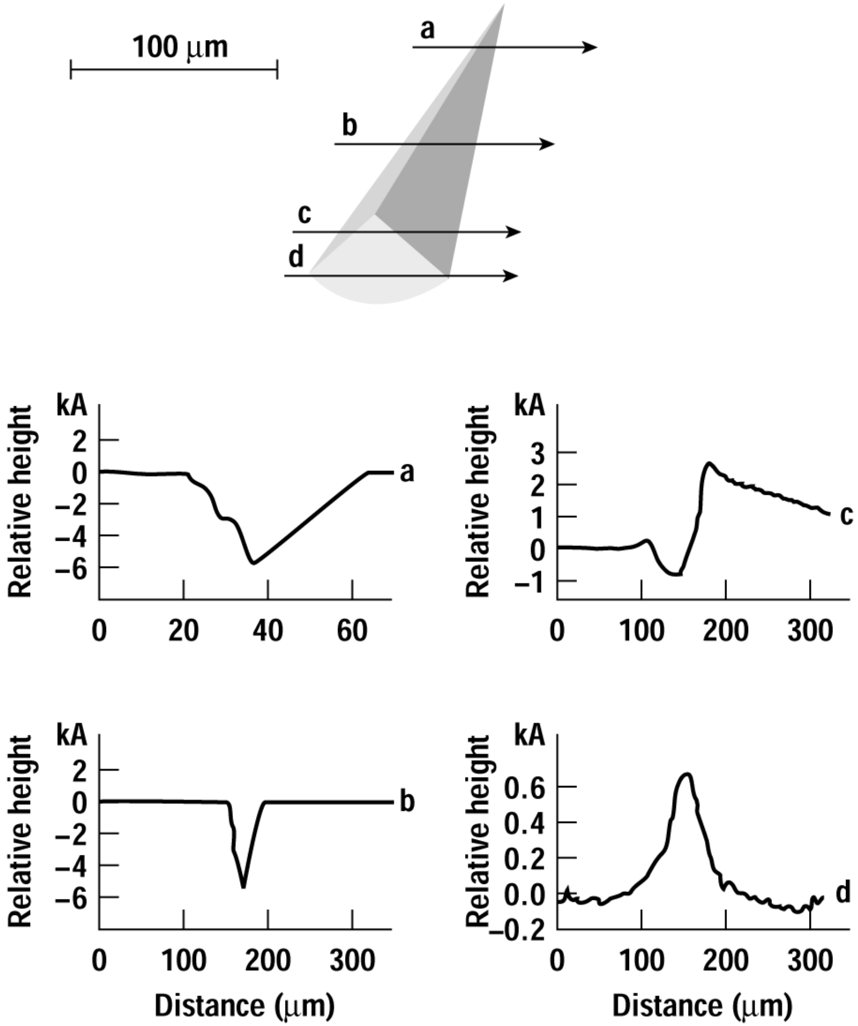
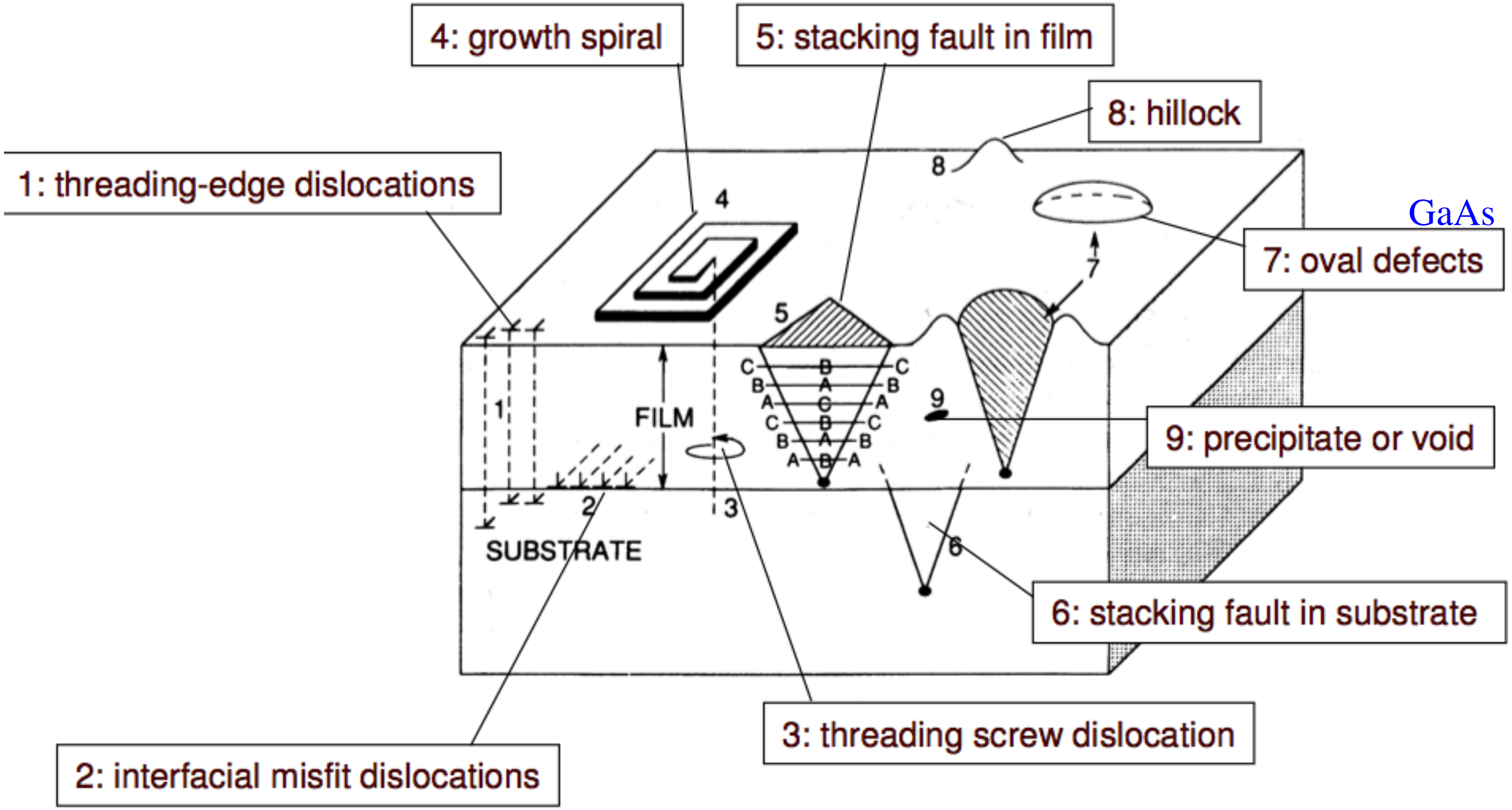


Figure 14.9 An electron micrograph of a stacking fault in an epitaxial layer grown on a (111) wafer. The lower plot shows mechanical scans of the surface topology at four sites on the fault *(reprinted from Liaw and Rose by permission, Academic Press).*

Dislocation types in epitaxial layers

Most-but not all-can occur for Si under certain conditions

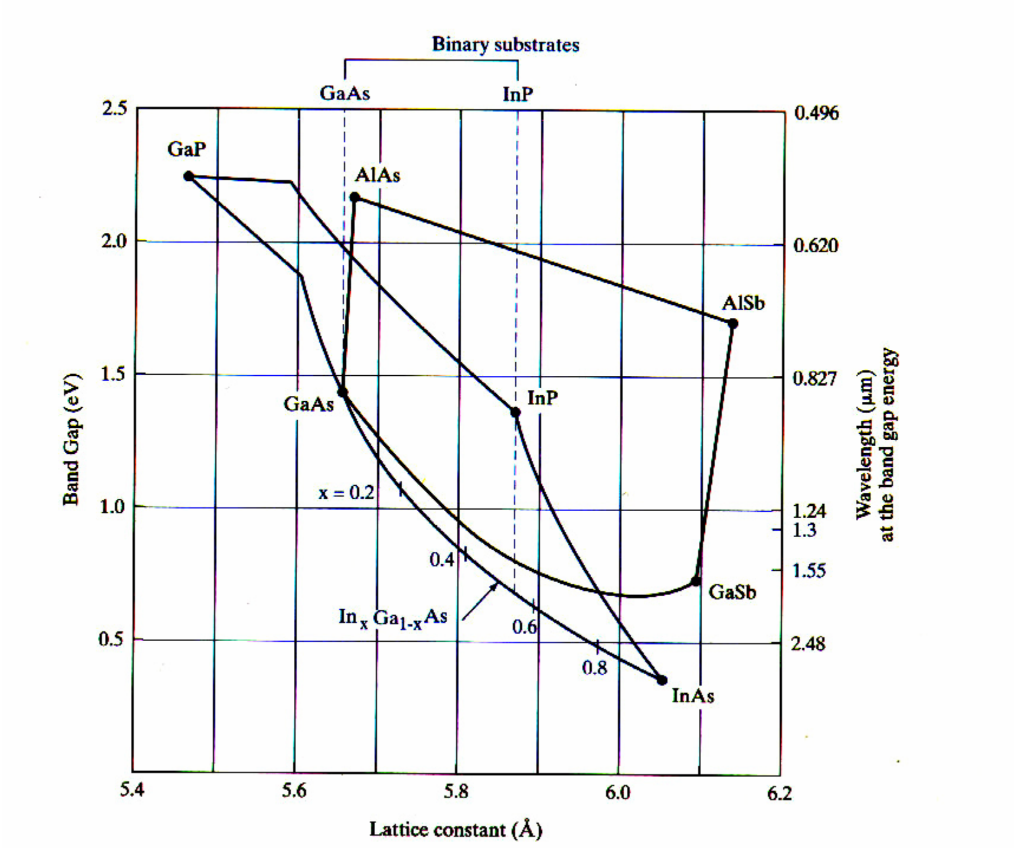


HETERO-EPITAXY

Lattice Matching in Epitaxial Growth

Heteroepitaxy: The expitaxial layer is different from the substrate.

Need Lattice Match ?



- $Al_xGa_{1-x}As$ on GaAs
- $In_{0.53}Ga_{0.47}As$ on InP
- $In_{0.5}Ga_{0.5}P$ on GaAs
- $In_xGa_{1-x}As_yP_{1-y}$ on InP or GaAs

Epitaxial Growth with Lattice Mismatch (1)

Gradual Lattice Matching

Example: $GaAs_{0.6}P_{0.4}$ on GaAs for red LED applications

(1) The growth is begun at a composition near GaAs

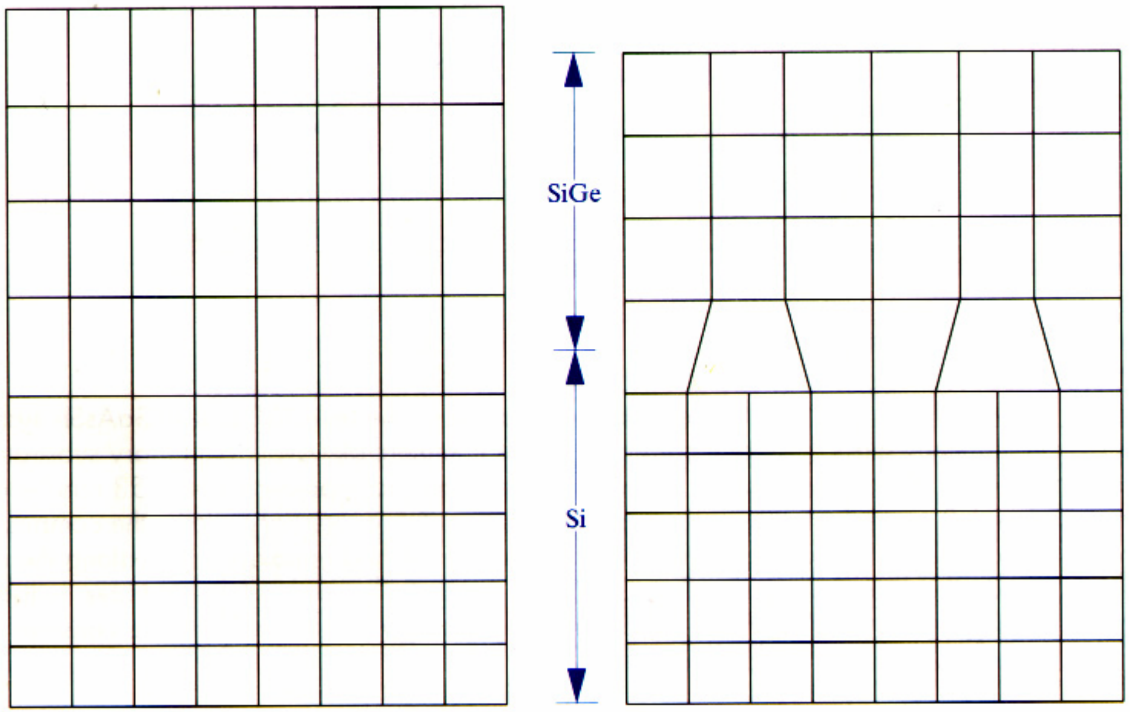
(2) A buffer region of 25 um is grown while gradually introducing phosphorus until the desired As/P ratio is achieved.

