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INTERNATIONAL CENTRE FOR THEORETICAL PHYSICS



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SCIENCE AND TECHNOLOGY OF THIN FILMS

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" Fabrication of quantum wells and superlattices by molecular beam epitaxy." (PART I)

presented by:

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These are preliminary lecture notes, intended only for distribution to participants.



# Fabrication of Quantum Wells and Superlattices by Molecular Beam Epitaxy

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## Outline

MBE--Method and equipment  
Growth mechanism of III-V-compounds

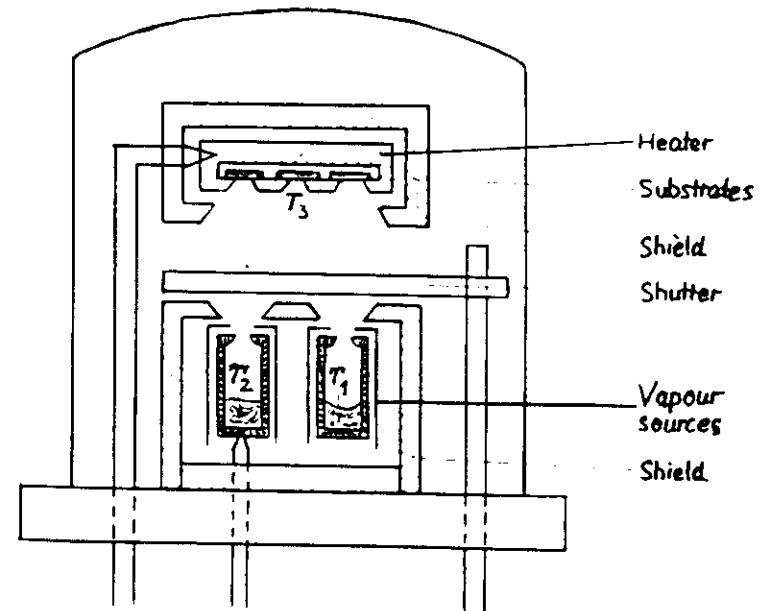
Homoepitaxy GaAs  
Heteroepitaxy I--AlAs/GaAs  
Single quantum wells

Heteroepitaxy II--doped structures  
Superlattices  
Strained layers

# Three-Temperature Method

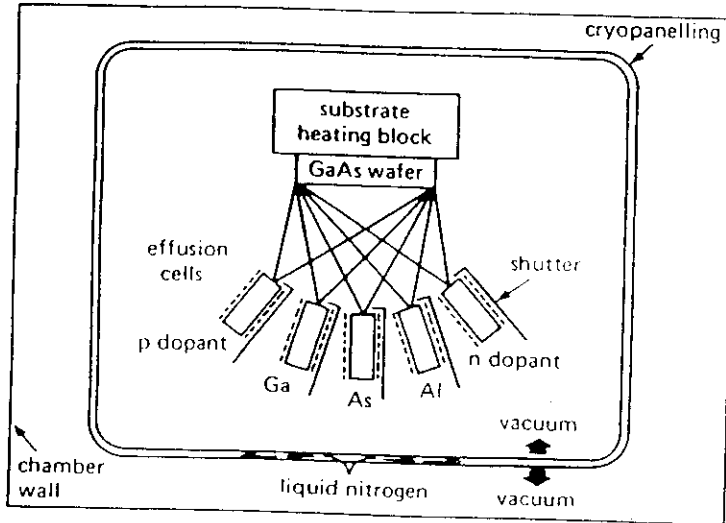
K.E. Günther (1977)

$$T_1 < T_2 < T_3$$



# Molecular Beam Epitaxy (MBE)

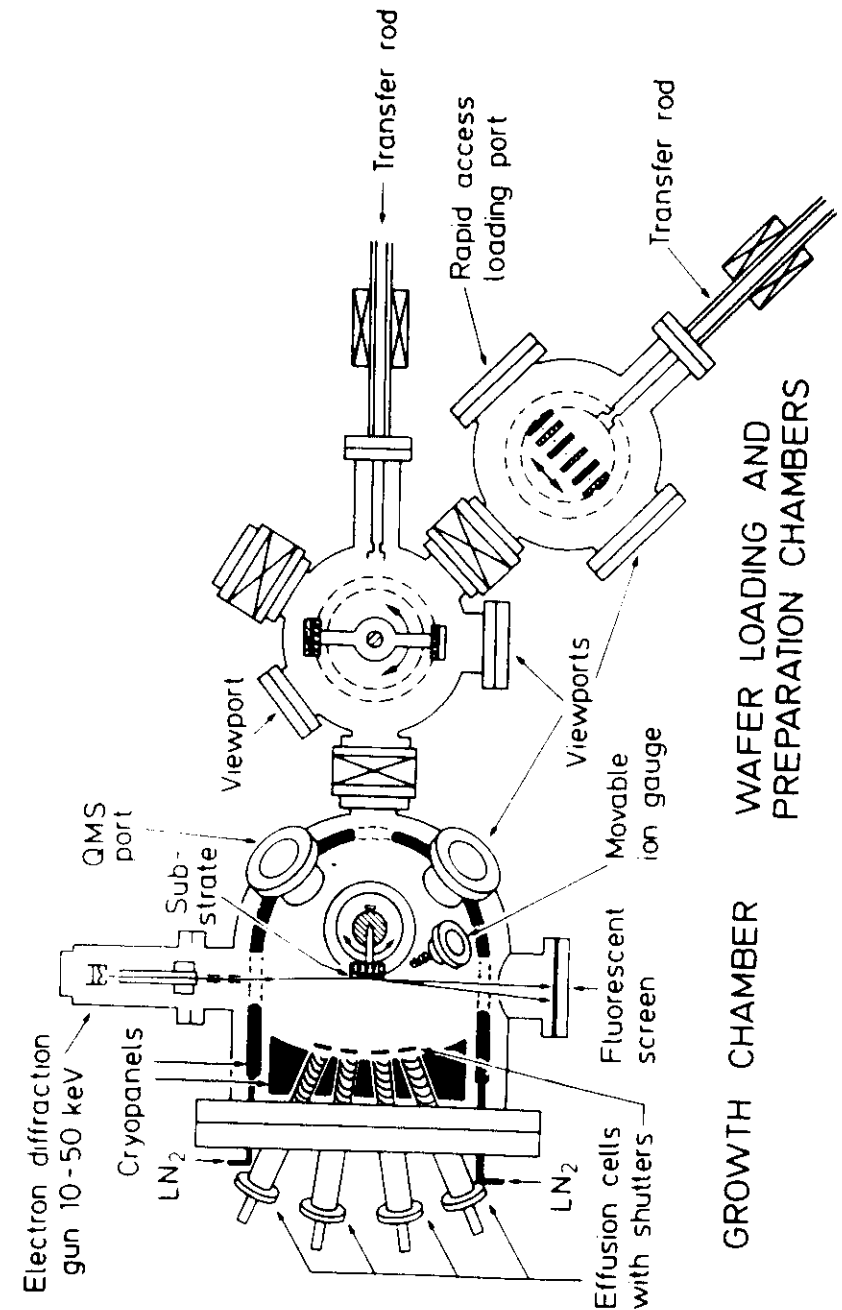
## Scheme



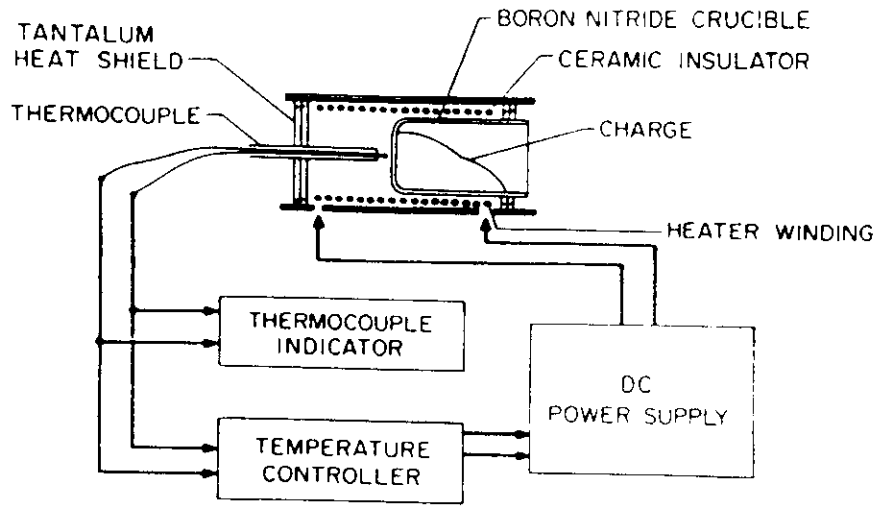
- ◆ ultra high vacuum conditions
- ◆ compatibility with in-situ surface - characterization techniques — RHEED
- ◆ thickness control down to sub-monolayer scale (growth rate  $\approx 0.1$ ---- $2$  ML/s)
- ◆ extreme sharp composition and doping profiles (low  $T_{sub}$ )

