# Crystal Growth: Physics, Technology and Modeling

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## Lecture 4. Molecular beam epitaxy

http://www.unipress.waw.pl/~stach/cg-2021-22

# Molecular beam epitaxy - MBE

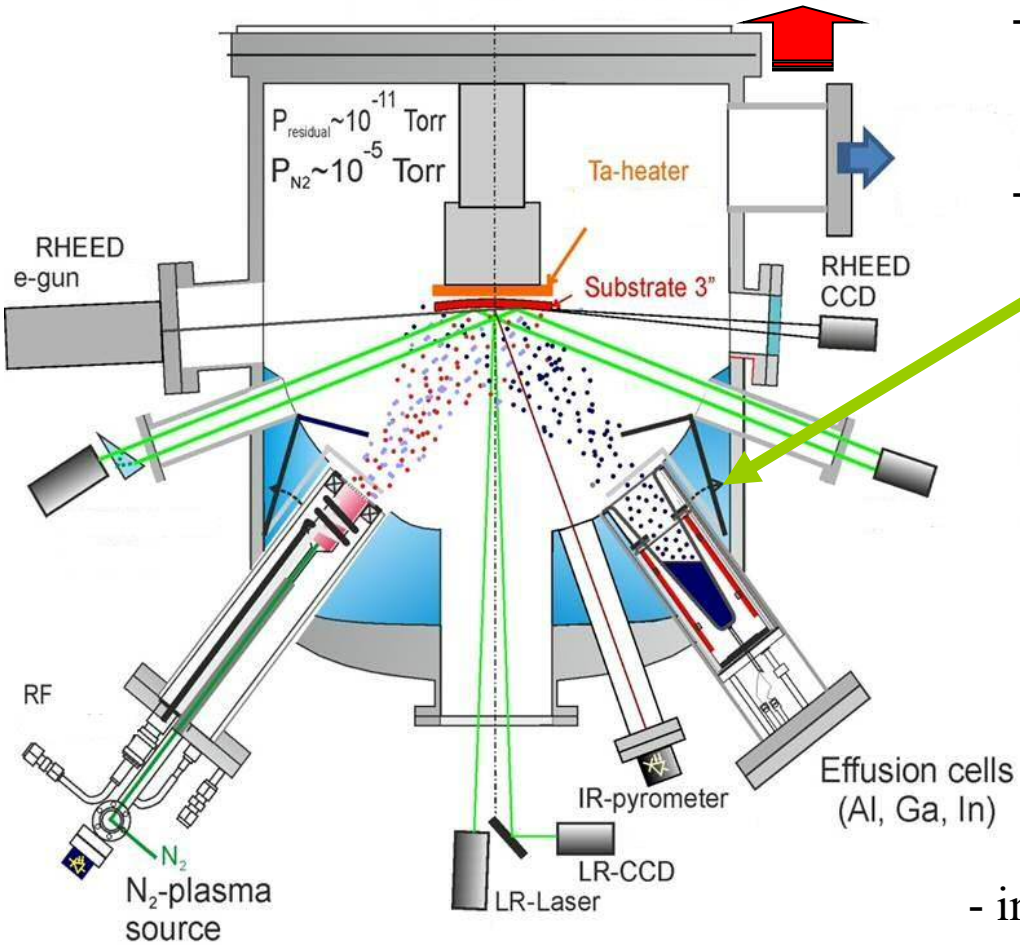
pol. epitaksja metodą (z) wiązek molekularnych

**Outline:**

- **idea and physical background of MBE**
- **technical aspect of MBE growth**
- ***in situ* monitoring of MBE growth**
- **examples of MBE grown structures**
  - **low-temperature growth**
  - **superlattices**
  - **quantum dots and nanowires**
- **summary**

# MBE system

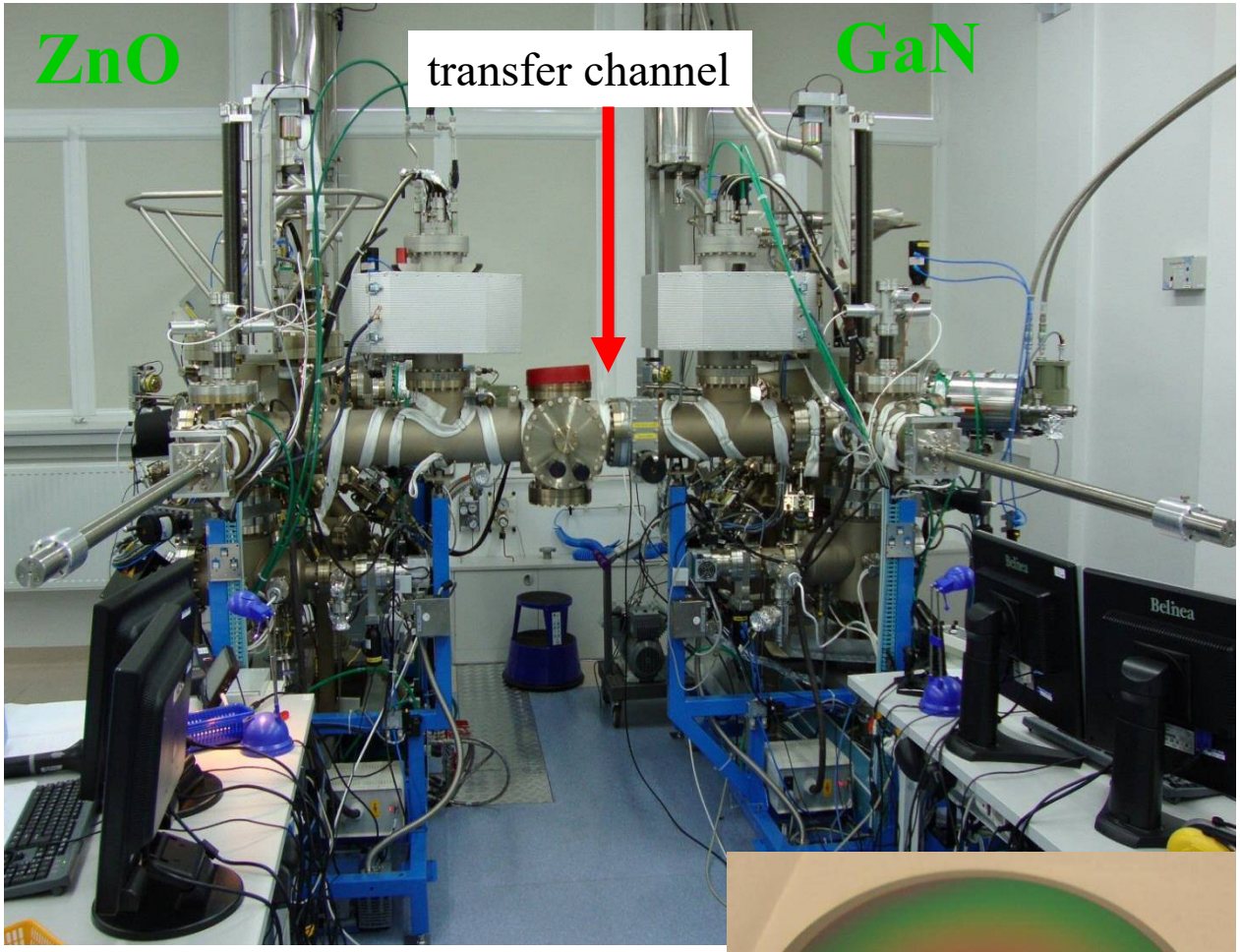
## pumping system

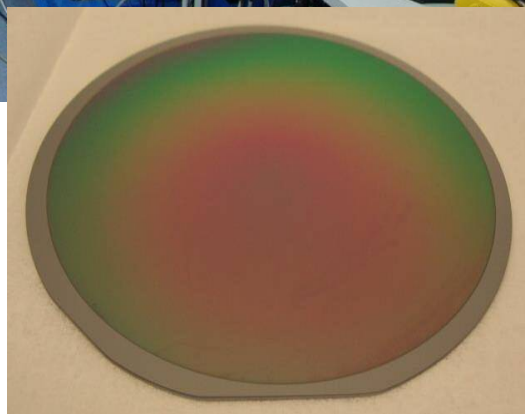



- UHV conditions
  - background pressure $10^{-10}$ – $10^{-11}$ Tr
  - ~ $10^{-5}$ Tr inside the molecular beam
- $LN_2$ filled cryoshroud :
  - additional pumping
  - freezing out atoms on the walls
  - lower „memory effect”
  - thermal separation of the sources

- independent sources of atoms/molecules;
  the flux usually controlled by $T_{source}$
- measurement of the flux – flux monitor
- mechanical shutters to open/close the source
- substrate heated by the heater
  T = ~200 °C - ~1000 °C
- many *in-situ* diagnostic tools available

# Plasma-Assisted MBE (PAMBE) Riber Compact 21



growth on
3" substrates
(4" possible)

**TOOLS:**

- optical pyrometer
- RHEED (k-Space)
- laser reflectometry
- LayTec EpiCurve TT (temperature, wafer curvature)
- line-of-sight quadrupole mass spectrometry (QMS)

**SOURCES:**

- Ga x2
- Al x2
- In
- RF nitrogen source
- Si x2
- Mg
- Fe

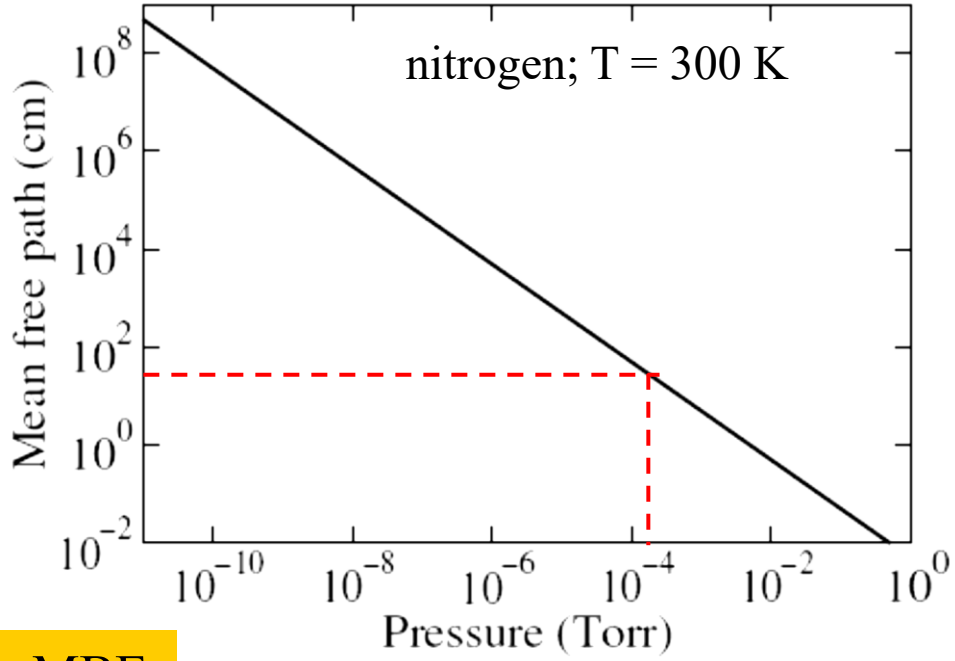
# UHV in MBE – meaning how much ?

condition 1: mean free path of atoms > source – substrate distance

mean free path of atoms λ in gas phase under pressure *p*

$$\lambda \approx \frac{5\times10^{-4}}{p[Tr]}[cm]$$

**p = $10^{-4}$ Tr ↔ λ = ~50 cm**
p = $10^{-7}$ Tr ↔ λ = ~0.5 km
p = $10^{-11}$ Tr ↔ λ = ~5 000 km




ballistic atom transport (no collisions) in MBE
- no UHV conditions needed

# UHV in MBE – meaning how much ?

## condition 2: high purity of MBE grown layer

assumption: all particles/atoms arriving stick to the substrate (no desorption)

flux of particles in a gas under pressure $p$ on area of 1 cm$^2$ in 1 sec.

$$J = \frac{p[Tr]}{\sqrt{2\pi m k_B T}}[cm^{-2}s^{-1}]$$

if m=40; T=300K to $J[cm^{-2}s^{-1}] = 3.2\times10^{20}\, p[Tr]$

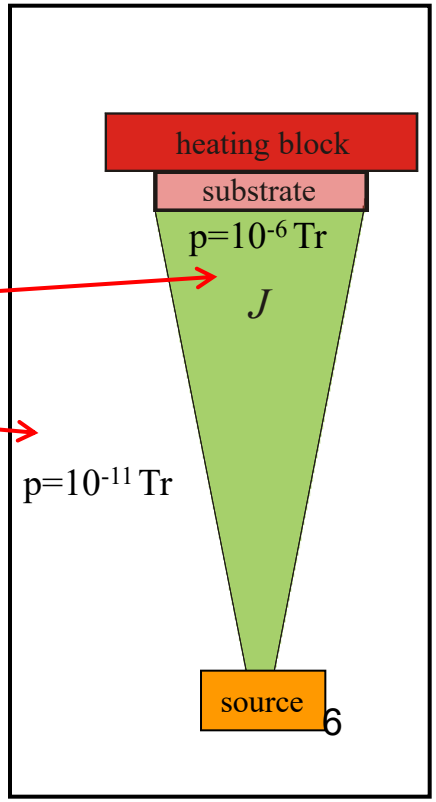
number of lattice places on Si surface $N = 3.2\times10^{14} cm^{-2}$

time to cover Si by 1 monolayer of particles (ML) $\tau[s] = \frac{N}{J} = \frac{10^{-6}}{p[Tr]}$

$p$ = $10^{-6}$ Tr $\leftrightarrow$ $\tau$ = 1 sec

$p$ = $10^{-11}$ Tr $\leftrightarrow$ $\tau \approx$ 28 h

$p$ = $10^{-11}$ Tr $\Rightarrow$ 1 impurity atom per $10^5$ Si atoms
impurity concentration in the bulk ~$10^{17}$ cm$^{-3}$



