Nanostructure Epitaxial Growth Techniques

ECE 598XL

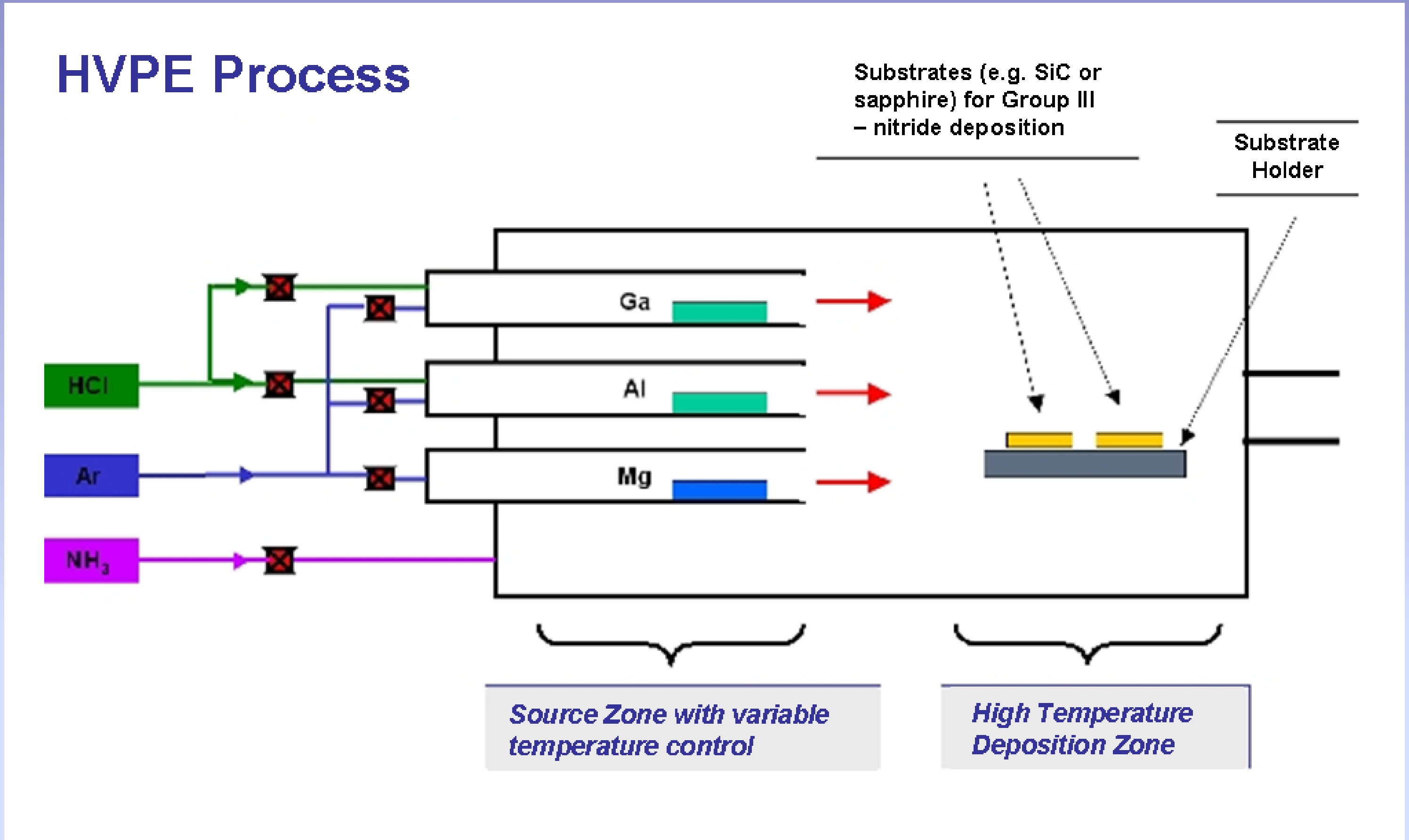
Fall 2009

Crystal Growth

- Advancement in crystal growth techniques is one of the major factors responsible for the nanotechnology momentum today.
- Thermodynamics
  - Chemical reactions
  - Phase diagrams
- Figure of merit: material quality, uniformity and controllability
  - Thickness
  - Composition
  - Interface
  - Doping
  - Defects

Crystal Growth

- Epitaxial growth techniques
  - LPE
  - HVPE
  - MOCVD
  - MBE
- Deposition of dielectric films or polycrystal semiconductors
  - PECVD
  - Evaporation
  - Sputtering



Hot HCl (g) + Ga (l) ------> GaCl (g)

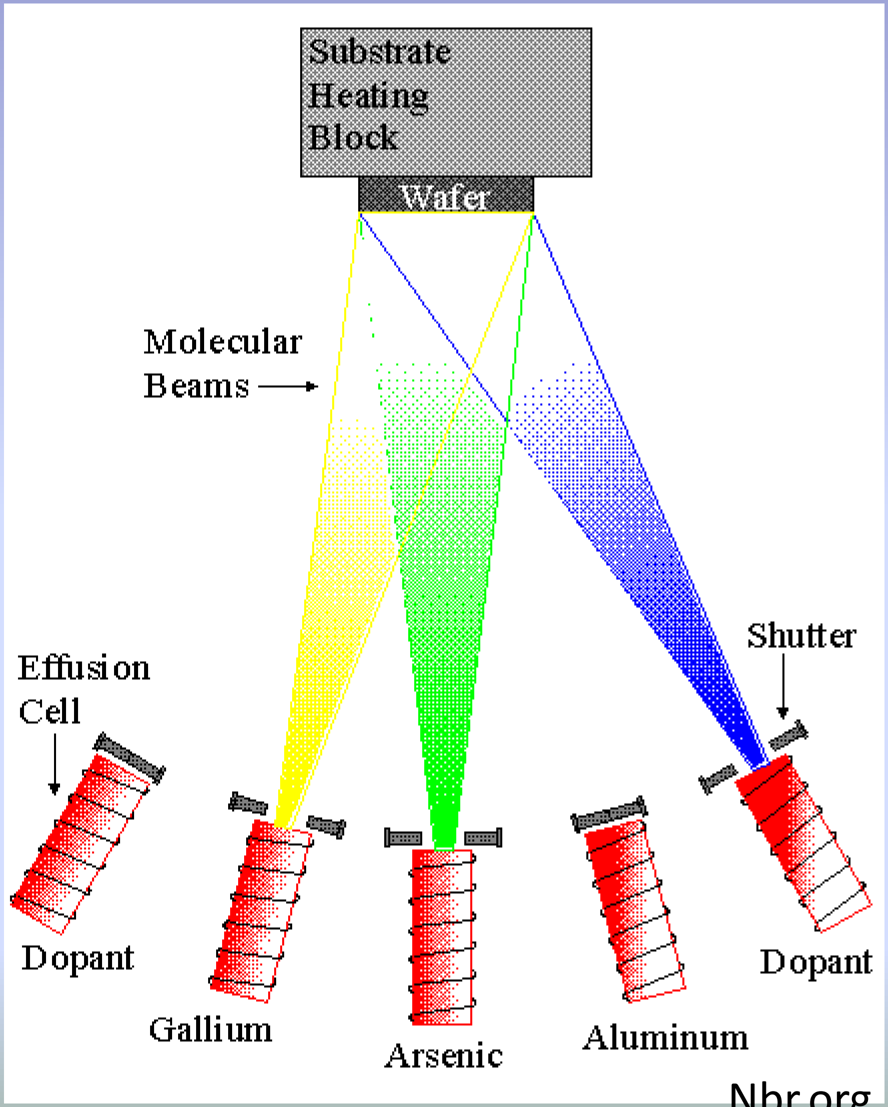
GaCl (g) + NH3 (g) -------> GaN (s) + HCl (g) + H2 (g)