⇒ *powerful technique for the preparation of artificially structured materials*

**Materials:** semiconductors, insulators, metals, high  $T_C$ - materials e.t.c.

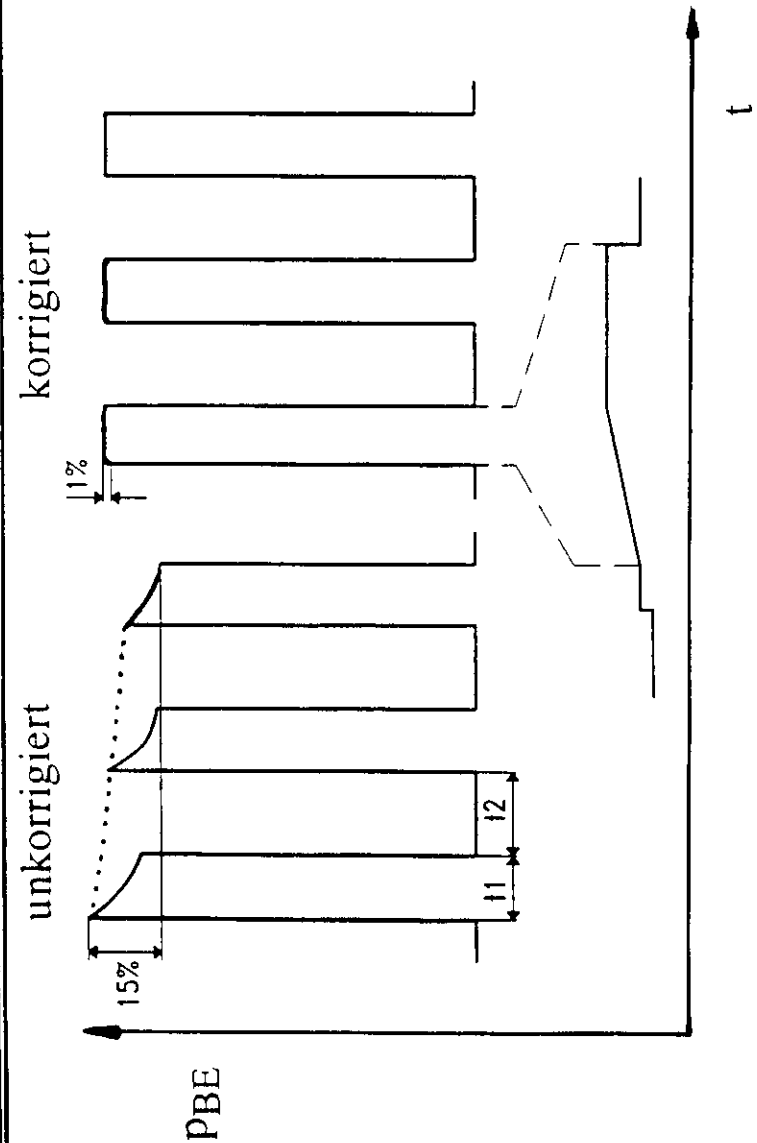


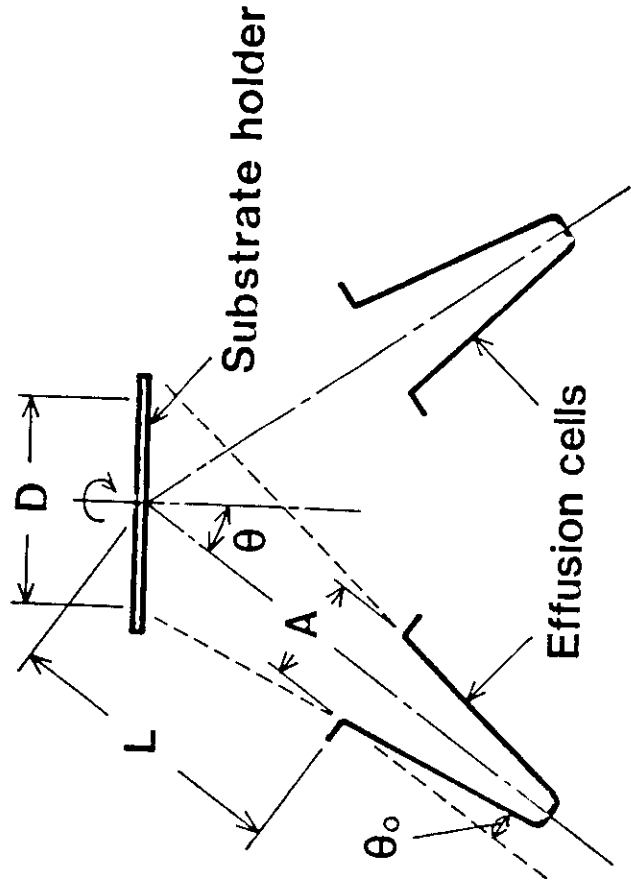
# Effusion Cell For MBE



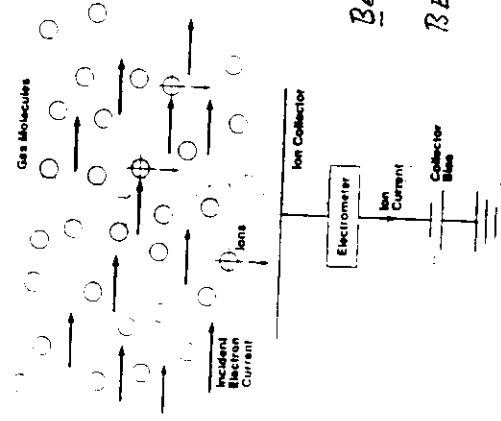
- Ta heater winding in mid a way that magnetic stray fields towards the substrate are avoided
- W/Re thermocouple to measure relative temperature
- PID regulator (having proportional, integral and differential adjustment)
- Operating temperature up to about 1500°C
- Accuracy of temperature control should be better than  $\pm 0.2^\circ$  at 1000°C, also the long-term stability.

## Einfluß der Transientenkorrektur auf ein Vielfachschichtsystem





$$I_{\text{eff}} = \frac{1}{4} n \bar{v} A \cos^2 \theta_0$$



Relative flux ratio:

$$\frac{J_1}{J_2} = \frac{BE_{P_1} \times M_2}{BE_{P_2} \times M_1} \sqrt{\frac{T_2 M_2}{T_1 M_1}}$$

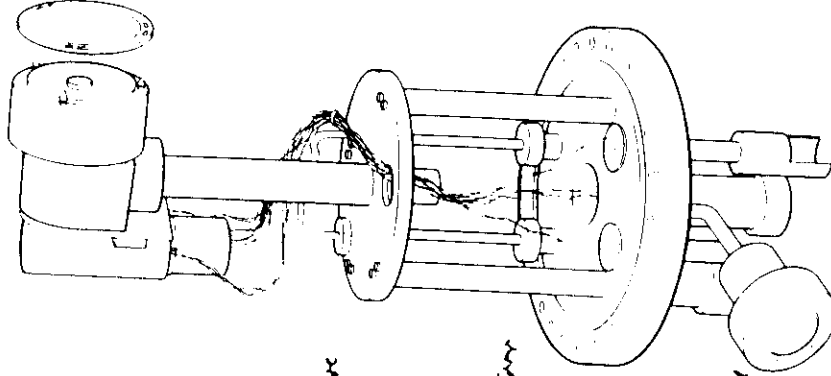
$J$  = beam flux

$T$  = cell temperature

$M$  = molecular weights

$m$  = ionization efficiency

Ion gauge to monitor beam flux



Beam Equivalent Pressure

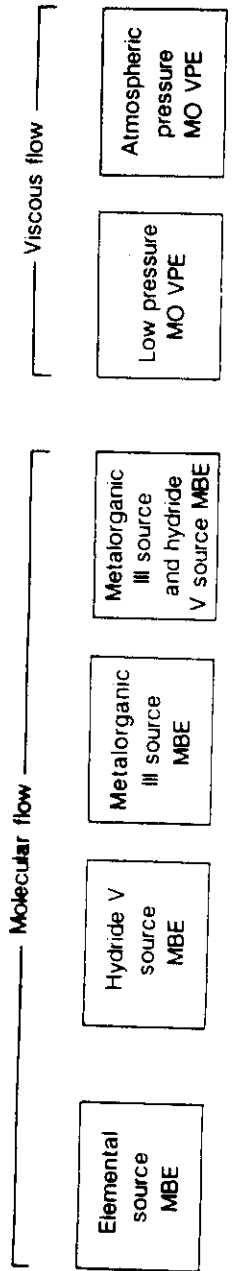
$$BE_{P_1} = P_{\text{open}} - P_{\text{closed}}$$