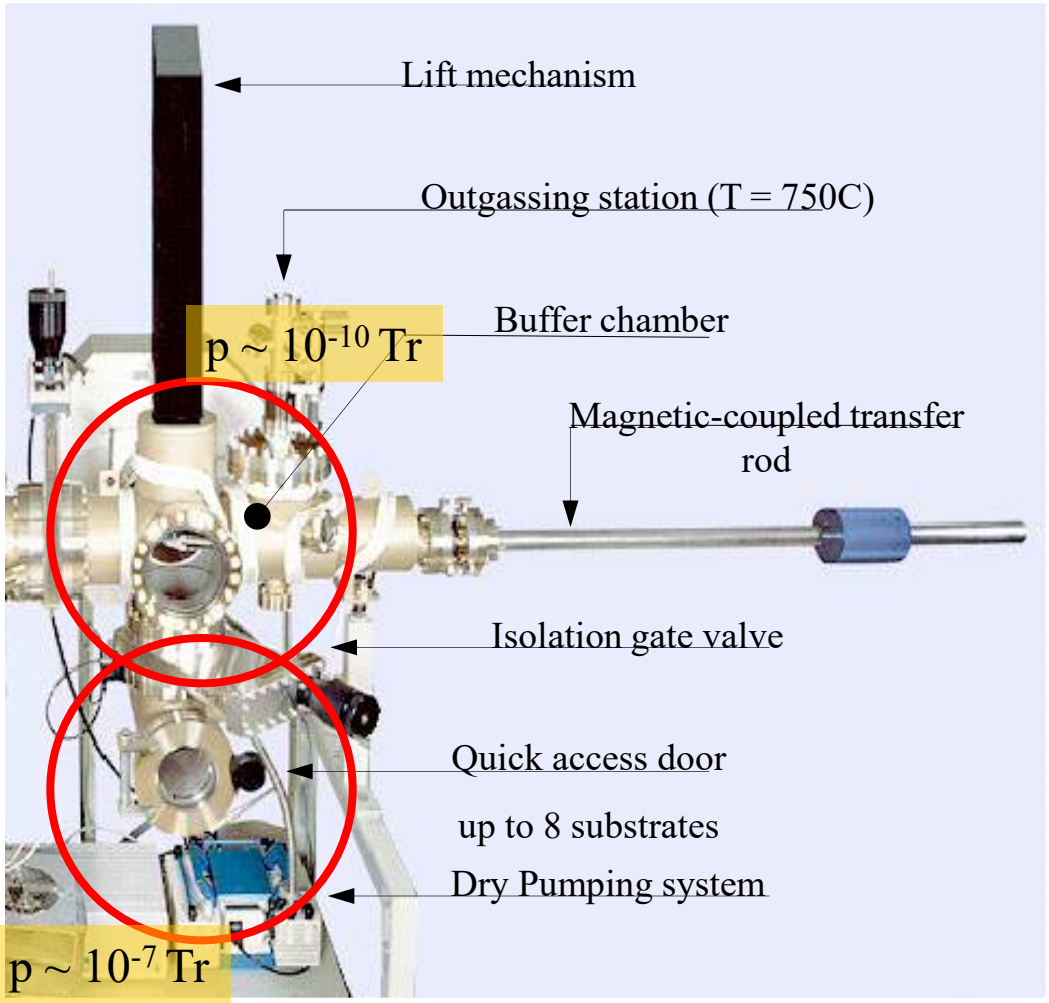

under real conditions: layers more pure (~$10^{14}$ cm$^{-3}$ possible) since:
- often sticking coefficient < 1 (desorption important)

# Three-chamber configuration of MBE system (example - Riber Compact 21)

growth chamber


$p \sim 10^{-11}$ Tr

loading and pre-annealing of the substrate




each chamber equipped with its own pumping system

# Generation of vacuum

- mechanical pumps - rough pumps (rotary, Scroll, membrane, ..) and turbomolecular (UHV)
- cryopumps
- ion and titanium pumps

pumping speed ($N_2$) 2800 l/sec

pumping speed ($N_2$) 1200 l/sec

Helix CTI-10; pumping speed ($N_2$) 3000 l/sec

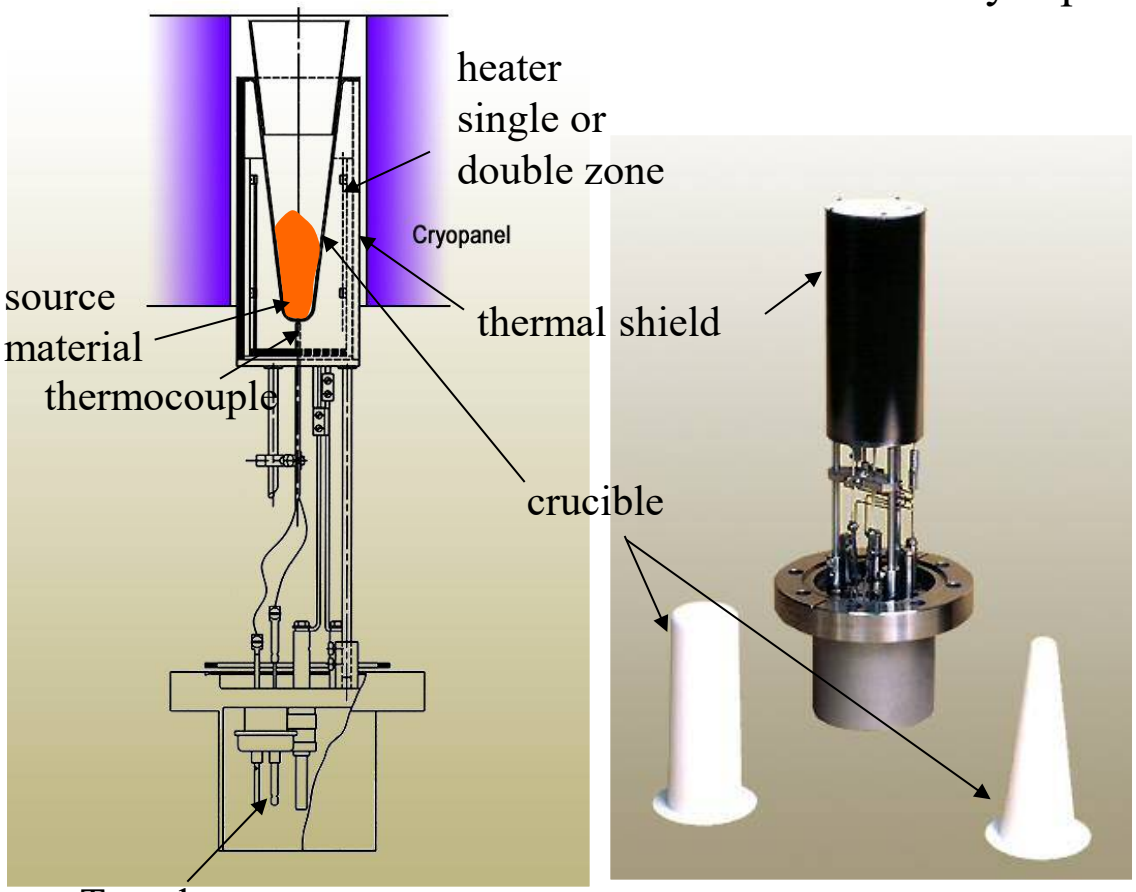
long annealling of all chambers at T ~ 150° C after each opening of the system to remove residual gases and water

# Generation of molecular beams – effusion (Knudsen) cell

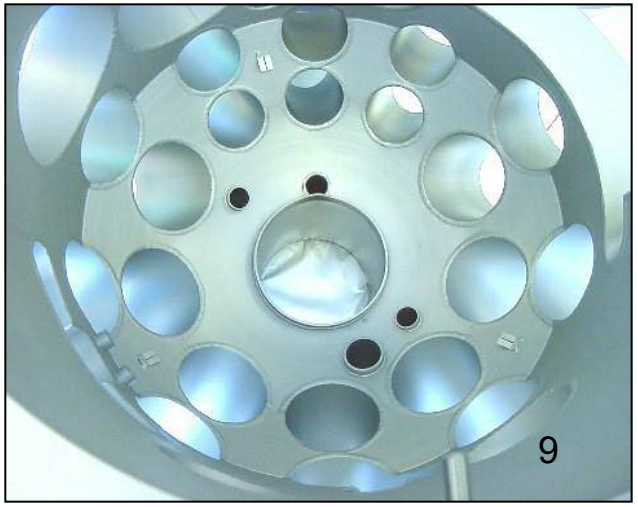
shutter

Modern molecular sources:

- many sources in one system (10 in Compact 21 Riber)
- sources centered at the substrate ⇒ flux uniformity
- high flux stability;
  flux drift < 1%/day⇒ ΔT < 1ºC @ T ~ 1000 ºC
- each cell equipped with its own shutter
- cells thermally separated from each other



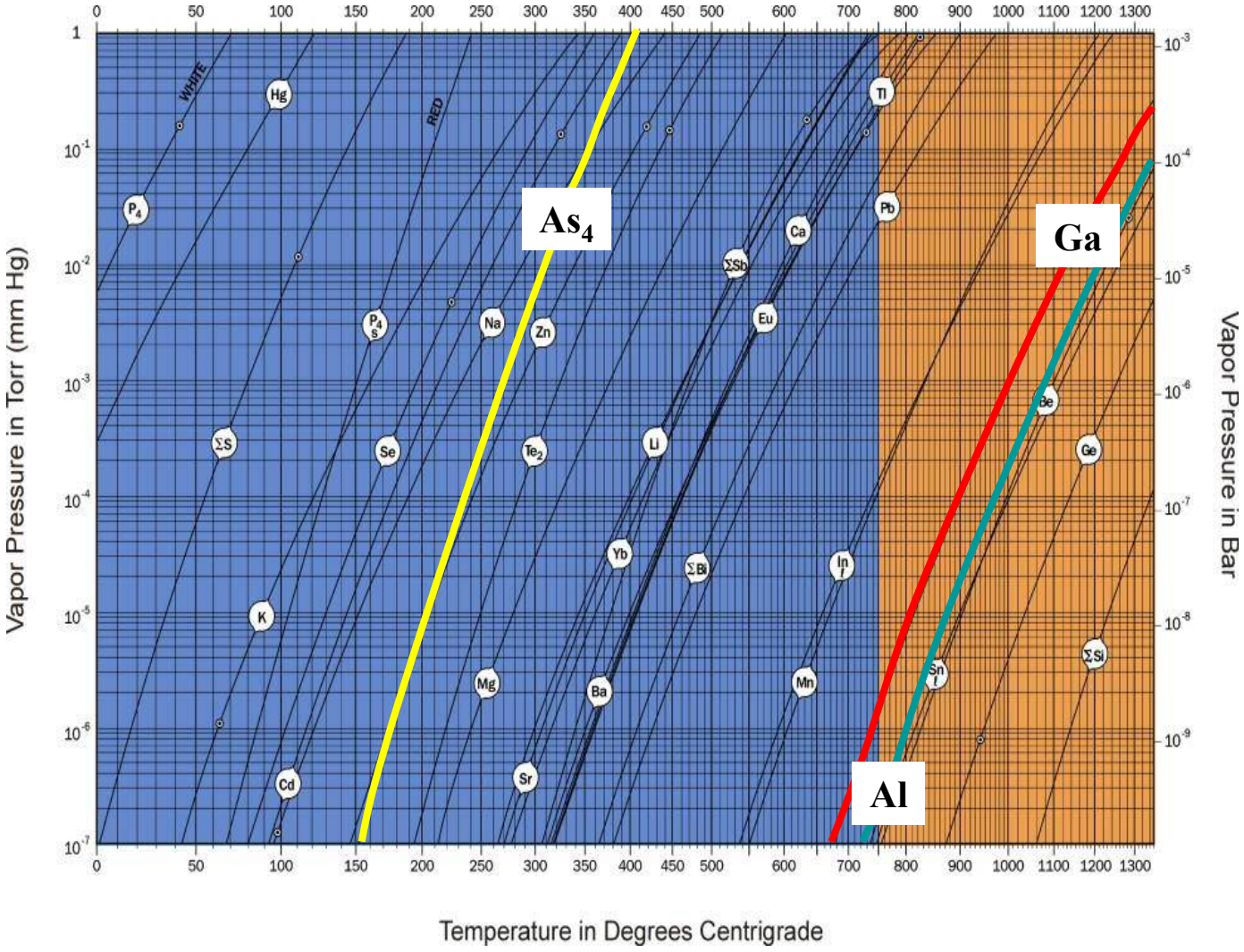

holes for sources and shutters in cryopanel of Compact 21 Riber system



# Generation of molecular beams – effusion (Knudsen) cell

**assumption:** vapor – liquid/solid equilibrium in the cell

vapor – liquid/solid equilibrium plots for selected elements

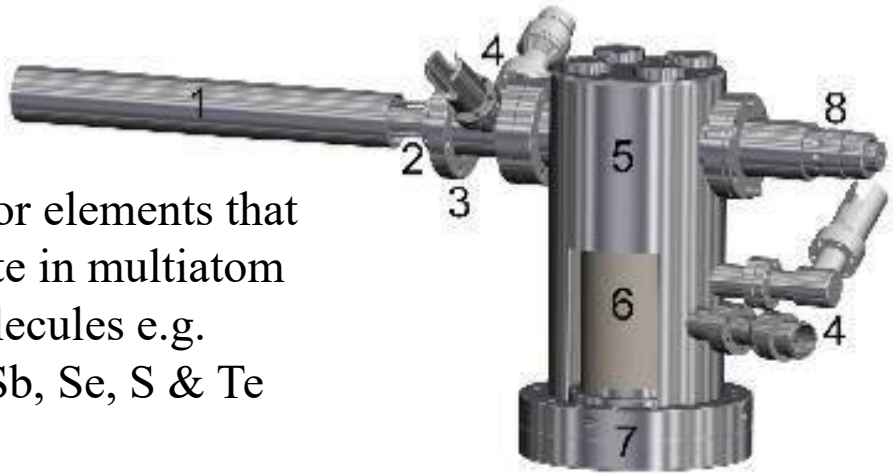



by changing $T_{source}$ the flux from the cell $p$ is controlled

# Generation of molecular beams –special sources

## valved cracker

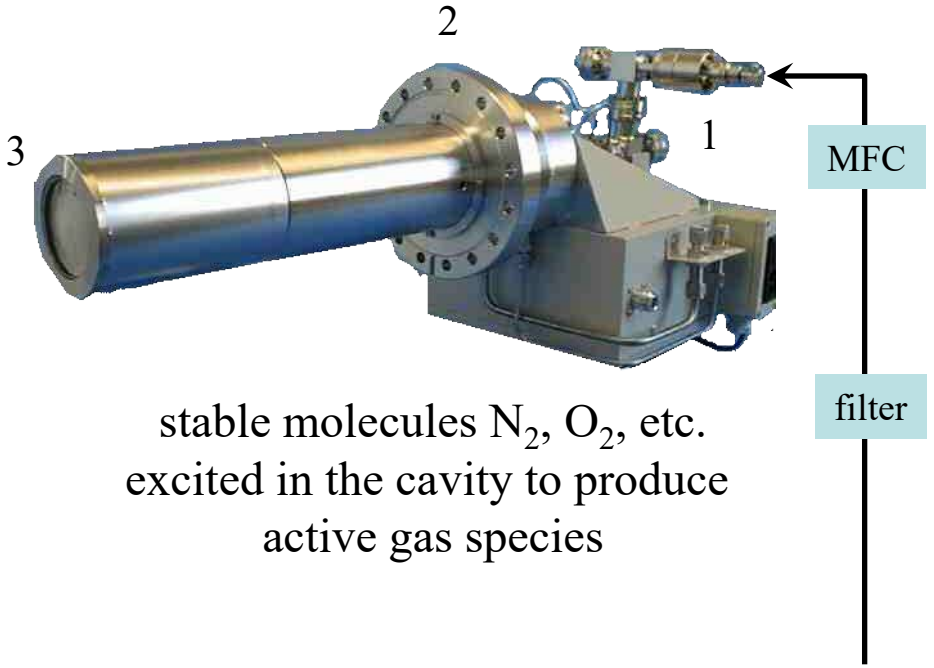
1. Cracking zone $As_4 \rightarrow As_2$
2. connector + needle valve
3. main flange
4. power and TC connection
5. generation of $As_4$ vapor
6. crucible with solid As




source for elements that sublimate in multiatom molecules e.g.
As, P, Sb, Se, S & Te