(3) The desired epitaxial layer is then grown

Epitaxial Growth with Lattice Mismatch (2)

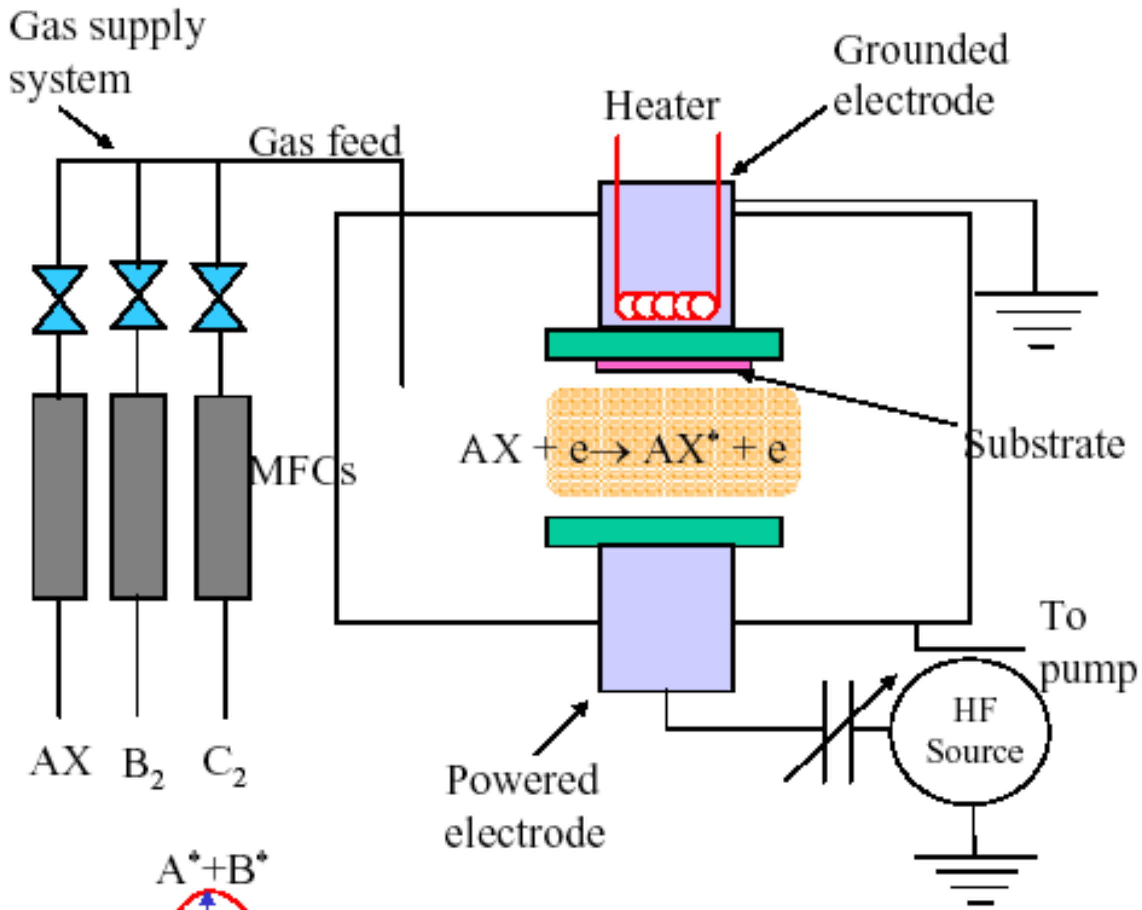
Critical Layer Thickness, t_c

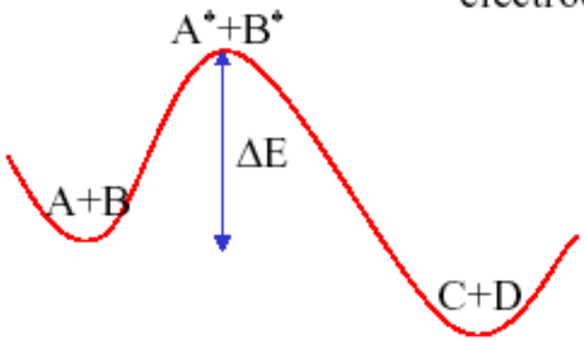
Lattice constant: *Si* = 5.43Å, *Ge* = 5.65Å. The lattice mismatch between SiGe and Si leads to compressive strain in the SiGe layer.



$t < t_c$ $t > t_c$

PECVD
Plasma enhanced/





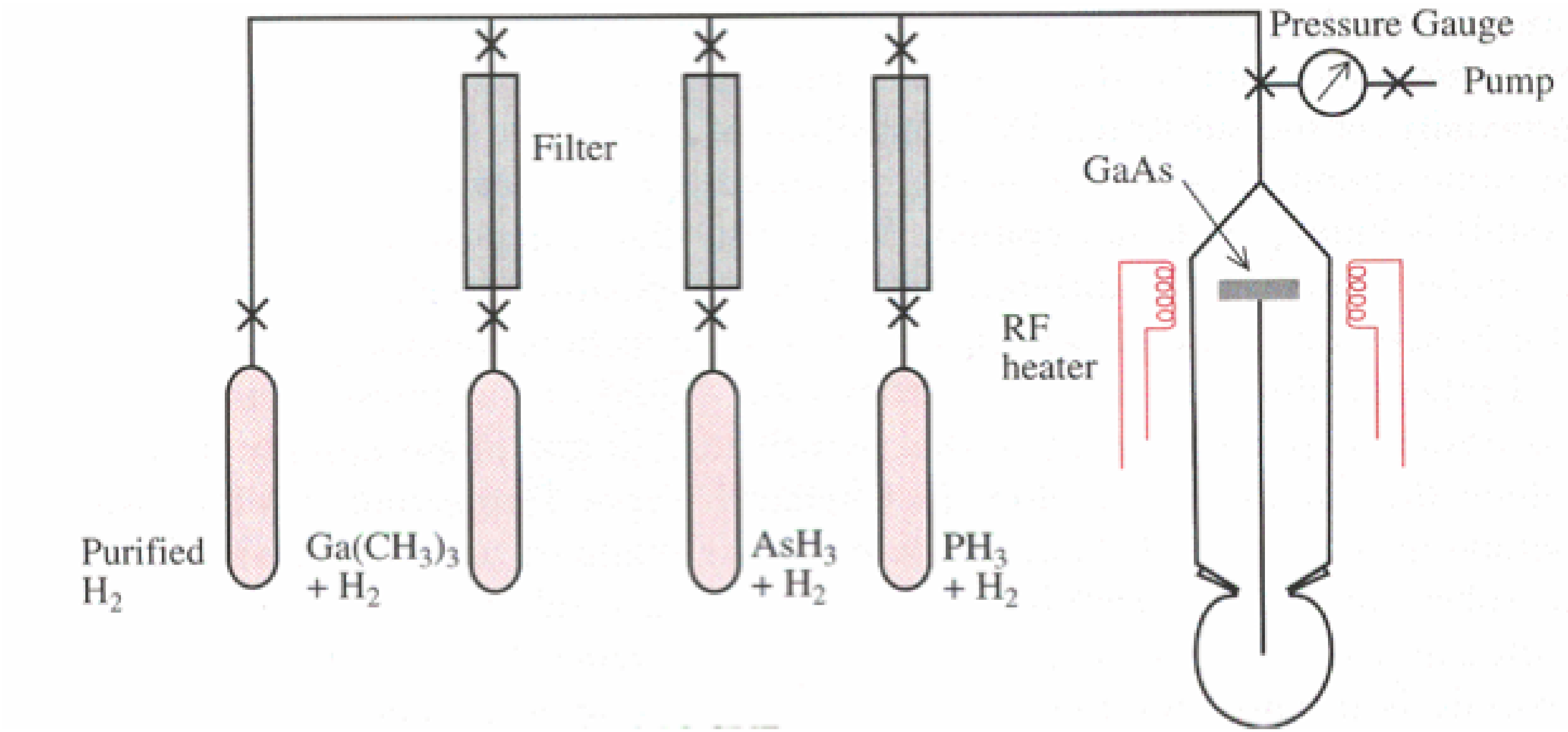
RX + e→ R + X + e

Collisional dissociation by electrons

Difference from sputtering?

High gas pressure (0.1 ~ a few Torr)

MOCVD Growth



$$Ga(CH3)3 + AsH3 \rightarrow 3CH4 + GaAs$$

Ref: Yu-Cardona

Britney and a real MOCVD machine

Measuring thickness of complicated device structures

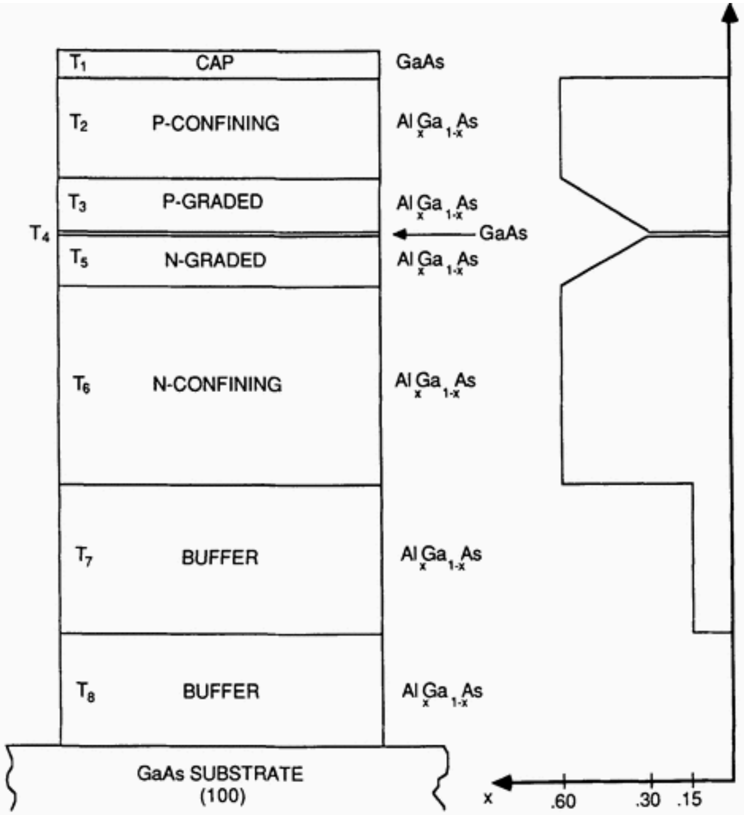


Fig. 1 — Schematic diagram of Graded Index Separate Confinement Heterostructure with a Single Quantum Well (GRINSCH-SQW), showing relative layer thicknesses and Aluminum concentration.