$$GAAs: BE_{P_{Ga}} \approx 5 \times 10^{-7} Torr$$

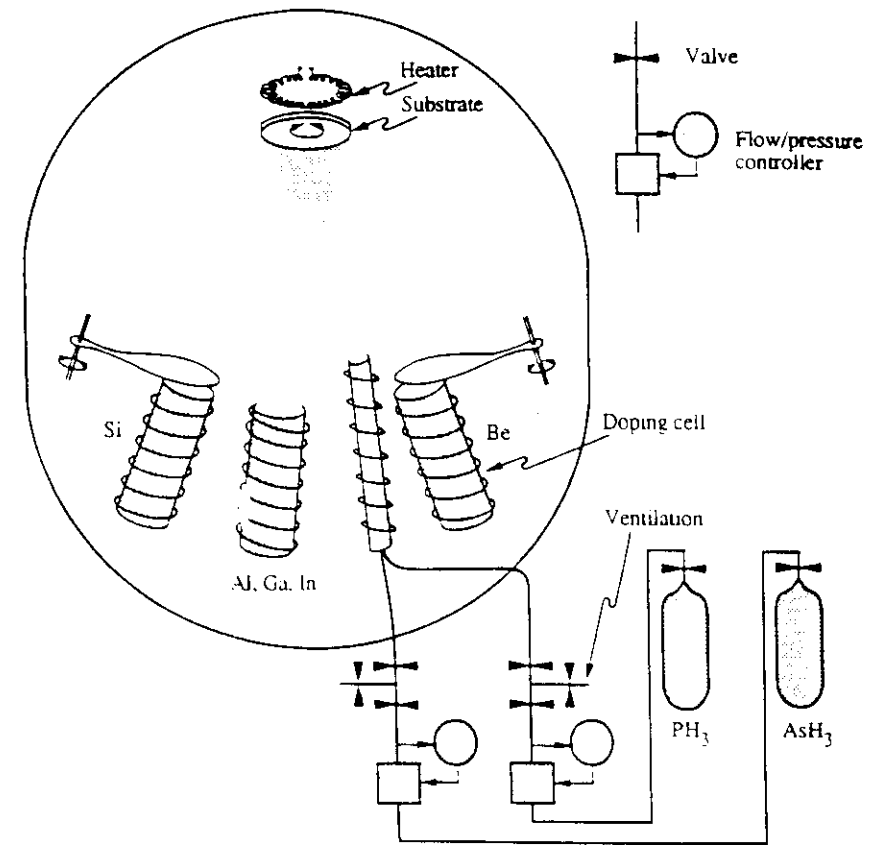
$$T^{1/2} \log BE_{P_1} \text{ vs. } A/P$$

Ratio of ionization efficiency is related to number of electrons,  $Z$ , in the atoms (underneath)

$$\frac{m_1}{m_2} = \frac{Z_1 \left( \frac{0.6}{A_1} + 0.4 \right)}{Z_2 \left( \frac{0.6}{A_2} + 0.4 \right)}$$



Pressure (Torr)	Source	Materials
$< 10^{-6}$	Gas source MBE	Group III and group V elements
$< 10^{-5}$		Group III elements and group V hydrides
$< 10^{-5}$		Alkyl group V compounds and group V elements
$< 10^{-4}$		Alkyl group III compounds and group V hydrides or alkyl group V compounds
$10^{-2} - 300$		Low pressure MO VPE
760		Atmospheric pressure MO VPE



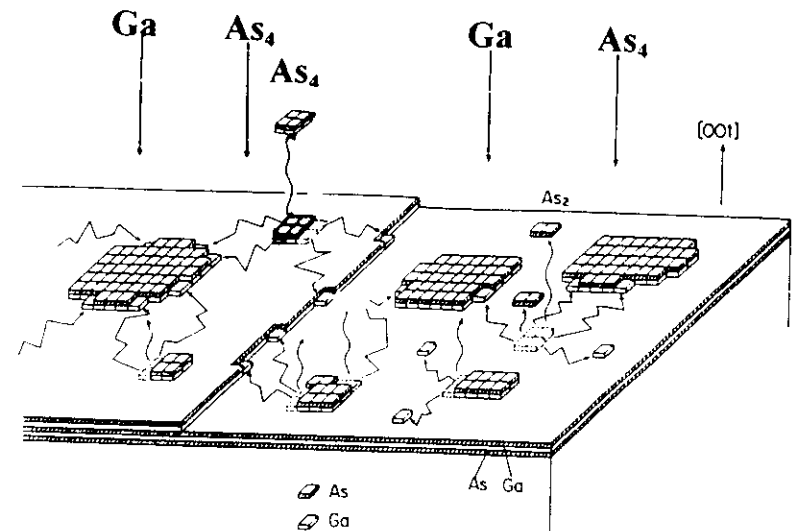
Schematic illustration of a gas source molecular beam epitaxy (GSMBE) system. Group - V elements are provided by hydrides (AsH<sub>3</sub> and PH<sub>3</sub>) which are thermally cracked upon entering the high vacuum chamber. Group - III elements and doping elements are provided by resistively heated effusion cells.

## GaAs substrate preparation

- Polishing with diamond paste
- Etch-polishing in NaOCl solution
- Treatment in sulfuric acid for 5 min at 300 K (twice)
  - removal of organic impurities
  - reaction with surface protrusions (etching)
- Careful rinsing in water
- Blowing dry with nitrogen gas
- Heating of the wafer in dust-free air to 300 °C for 5 min

## Growth Mechanism

### III-V compounds



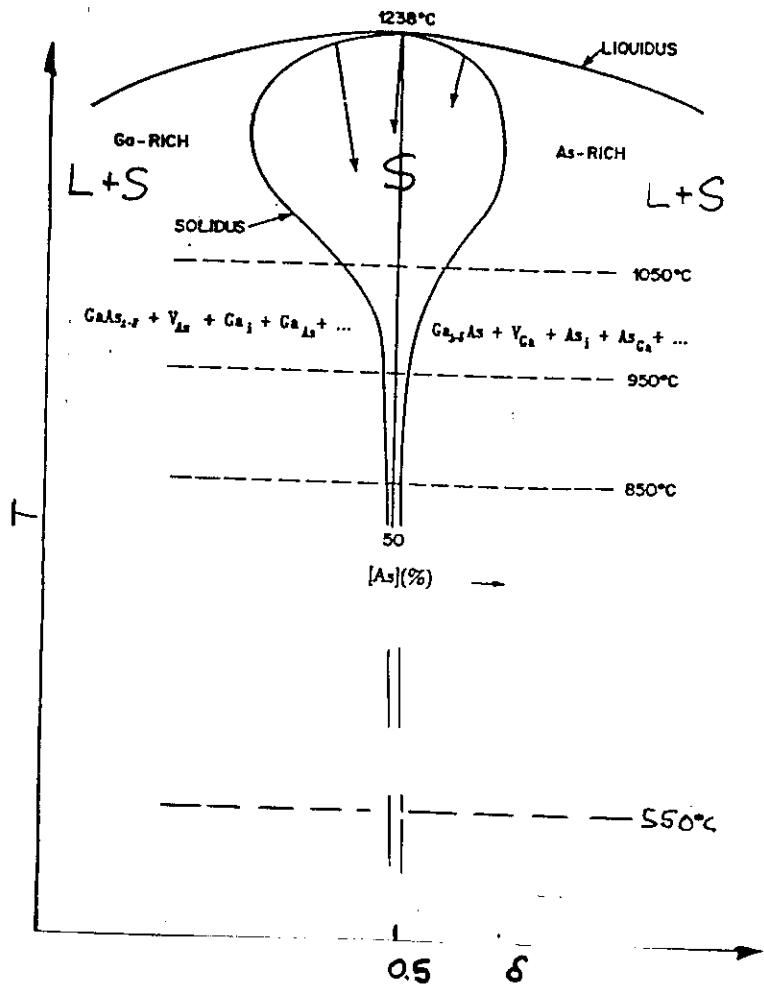
Deposition and 2-dim growth process of GaAs on a (001) GaAs surface in conventional MBE  
Y Honkoshi and M Kawashima J.Cryst. Growth 95 (1989) 17