## plasma source

1. inlet of purified gas (MFC)
2. RF cavity
3. exit aperture (plate with small holes)




## gas injectors

gas sources with needle valve to deliver precursors used in Gas Source MBE (e.g. $SiH_4$) or metalorganics in MO MBE

stable molecules $N_2$, $O_2$, etc. excited in the cavity to produce active gas species

# growth rate in MBE – example GaAs

growth under As-rich conditions;
growth rate $V_{gr}$ controlled by Ga flux;
assumption: no Ga desorption

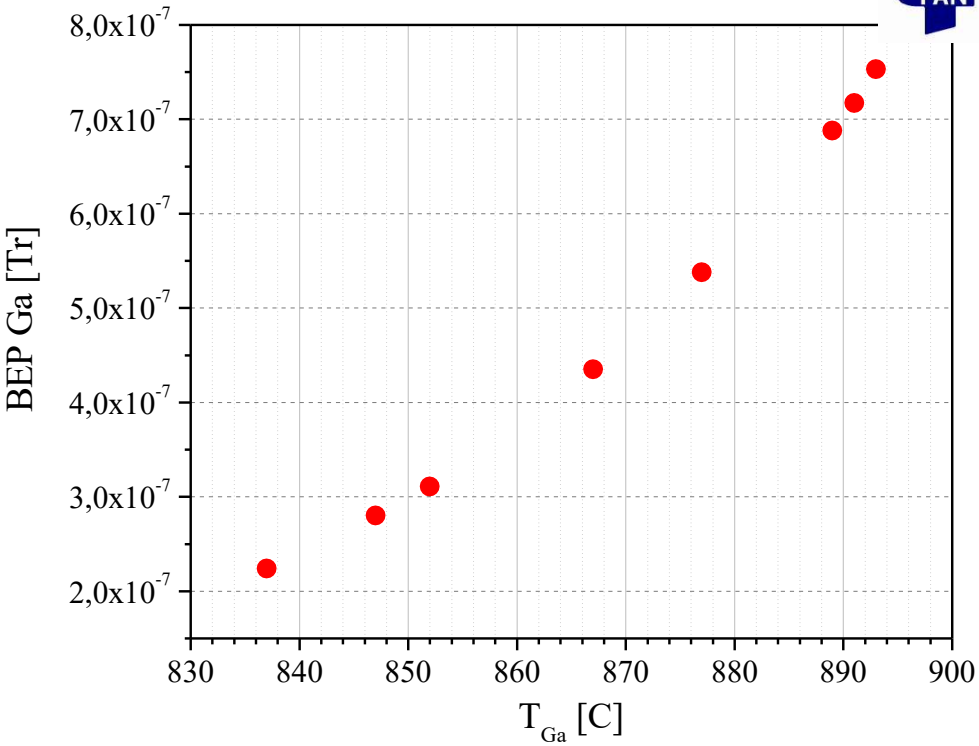
Ga flux $J = 1.18 \times 10^{15} \frac{at}{cm^2 s}$

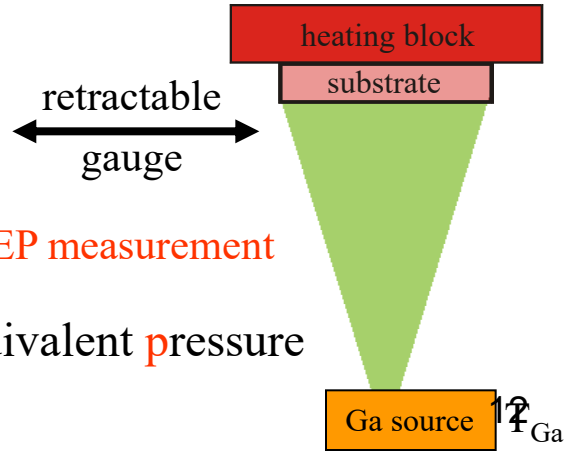
spec. volume of GaAs $\Omega_0 = 2.27 \times 10^{-23} cm^3$