- Hydride gaseous source
- Metal liquid atomic source
- Fast growth rate (> 100 um/h)
- Surface defects for non-nitride materials

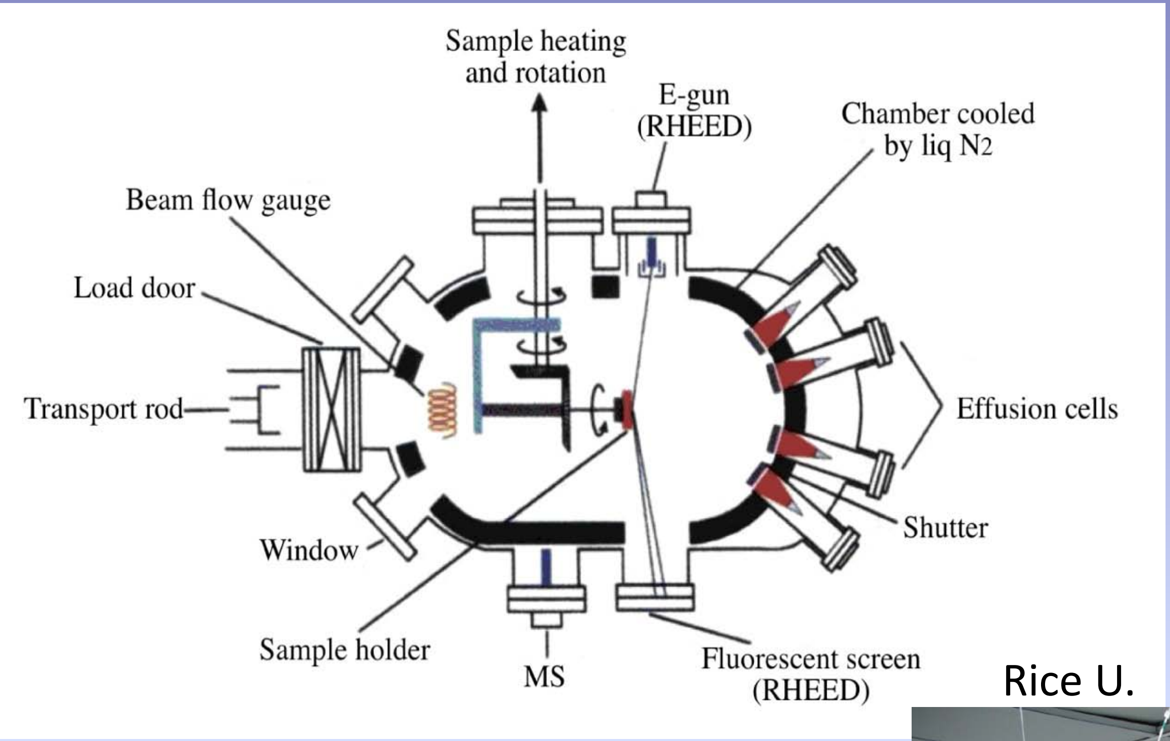
Oxford Instruments

MBE

- Inventor:
  - Bell Lab, Arthur and Alfred Cho
- UHV : 10^{-11} torr
  - Not thermodynamic equilibrium condition
  - Governed by the kinetics of the surface process
- Solid atomic source – effusion cell-controlled vapor pressure
- Shutters
- Substrate-heated
- GSMBE and MOMBE (CBE)
- Slower growth rate
- Better thickness and heterojunction control
- Lower growth temperature
- High cost



Nbr.org



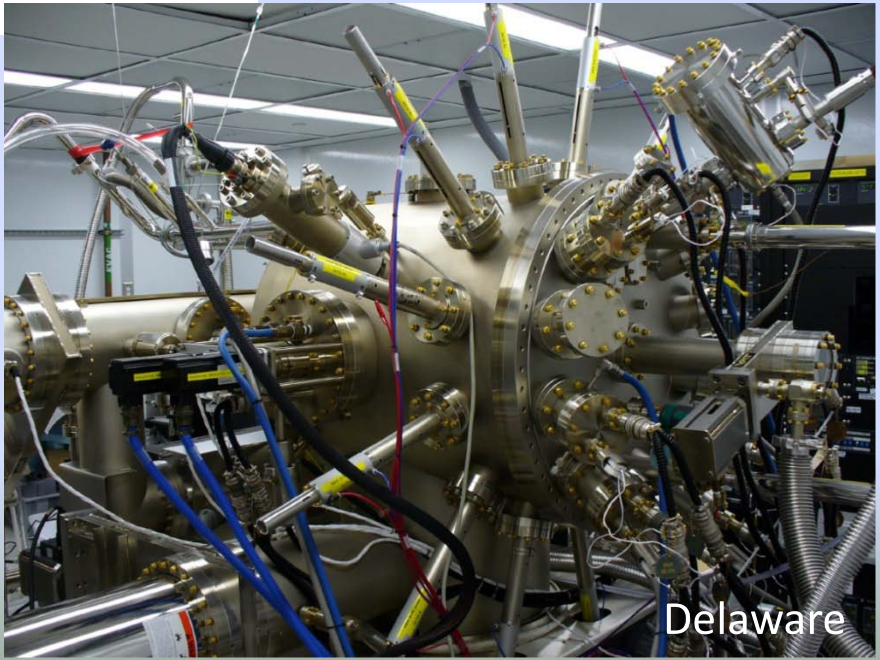
Rice U.