Moellering et al J. Electronic Mat.19,181(1990)

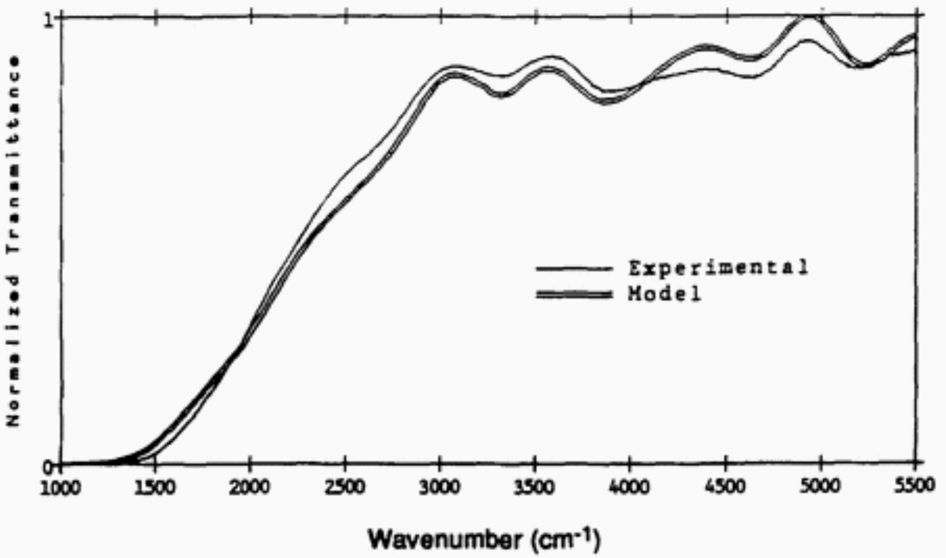
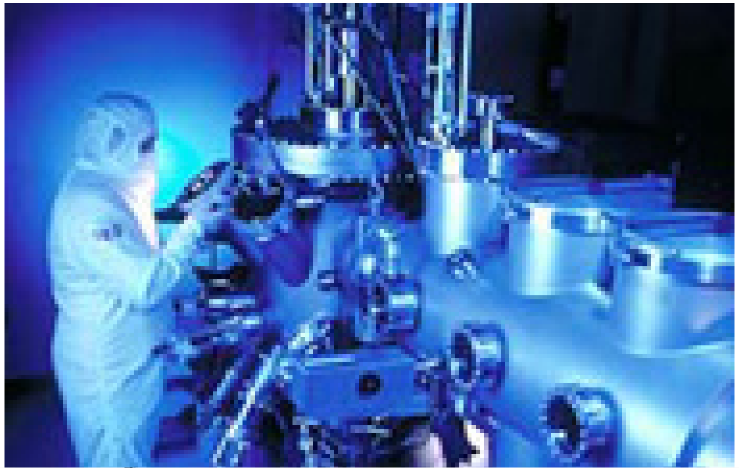
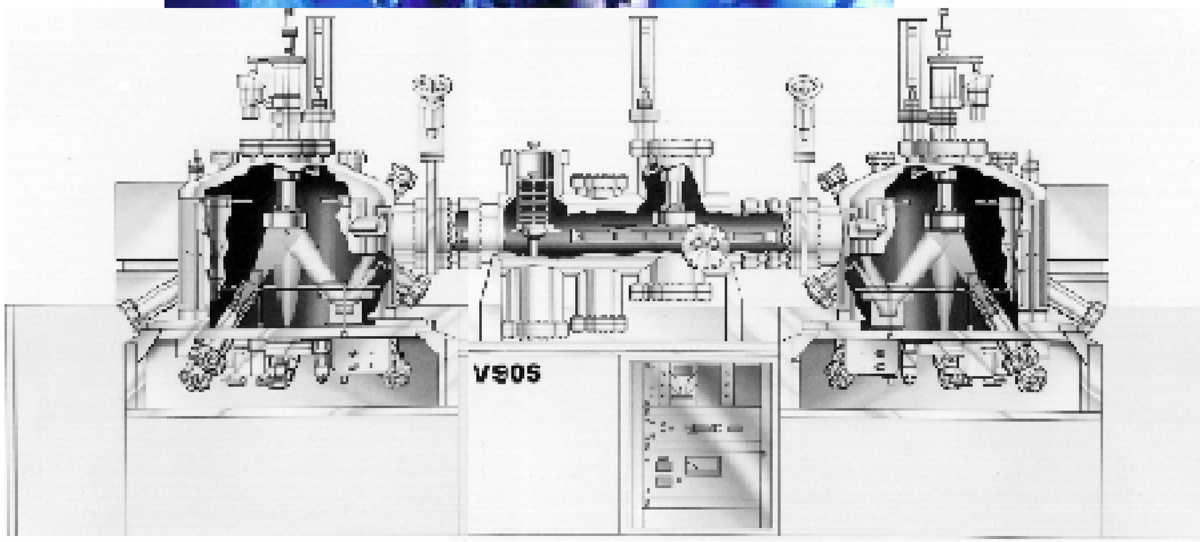


Fig. 2 — Example of curve fitting the characteristic matrix method transmission spectrum to experimental FTIR data. The fringe peak-to-peak spacing is not constant for the complicated epitaxial structure, confriming the need for a computer model. The fall in transmission at wavenumbers less than 3000 cm^{-1} is due to free carrier absorption.

GRINSCH Laser
Graded Index Spatial Confinement Heterostructure
SQW Semiconductor Quantum Well

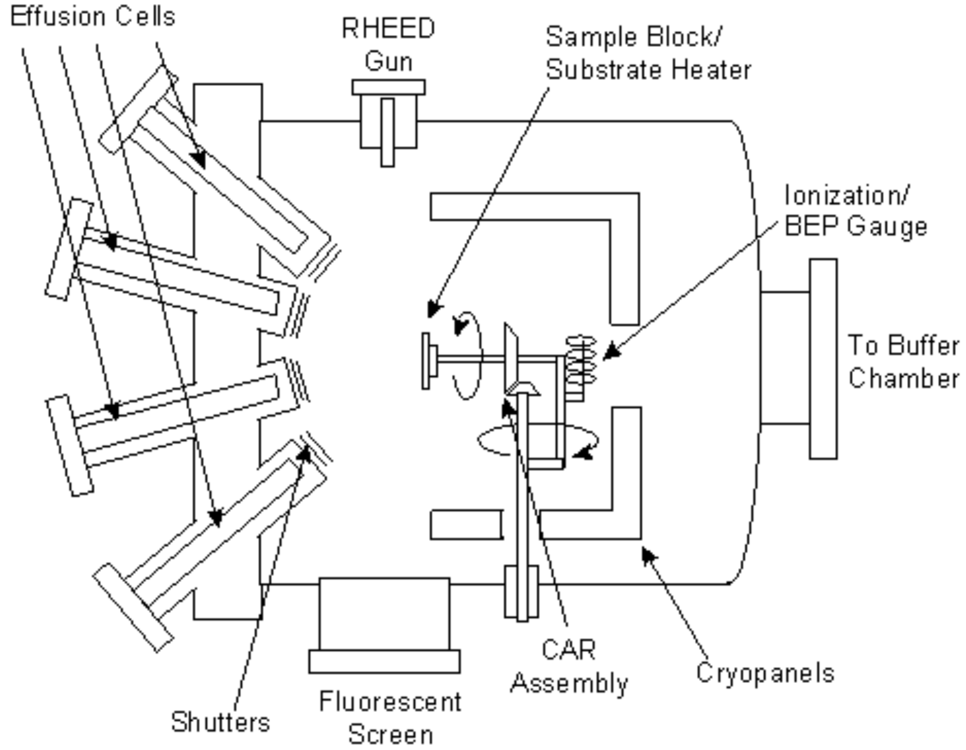
MBE





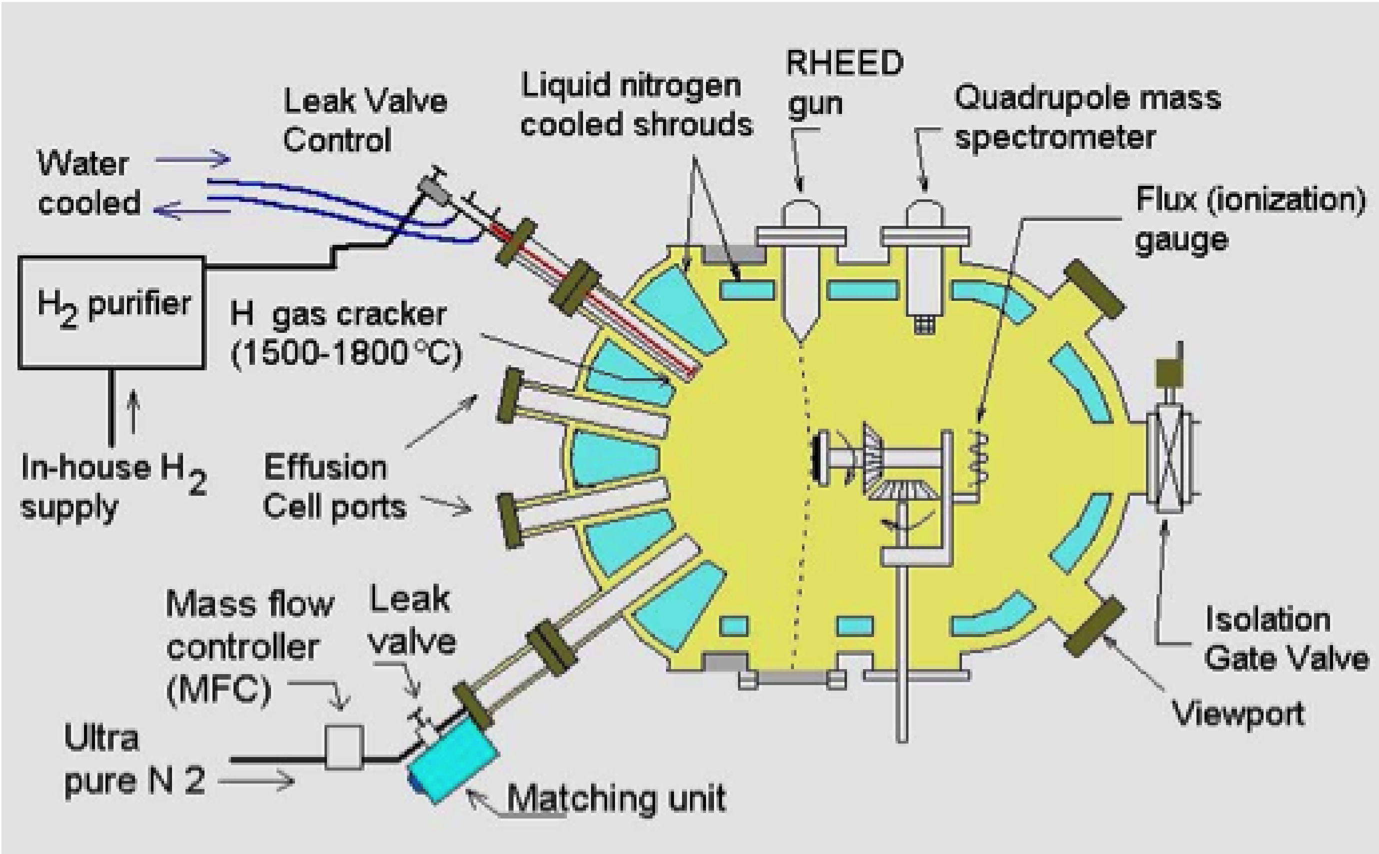
Molecular Beam Epitaxy (MBE)

The expitaxial layer is formed by the impingement of molecular or atomic beams of constituents upon the substrate surface in a high vacuum chamber.