$V_{gr} = J\Omega_0$

$V_{gr} = 2.67$ Å/s $= 1\,ML/s = 0.96\,\mu m/h$

controlled growth of very thin (~1 ML) layers and epitaxial structures



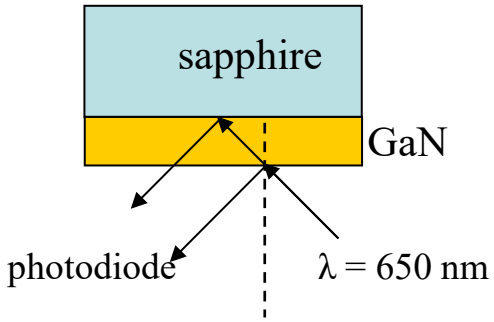

BEP = beam equivalent pressure

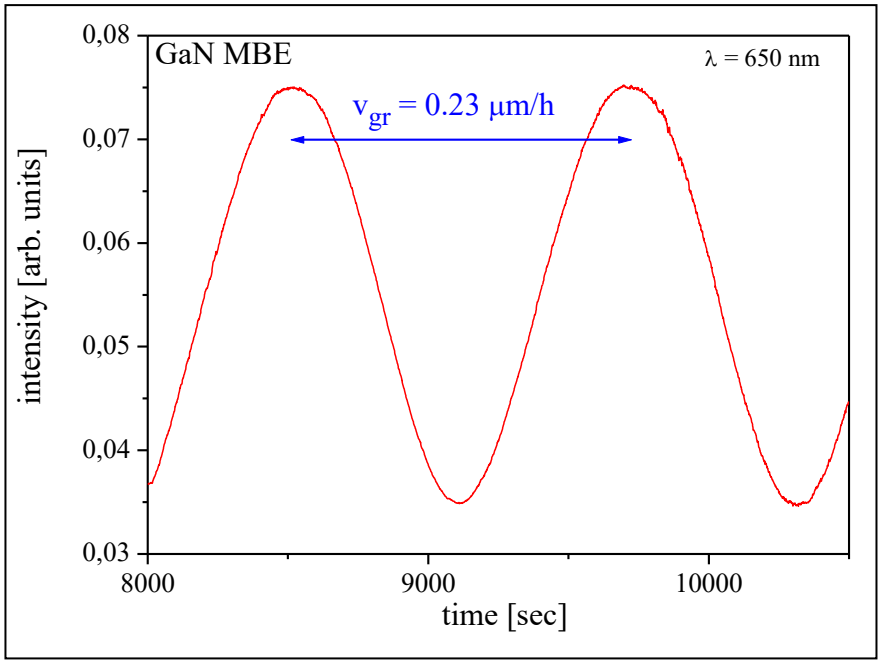
# *in situ* growth monitoring

**vacuum is transparent for light, electrons, X-rays, …**
wide possibilities to „observe" surface of growing epilayer

## laser reflectometry

*growth rate, evolution of surface roughness, …*




## optical pyrometry *measurement of sample T based on the black body emission spectrum*

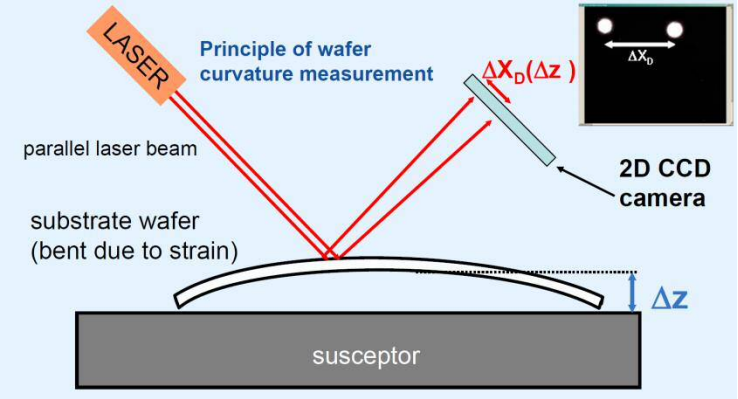
to be discussed later

## ellipsometry

# *in situ* growth monitoring

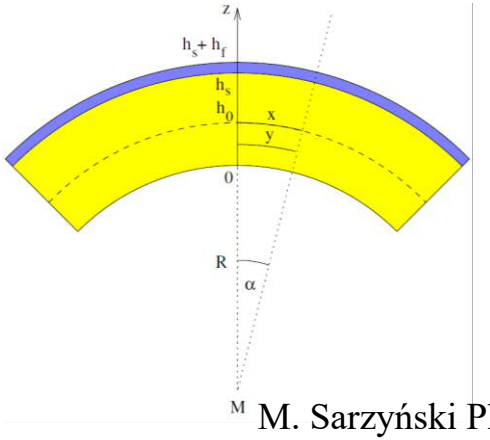
## sample curvature

*stress and bow evolution in real time*



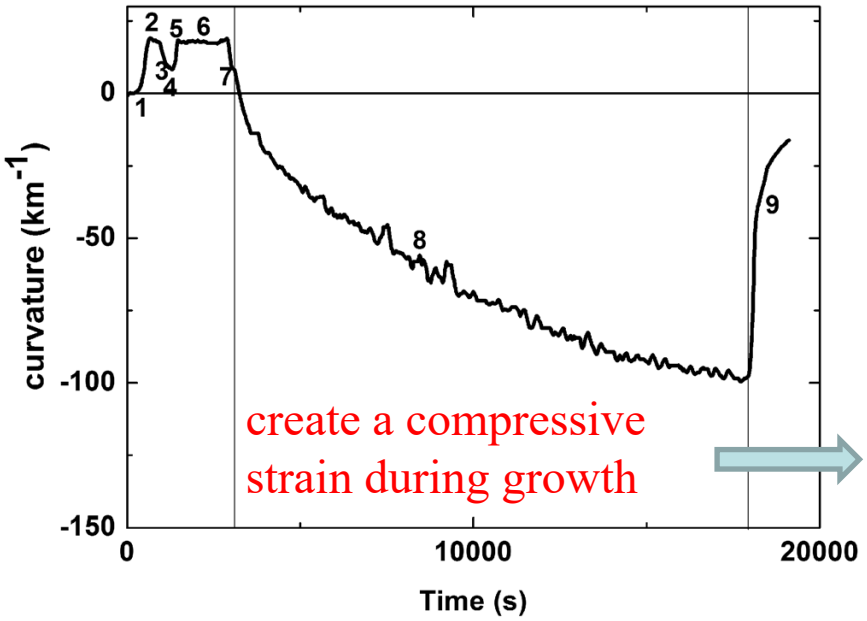

*laytec.com*

LayTec – EpiCurve; Riber – EZ-Curve, k-Space - kSA MOS…




M. Sarzyński PhD 2007

Stoney formula



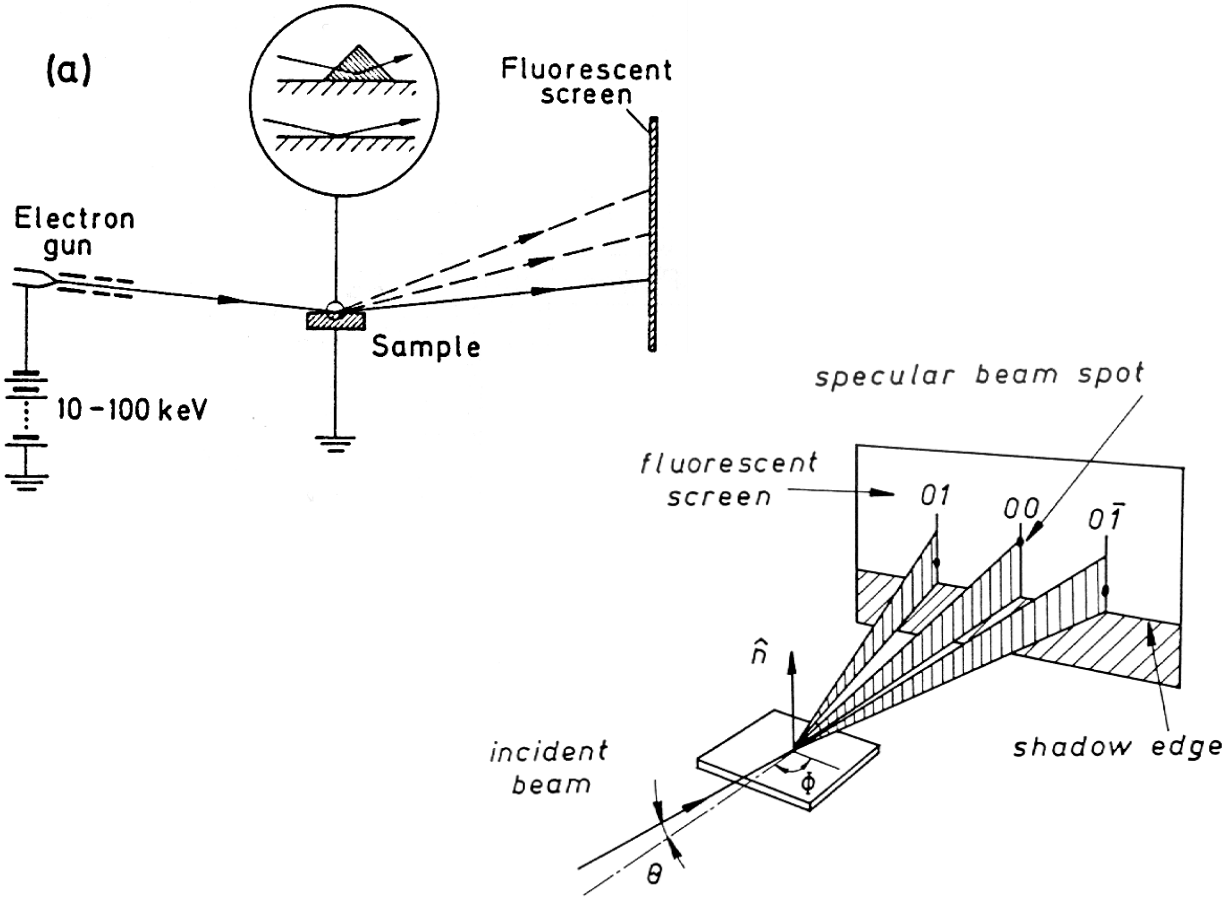

PAMBE growth of GaN/AlGaN on Si(111): mismatch of thermal contraction leads to tensile strain and cracking upon cooling

thick GaN buffers can be grown on Si w/o cracks

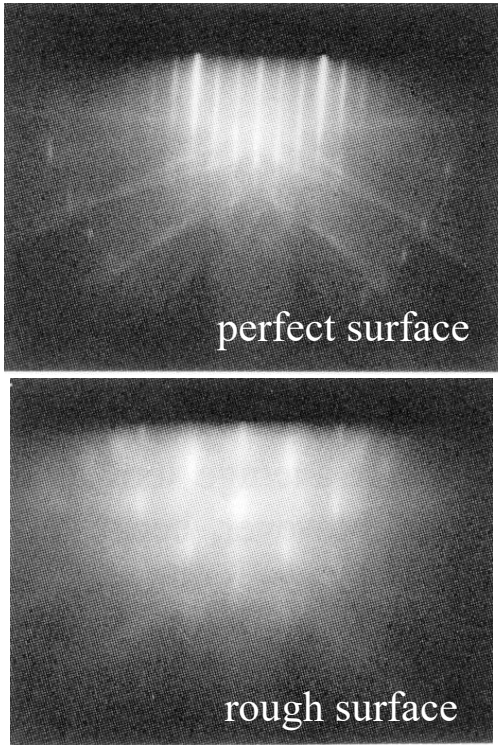
Aidam et al., J. Appl. Phys. 111, 114516, 2012

# *in situ* growth monitoring - reflection high energy electron diffraction (RHEED)

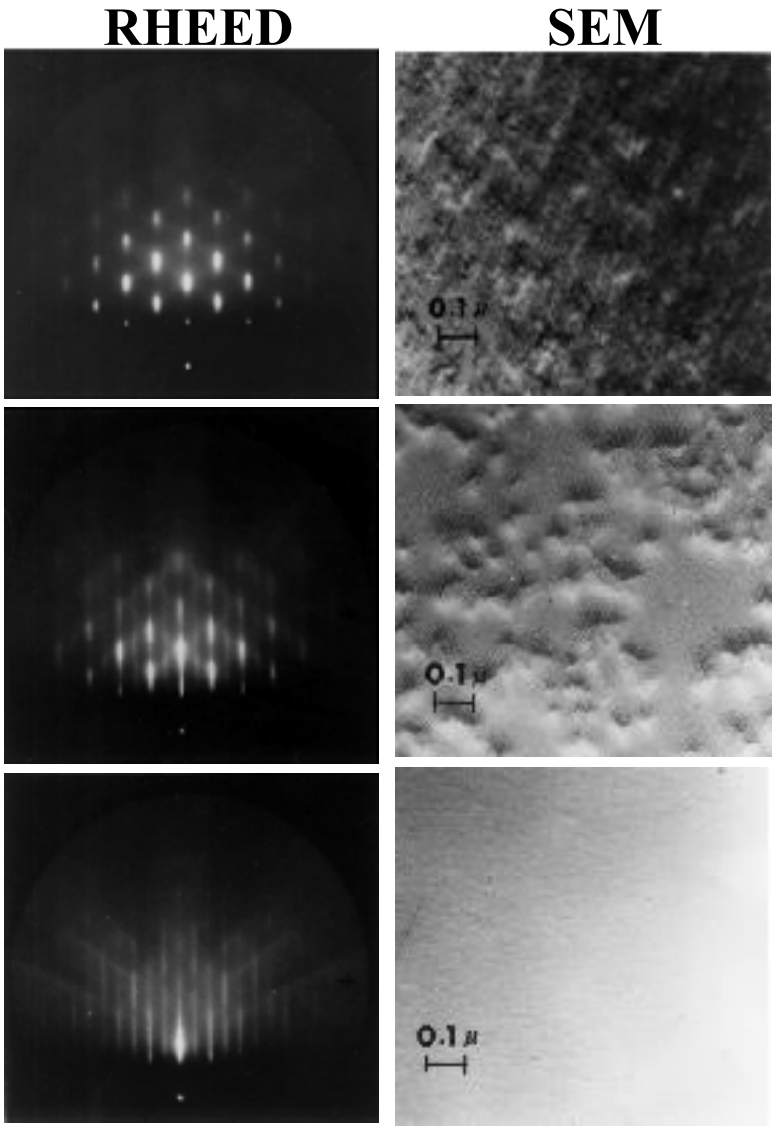
- probing of surface by diffraction of electron beam striking the sample at a very small angle relative to the sample surface ($1^o$ – $3^o$)
- electron energy 5 – 20 keV; wavelength ~0.1Å
- ideal 2D surface – set of parallel streaks




**Si(001) RHEED patterns**
**sputter-cleaned surface**



## *in situ* growth monitoring - reflection high energy electron diffraction (RHEED)




GaAs substrate after oxide desorption

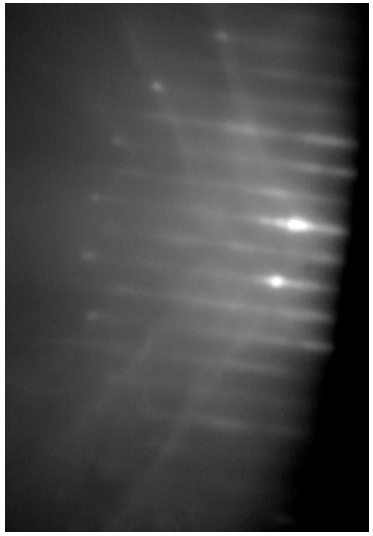
+ MBE growth of 15 nm GaAs

+ MBE growth of 1 μm GaAs

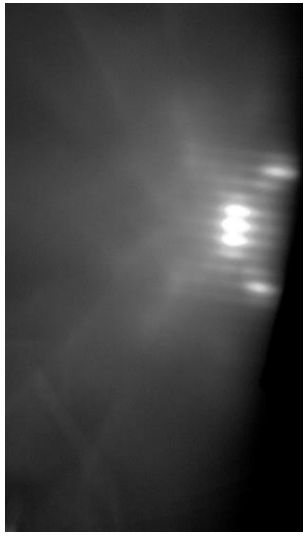
Alfred Yi Cho, J. Cryst. Growth **201/202** (1999) 1

# *in situ* growth monitoring – RHEED – (2x4) GaAs surface reconstruction

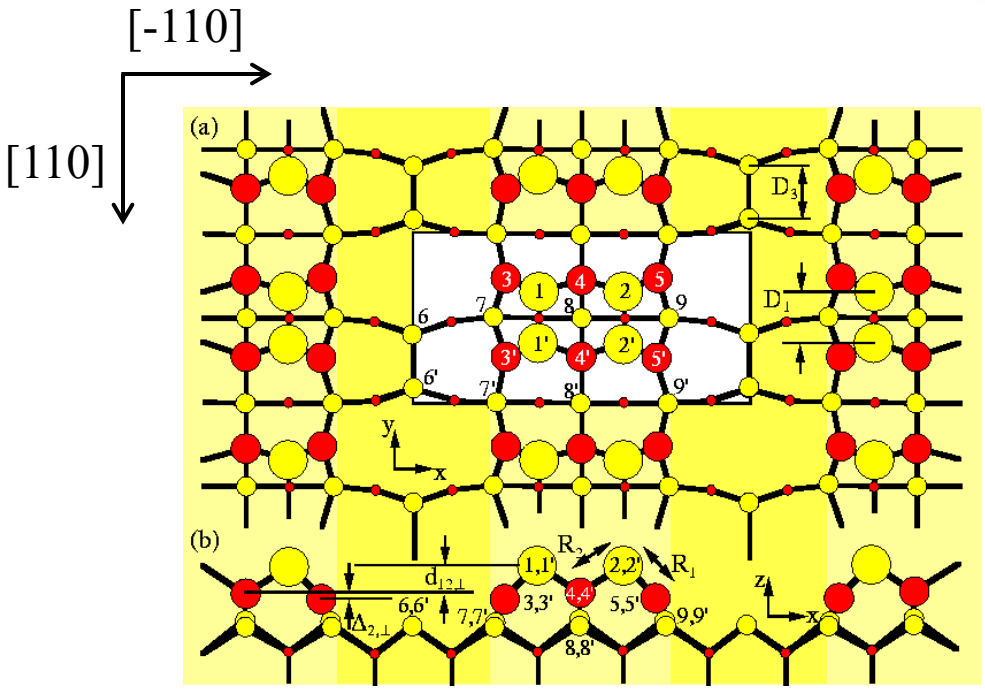
RHEED pattern depends on the azimuth



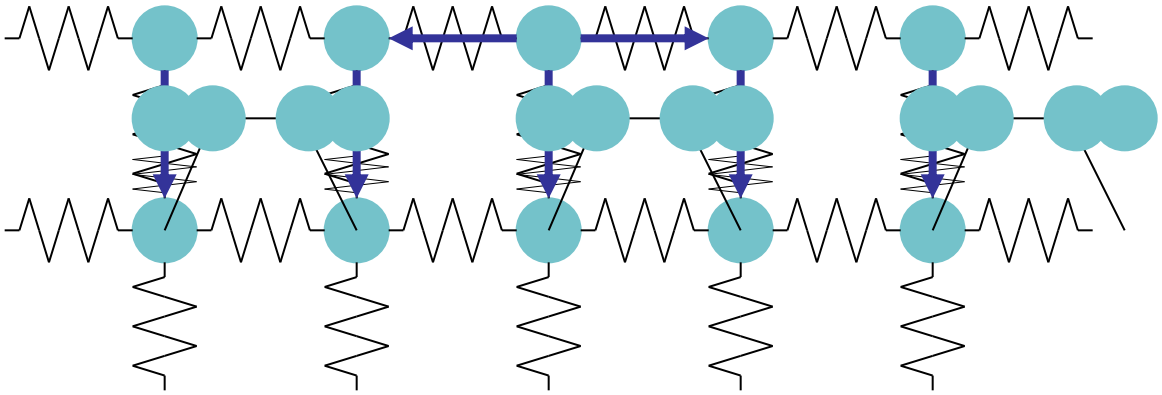
azimuth [110] (2x)



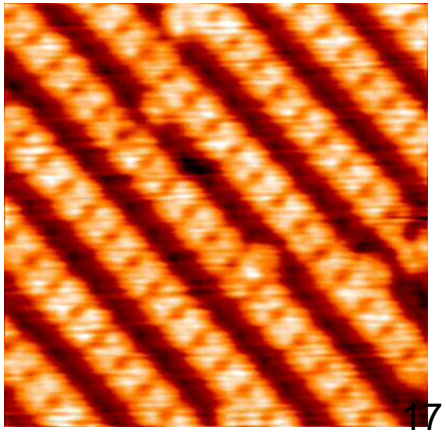
azimuth [-110] (4x)