UHV

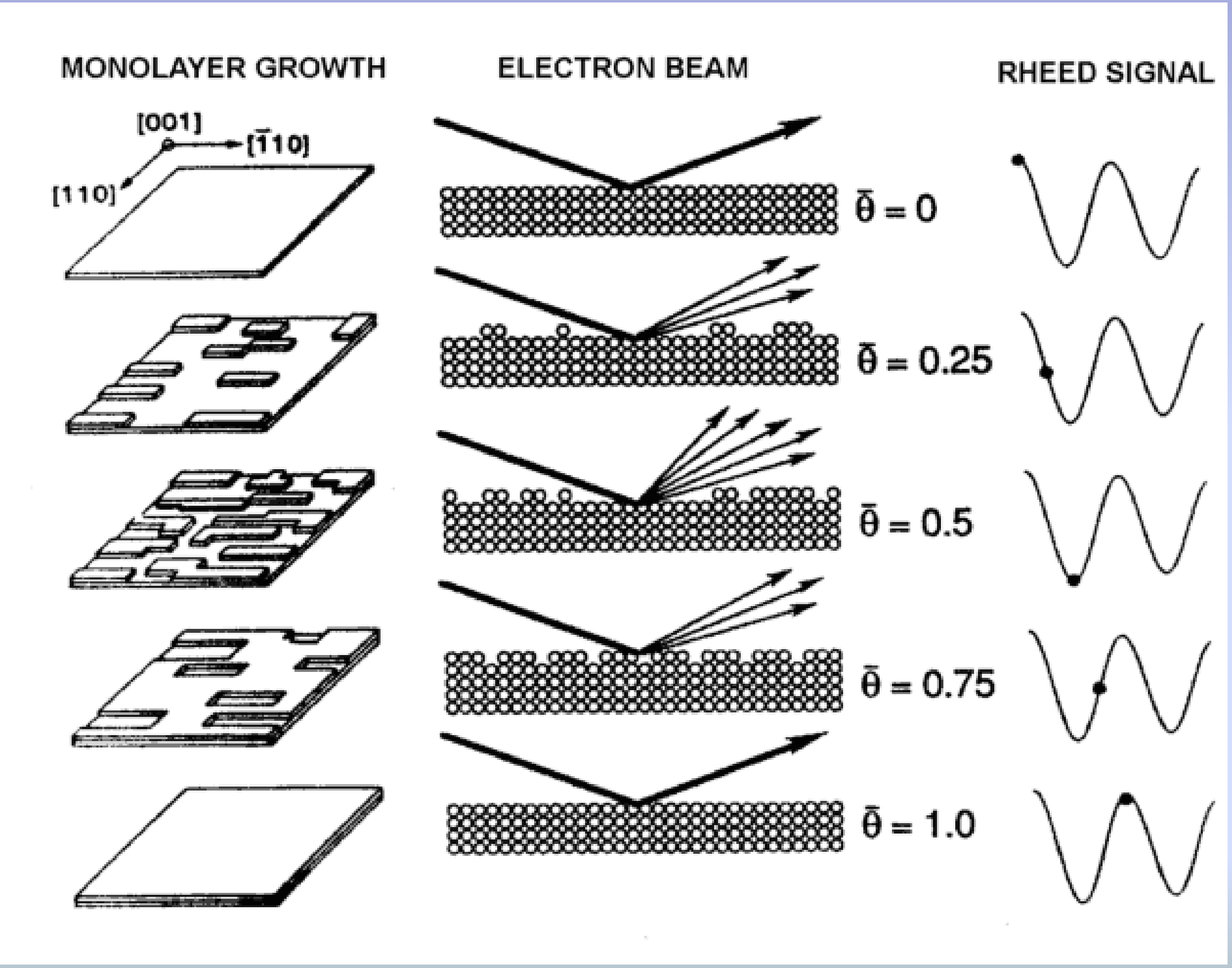
↕

in situ monitoring

- RHEED
  - 5- 50 keV
  - Glancing angle incidence
  - Surface sensitive – ML



Reflection High Energy Electron Diffraction (RHEED): principle



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

Layer-by-layer 2D growth

- RHEED oscillation
  - Growth rate
  - Growth condition

RHEED Patterns for Nanostructures

APPLIED PHYSICS LETTERS 91, 251902 (2007)

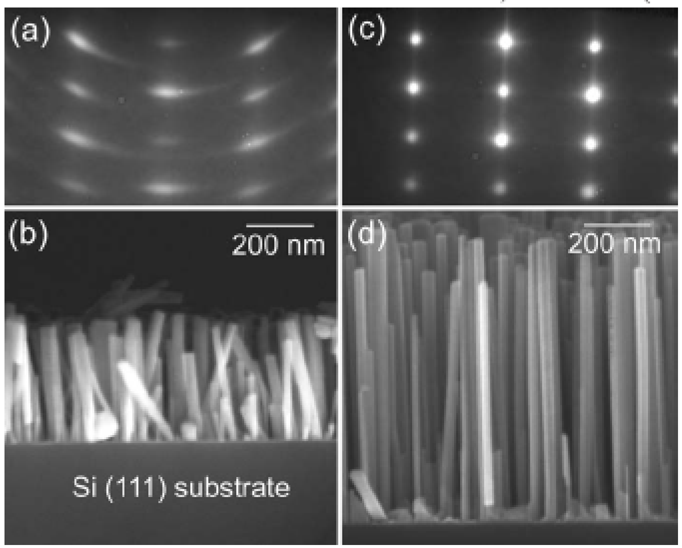
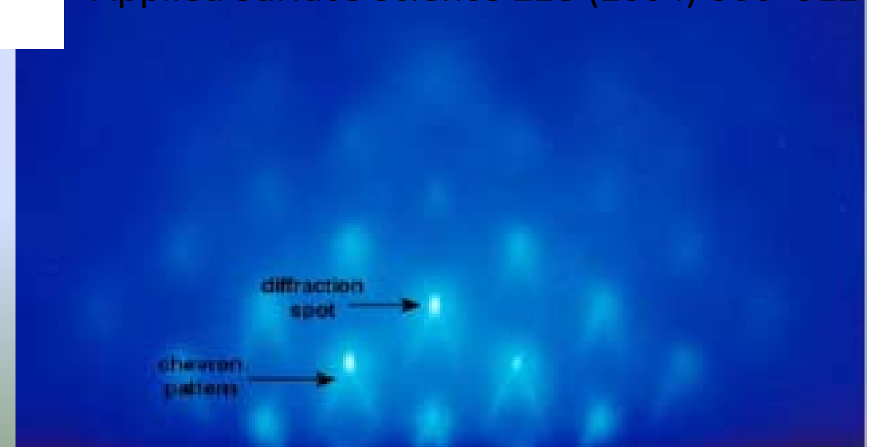


