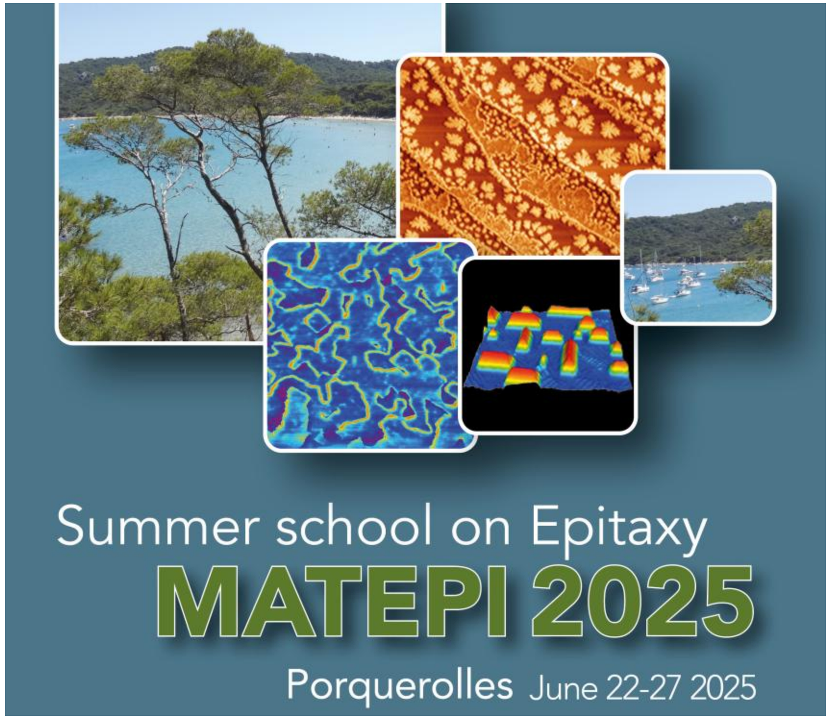


Summer school on Epitaxy

MATEPI 2025

Porquerolles June 22-27 2025

Instrumental Epitaxy

Noëlle Gogneau

C2N
Centre
DE Nanosciences
& DE Nanotechnologies

Dr. Noëlle Gogneau

Growth of III-N NWs for nano-energy

NW growth by PA-MBE

Single NW characterization

Understanding of nanometer scale phenomena

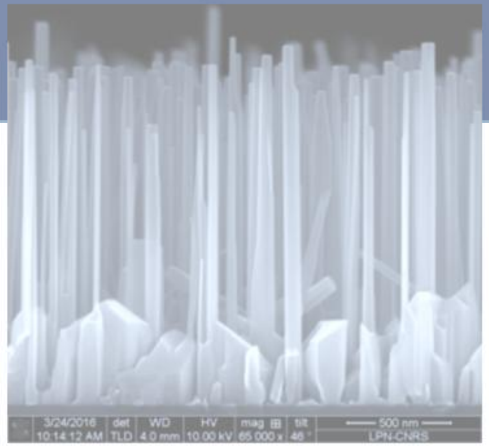
Design, Fabrication & Testing of NW-based devices

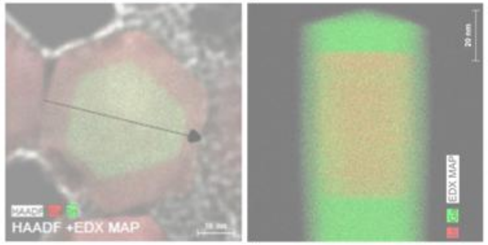
C2N Centre de Nanosciences & de Nanotechnologies

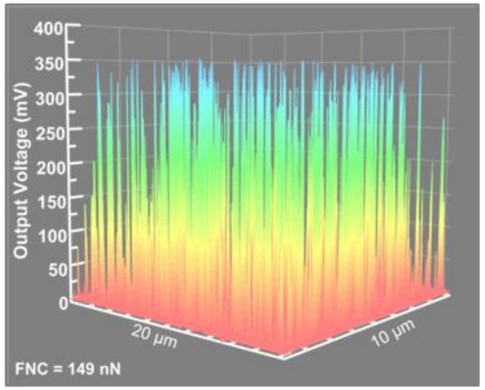
cnrs

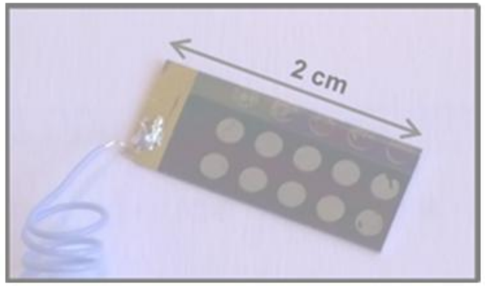
université PARIS-SACLAY

Université de Paris









Outline

Epitaxy – a little history !

Why epitaxy ?

Epitaxial techniques

- *Liquid Phase Epitaxy (LPE),*
- *Molecular Beam Epitaxy (MBE) and the hybrid systems*
- *Vapor Phase Epitaxy (VPE) and the related techniques*