**surface reconstruction** – change of periodicity



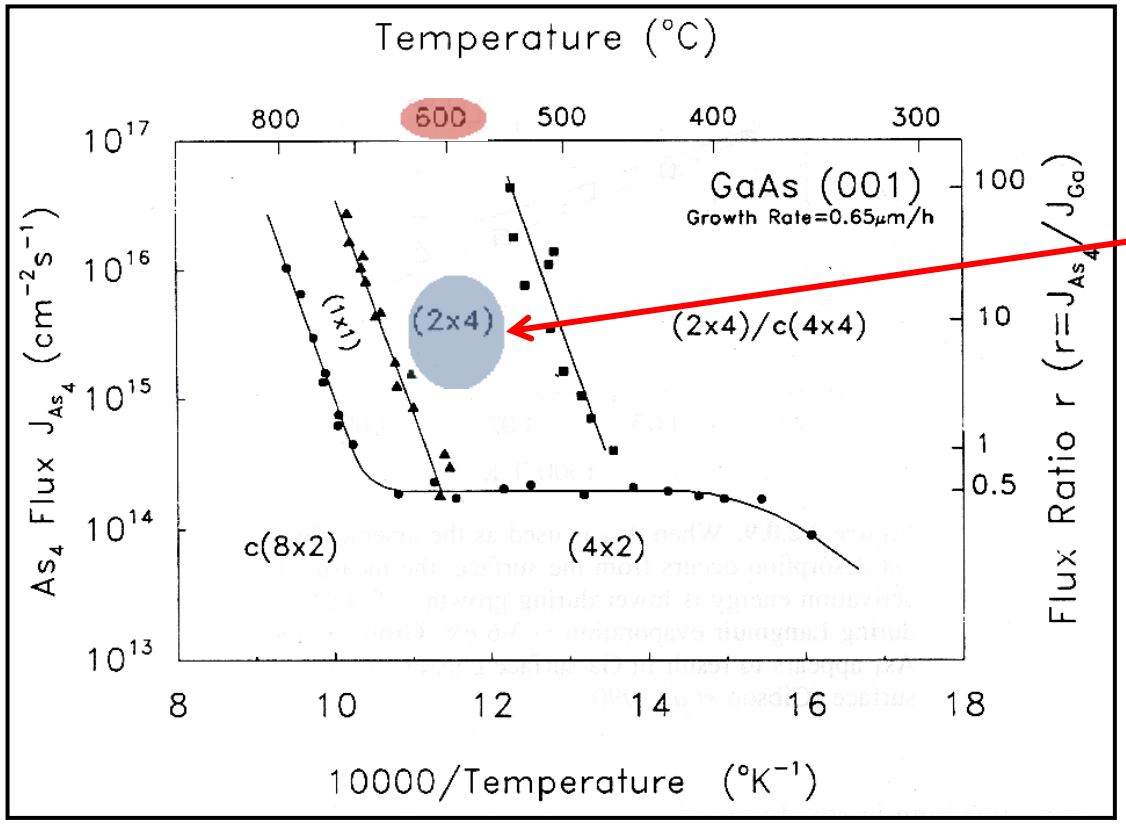
GaAs(001) - STM



V. P. LaBella *et al.*, PRL 83, 2989 (1999)

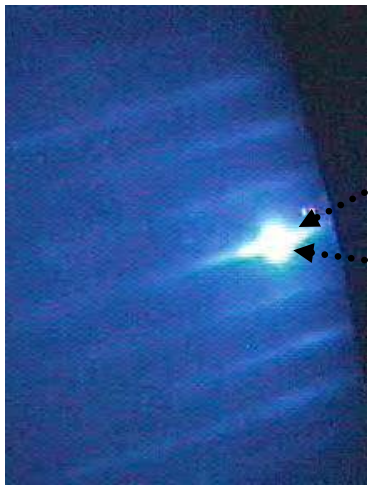
# RHEED – surface phase diagram of GaAs

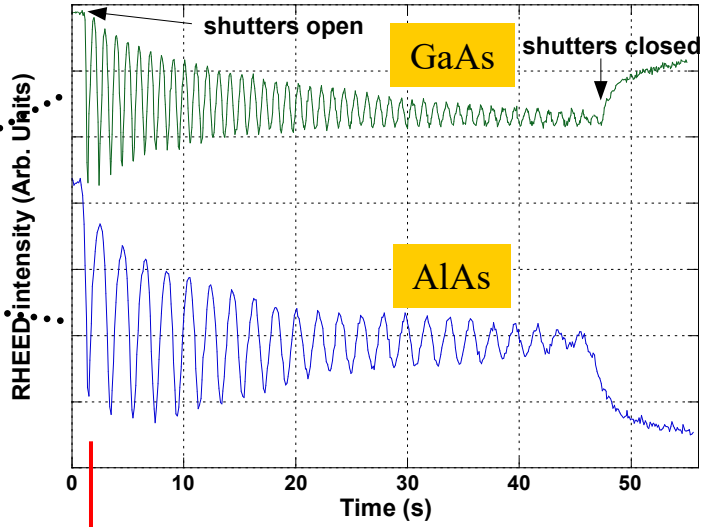
various surface reconstructions depending on T, As/Ga ratio, …




- As-stable (2 × 4): typical GaAs growth conditions by MBE
- surface reconstruction strongly depends on surface temperature – RHEED as surface thermometer

# RHEED – growth rate measurements (RHEED oscillations)





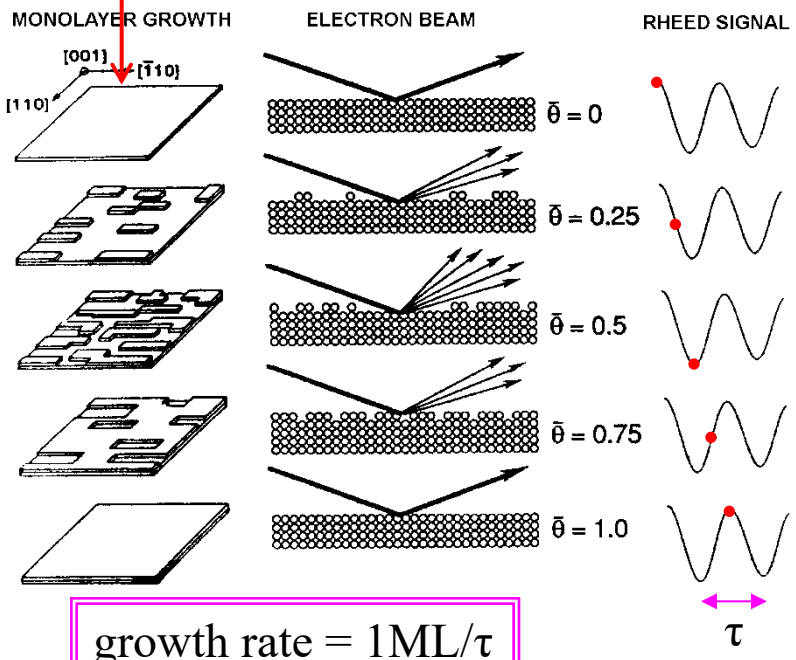

Ga shutter closed:

**GaAs:** signal recovery ⇒ high surface mobility of Ga adatoms, smoothing of the surface

Al shutter closed:

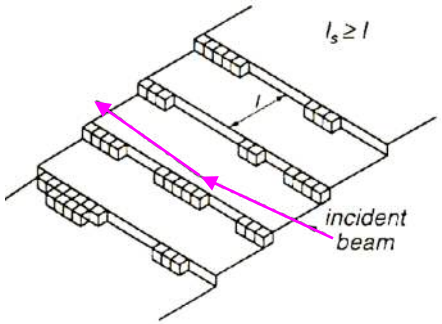
**AlAs:** signal damping ⇒ no surface smoothing; low surface mobility of Al adatoms

**start of growth**




growth rate = 1ML/τ

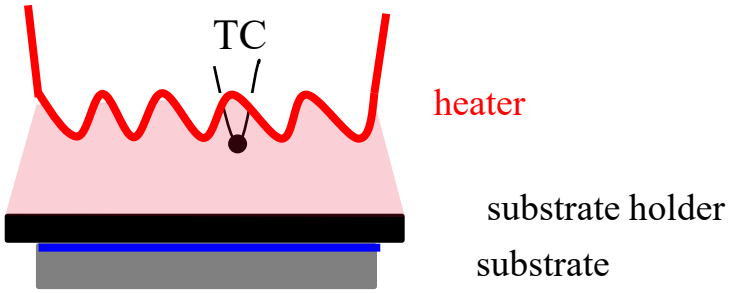
- RHEED oscillations – observation of periodic change of surface roughness as the layer grows
- required: 2D nucleation – layer by layer growth
- no RHEED oscillations for step flow growth




- V element-rich conditions

# substrate temperature measurement in MBE

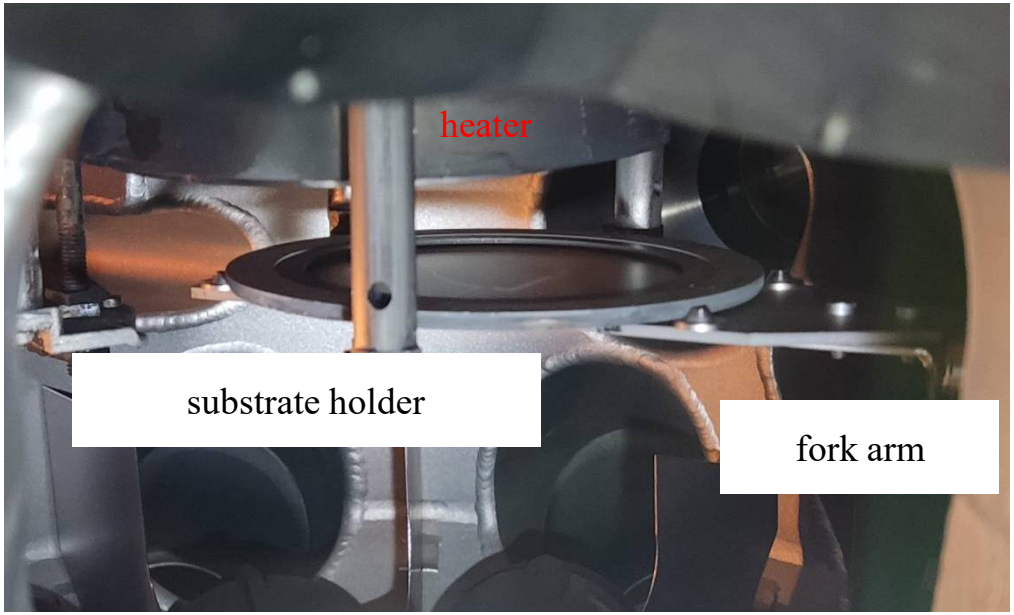
under vacuum heat transport by radiation only




for low T growth substrate glued by In or In/Ga to improve thermal contact of the substrate and the holder

often TC reading used as the measure of the substrate surface T

- TC measures T of the heater !!!
  (TC has no thermal contact with the substrate)
- even if reproducible (?) then for the particular system only
- T values useless for others




**Do not do that !!!!**

*ethical guidelines in science require that your data are presented in the way allowing others to repeat (verify) your experiment !!!!*

# substrate temperature measurement in MBE

optical pyrometry in IR $\lambda = 1 - 3$ µm *measurement of sample T based on the black body emission spectrum*

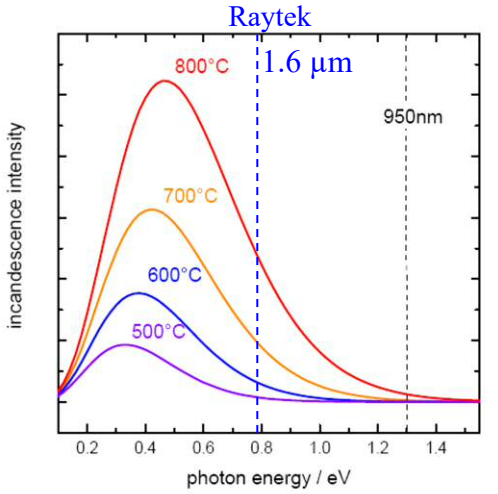
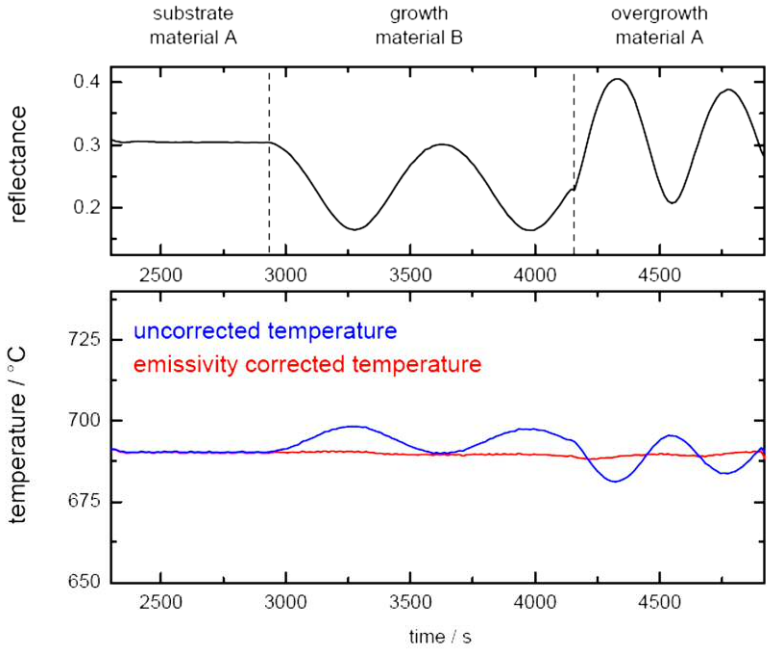



**Fig. 1:** Emission of a black body according to Planck's law: the emitted radiation power increases together with the temperature, the maximum of the curves shifts to higher photon energies.




IR light interference leads to oscillations of the signal; thus to artificial oscillations of T reading

emissivity corrected pyrometry – simultaneous measurement of pyrometry signal and light reflection; allows to eliminate interference-induced oscillations

- still the problem exists if the viewport transmission changes during a long growth campaign

substrate holder

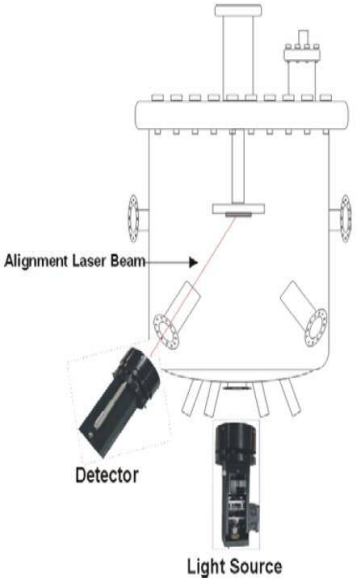
substrate

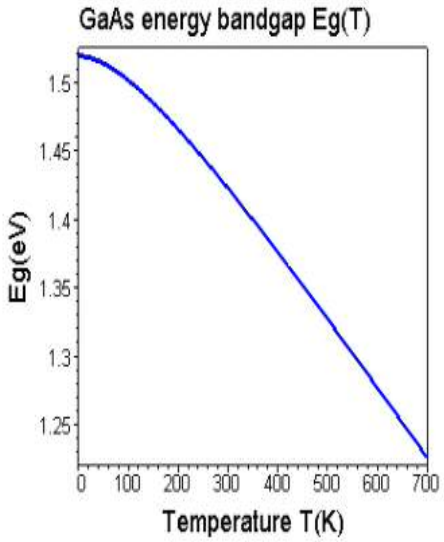
- T of which part pyrometry measures if the substrate is transparent (e.g. sapphire, GaN, ZnO, ….) ?