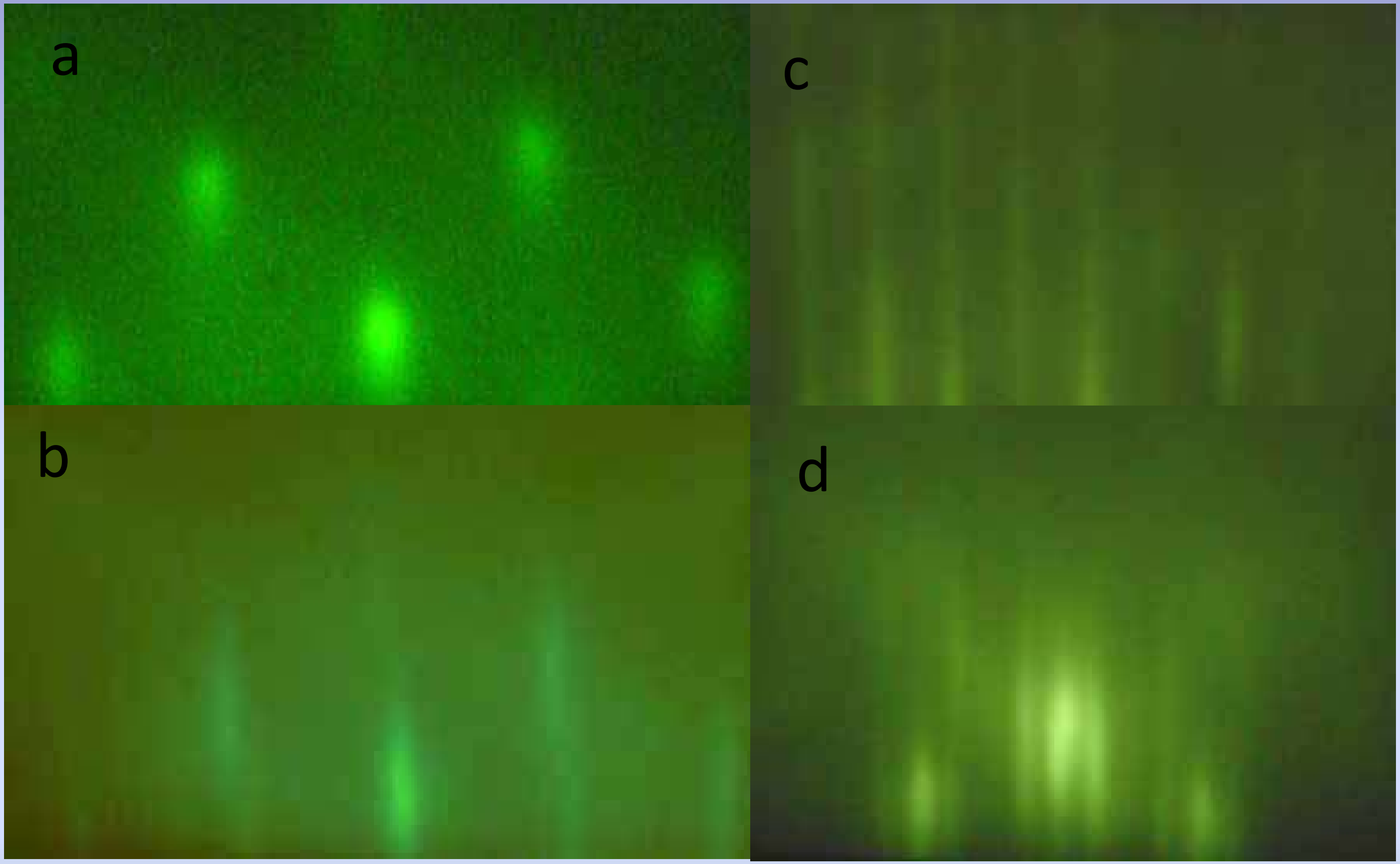
FIG. 1. RHEED patterns and corresponding SEM images of GaN nanowires [(a) and (b)] grown directly on Si (111) substrate and [(c) and (d)] on AlN thin buffer layer on Si (111) substrate.

– RHEED image
  - Sharp vs diffuse
  - Streaky line -2D
  - Spotty – 3D
  - Chevron –QD facet

Applied Surface Science 228 (2004) 306–312



RHEED patterns for various stages of LT-GaAs on Si growth. (a) Typical pattern after exposure to arsenic and MEE cycles. (b) After LT-GaAs growth. (c) [011] azimuth after in-chamber annealing. (d) [0-11] azimuth after in-chamber annealing.

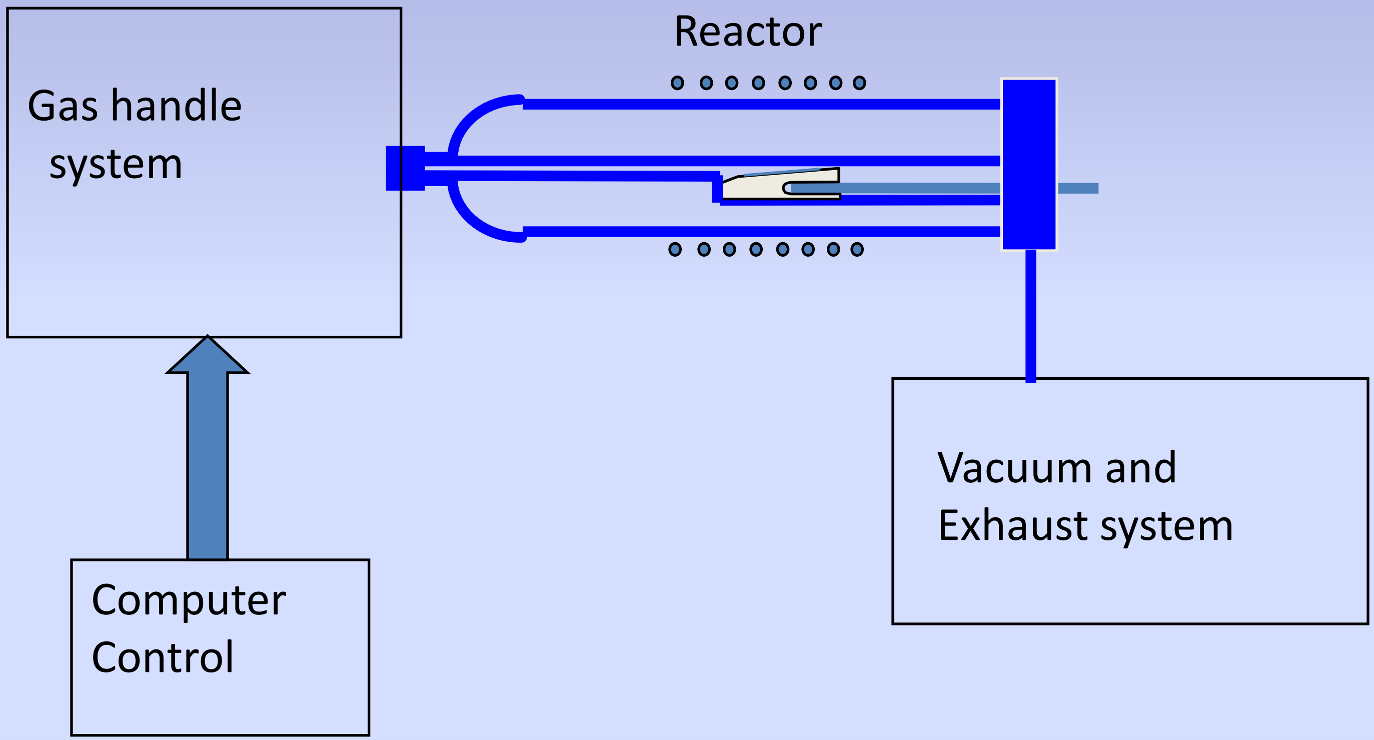


Ma et al. Harris group, 2003, MRS proc.