Epitaxy - Definition

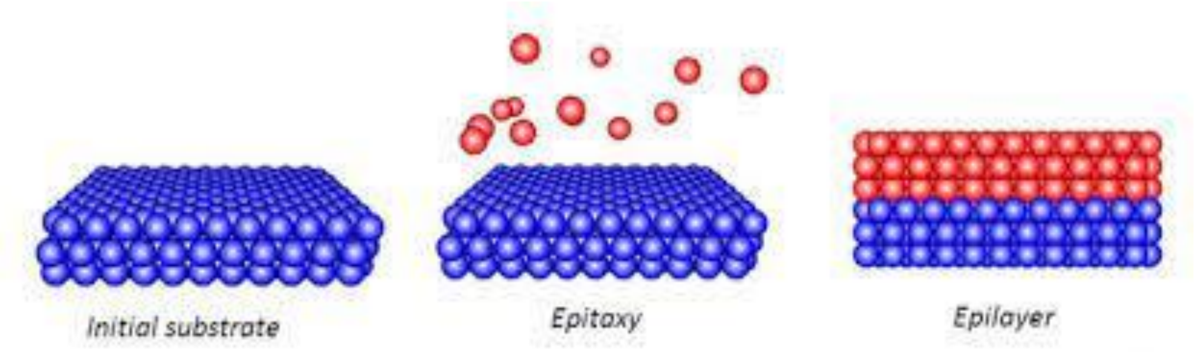
Epitaxy

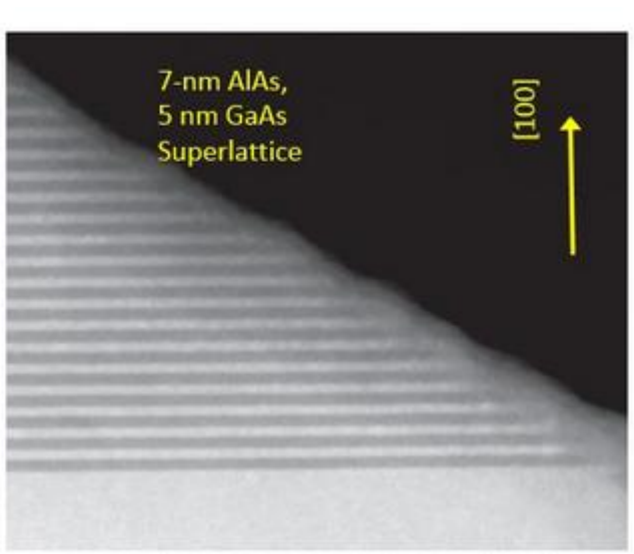
The word ***epitaxy*** derives from the **Greek prefix**

epi meaning “upon” or “over”

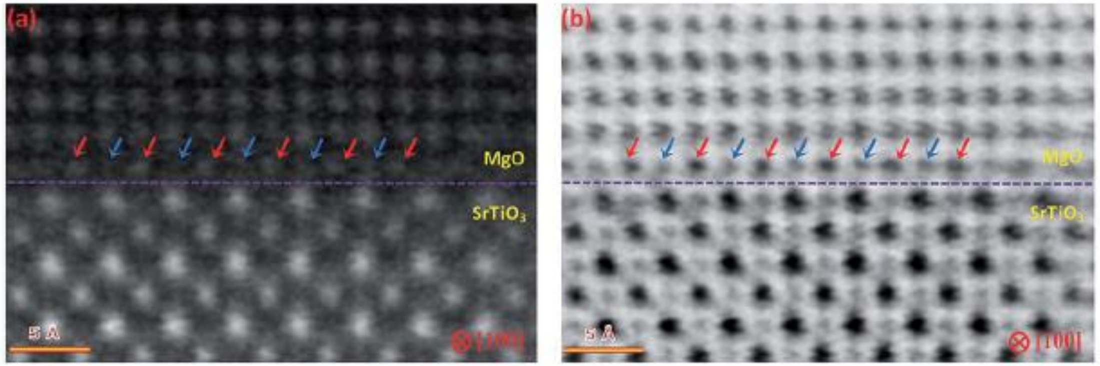
taxis meaning “arrangement” or “order”

Refers to the growth of a material with a highly ordered atomic arrangement (thin films, nanostructures, 2D materials, inorganic or organic materials) on top of another one (crystalline, amorphous material)

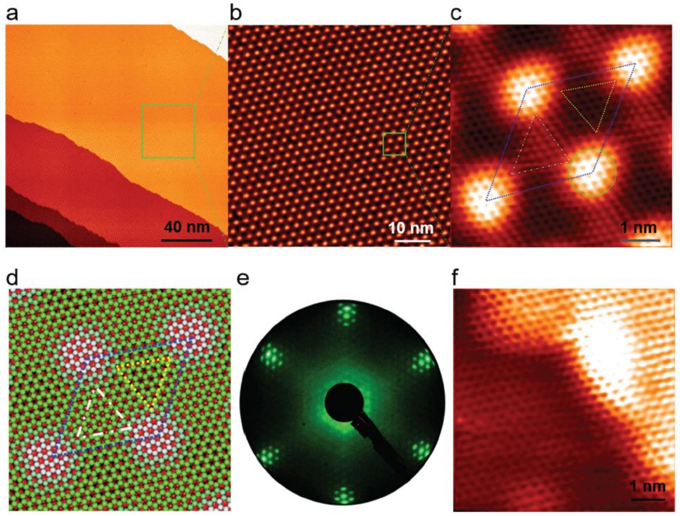




MBE of AlAs/GaAs superlattice [1]



(a) HAADF and (b) ABF STEM image of the MgO/STO heterointerface [2]



Epitaxially-grown wafer-size graphene on a Ru(0001) surface [3]

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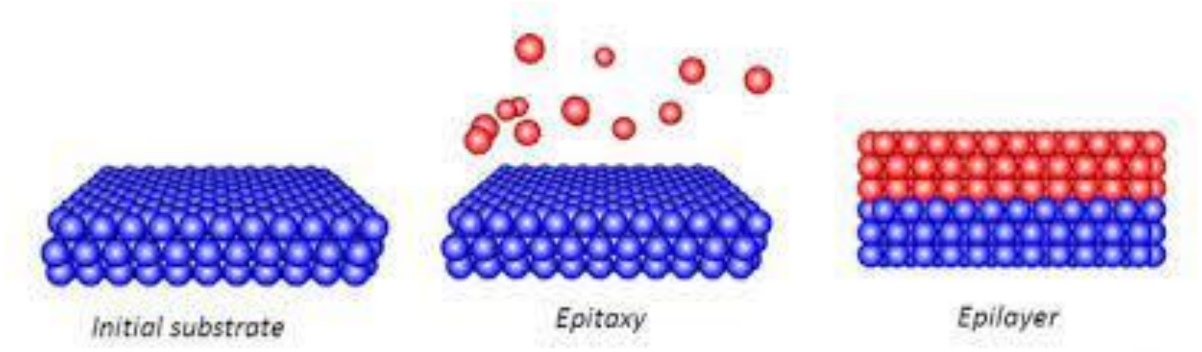

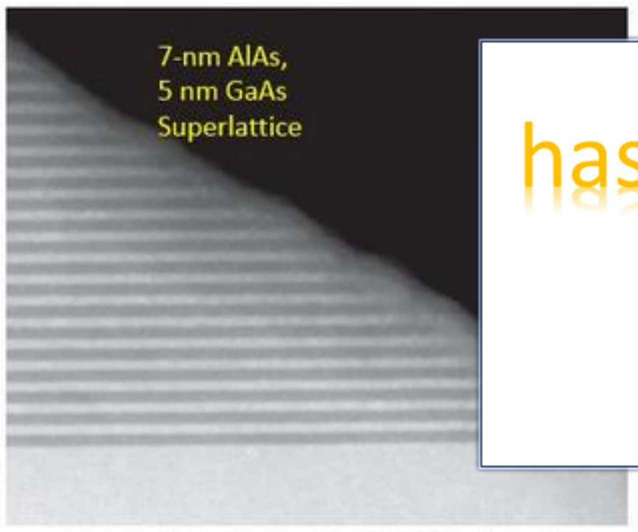

has always been a driver of innovation

having a direct impact on the social, economic, environmental and technological transformations of human activities