### *self-regulating deposition process conserving stoichiometry in a wide range of growth parameters*

- Growth rate determined by condensation ratio of group III -element (excessive Group V-element reevaporates)
- two-dimensional layer-by-layer-growth

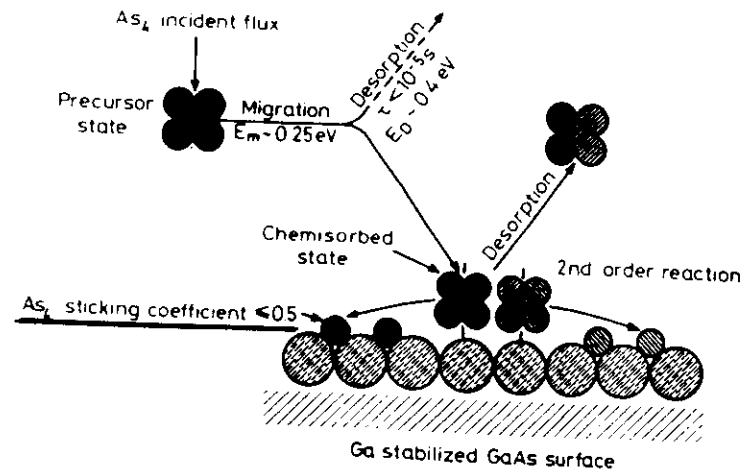
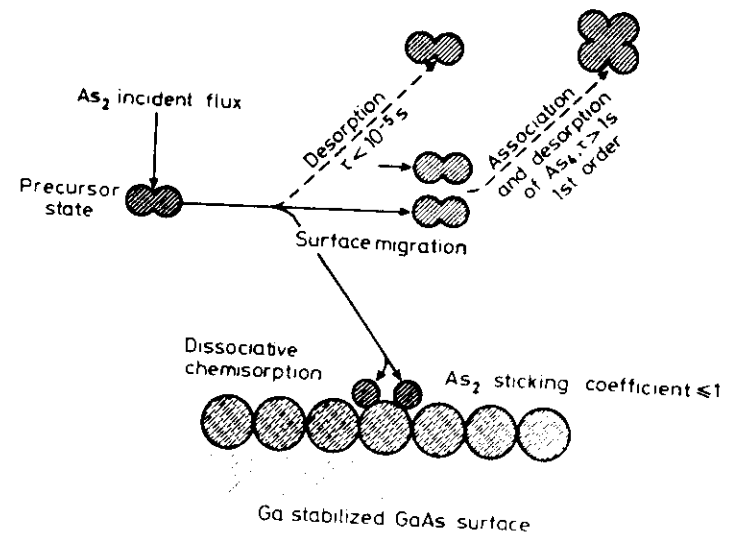


# Partial phase diagram for GaAs



J. M. Parisey et al. Nat. Res. Soc. Symp Proc Vol 104 (1988) 429

## Dimer $\leftrightarrow$ Tetramer sticking coefficient



# Step Propagation and 2-Dimensional Nucleation

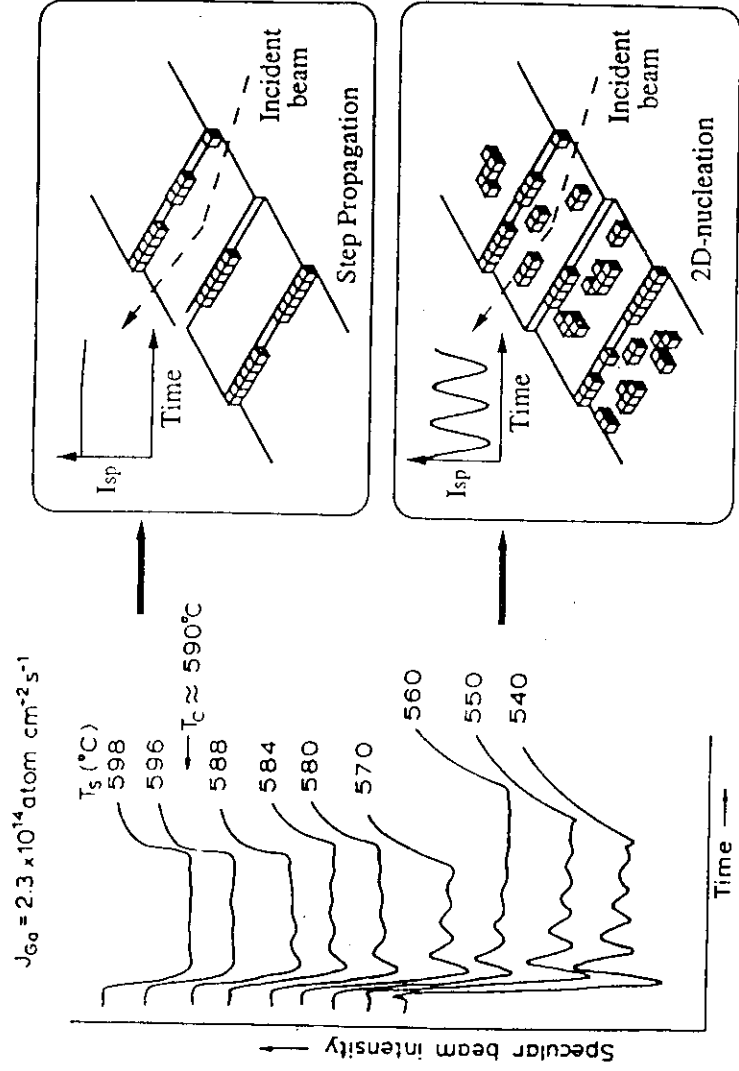
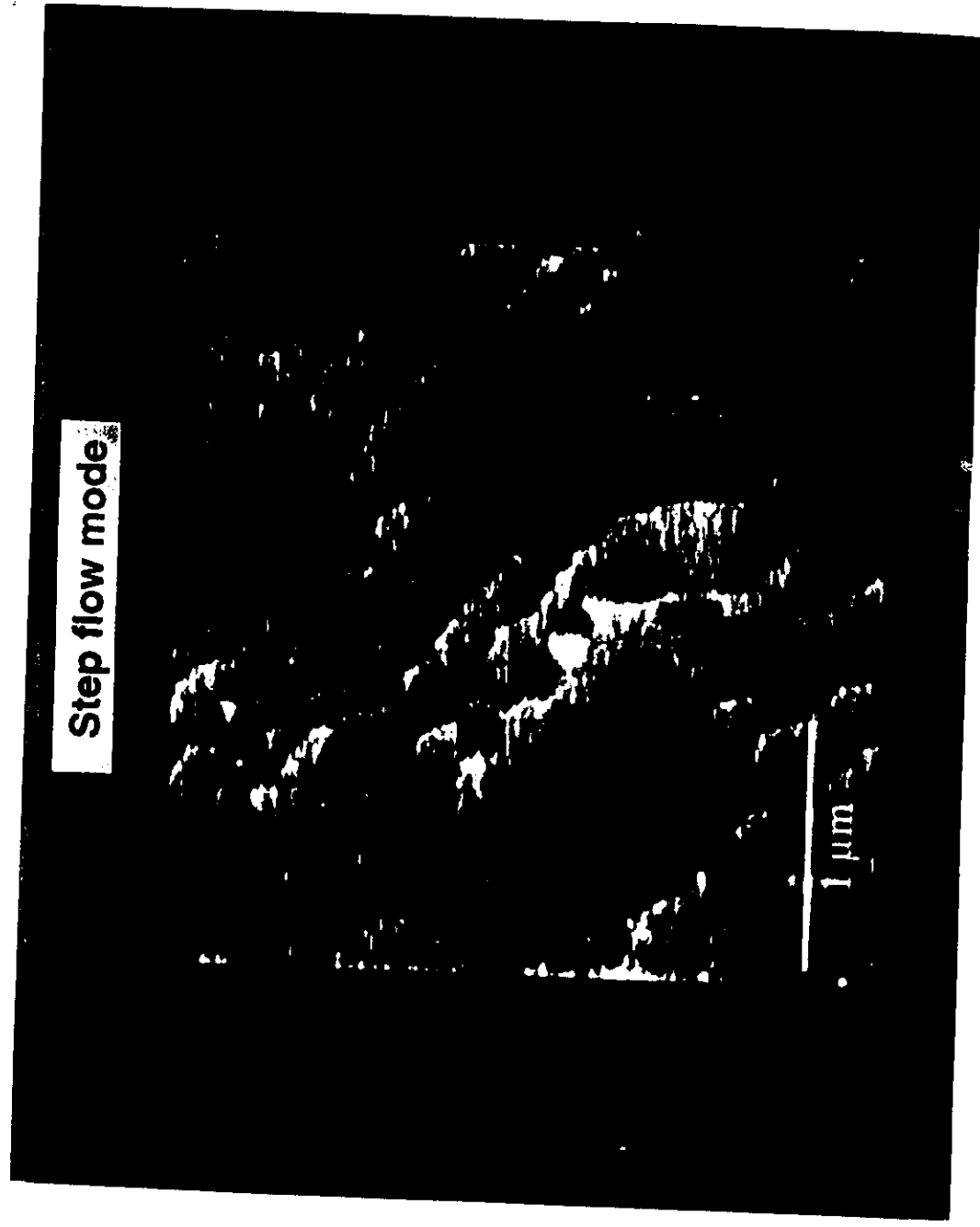
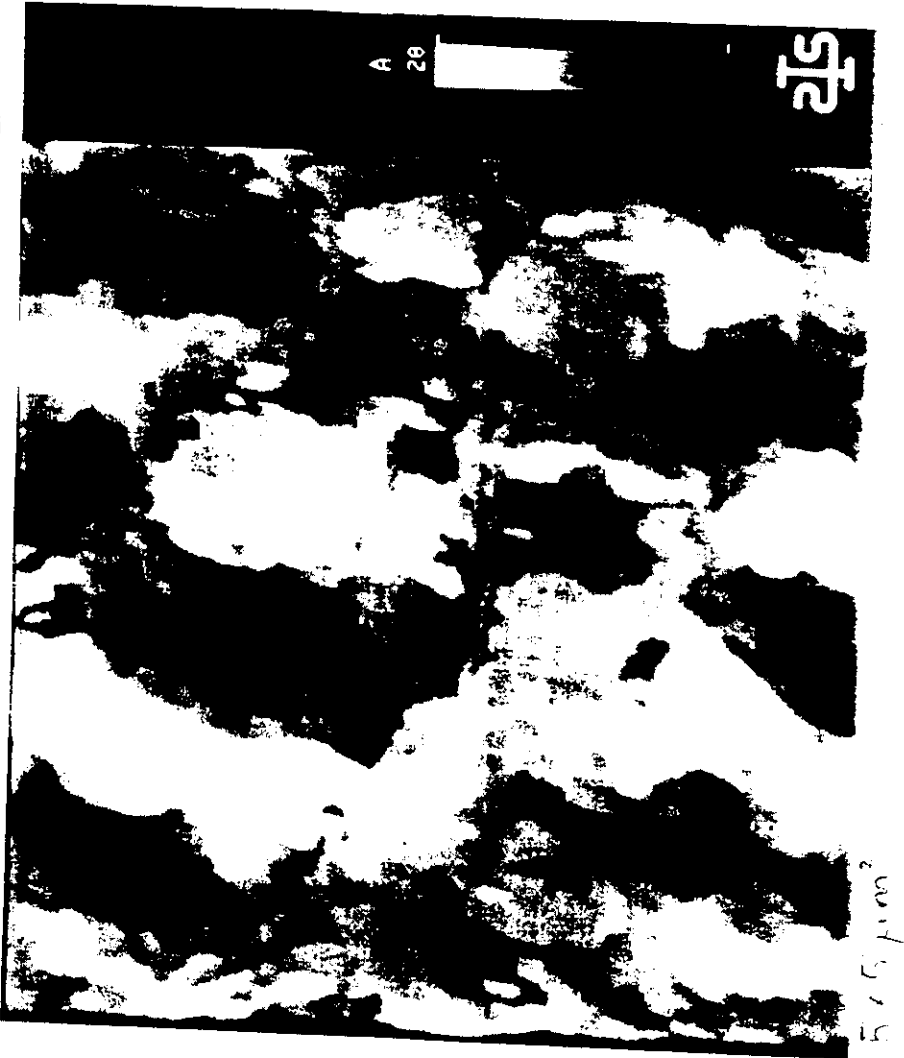