MOCVD

- Nomenclature
  - MOCVD
  - OMVPE
  - MOVPE
  - OMCVD
  - AP-MOCVD
  - LP-MOCVD
- Most widely used epitaxial technique at commercial scale
- Major components:
  - Gas handling system
  - Reactor chamber
  - Heating system
  - Exhaust system

MOCVD Growth System



KSU

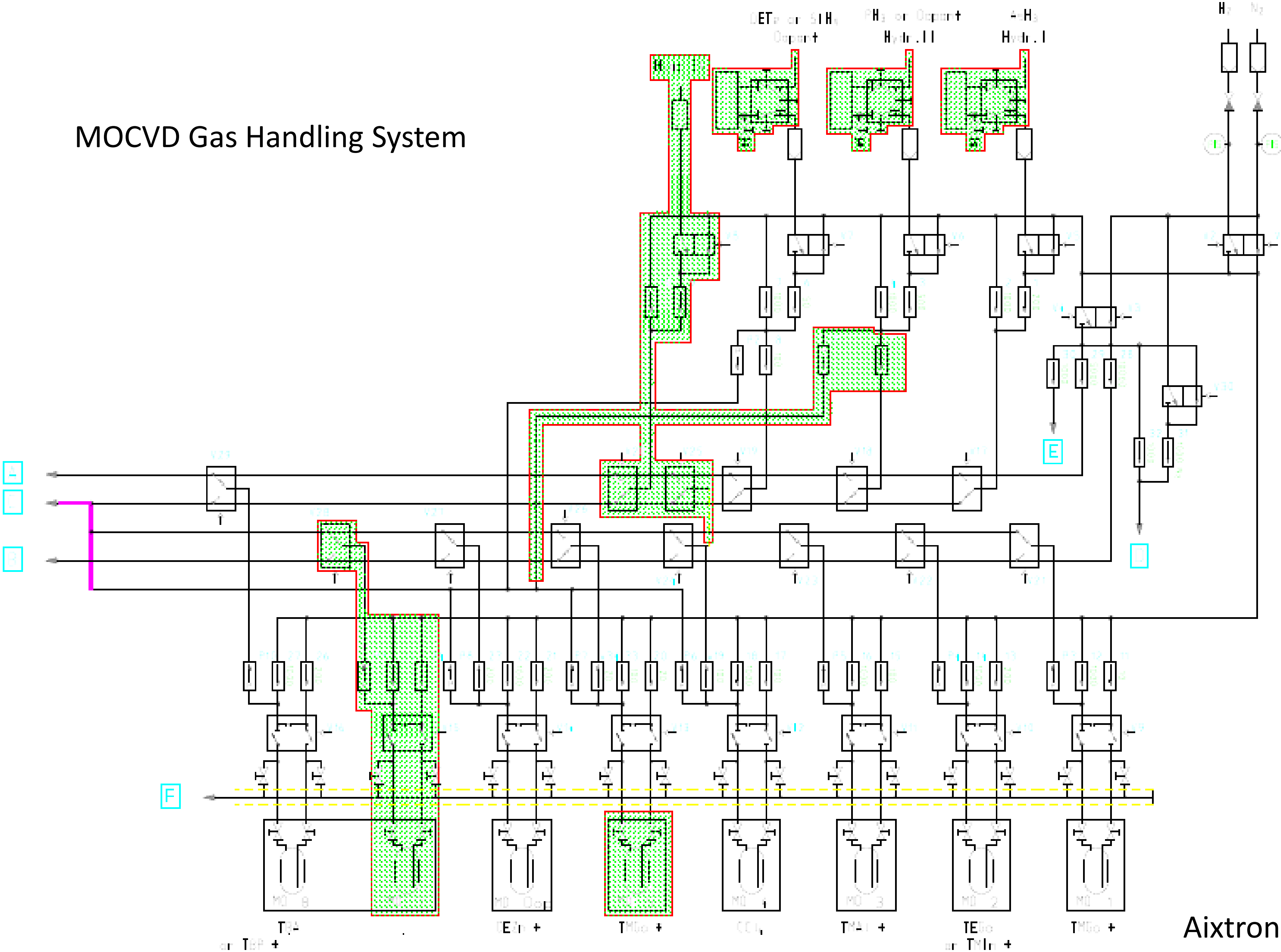
A MOVD growth system

In Xiuling Li's group, UIUC

Gas Handling System

- Sources:
  - Metalorganics (MO) or alkyls:
    - TMGa, TEGa, TMAl, TMIn, DMZn, etc.
    - Bubbler
  - Hydride: AsH3, PH3, NH3, Si2H6
    - Cylinder
    - Gas cabinet
- Carrier gas: H_2 or N_2
  - H2 purifier
- Valves, MFCs, tubes, pumps etc.
- Purity, cleanness, leak-tight

MOCVD Gas Handling System



Aixtron

ling system


PHOSPHINE


UNGLE
MAINTENANCE IN PROGRESS
PLEASE STAY OUT OF AREA
PLEASE STAY OUT OF AREA

Calculate mol flow rate of MO sources

- The flow rate of a source is normally expressed in **mol/min**

F (mol/min)$=p_{MO}/p_{Bubbler}$*[flow rate (ml/min)]/22400 (mol/ml)

- Use the mole flow rate
  - calculate growth rate:
  - estimate alloys composition, assuming the pyrolysis and incorporation efficiencies of Al and Ga sources are the same.