Schematic diagram of a MBE machine

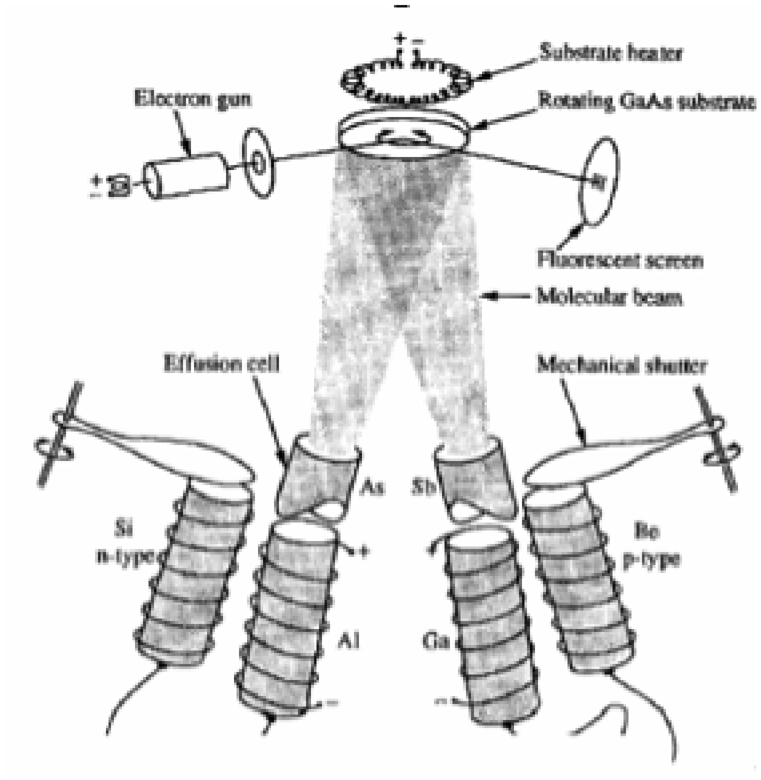
http://britneyspears.ac/physics/fabrication/fabrication.htm

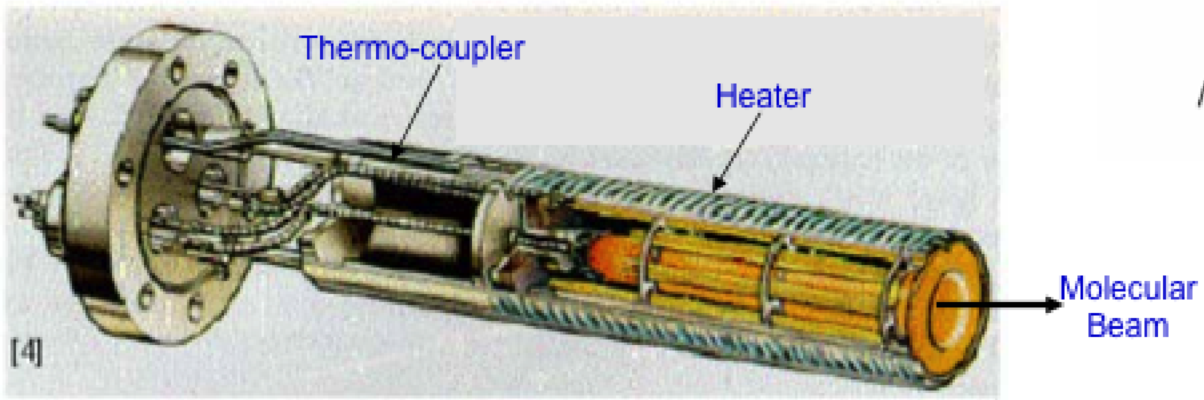

Water
cooled
Leak Valve
Control
Liquid nitrogen
cooled shrouds
RHEED
gun
Quadrupole mass
spectrometer
Flux (ionization)
gauge
H_2 purifier
H gas cracker
(1500-1800 °C)
In-house H_2
supply
Effusion
Cell ports
Mass flow
controller
(MFC)
Leak
valve
Ultra
pure N 2
Matching unit
Isolation
Gate Valve
Viewport

n6

MOLECULAR BEAM EPITAXY

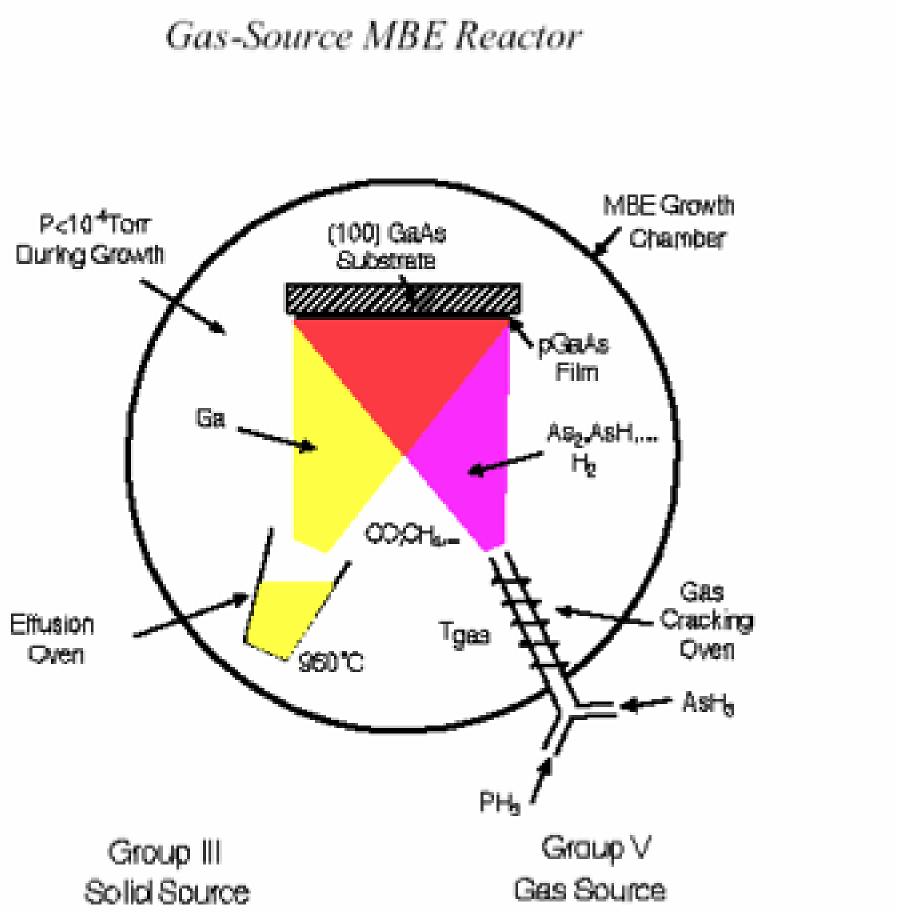
- Hot ovens (effusion or Knudsen cells) contain elements to be grown.
- Place in an extremely high vacuum (e.g. <10^{-10}torr)
- Beams of atoms or molecules of the elements evaporate from the cells
- Low pressure is desired so that these remain as beams and no chemical reactions before the atoms reach the substrate
- Atoms reach the heated substrate, react and materials grow epitaxially.
- Substrate rotation is important to improve growth uniformity.





Effusion (Knudsen) Cell

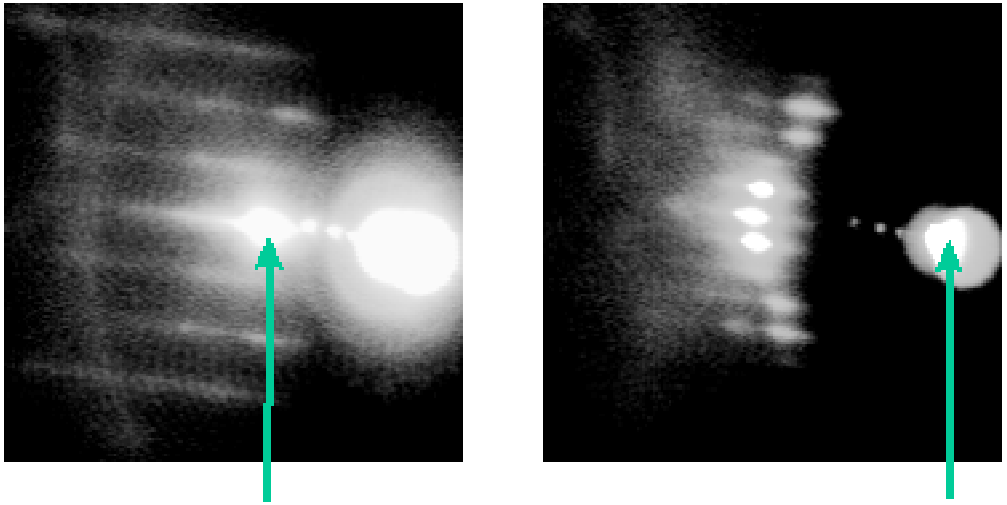
GAS-SOURCE MBE SYSTEM



Reflection High-Energy Electron Diffraction (RHEED)

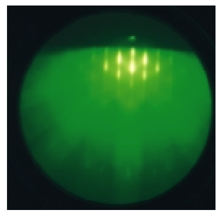
Purpose: **Ascertain substrate cleanlyness, visualize natural oxide blown off, ascetain flux ratios by observing phase transitions in surface reconstructions, calibration of sources by observing growth rate by osc.(next)**

'2 x' Pattern **'4 x' Pattern**



Specular Reflection Straight-Through Beam

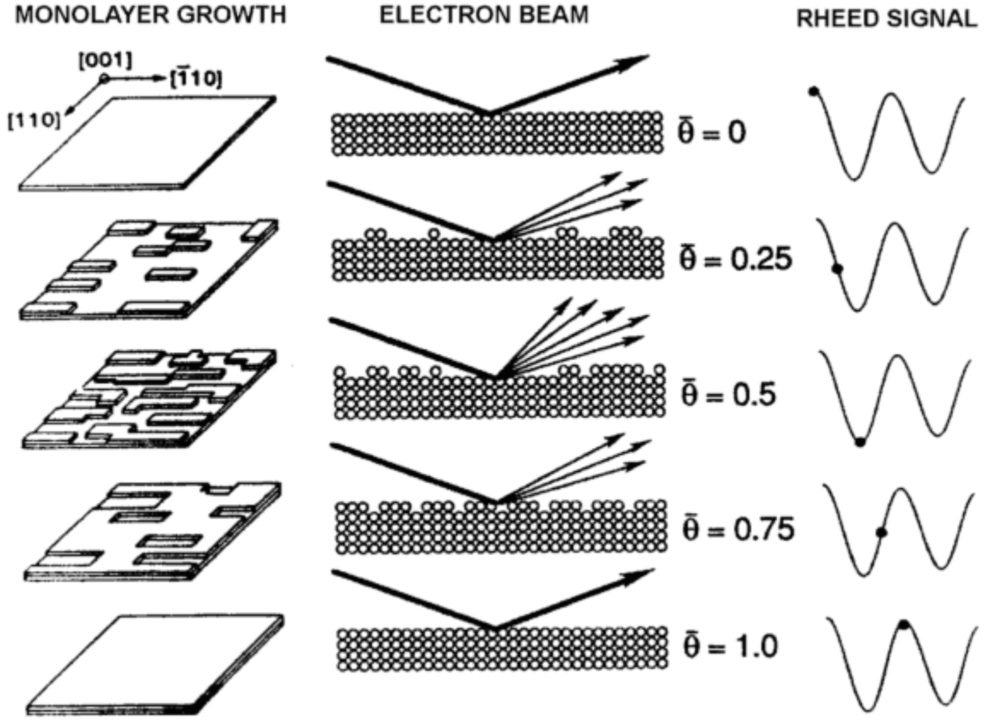
Reflection High-Energy Electron Deflection (RHEED) measurement



Pattern =Fourier transform of surface

Reflection High-Energy Electron Diffraction (RHEED)

Purpose: To monitor the oscillations in the reflectivity and estimate the thickness and rate of growth of the epitaxial material.