Figure 2.5: The temperature dependence of the RHEED oscillation (left) and growth modes on the vicinal surface (right). (Neave *et al.* [14])



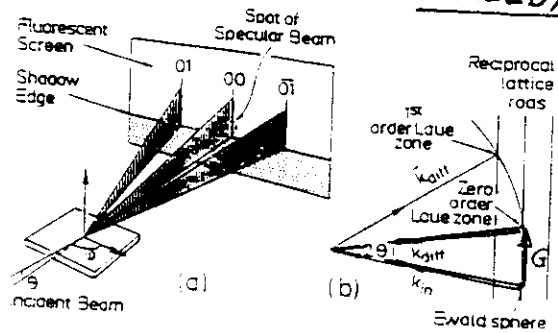
21. Micrograph in growth mode.



### Methods for in-situ monitoring of MBE growth

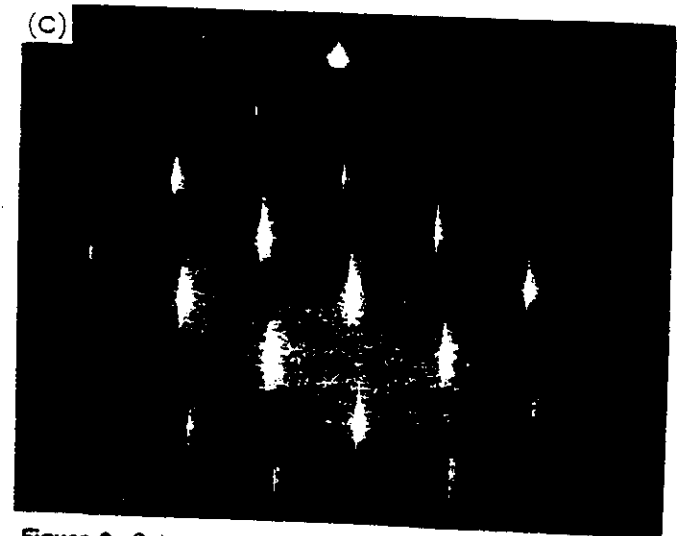
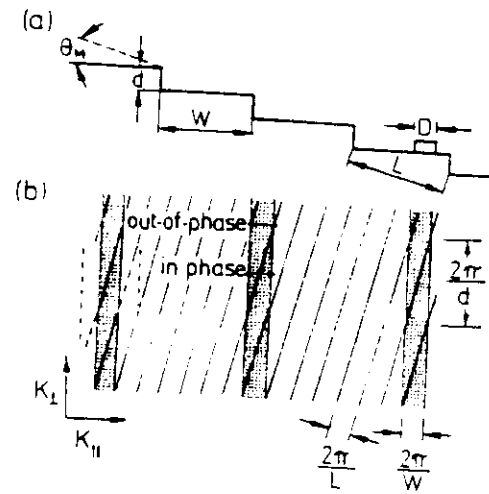
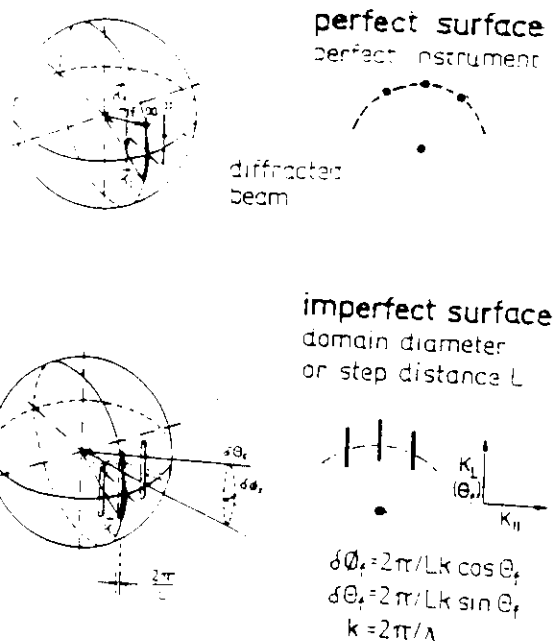
- ◆ Reflection High-Energy Electron Diffraction (RHEED)
- ◆ Reflectance Anisotropy Spectroscopy
- ◆ Near-Threshold Photoemission of Electrons
- ◆ Optical Pyrometry
- ◆ Desorption Mass Spectroscopy
- ◆ Scattered Light Intensity Measurements