    - $x_{Al}=F_{Al}/(F_{Al}+F_{Ga})$

Vapor pressure of most common MO compounds

Compound		P at 298 K (torr)	A	B	Melt point (^oC)
$(Al(CH_3)_3)_2$	TMAl	14.2	2780	10.48	15
$Al(C_2H_5)_3$	TEAl	0.041	3625	10.78	-52.5
$Ga(CH_3)_3$	TMGa	238	1825	8.50	-15.8
$Ga(C_2H_5)_3$	TEGa	4.79	2530	9.19	-82.5
$In(CH3)_3$	TMIn	1.75	2830	9.74	**88**
$In(C_2H_5)_3$	TEIn	0.31	2815	8.94	-32
$Zn(C_2H_5)_2$	DEZn	8.53	2190	8.28	-28
$Mg(C_5H_5)_2$	Cp2Mg	0.05	3556	10.56	**175**

Log[p(torr)]=B-A/T

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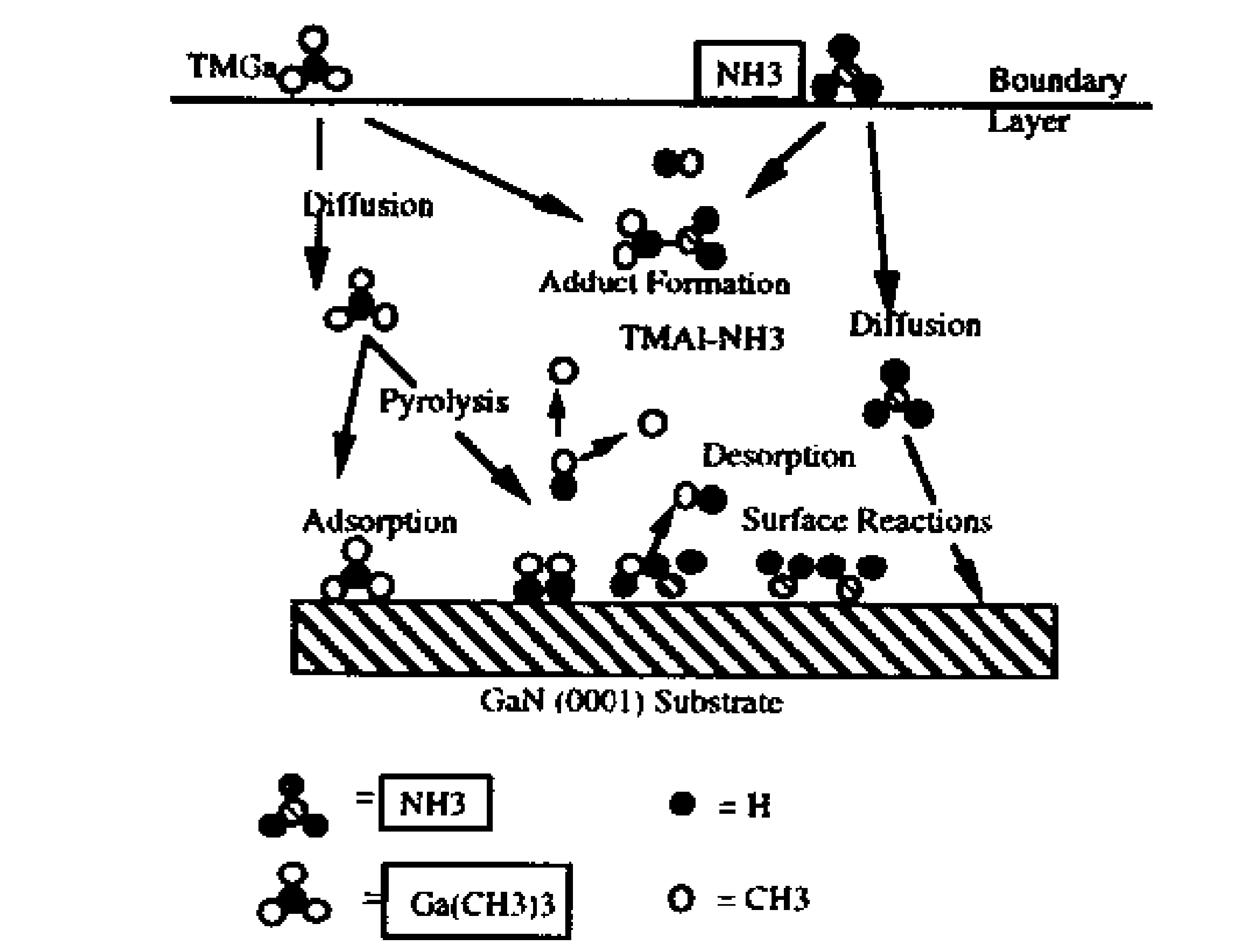
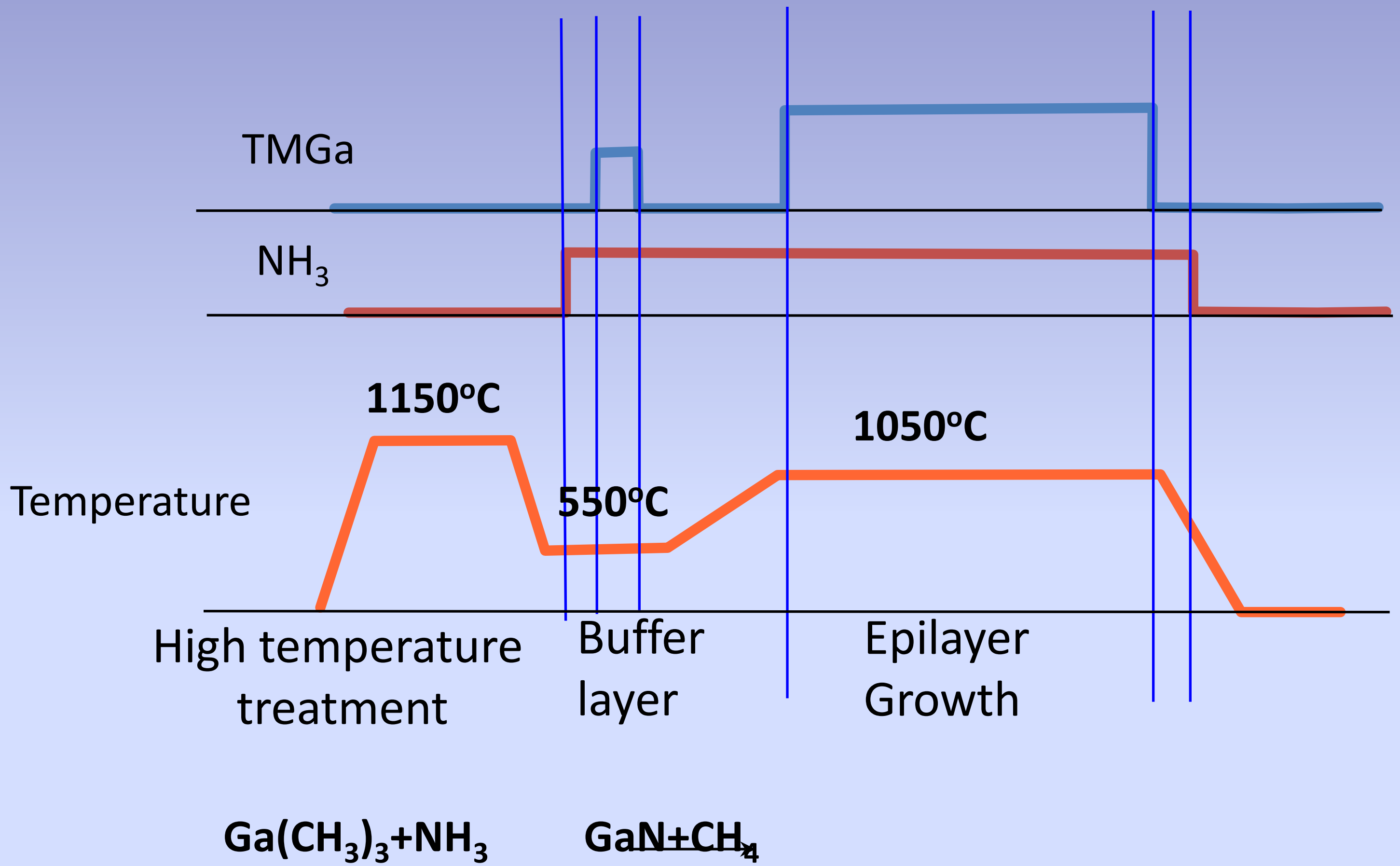
it is easier to control the delivery from a liquid than from a solid