Reflection High-Energy Electron Deflection (RHEED) measurement system
http://britneyspears.ac/physics/fabrication/fabrication.htm

STRENGTHS & WEAKNESSESS OF MBE

Strengths

- Excellent surface/interface morphology and thickness control
- Precisely controlled abrupt heterostructions
- Possible to grow many (100s) layer complex heterostructures
- In-situ characterization tools (RHEED, Mass Spect. Reflectivity)
- Easier to grow mixed column III alloys (GaInAl) and dilute nitrades (Nas, NP, NAsSb)
- High purity elemental starting materials readily available
- No toxic gases, easily handled solids
- Relatively simple chemistry

Weaknessess

- Complex graded interfaces difficult
- Structures with many different compositions (only 4 metal sources in most machines – now overcome in vertical production machines)
- Flux transients
- Run-to-run reproducibility of layer thickness and composition
- Surface 'oval defects'
- Nucleation of GaN and AlN

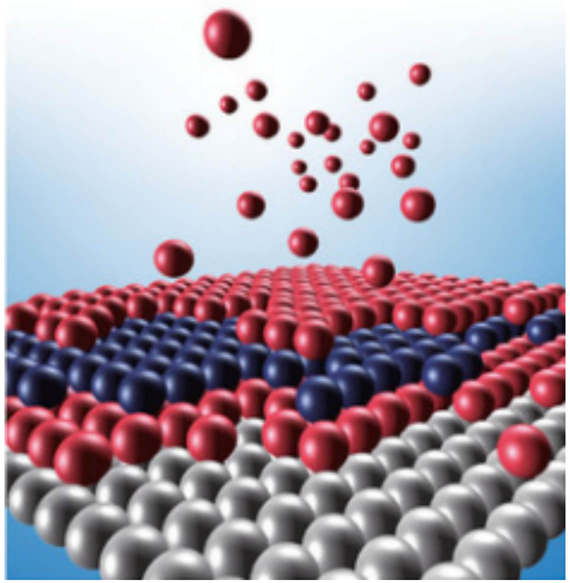
ALE Atomic layer epitaxy

used for II-VI semicond

ALD Atomic layer deposition

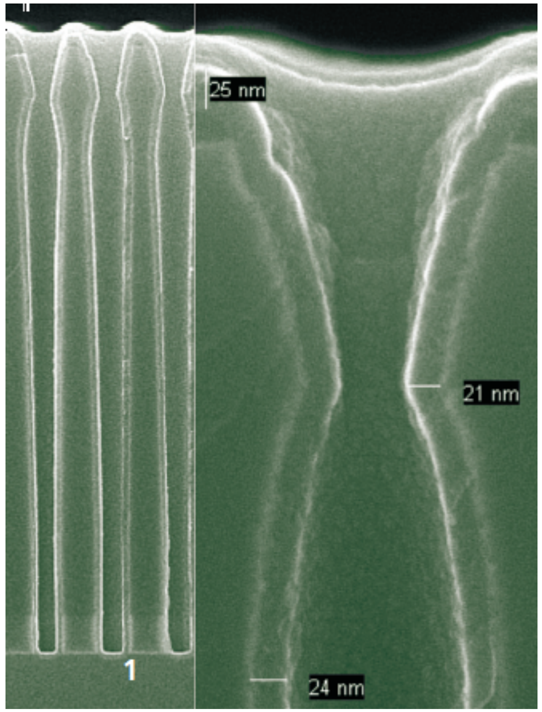
used for all kind of films

metals - insulators



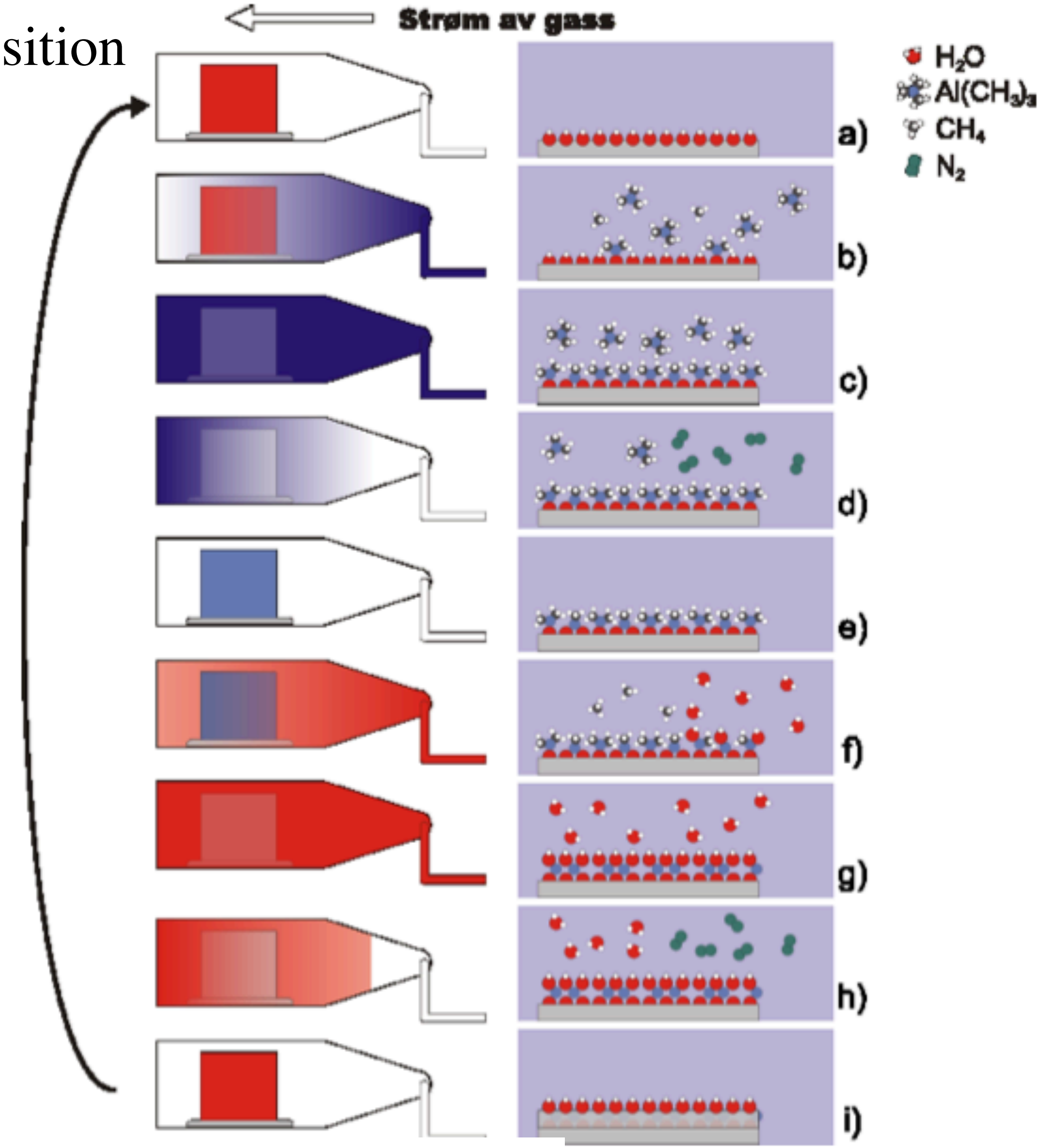
avantage

Good step coverage



ALD Atomic layer deposition

Example deposition of Al2O3



$$2 * Al(CH_3)_3 + 3 * H_2O \rightarrow Al_2O_3 + 6 * CH_4$$

ALD at MiNaLab

Al_2O_3, ZnO, TiO_2

Thickness: sub nm - 400 nm

Growth models

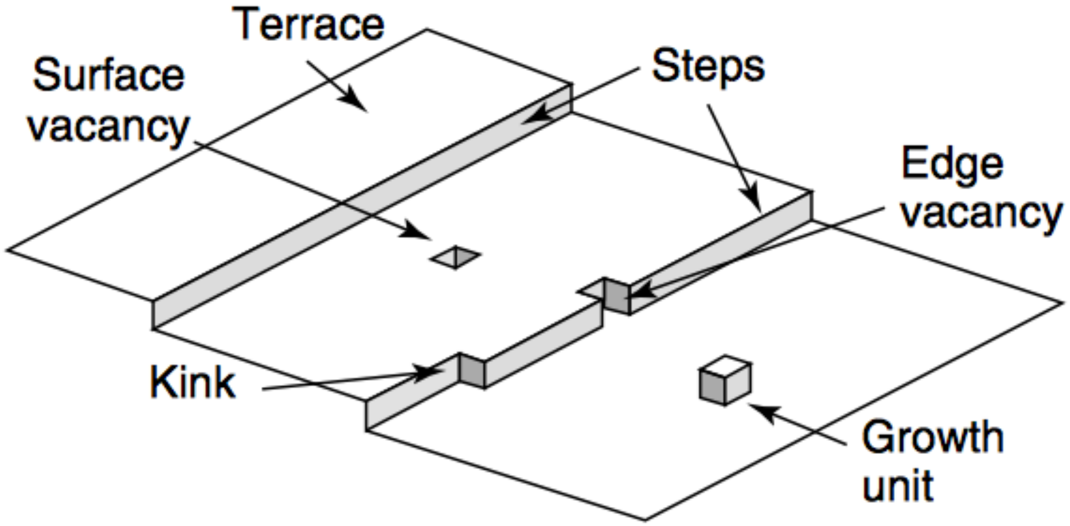


Figure 1.4 Kossel model of a crystal surface.