(a) HAADF and (b) ABF STEM image of the MgO/STO heterointerface [2]

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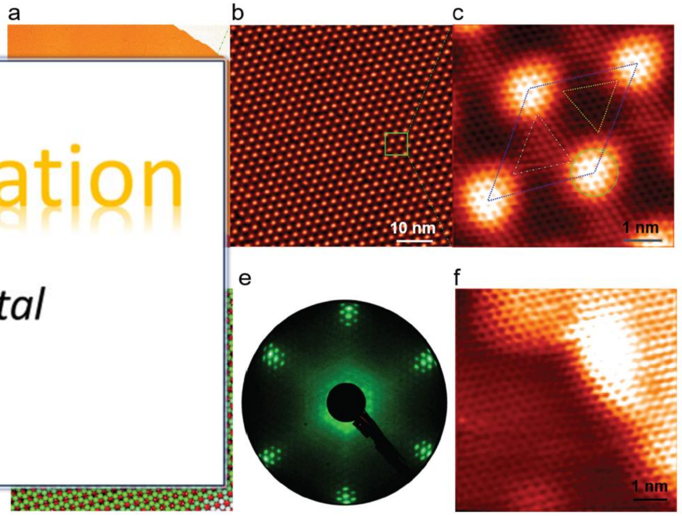


Epitaxially-grown wafer-size graphene on a Ru(0001) surface [3]

Epitaxy – A little history

[4] CHM Computer History Museum

"In 1951 Gordon Teal and Howard Christensen at Bell Labs developed a process, now called epitaxial deposition, to grow a thin layer of material on a substrate that continues the underlying crystalline structure. Sheftal', Kokorish, and Krasilov described similar work on germanium and silicon in the U.S.S.R. in 1957"

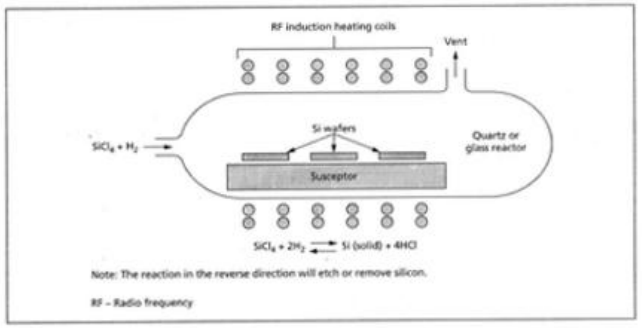
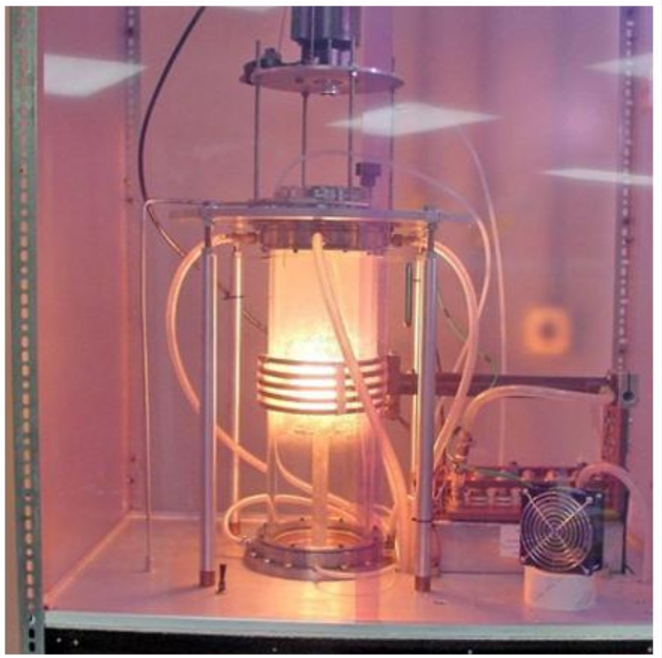
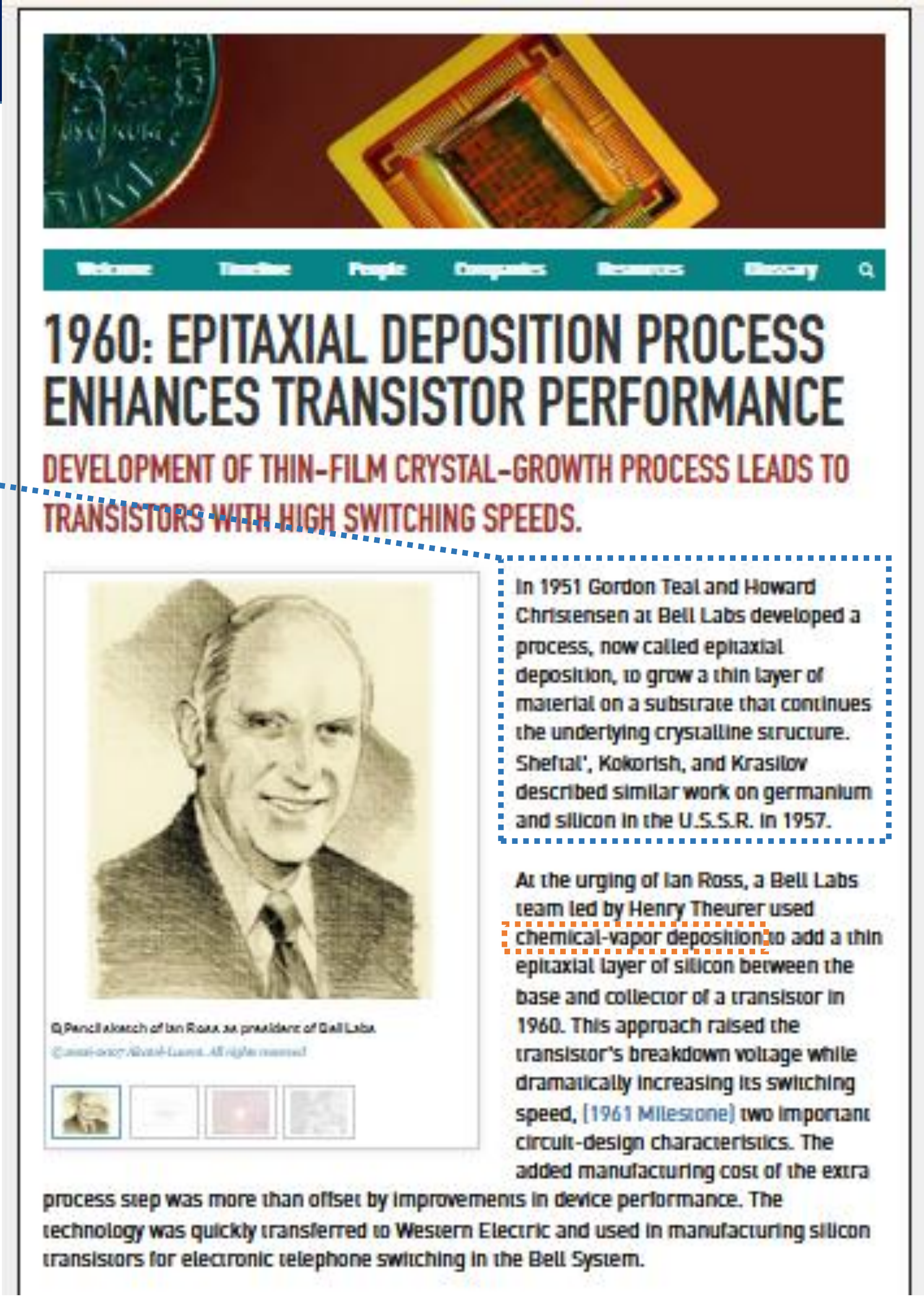