MOCVD mechanism



MOCVD growth process of GaN and related materials



Two Step MOCVD Growth procedure

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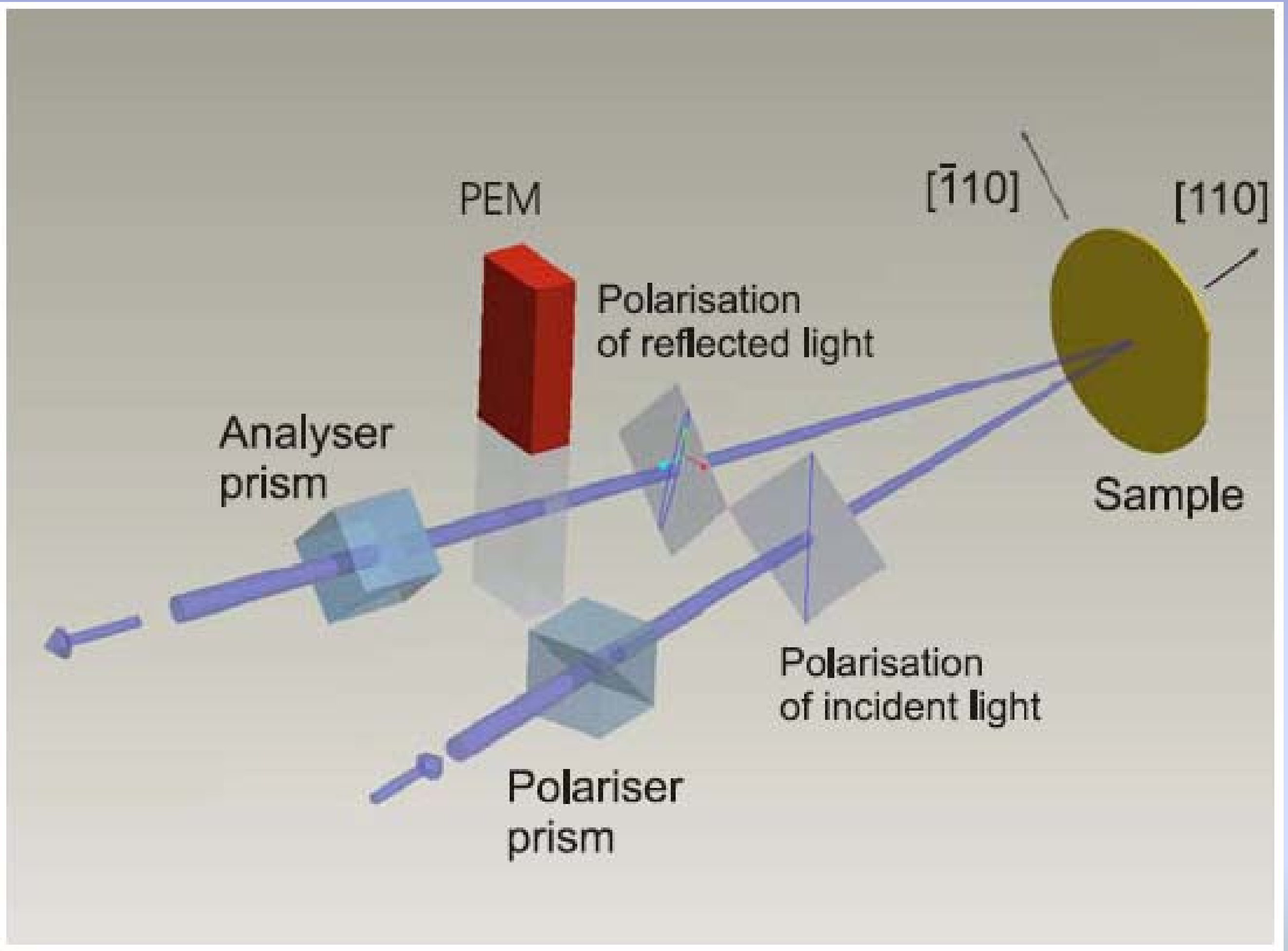
In situ Monitoring in MOCVD: epiRAS

Optical

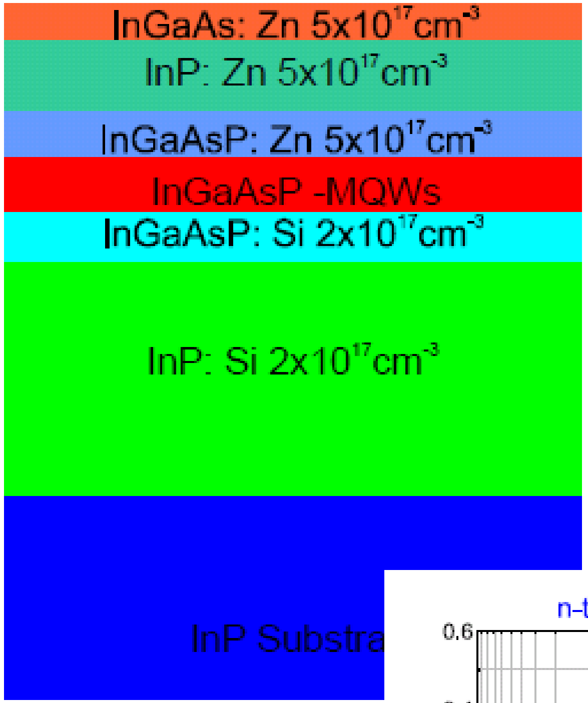
- **Conventional reflection spectroscopy:**
  - Growth rate
  - Layer thickness
  - Composition
- **Reflectance Anisotropy Spectroscopy (RAS)**
  - reflectance difference spectroscopy
  - Sensitive to surface, interface, doping induced surface electrical fields
  - For cubic crystal only
  - For surface that absorbs incoming light
  - Artifacts