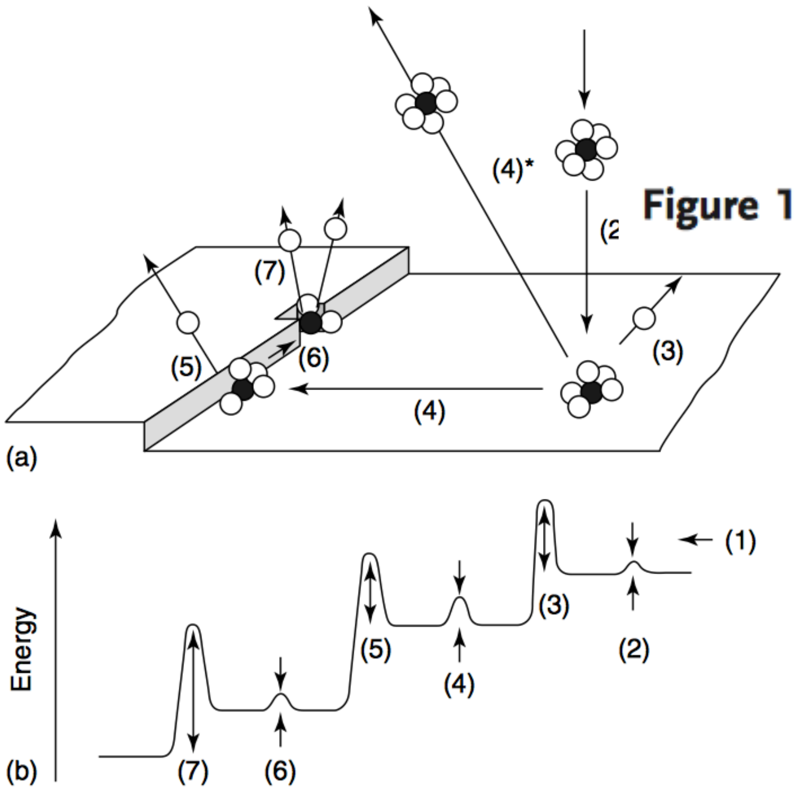
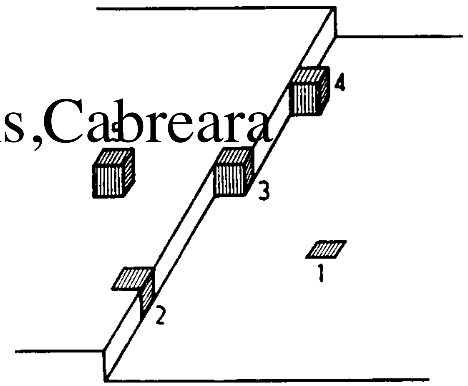


Figure 1.3 (a) Schematic representation of processes involved in the crystal growth: (1) Transport of solute to a position near the crystal surface; (2) diffusion through boundary layer; (3) adsorption onto crystal surface; (4) diffusion over the surface; (4*) desorption from the surface; (5) attachment to a step or edge; (6) diffusion along the step or edge; (7) Incorporation into kink site or step vacancy. (b) Associated energy changes for the processes depicted in (a). Figure modified from Elwell *et al.* [7].

BCF model

Burton, Franks,Cabreara



Position of atom	No. of saturated bonds
Within Face (1)	5
Within Step (2)	4
Within Kink (3)	3
Upon Step (4)	2
Upon face (5)	1

Equilibrium density absorbed atoms,

$$n_{seq} = N_s \exp(-W_s / \mathrm{k}T)$$

W_s act.energy for liberation from kink (or controlling site)

N_s density of surface positions

Surface diffusivity,

$$D_s = a^2 f \exp(-U_s / \mathrm{k}T)$$

U_s act.energy for surface jump

Stay time,

$$1/\tau = f' \exp(-E_d / \mathrm{k}T)$$

E_d act.energy for desorption

Migration length,

$$\lambda_s = \sqrt{D_s \tau} \approx a \exp(-(E_d - U_s) / \mathrm{k}T)$$

Desorbing flux,

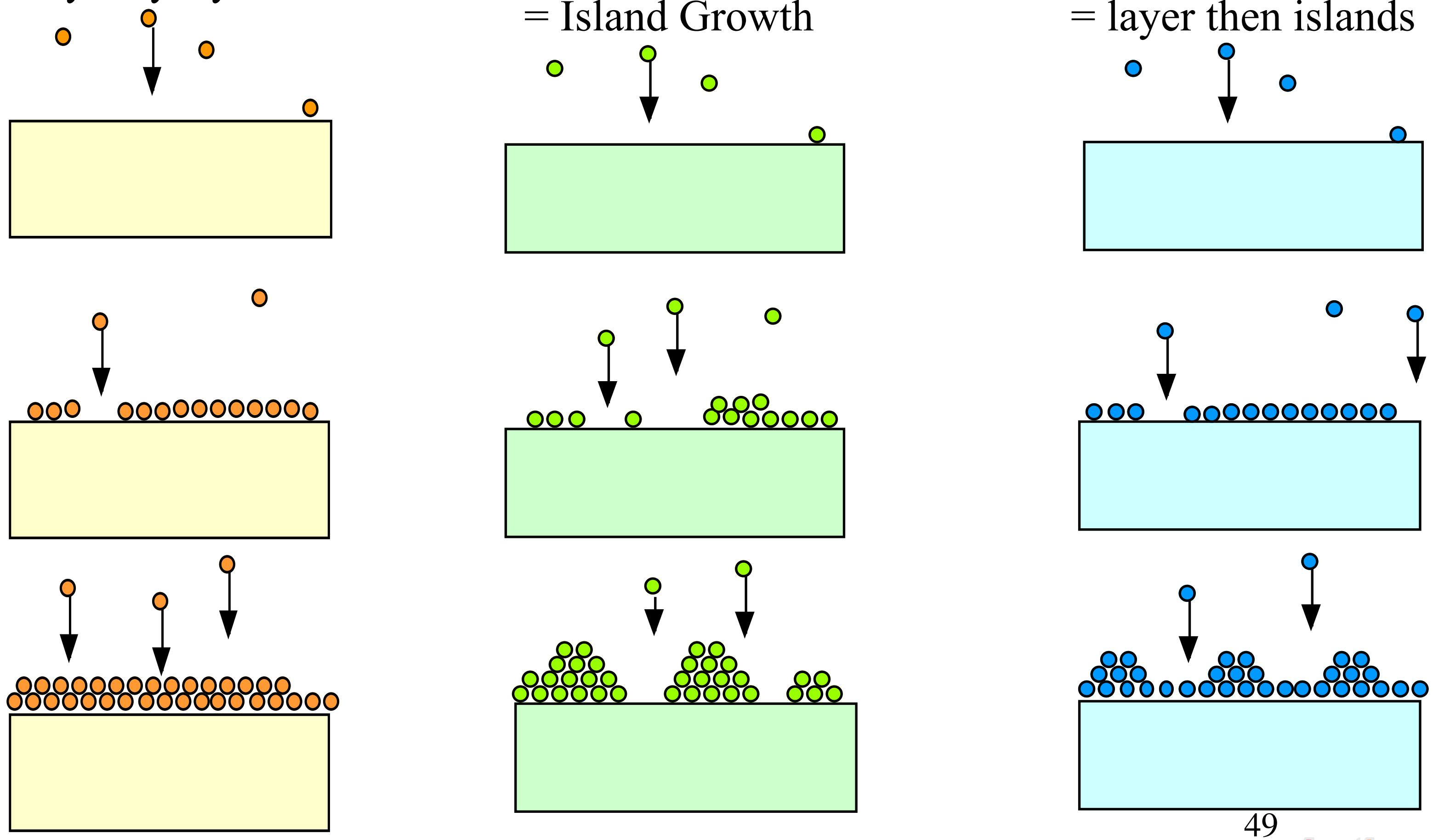
$$F_0 = \frac{n_{seq}}{\tau} = N_s f' \exp(-(E_d - W_s) / \mathrm{k}T)$$

Three growth modes during thin film epitaxial growth

1: Frank -van der Merwe
= layer by layer

2: Volmer -Weber
= Island Growth

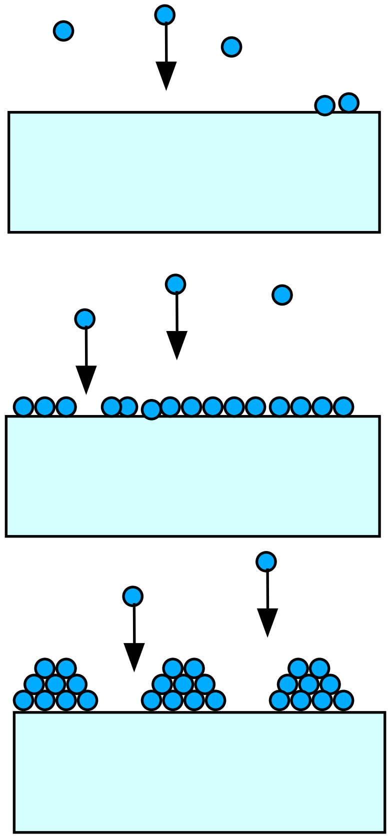
3 Stranski - Krastanow
= layer then islands



Is there a 4th?

Growth between V&B and S&K

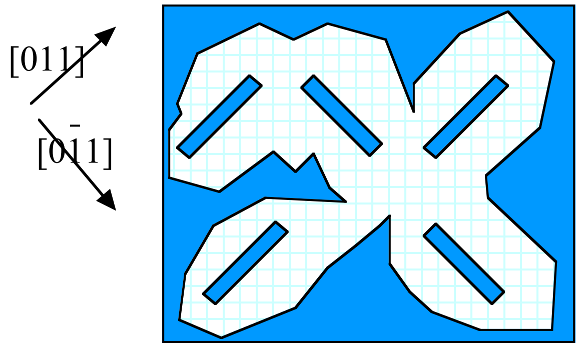
4 **layer, then islands+no layer**
(finstad palmstrøm)



GaAs on $Sc_xEr_{1-x}As$

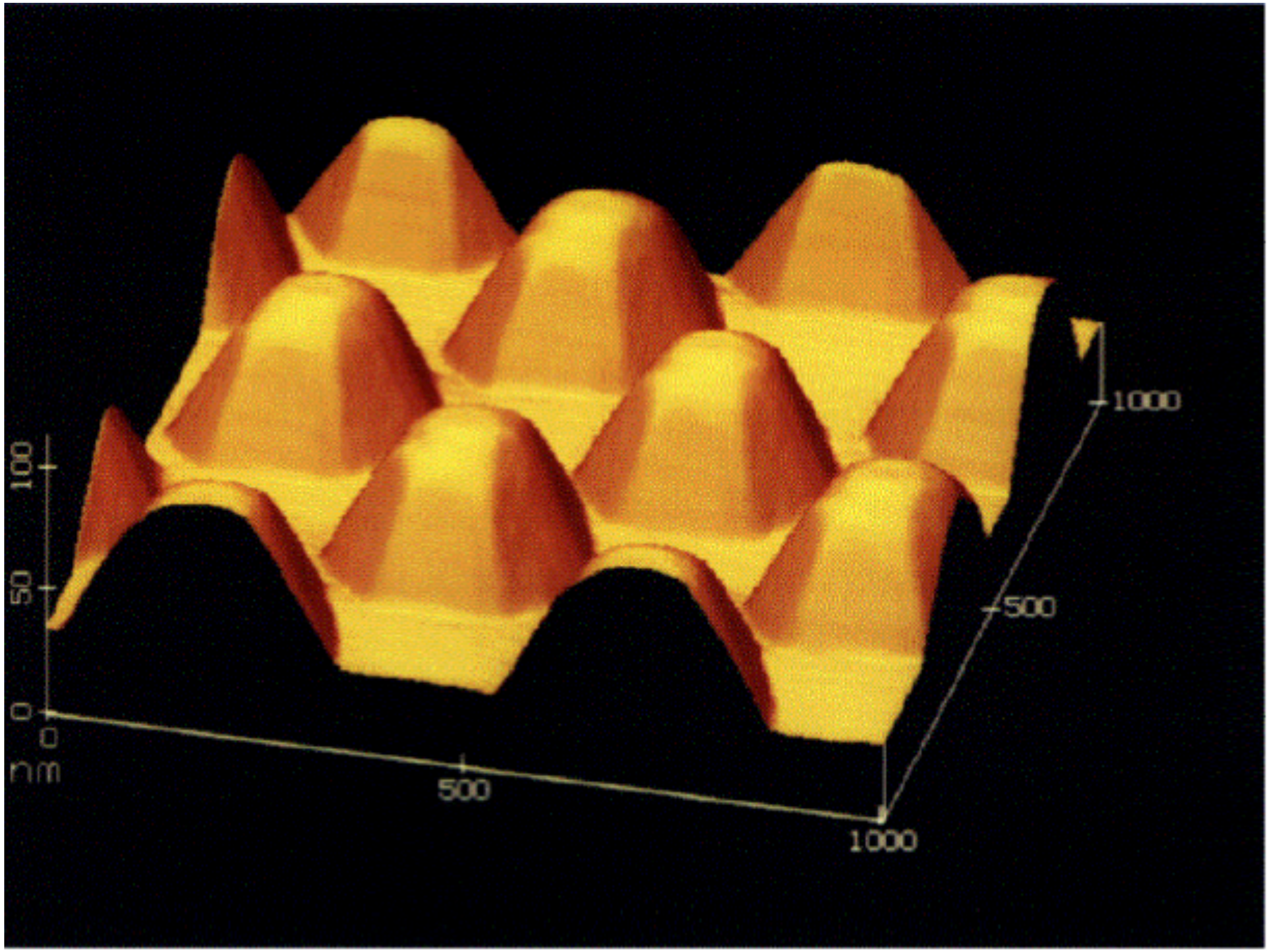
GaAs ZinkBlende
ErAs NaCl
$Sc_xEr_{1-x}As$ lattice matched
$Sc_xEr_{1-x}As$ 1r by 1r GaAs