Diagram of a simple epitaxial reactor
© 2006-2007 Alcatel-Lucent. All rights reserved



A research-scale epitaxial reactor in operation
Credit: University of South Carolina



1960: EPITAXIAL DEPOSITION PROCESS ENHANCES TRANSISTOR PERFORMANCE

DEVELOPMENT OF THIN-FILM CRYSTAL-GROWTH PROCESS LEADS TO TRANSISTORS WITH HIGH SWITCHING SPEEDS.

In 1951 Gordon Teal and Howard Christensen at Bell Labs developed a process, now called epitaxial deposition, to grow a thin layer of material on a substrate that continues the underlying crystalline structure. Sheftal', Kokorish, and Krasilov described similar work on germanium and silicon in the U.S.S.R. in 1957.

At the urging of Ian Ross, a Bell Labs team led by Henry Theurer used chemical-vapor deposition to add a thin epitaxial layer of silicon between the base and collector of a transistor in 1960. This approach raised the transistor's breakdown voltage while dramatically increasing its switching speed, [1961 Milestone] two important circuit-design characteristics. The added manufacturing cost of the extra process step was more than offset by improvements in device performance. The technology was quickly transferred to Western Electric and used in manufacturing silicon transistors for electronic telephone switching in the Bell System.

Pencil sketch of Ian Ross as president of Bell Labs
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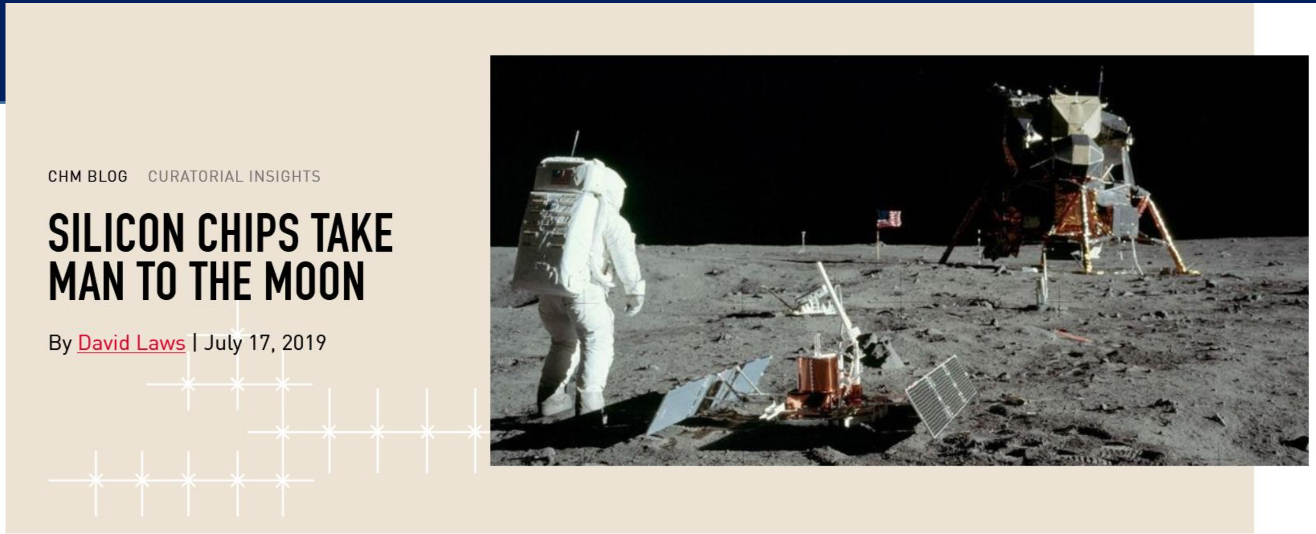
Epitaxy – A little history

[4] CHM Computer History Museum



CHM BLOG CURATORIAL INSIGHTS

SILICON CHIPS TAKE MAN TO THE MOON

By David Laws | July 17, 2019

Micrologic—The First “Planar” Integrated Circuit

Fairchild introduced its first commercial IC, a flip-flop element mounted in a round metal can package, under the trade name Micrologic at a New York press conference in March 1961.

Fairchild's first IC, the “F” element flip-flop compared to a dime coin.
Photo: Getty Images

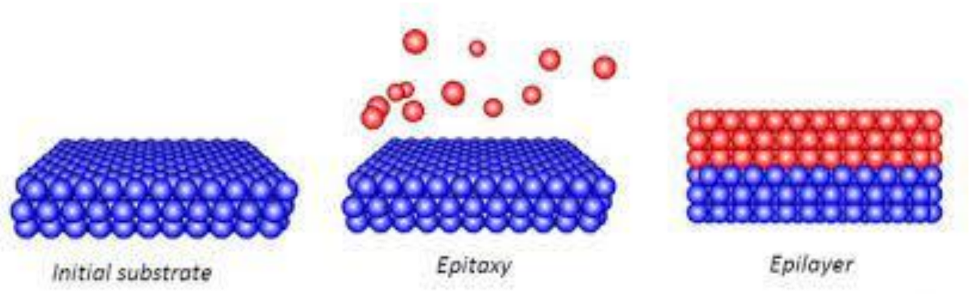
Ed Porter (…) **suggested that they try a new method of growing special silicon layers on the wafer, called epitaxy,** that had recently been developed for transistors. When implemented in production, yields improved by a factor of more than 25 times…

Coupled with advances in manufacturing equipment, the epitaxial process also enabled the design of smaller, faster, and lower power circuits…