# Reflection High-Energy Electron Diffraction (RHEED)



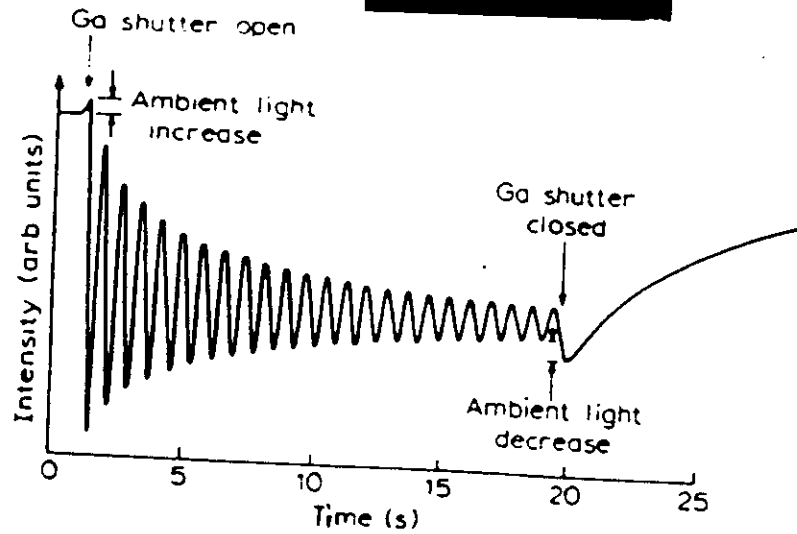
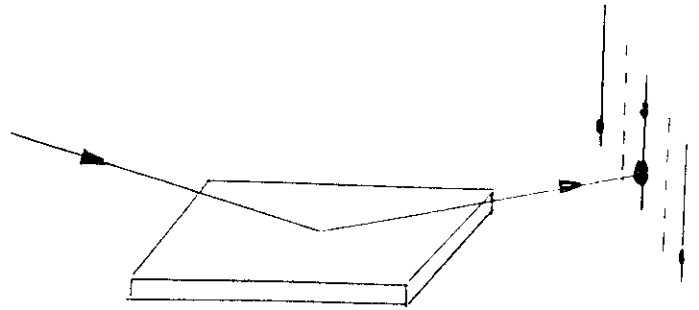
Geometric arrangement of RHEED with grazing-angle incidence used as in-situ analytical tool during MBE (a); Ewald construction to interpret the diffraction pattern (b)

$$k_{diff} - k_{in} = G$$

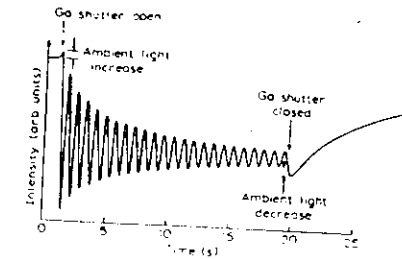
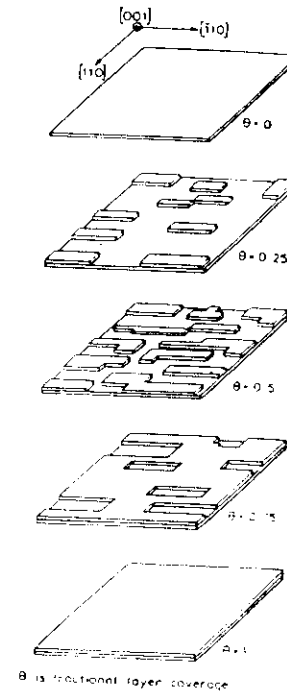


**Figure 9.** Schematic drawing of a regularly stepped vicinal surface with islands on the terraces (a) and the associated reciprocal lattice (b) and a RHEED pattern from an MBE-grown GaAs(001) surface misoriented  $5.9^\circ$  towards  $(111)$ . As recorded with the incident beam parallel to the step edges (c). To image the reciprocal lattice plane the sample has been oscillated during recording of the pattern. The pattern corresponds to the slashes drawn as thick lines in (b). For the 00 rod an additional broadening due to islands is indicated.

# RHEED---Specular Reflected Beam



# Intensity Oscillations of the Specular Reflected Electron Beam



J H Neave et al Appl. Phys. A31 (1983) 1

- ⇒ • process control
- information on structural imperfections on and near to the surface