3X3 reconstructed sp2 bonded
monolayer GaAs weak bonding to substate

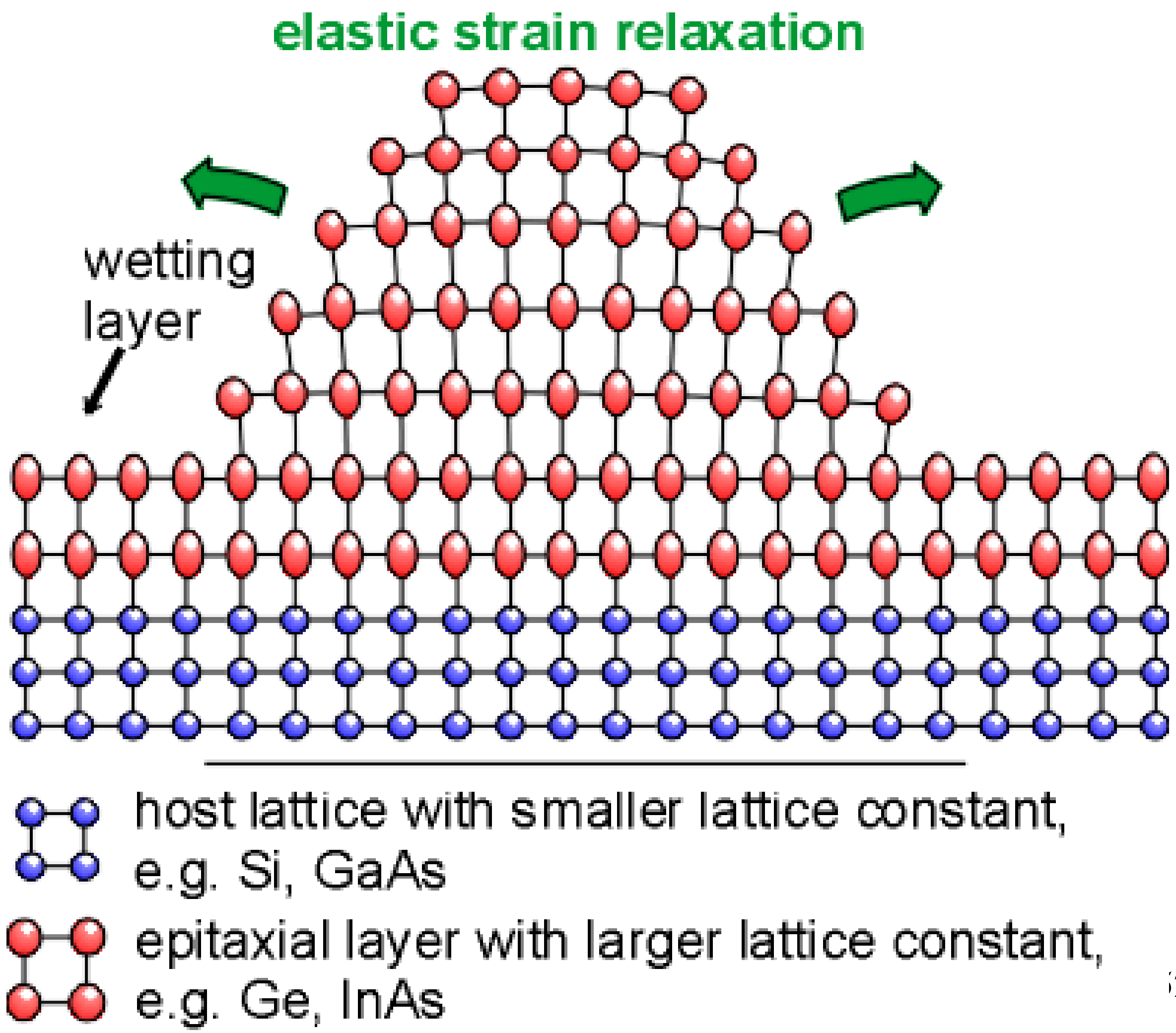


Stranki-Krastanow growth for QD

AFM In(Ga)As on GaAs



Stranki-Krastanow growth for QD



Stranski-Krastanow growth for QD

Stack of InAs islands in GaAs

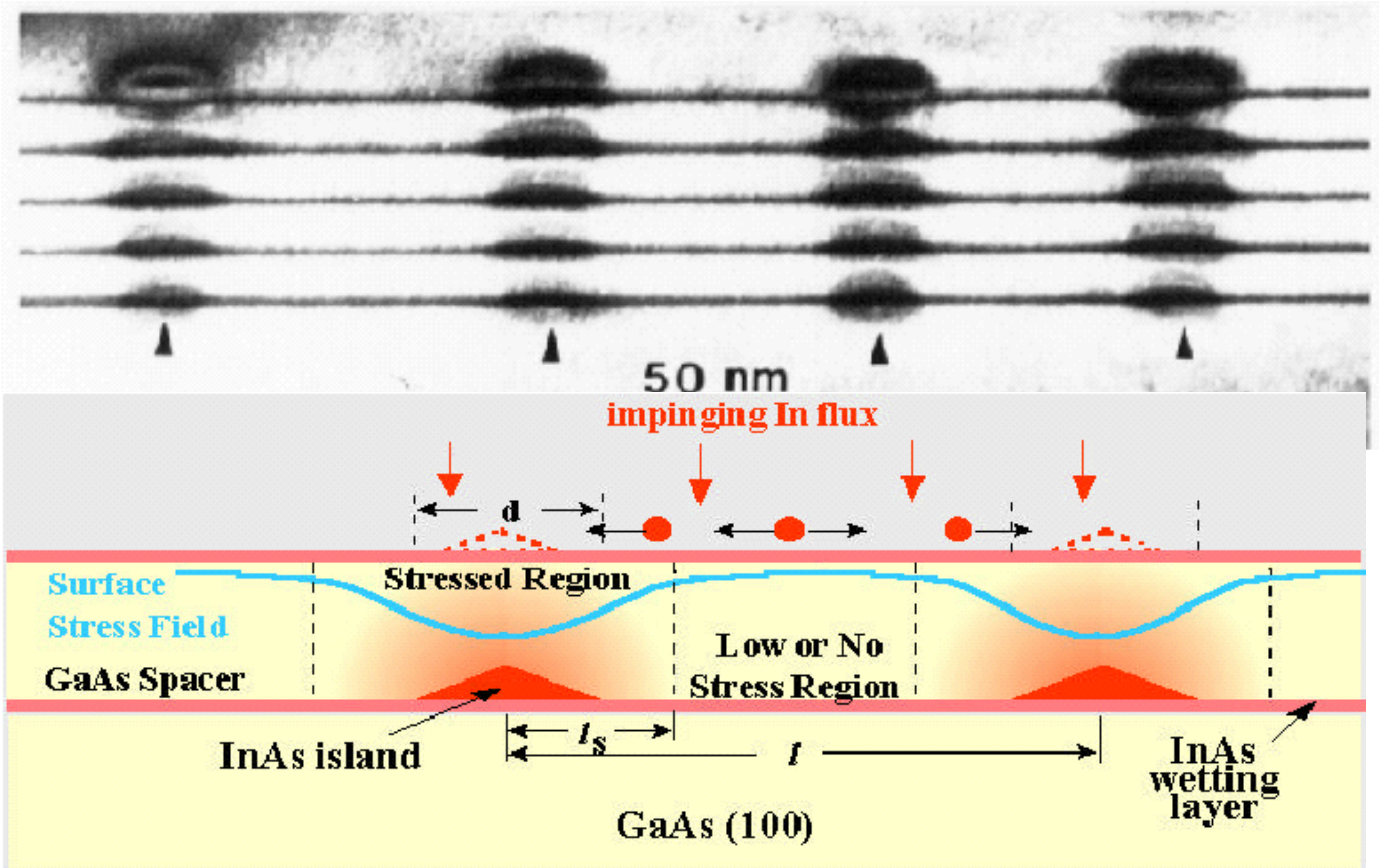


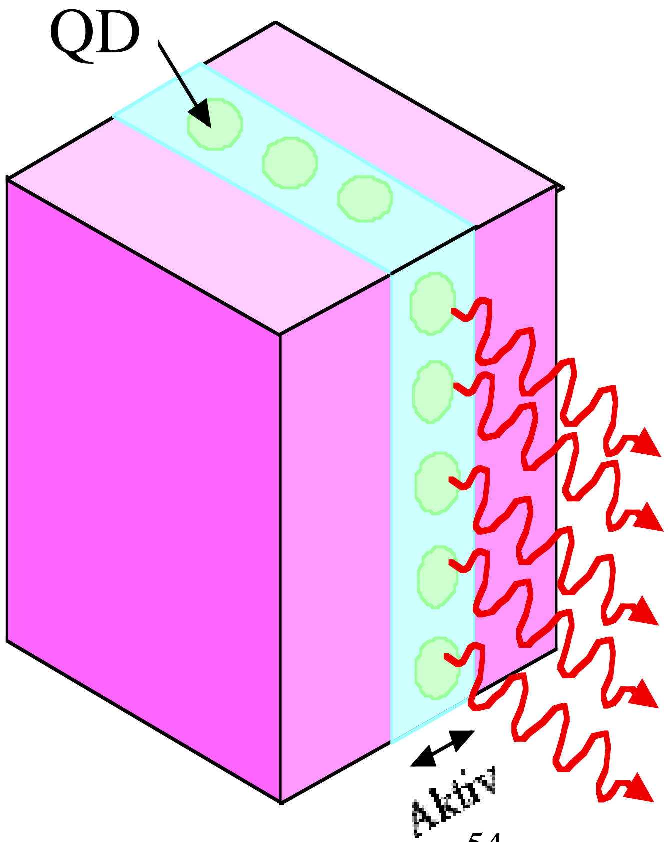
Fig 6. *Schematic of spontaneous synthesis of nanostructures via growth of highly strained materials*