Epitaxy – A little history

Epitaxy

Refers to the growth of a material with a highly ordered atomic arrangement (thin films, nanostructures, 2D materials, inorganic or organic materials) on top of another one (crystalline, amorphous material)



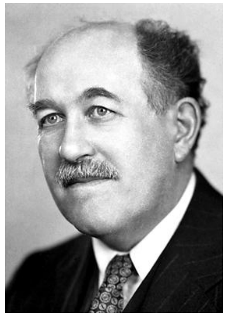
has always been a driver of innovation

having a direct impact on the social, economic, environmental and technological transformations of human activities

The importance of epitaxial structures in materials science can be illustrated by the numerous researchers in this field awarded over the past decades, including Nobel Prize recipients

Epitaxy – A little history

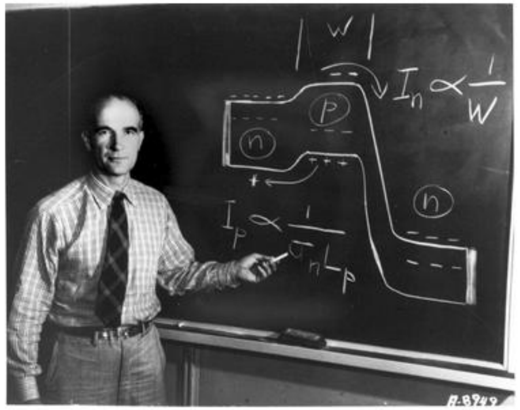
In 1943, epitaxy was highlighted for the first time with the Nobel Prize of



1943, O. Stern *"for his contribution to the development of the molecular ray method"*

In 1956, another milestone was achieved W.Shockley, J.Bardeen and W.H.Brattain, who were awarded by Nobel Prize

1956, W. Shockley, J. Bardeen & W.H. Brattain*, "for their researches on semiconductors and their discovery of the transistor effect"*



Dr. William Shockley joined Bell Telephone Laboratories in 1936. Under Shockley's direction, John Bardeen and William Brattain demonstrated the first semiconductor amplifier: the point-contact transistor. Shockley invented the more robust junction transistor. The three shared the 1956 Nobel Prize in Physics for their inventions. Reprinted with permission of Alcatel-Lucent USA Inc.

➡ ***This is believed to be the starting point of the microelectronics industry in the Silicon Valley.***

Epitaxy – A little history

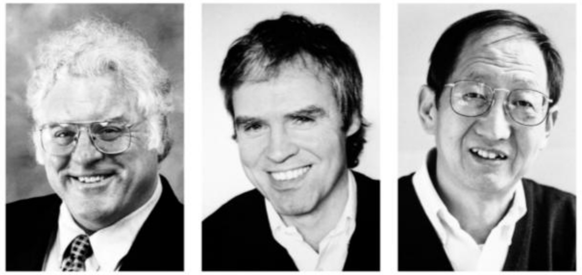
1973, L. Esaki *"for his pioneering work on electron tunneling in solids"*

He took the epitaxial growth to another level, demonstrating the importance of quantum structures that are widely used today in electronics and optoelectronics.

1985, K. V. Klitzing, *"for the discovery of the quantized Hall effect"*

The discovery of the quantum Hall effect (K. V. Klitzing,1985) and its fractional version (L. Störmer, D. Tsui, R. B. Laughlin, 1998) with epitaxial metal-on-semiconductor structures were also awarded the Nobel Prize few years later.

1998, L. Störmer, D. Tsui, & R. B. Laughlin *"for their discovery of a new form of quantum fluid with fractionally charged excitations."*

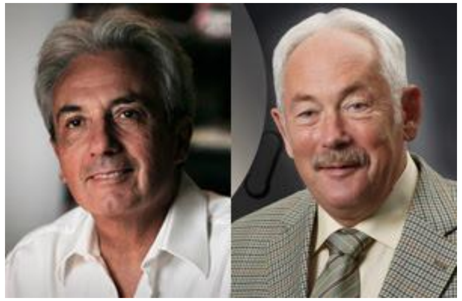


Epitaxy – A little history

The beginning of the 21st century is also marked by Nobel Prizes highlighting the strong impact of epitaxy in research and innovation

Between 2009 and 2014, the Nobel Prize foundation has honored numerous scientists for their **works using epitaxy and has enabled and encouraged applications that are now commonly used**

2000, H. Kroemer & Z. I. Alferov
"for developing semiconductor heterostructures used in high-speed- and opto-electronics"



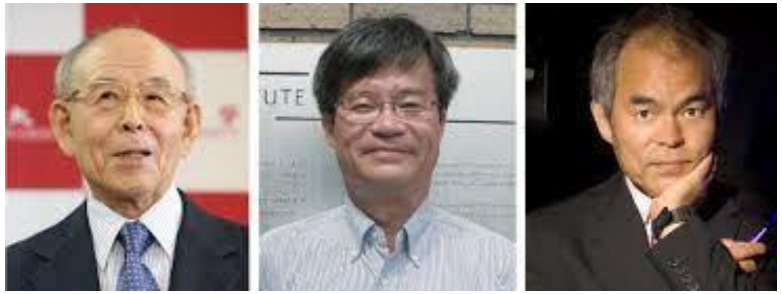
2007, A. Fert and P. Grünberg
"for the discovery of Giant Magnetoresistance."

2009, W.S. Boyle & G. E. Smith
“for the invention of an imaging semiconductor circuit – the CCD sensor“

Epitaxy – A little history

The beginning of the 21st century is also marked by Nobel Prizes highlighting the strong impact of epitaxy in research and innovation

2014, I. Akasaki, H. Amano & S. Nakamura *“for the invention of efficient blue light-emitting diodes which has enabled bright and energy-saving white light sources"*



Why It Was Almost Impossible to Make the Blue LED

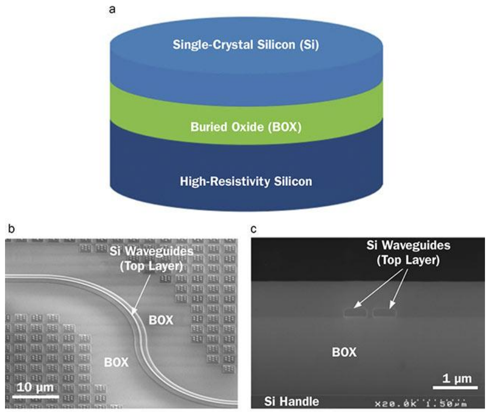
More recently, the theoretical discovery of topological insulators (F. Duncan, M. Haldane and J. M. Kosterlitz, Nobel Prize 2016) has been demonstrated experimentally for the first time with epitaxial layers of HgTe in 2007 and BiSe