T of the substrate holder !!!!!

it may differ from the substrate surface T by tens of °C

# substrate temperature measurement in MBE



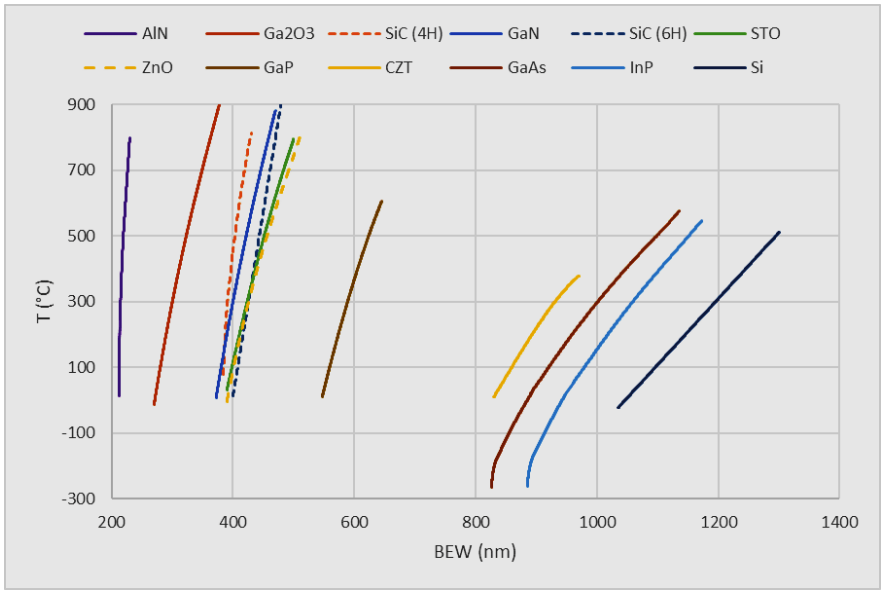




BandiT – k-Space Inc.

- measurement of the substrate optical absorption edge (not the light intensity), the absolute temperature of the wafer can be determined. This absorption edge, which is directly proportional to the band gap of the material, is temperature dependent.

$$Eg(T) = 1.519 - 5.408 \cdot 10^{-4} T^2/(T + 204)$$

J. S. Blakemore J. Appl. Phys. 53 (1982)




k-Space Associates, Inc.

- immune to changing viewport transmission, stray light, and signal contribution from substrate or source heaters, all sources of measurement error for pyrometers

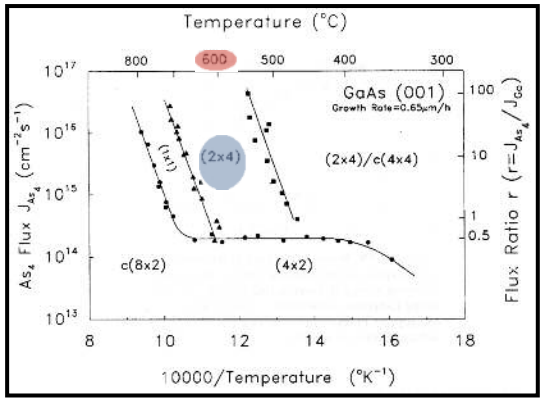
- requires that your substrates are carefully calibrated (factory calibration files)
- different substrate doping can change the result
- does it measure substrate *surface* T ?

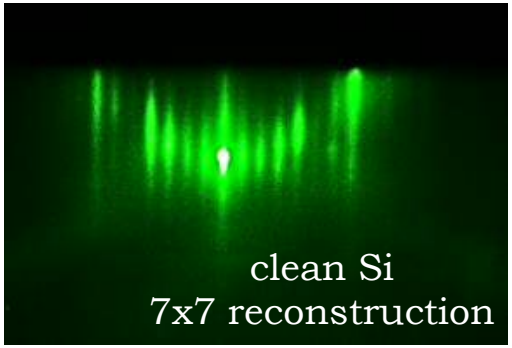
# substrate temperature measurement in MBE

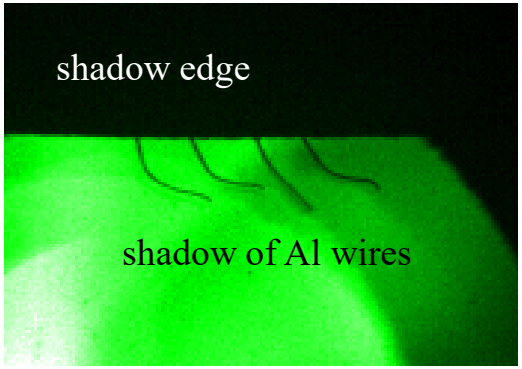
relay on surface phenomena if possible

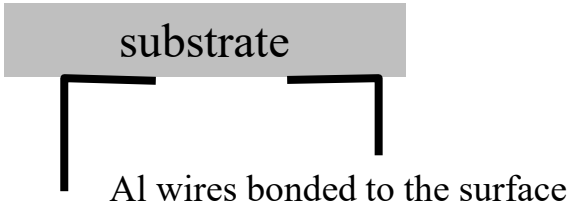
some examples:

1. oxide desorption from GaAs (RHEED observation) ~560°C
2. change of surface reconstruction (RHEED pattern) of GaAs
3. change of surface reconstruction of Si(111) 7×7 → 1×1 @ 830°C
4. melting point of suitable metal (Al 660.3°C)
5. desorption rate of deposited metal (e.g. Ga from GaN surface)
6. others, depending on your material system



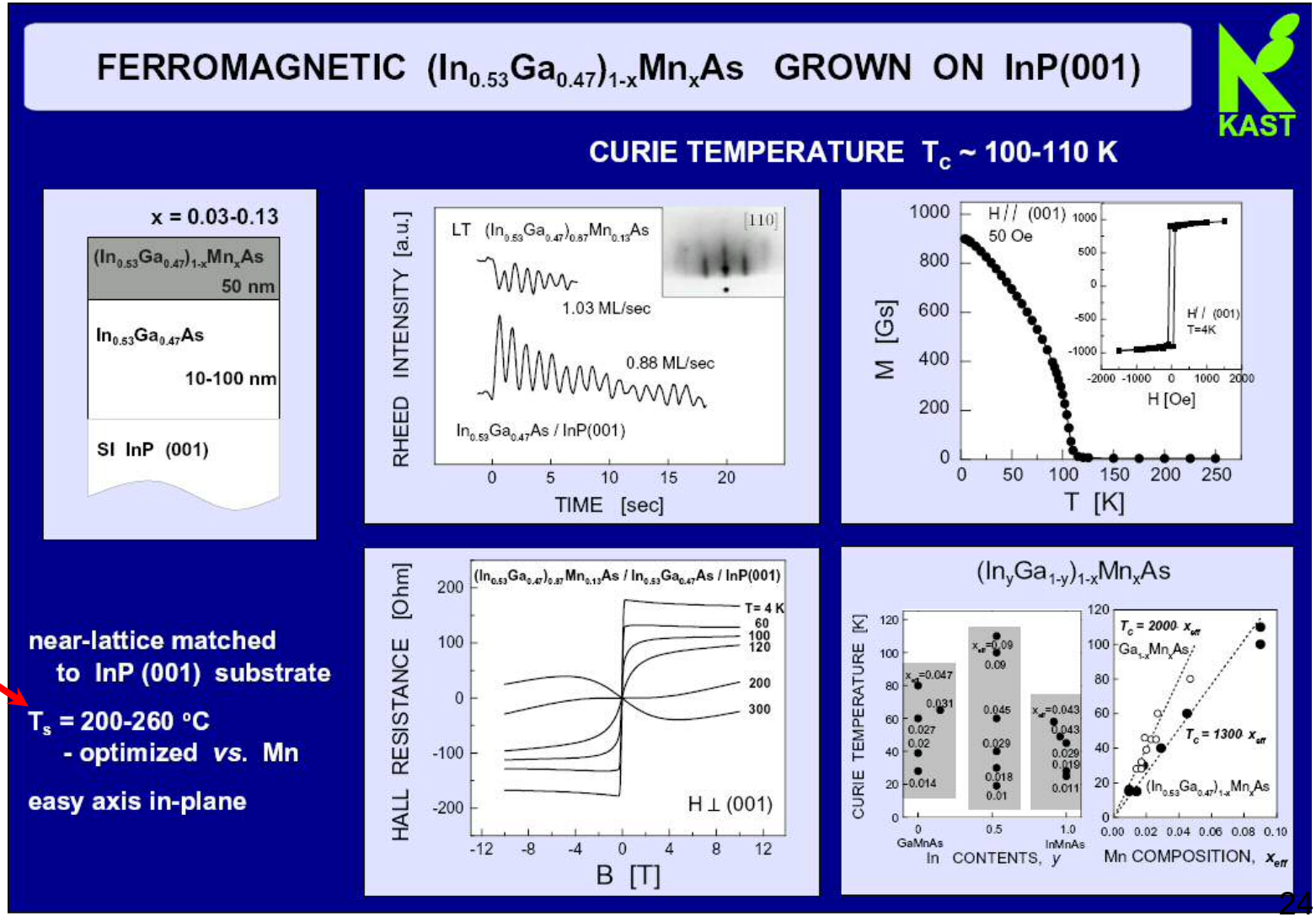




Try to calibrate surface T as precisely as possible. For you the run to run T reproducibility is the most important. In some cases differences in T readings between various MBE systems as large as ±50 °C are standard. It is crucial to describe in details the way of substrate T measurement in your experiment !!!

# **Application of MBE:** incorporation of Mn above the solubility limit in III-V's

nonequilibrium growth in MBE ⇒ possibility to grow (Ga, In)As layers with high concentration of randomly distributed Mn



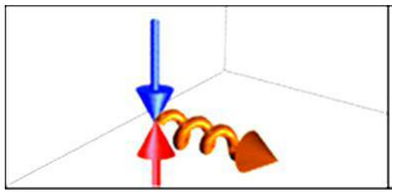

!!!!!!

**T. Slupinski**

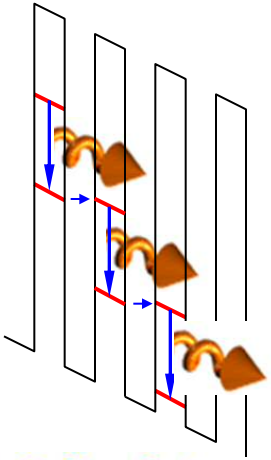
T. Slupinski et al. APL (2002)

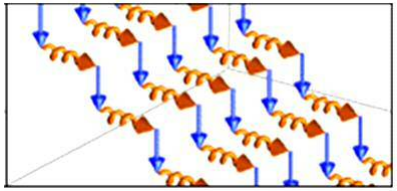
# **Application of MBE:** superlattices in optical devices

conventional laser



cascade laser

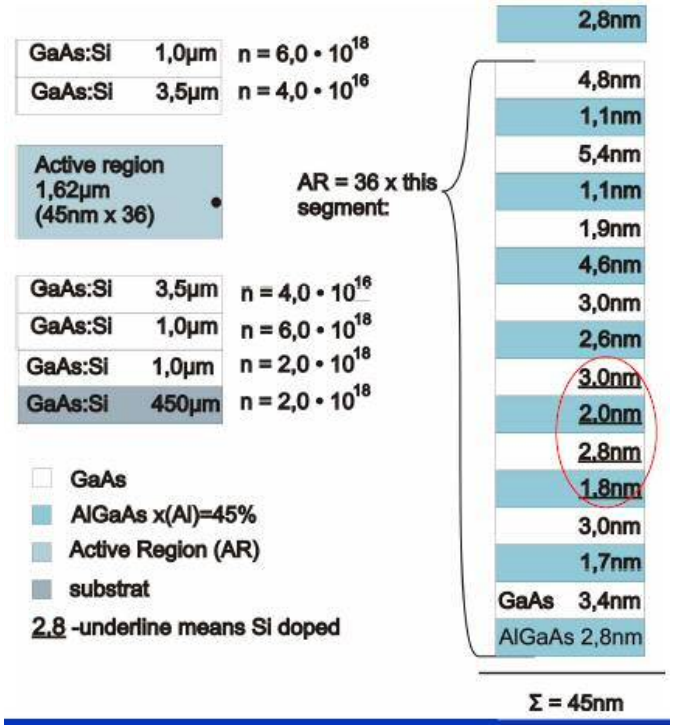


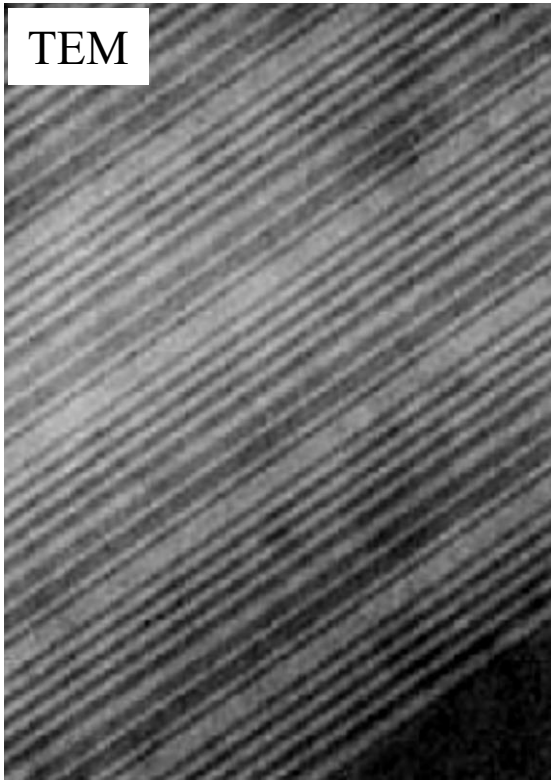


„cascade of electrons”
multiple photon emission from one electron

www.bell-labs.com/org/physicalsciences/projects/qcl/qcl2.html

cascade IR laser GaAs/AlGaAs (~9μm)




ITE Warszawa - Kosiel et al. EuroMBE 2009, Zakopane

MBE allows growth of complicated set of superthin epilayers with very high crystallographic quality