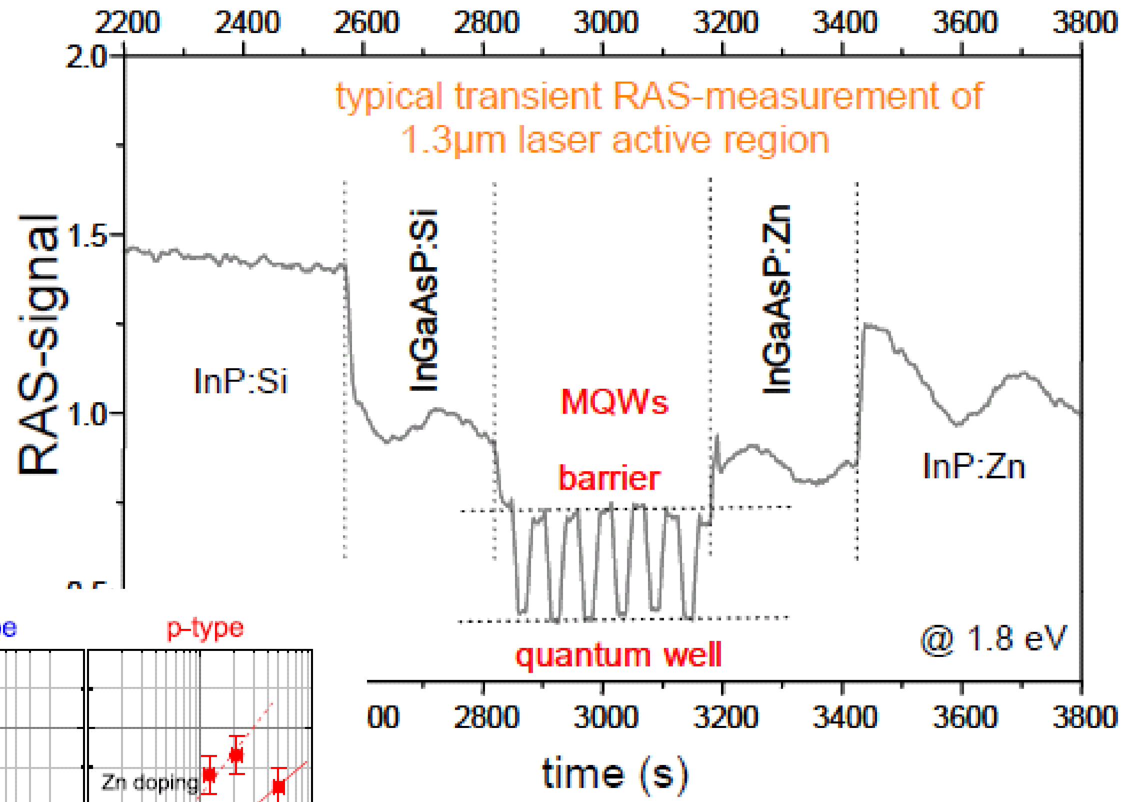
$$\frac{\Delta R}{R} = 2\frac{R_x - R_y}{R_x + R_y}$$

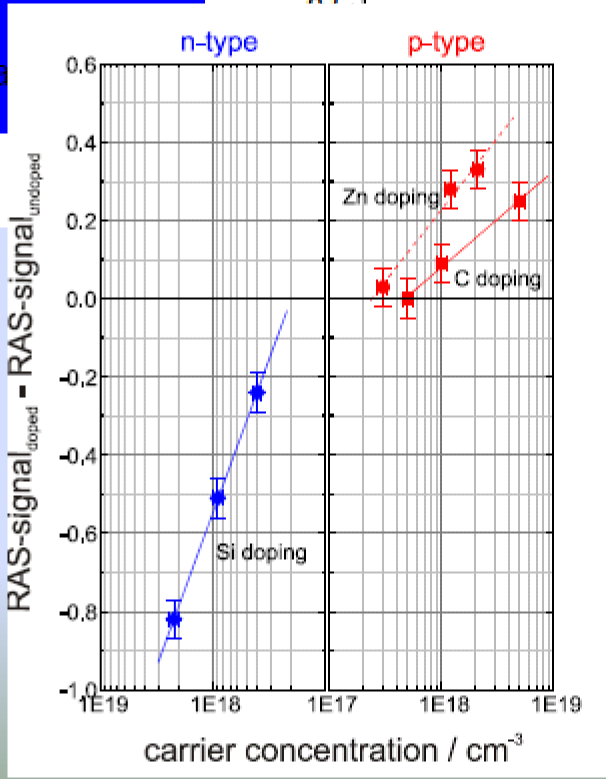
RAS setup



LayTec, Inc.


InGaAs: Zn 5x10^17 cm^-3
InP: Zn 5x10^17 cm^-3
InGaAsP: Zn 5x10^17 cm^-3
InGaAsP -MQWs
InGaAsP: Si 2x10^17 cm^-3
InP: Si 2x10^17 cm^-3
InP Substra


typical transient RAS-measurement of
1.3µm laser active region
RAS-signal
InP:Si
InGaAsP:Si
MQWs
barrier
quantum well
InGaAsP:Zn
InP:Zn
@ 1.8 eV
time (s)
2200
2400
2600
2800
3000
3200
3400
3600
3800
2.0
1.5
1.0


n-type
p-type
RAS-signal doped - RAS-signal undoped
Zn doping
C doping
Si doping
carrier concentration / cm^-3
1E19
1E18
1E17
1E18
1E19
0.6
0.4
0.2
0.0
-0.2
-0.4
-0.6
-0.8
-1.0

LayTec, Inc.

Control Parameters

- Temperature
- Pressure
- Growth rate
- V/III ratio
- Doping
- Growth pulse
- Substrate orientation
- Desorption condition

Black box?

Comparison of Epitaxial Techniques

Growth method	time	features	limitation
LPE (Liquid phase epitaxy)	1963	Growth from supersaturated solution onto substrate	Limited substrate areas and poor control over the growth of very thin layers
VPE (Vapor phase epitaxy	1958	Use metal halide as transport agents to grow	Surface roughness thick layer
MBE (Molecular Beam Epitaxy)	1958 1967	Deposit epilayer at ultrahigh vacuum	Slow and hard to grow materials with high vapor pressure
MOCVD (Metal-Organic Chemical Vapor Deposition)	1968	Use metalorganic compounds as the sources	Some of the sources e.g. $AsH_{3,}$ are very toxic.

SOLUTIONS FOR A WIDE VARIETY OF DEVICES		
Applications	MBE	MOCVD
Wireless telecom	InP, GaAs, GaN	InGaP, GaAs, GaN, SiC
Optical telecom	InP, GaAs	InP/As
Lighting-LEDs	ZnO, ZnSe	GaN, AlGaAs; As/P
Research	Across periodic table	GaN, As/P, SiC
Data storage	Metal oxides	GaN, AlGaAs
Si semiconductor	Oxide, novel materials	GaN

Veeco.com