2016, F. Duncan, M. Haldane & J. M. Kosterlitz,
“for theoretical discoveries of topological phase transitions and topological phases of matter”

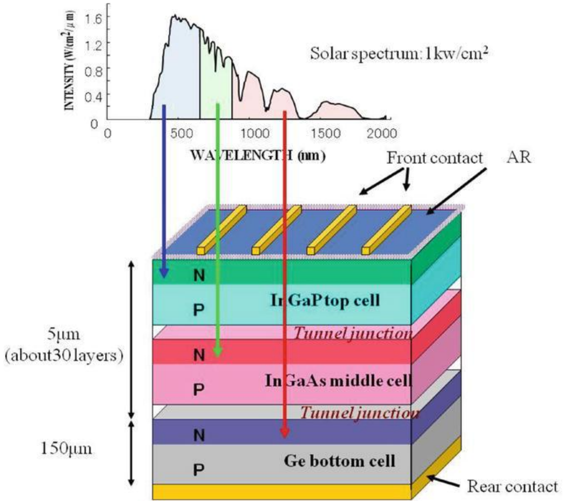
Epitaxy – Towards applications

“Conventional” semiconductors, the first grown, represent the most prominent used materials in applications of epitaxy

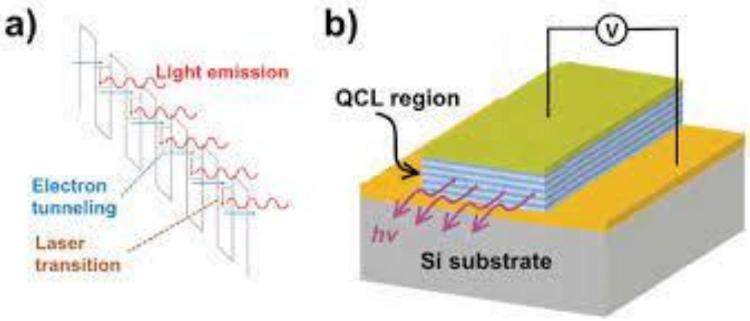
High potential in terms of innovation



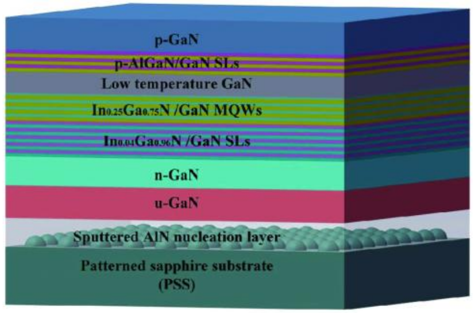
SOI Technology Lights Up the Next Wave of Photonics Solutions [10]



High-Efficiency GaAs-Based Solar Cells [9]



Quantum Cascade Laser [5-7]



Green light-emitting diode (LED) epitaxial structure [8]

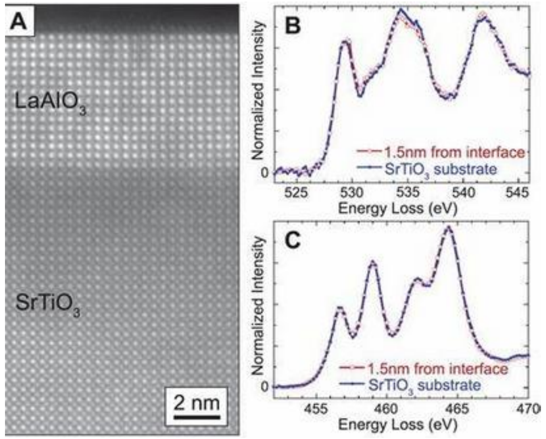
Although epitaxial 2D-layers based on silicon and III-V semiconductors have largely demonstrated their potential in terms of innovation, continuous efforts in the development of epitaxy have realized new breakthroughs opening the way towards more efficient, low cost and/or more eco-friendly devices.

Epitaxy – Towards applications

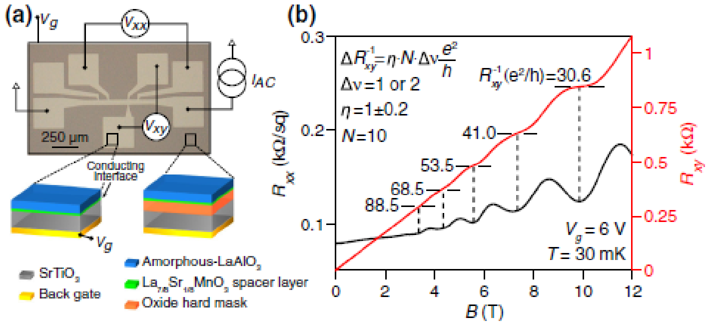
The past two decades have also seen an impressive boom and development of a wide range of novel epitaxial materials, combinations and forms of materials

Functional oxides include a wide diversity of material systems ranging from simple binary materials to complex oxide heterostructures

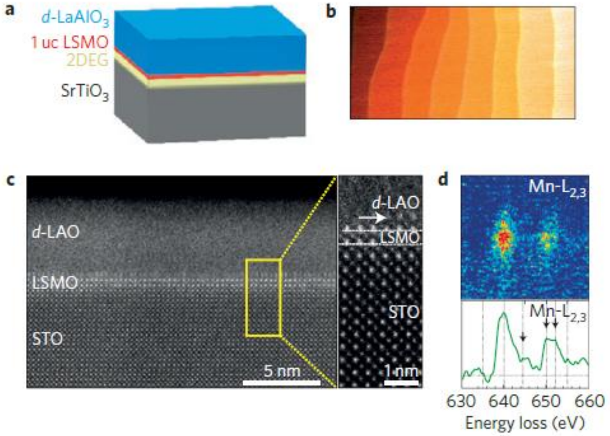
Their large variety of properties offers a step change across a multitude of applications spanning from electronic devices to energy applications [11-12]



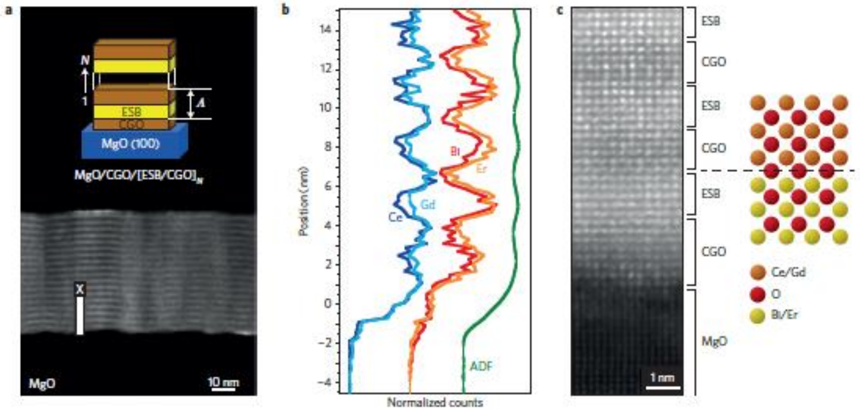
Superconductivity [16]