QuantumDot(QD)-laser

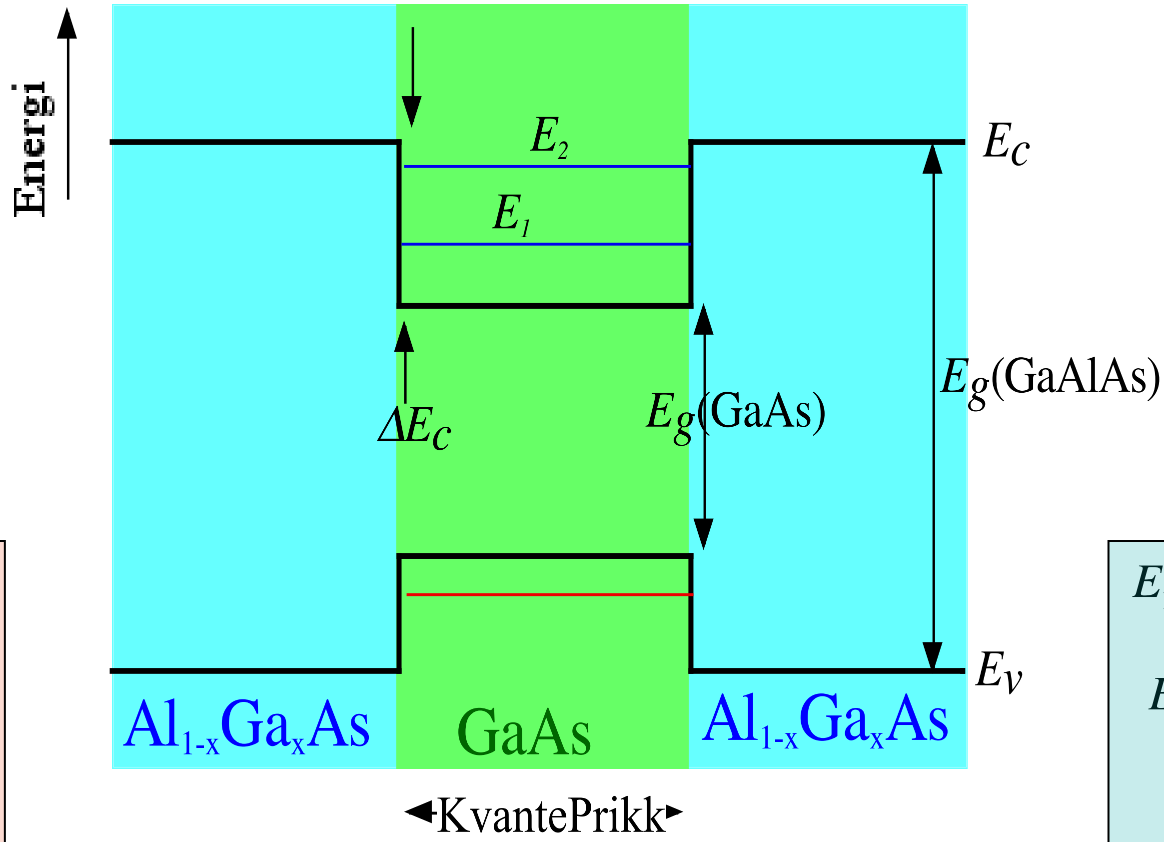
(advertisement)

quantum dot solutions

- Row of QD in active layer
- Selforganized stack of QD
- Large quantum efficiency
- Very good temperture stability
- Small threshol voltage
- Long time to develop
- On the marked



Quantum-laser Energy diagram



$$E_2 - E_1 \geq \mathrm{k}T$$

$$E_n = n^2 \frac{(\hbar\pi)^2}{2mD_{\min}^2}$$

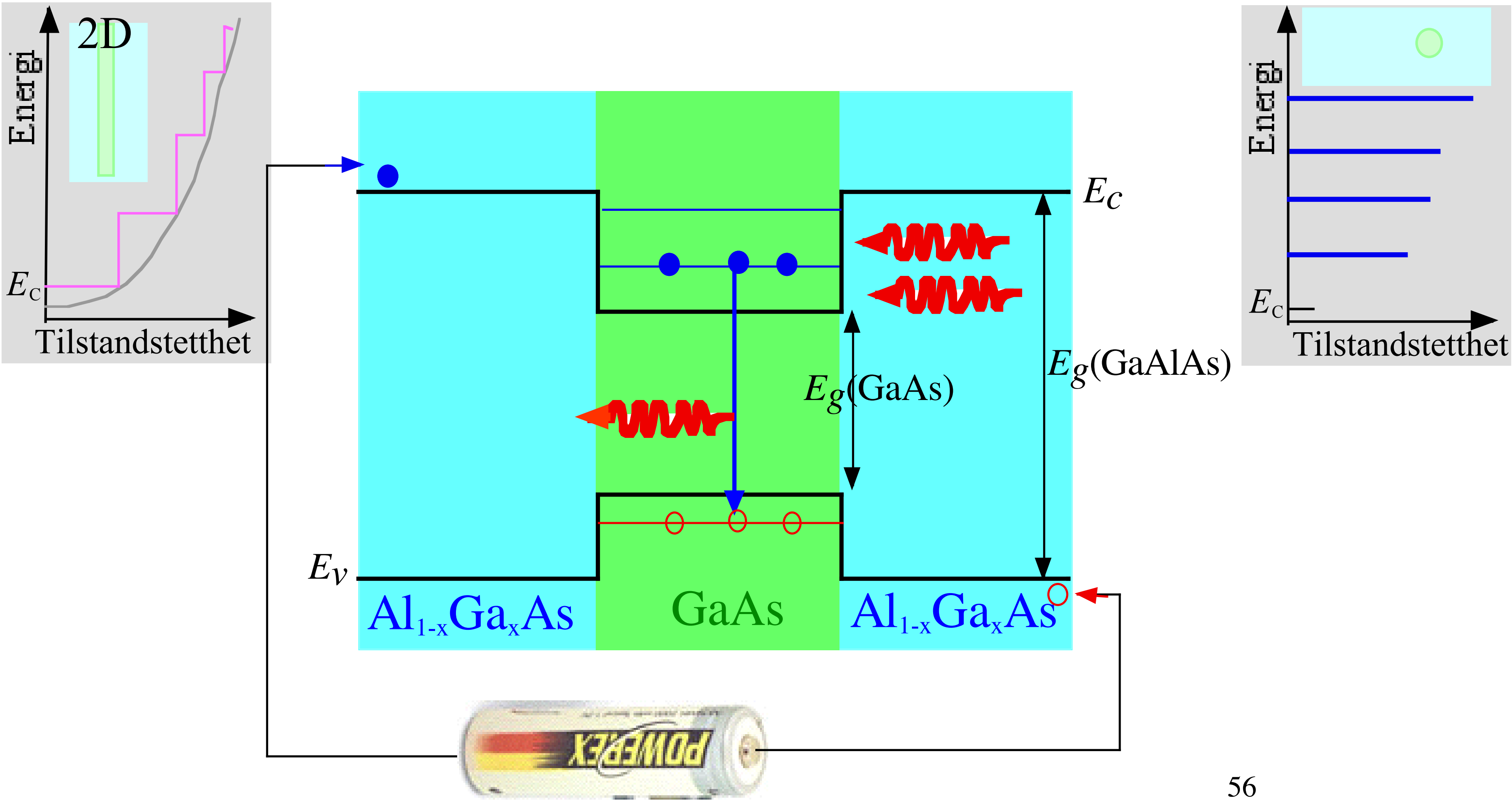
$$D_{\max} \leq 12\,\mathrm{nm}$$

$$E_1 \leq \Delta E_C = 0.3\,\mathrm{eV}$$

$$E_n = n^2 \frac{(\hbar\pi)^2}{2mD_{\min}^2}$$

$$D_{\min} \geq 4\,\mathrm{nm}$$

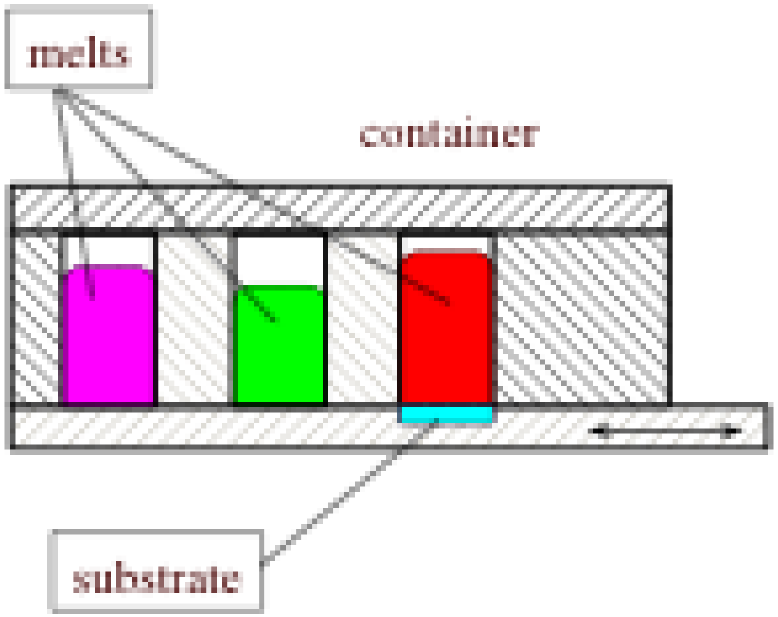
QuantumDot-laser: Work principle

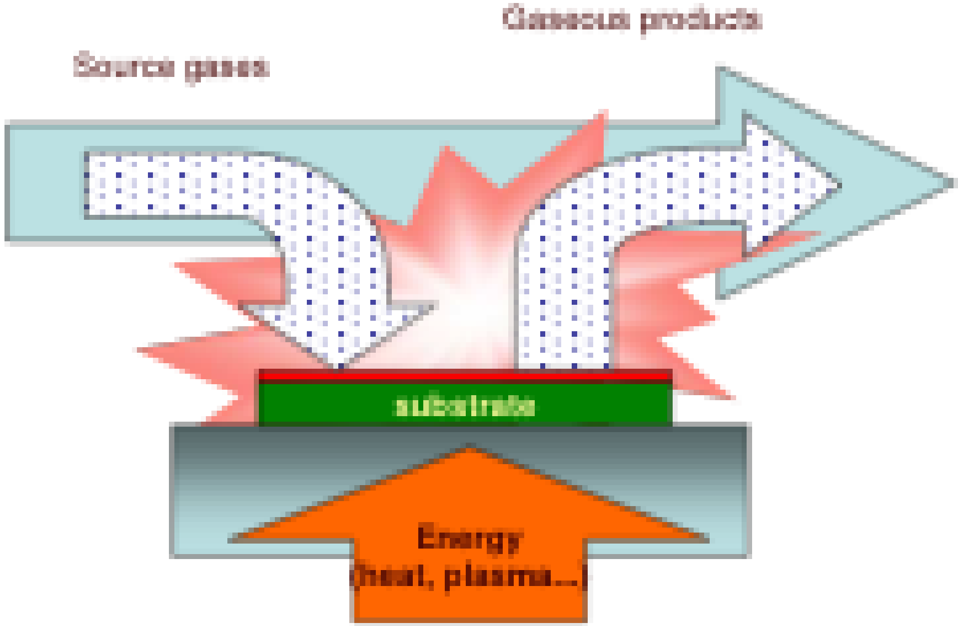


Epitaxy

High-Temperature Deposition Methods

- Liquid-Phase Epitaxy (70% of light-emitting diods)
- CVD-Based Epitaxy





Comparison of LPE, MOCVD & MBE

	LPE	MOCVD	MBE
Pressure	760torr	25-760torr	10^{-10}torr
Reactant transport	Liquid phase	Vapor phase	Atomic & molecular beams
Temperature control	Source & substrate	Substrate	Source & substrate
Heterostructure formation	Sliding speed	Gas flow control	Shutter control
In-situ diagnostic	no	no	RHEED, reflectivity Mass spectroscopy
Growth rate (um/min)	0.1 ~10	0.005~1.5	0~0.05
Minimal thickness (A)	500	20	5
Uniformity	Good (small wafer)	good	good
Surface quality	bad	good	good
Interface sharpness	bad	good	good
Doping Range (cm^{10})	10^{14} ~10^{19}	10^{14} ~10^{19}	10^{14} ~10^{19}
Process yield	low	high	Very low