# Application of MBE: modulation doping (δ-doping)

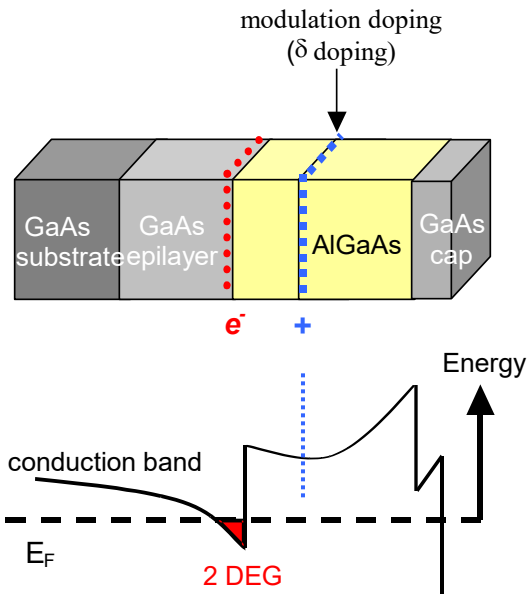
**problem:** doping required for high electrical conductivity

**BUT**

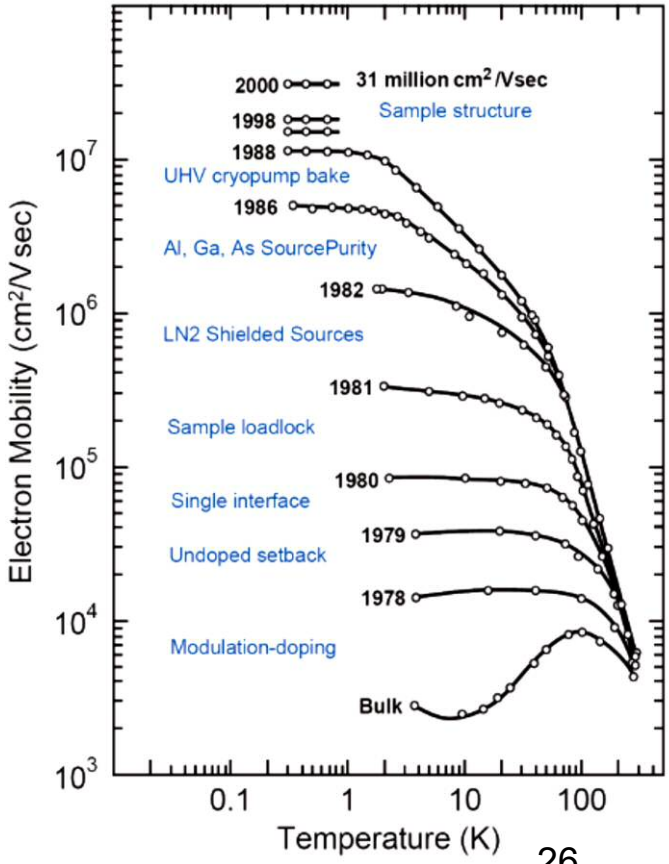
impurities scatter charge carriers ⇒ lower mobility at low T

**solution:** separate in space source of charge carriers (dopants) from the electrical conductivity channel

70ties, Art Gossard i Horst Störmer z Bell Labs.




transfer of charge carriers into the 2D channel and their separation from dopants ⇒ higher μ

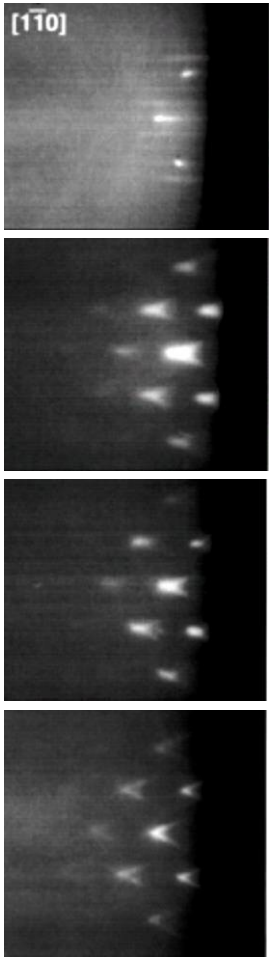



H. Störmer, Surf. Sci.132 (1983) 519

http://www.bell-labs.com/org/physicalsciences/projects/correlated/pop-up2-1.html;
L. Pfeiffer and K. West, Physica E **20**, 57 (2003).

# **Application of MBE:** self-organized quantum dots (QD)

InAs/(001) GaAs
azimuth [1-10]

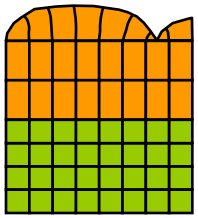



growth 3D

H. Yamaguchi et al. APL (1996)

lecture 8.03.2022 - surface deformation as the way to relax lattice mismatch strain

7% lattice mismatch in the InAs/GaAs system

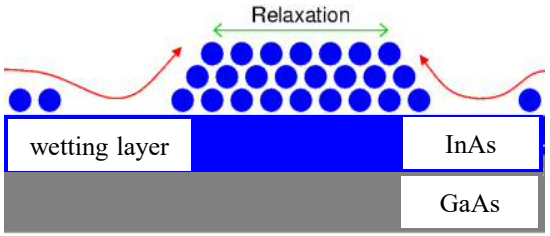


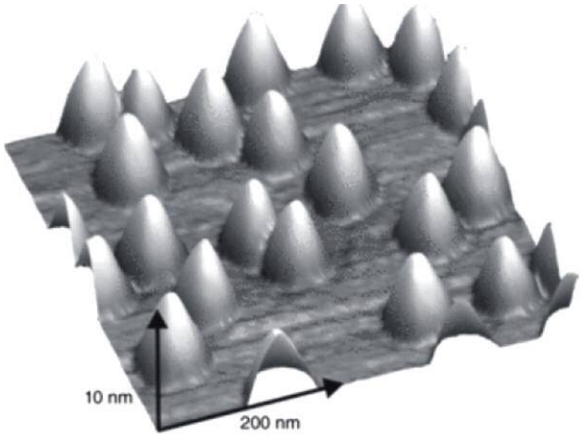
**growth modes:**

Frank-van der Merwe (layer-by-layer)

**Stranski-Krastanov (layer + island)**

Volmer-Weber (island)




InAs QDs on GaAs:

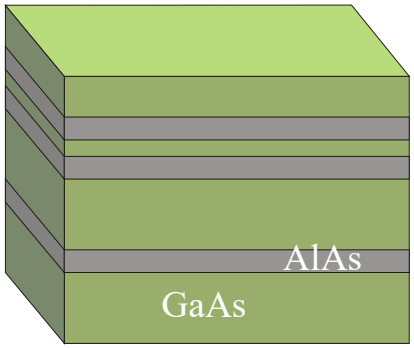
- dislocation free
- diameter ~20nm
- heigth a few nm
- broad distribution of dimensions
- random positions on the substrate

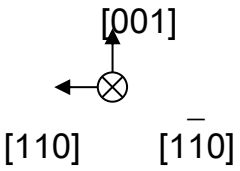
(self-organization)

# **Application of MBE:** organized quantum dots (QD)

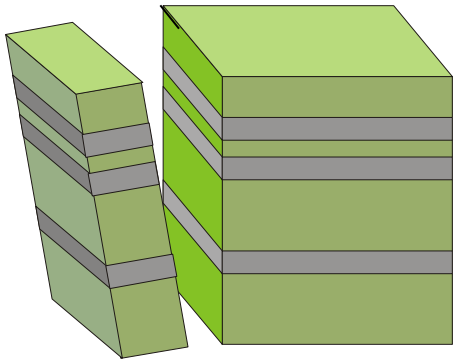
E. Uccelli et al. EuroMBE 2009, Zakopane

1. growth of AlAs/GaAs (001) layers

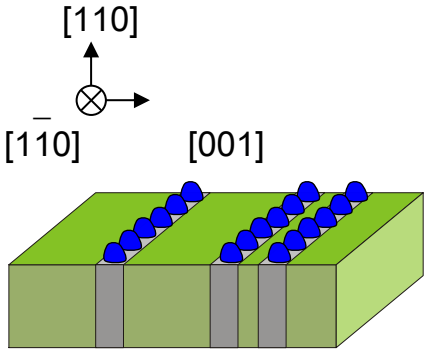


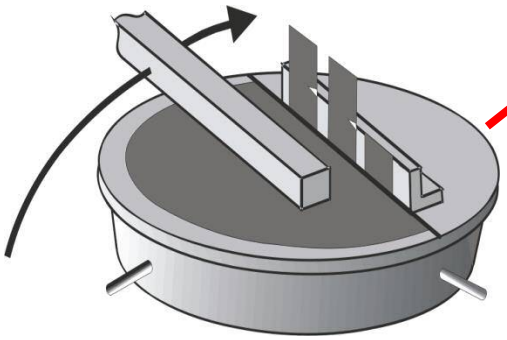




2. *In situ* cleavage: (110) flat surface

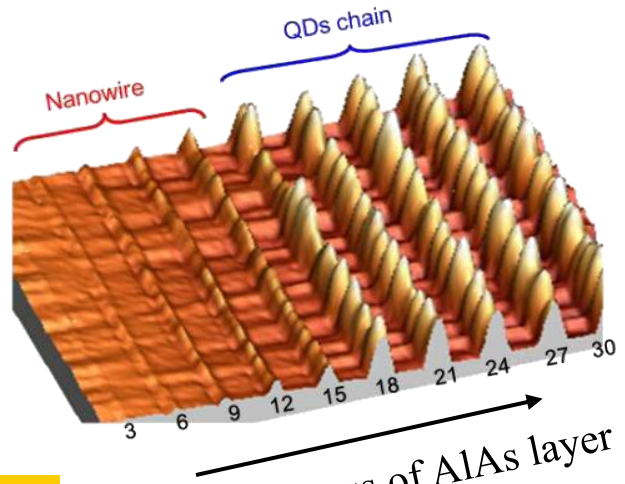


3. growth of InAs on the cleaved (110) surface



shutter blade cuts the wafer



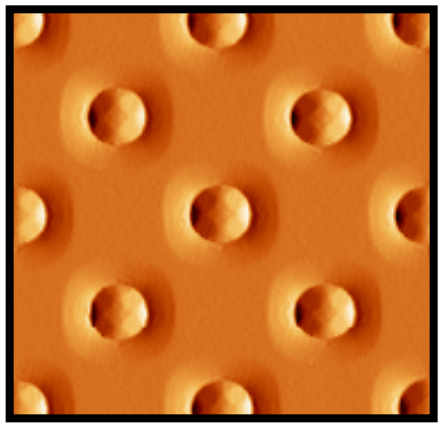

- in-plane nanowires for thin AlAs layers
- QDs for thicker AlAs layers

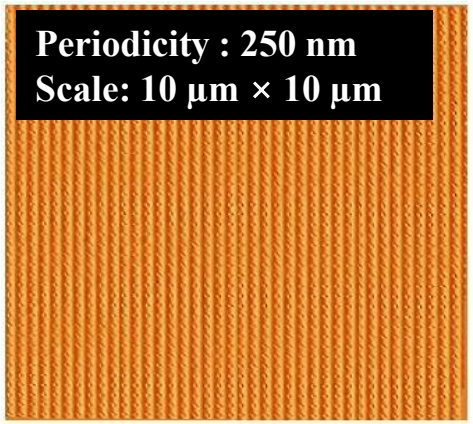
# **Application of MBE:** organized quantum dots (QD)

advantages of ordering:

- better uniformity of QDs' dimensions (more uniform light emission λ)
- single QD can be adressed
- …

G. Chen (EuroMBE 2009, Zakopane)
E-beam lithography + RIE





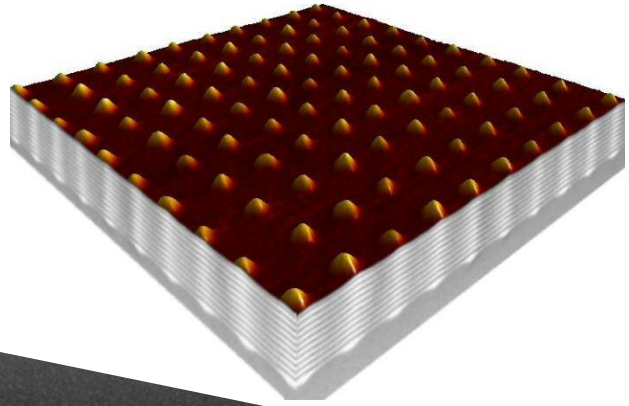

## Ge QDs on Si substrate

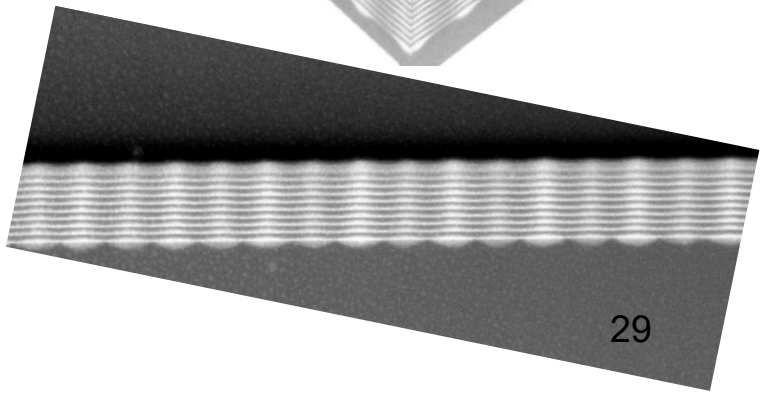
- lithography of the substrate (e-beam or X-Ray)
- etching of the pattern (RIE)
- MBE growth of QDs

- positions of QDs in the next layer reflects their distribution in the layer underneath
  (coupling via the strain field)