Observation of the quantum Hall effect [15]



2D electron gas [13] with high mobilities [14]



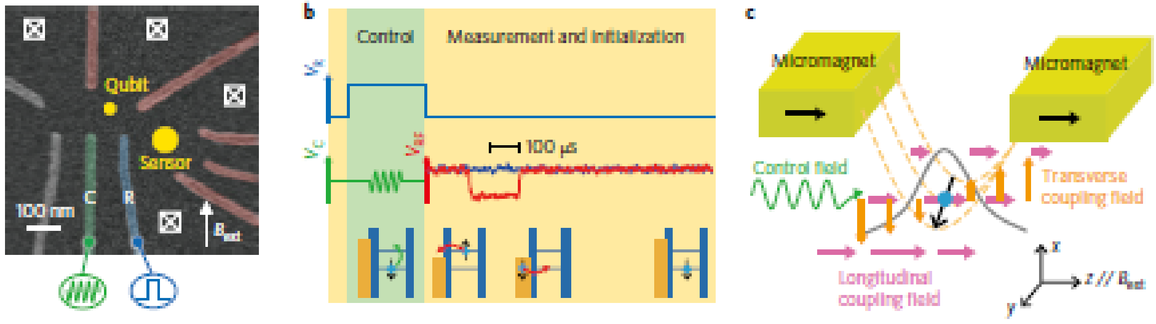
Energy [17]

Epitaxy – Towards applications

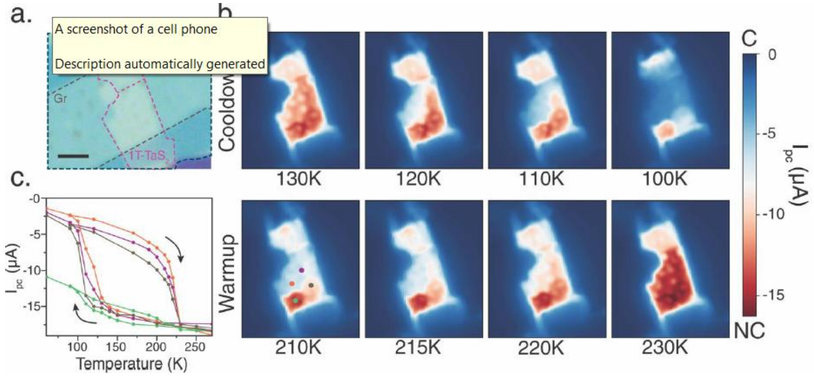
The past two decades have also seen an impressive boom and development of a wide range of novel epitaxial materials, combinations and forms of materials

2D-materials have unambiguously demonstrated their high potential for the observation of novel quantum phenomena such as in electronics and photonics [28]

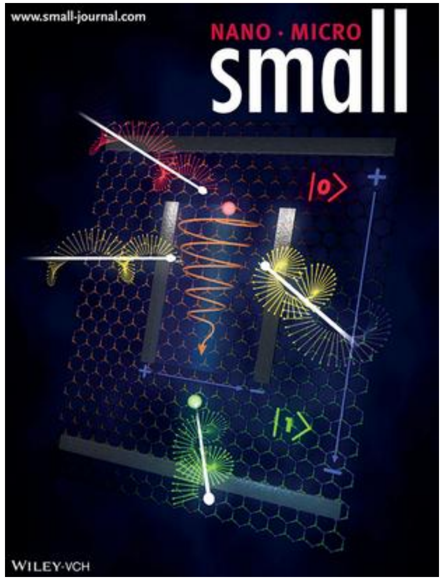
Recent works on graphene- and beyond-graphene-materials have established their large capacity for applications in various domains



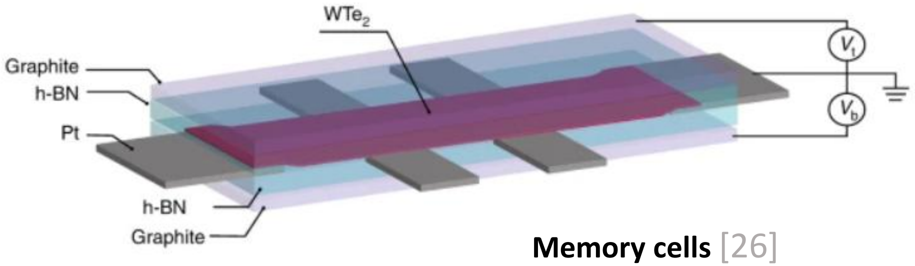
Transistors [18-19]



Photodetectors [20-21]



Valleytronics [27]



Memory cells [26]

Batteries [22]
Transparent electrodes [23]
Energy storage [24-25]

Epitaxy – Towards applications

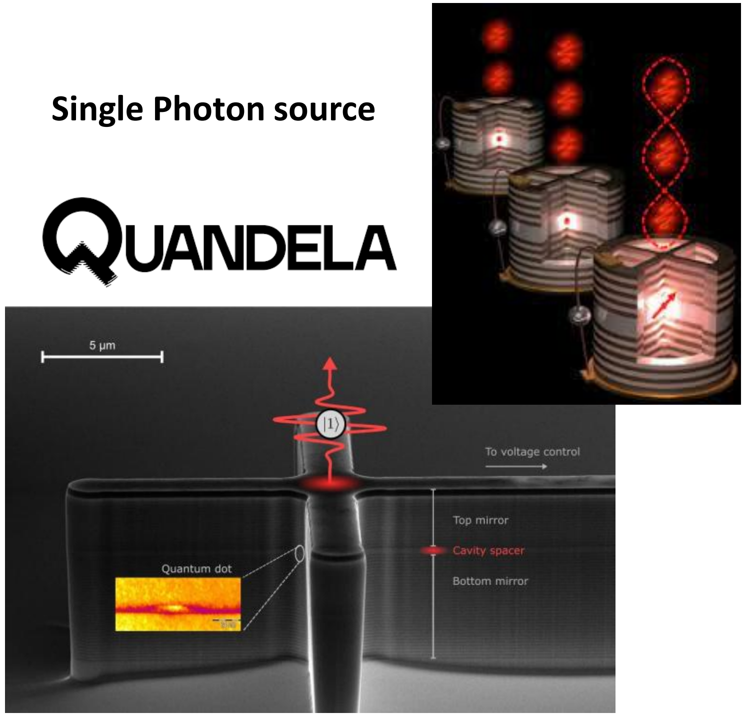
The past two decades have also seen an impressive boom and development of a wide range of novel epitaxial materials, combinations and forms of materials