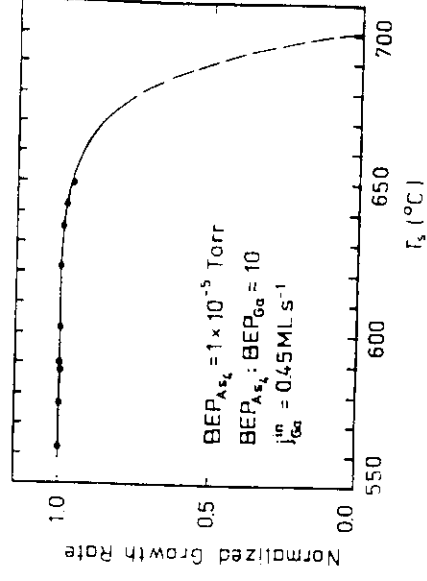
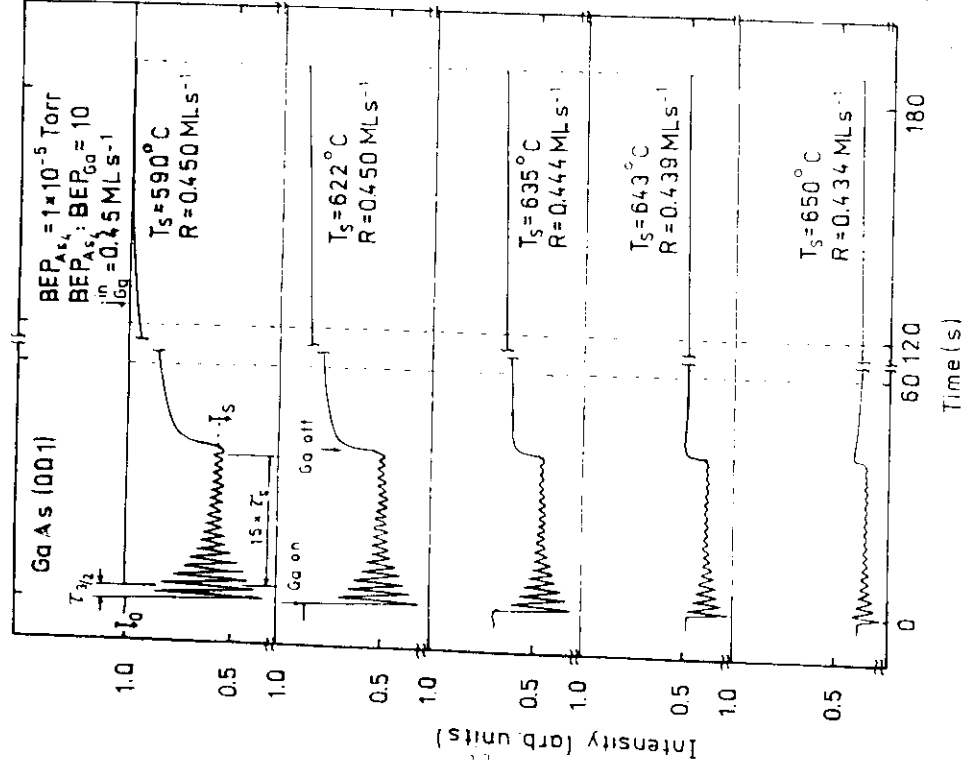
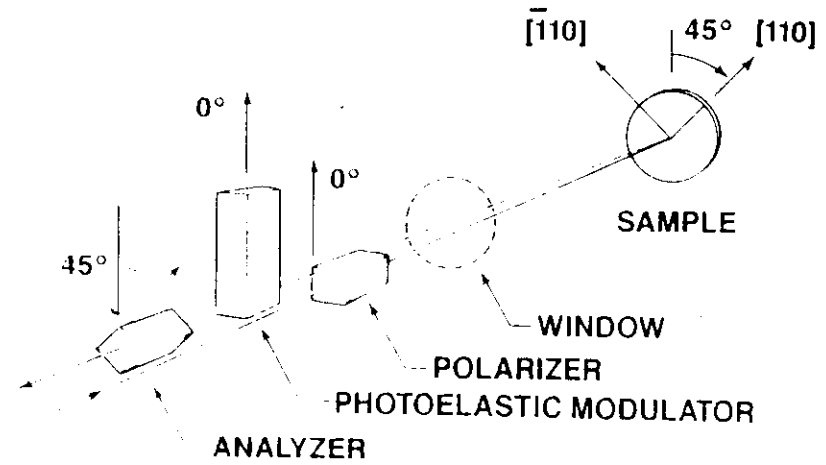
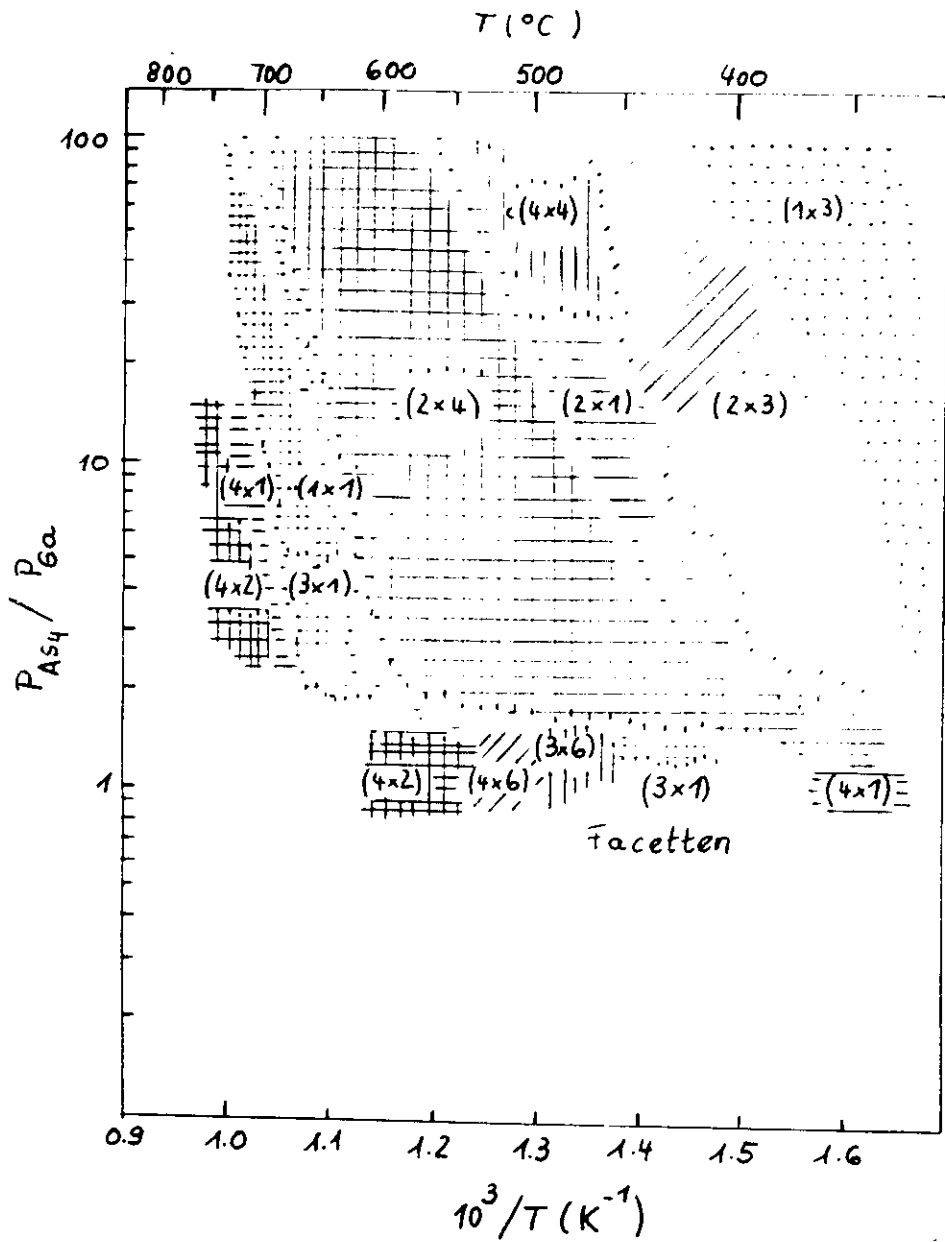


Table 2 Approximate loss rate of group-III-elements in monolayer per second from the surface of ternary III-III-V semiconductors estimated from vapour pressure data

Temperatur (°C)	Al	Ga	In
550	-	-	0.03
600	-	-	0.3
650	-	0.06	1.4
700	-	0.4	8
750	0.05	2	30



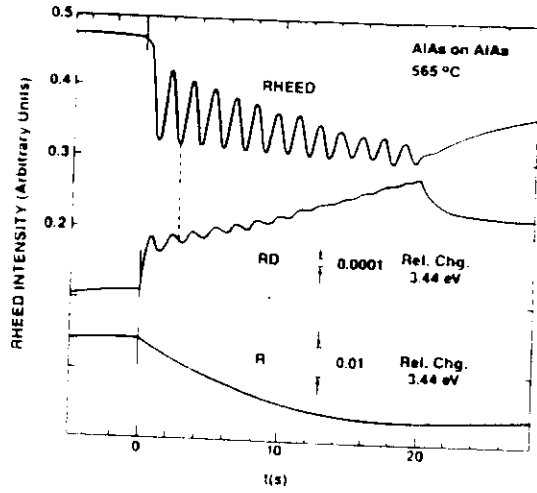
Configuration of reflectance anisotropy spectroscopy during MBE

accessible spectral range: 1.6 to 5.3 eV

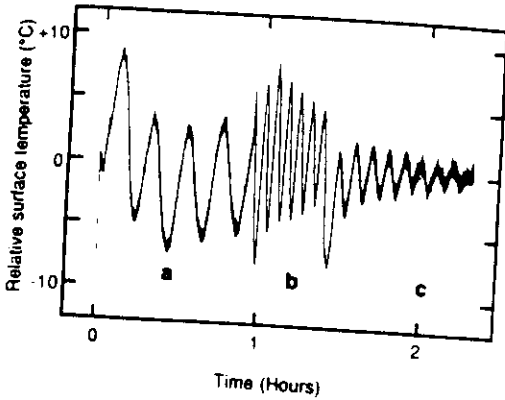
photon energy for RAS monitoring 2.6 eV  
mainly sensitive to As surface dimer transitions

$$\frac{\Delta r}{r} = \frac{r_{[110]} - r_{[\bar{1}\bar{1}0]}}{r_{[110]} + r_{[\bar{1}\bar{1}0]}}$$

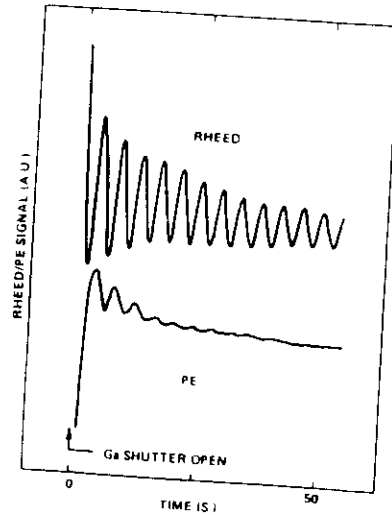
# Reflectance Difference Spectroscopy



Averages of nine RHEED (upper), RD (middle), and reflectance (R) (lower) signals upon initiation and termination of AlAs growth on an As-stabilized (2 × 4) AlAs surface



Oscillations in apparent surface temperature



RHEED and photoemission (PE) transients recorded separately for a growth rate of 0.25 ML/s

## Conventional molecular beam epitaxy (MBE)

- continuous flux of group III and group V elements
- growth temperature > 500°C for high-quality GaAs