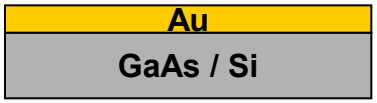
G. Mussler (EuroMBE 2009, Zakopane)
X-ray lithography + RIE

crystal of Ge QDs

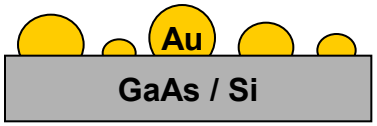




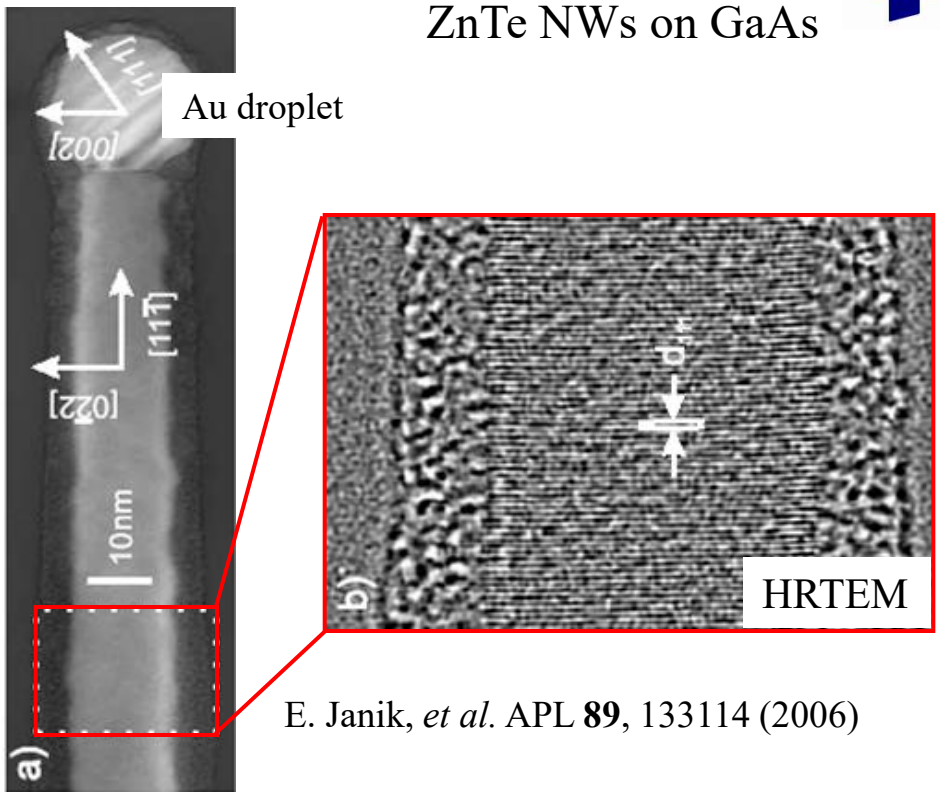
# **Application of MBE:** self-organized nanowires (NWs)





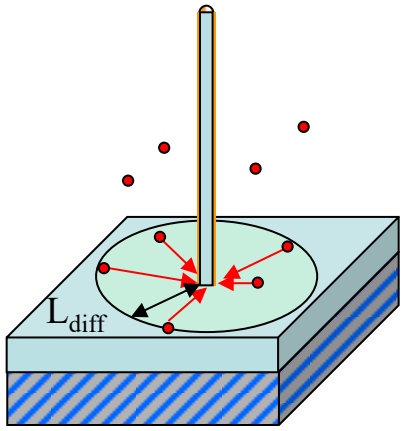



ZnTe NWs on GaAs

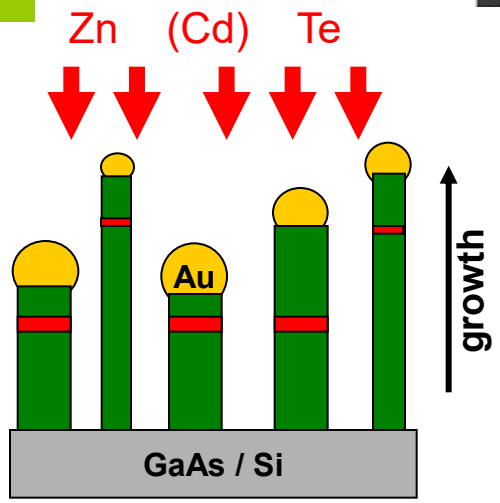


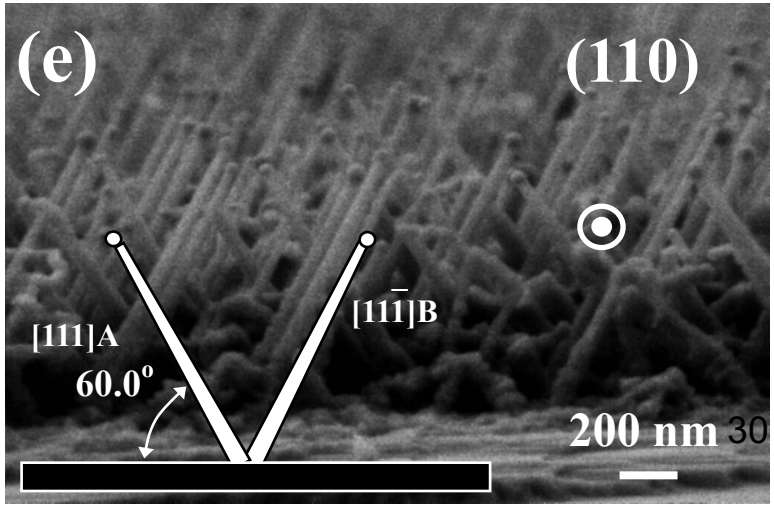

E. Janik, *et al.* APL **89**, 133114 (2006)

growth mode:
vapor – liquid – solid VLS



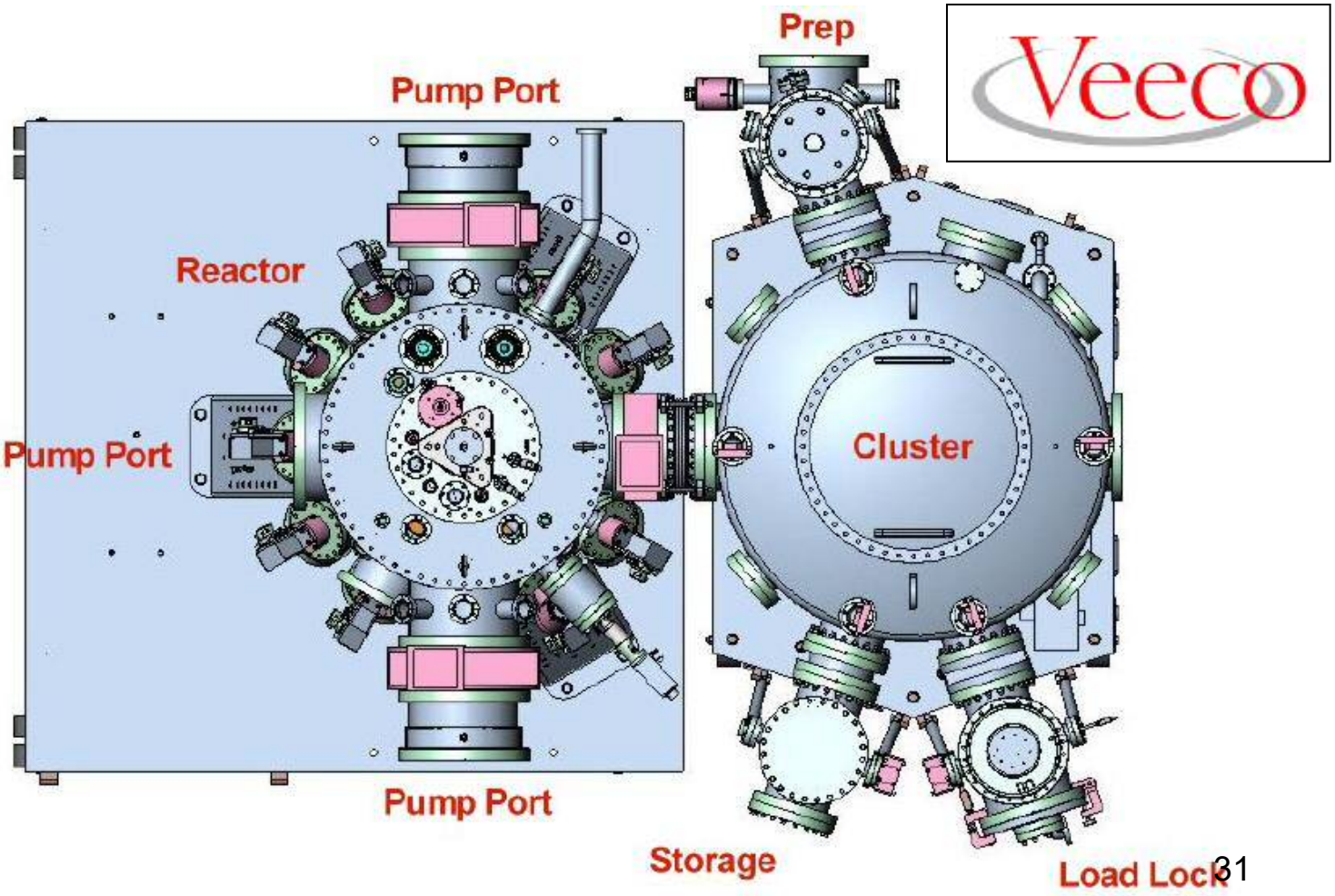

Molecular beams



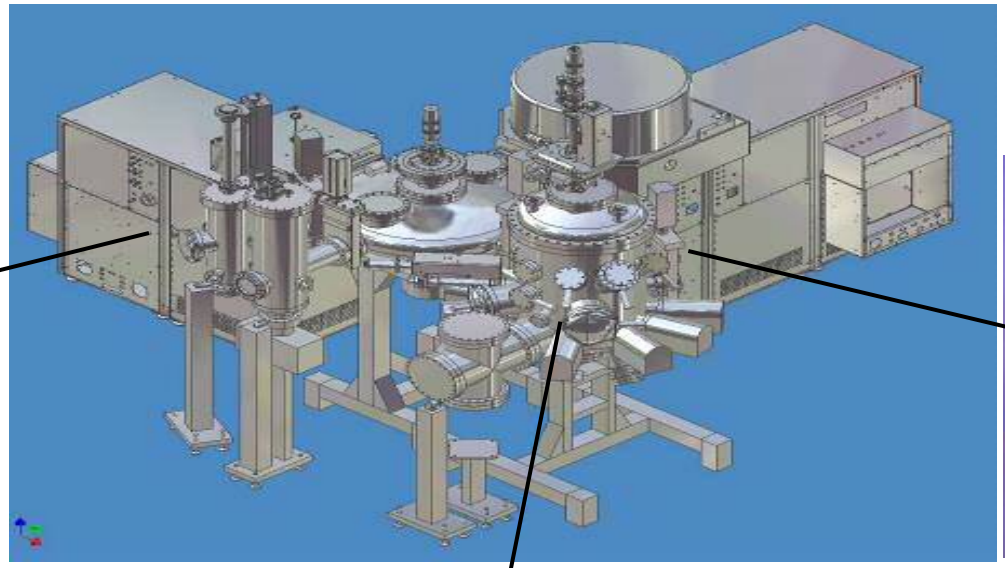



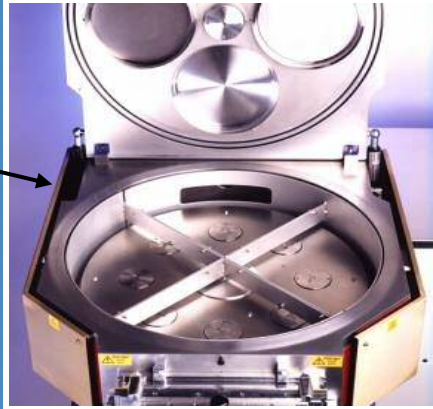
# New generation of MBE systems - clusters

- simultaneous growth on large substrates; multi-wafer substrate holders; to increase yield
- min 12 source ports + extra ports for surface analysis tools
- cluster design – independent growth and surface preparation (plasma etching, metallization, …) chambers
- additional chambers for surface analysis (STM, …); sample transfer under UHV

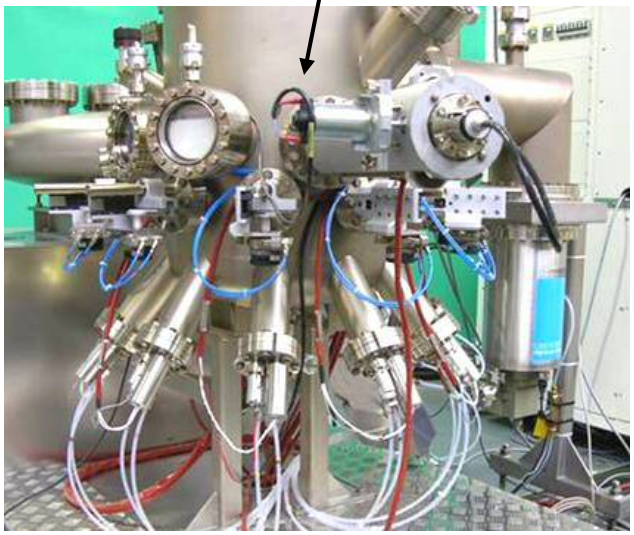


# New generation of MBE systems - clusters





Etch Module (ICP)
for Clusterlab 600



Deposition Module
(RF Magnetron Sputter)
for Clusterlab 600

Epitaxial Growth Module
(MBE V60) for
Clusterlab600

# Summary

**advantages of MBE:**

- high purity of epilaters
- precise growth control
- perfect for fabrication of low-dimensional structures; sharp interfaces
- wide range of *in situ* growth monitoring tools; important for R&D
- large variety of materials/compounds that could be grown
- strongly nonequillibrium growth technique; solubility limit can be overcome

**disadvantages of MBE:**

- measurement of REAL substrate surface temperature difficult
- high costs (purchase, installation and every-day use)
- high failure rate (typical for complicated UHV systems)

  Most Broken Equipment

  Multi Bucks Evaporator …..
- selective area growth (SAG) difficult

# For further reading

*1) M.A. Herman, H. Sitter "Molecular Beam Epitaxy, Fundamentals and Current Status", Springer, 1996*

*2) ed. A. Cho "Molecular Beam Epitaxy", AIP, 1994*

*3) review papers by T. Foxon; B.A. Joyce; etc.*