Advantages: · reasonable growth rates

· excellent material quality for lattice-matched systems

· reasonably abrupt interfaces

Problems: · formation of "oval" defects

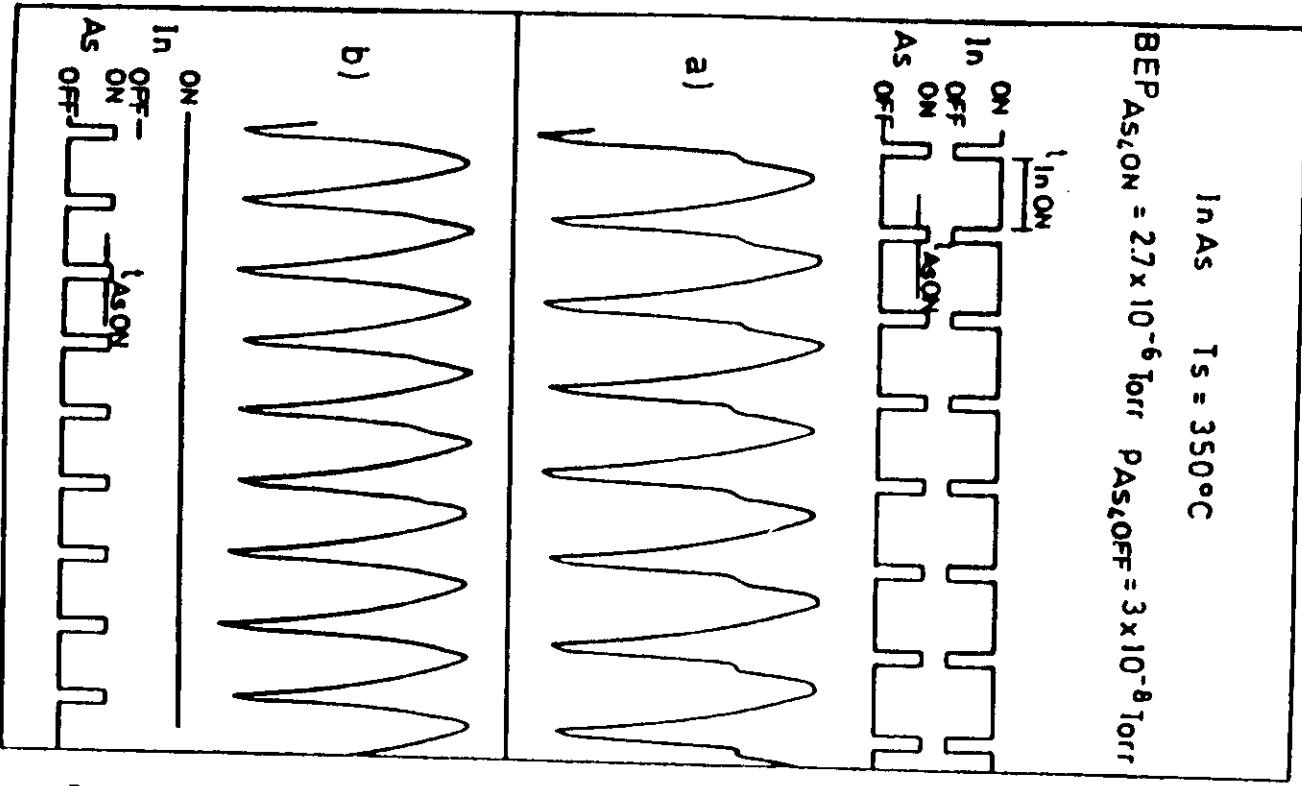
· interfaces in ultrathin-layer SL

· strained-layer heterostructures

Application: · standard heterostructures

· production of material for device fabrication





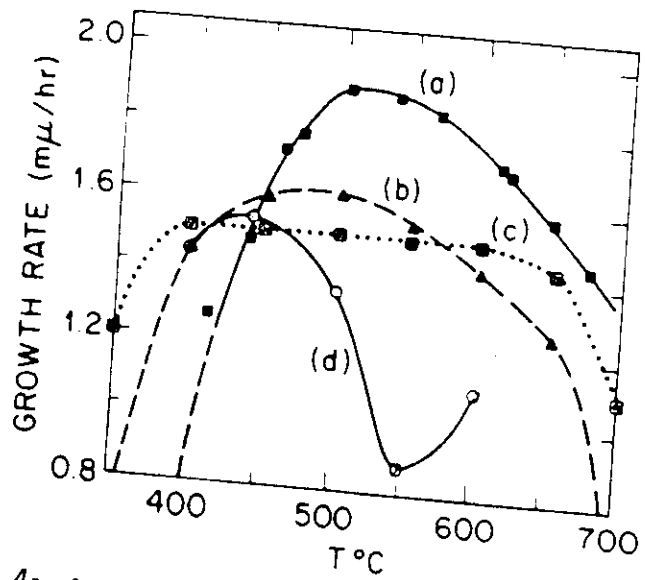
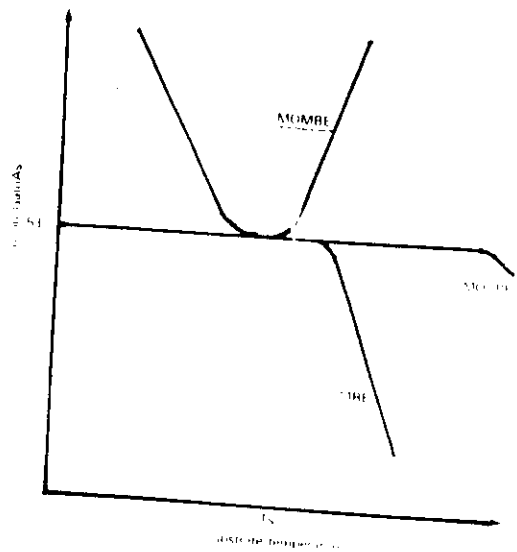
MEE

Honkoki et al  
 7 pm. 7. Appl. Phys.  
 27, 169 (1989)

ALMBE

Briones et al.  
 NAFD ASI  
 37 (1989)

	CONVENTIONAL MOLECULAR BEAM EPITAXY (MBE)	MIGRATION ENHANCED EPITAXY (MEE)	ATOMIC LAYER MOLECULAR BEAM EPITAXY (ALMBE)
Characteristic features	<p>Continuous flux of group III and group V elements; Substrate temperature <math>&gt; 500^{\circ}\text{C}</math> for high-quality GaAs</p>	<p>Periodic modulation of both the group III and group V element flux synchronously with the atomic layer-by-layer sequence (RHEED oscillations); Growth temperature lowered by <math>200^{\circ}\text{C}</math> as compared to MBE</p>	<p>Continuous flux of group III element(s), but short pulses (modulation) of the group V flux synchronously with RHEED intensity oscillations; Growth temperature lowered by <math>200^{\circ}\text{C}</math> as compared to MBE</p>
Advantages	<p>Reasonable growth rates; Excellent material quality for lattice-matched systems; Reasonably abrupt interfaces</p>	<p>Excellent surface morphology (no "oval" defects); Low growth temperature; Abrupt interfaces in ultrathin-layer superlattices; 2D growth in lattice mismatched systems; Controlled incorporation of two group V elements</p>	<p>Excellent surface morphology (no "oval" defects); Low growth temperature; Reasonable growth rates; Abrupt interfaces in ultrathin-layer superlattices; 2D growth in lattice-mismatched systems; Controlled incorporation of two group V elements</p>
Problems	<p>Formation of "oval" defects; Interfaces in ultrathin-layer superlattices; Strained-layer heterostructures</p>	<p>Low growth rate; Accurate control of group III flux required to deposit exactly one monolayer; High mechanical load for shutters</p>	<p>Mechanical design of group V element shutters; Substrate rotation vs. RHEED intensity oscillations</p>
Applications	<p>Standard heterostructures; Production of material for device fabrication</p>	<p>Low-temperature growth on processed substrates; Controlled 2D growth of lattice-mismatched materials (e.g. GaAs on Si); Ultrathin-layer superlattices with very abrupt interfaces; Layered structures composed of two different group V elements (e.g. P and As)</p>	<p>Low-temperature growth on processed substrates; Controlled 2D growth of lattice-mismatched materials (e.g. GaAs-on-Si); Ultrathin-layer superlattices with very abrupt interfaces; Layered structures composed of two different group V elements (e.g. P and As)</p>



- (a) GaAs grown with TEG and AsH<sub>3</sub>
- (b) GaAs grown with TEG and As<sub>4</sub>
- (c) Al<sub>x</sub>G<sub>1-x</sub>As with TEG, Al, and As<sub>4</sub>