Nanostructuring the material with at least sub-100 nm in one of the dimensions (quantum dots, 1D-nanostructures) offers unique properties in comparison with their bulk and thin film counterparts

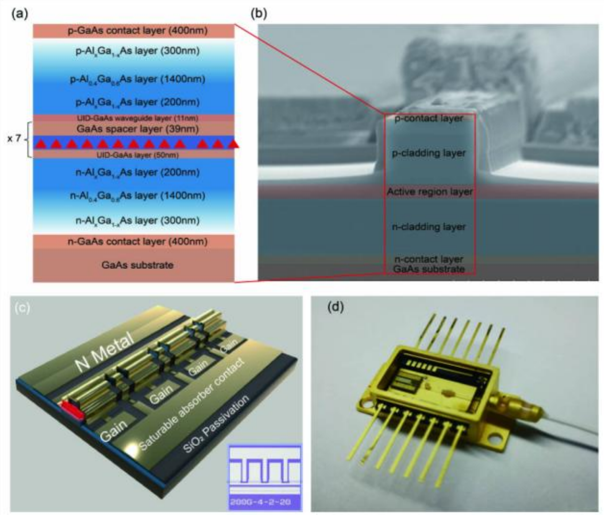
Engineering materials at the nanoscale is of great interest for a wide range of applications

Single Photon source

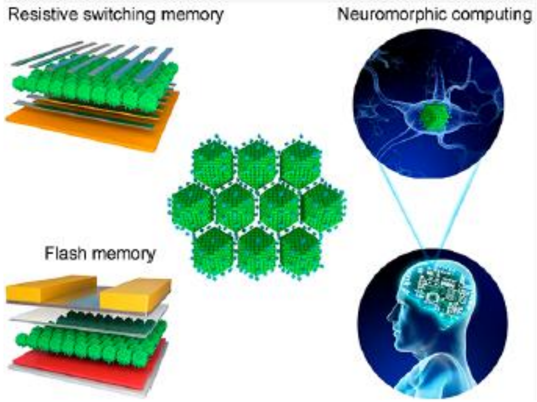
QUANDELA



pulse mode-locked laser for high-power optical comb generation



Intracellular recording



Semiconductor Quantum Dots for Memories and Neuromorphic Computing Systems [35]

Epitaxy – Towards applications

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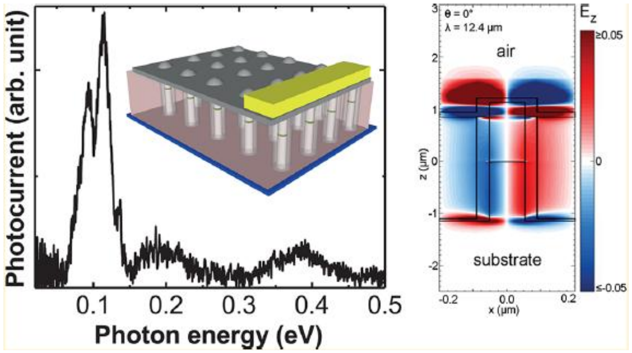
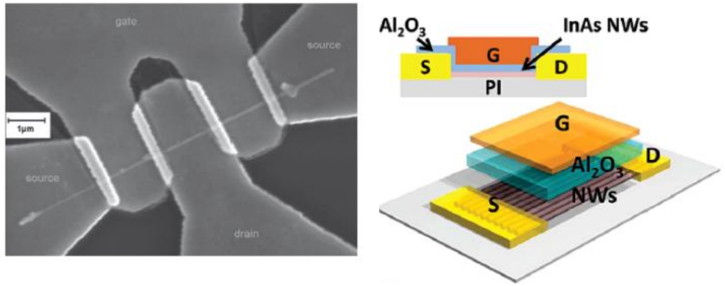
Photodetectors



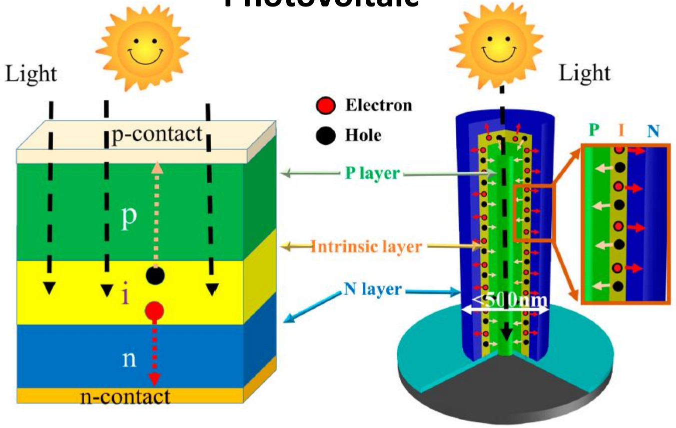
Intersubband Quantum Disc-in-Nanowire Photodetectors [32]

Electronics

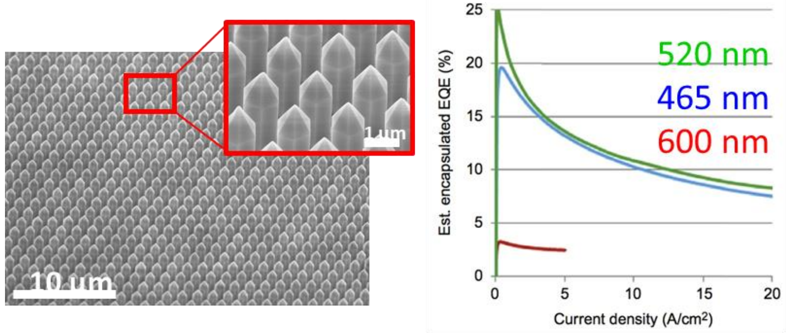


Lateral single nanowire InAs MOSFET & InAs nanowire FET [29]

Photovoltaic



Nanowires for High-Efficiency, Low-Cost Solar Photovoltaics [34]



LEDs

InGaN nano-sized LEDs [33]

Why epitaxy ?

What do all these applications have in common?

Epitaxy

Epitaxial materials are the basis for device innovation

Motivations

- Epitaxial growth is useful for applications that place stringent demands on a deposited layer:
  - * High purity
  - * Low defect density
  - * Abrupt interfaces
  - * Controlled material thickness and carrier concentration
  - * Controlled doping profiles
  - * Possibility to grow p-n junction & other multilayer structures

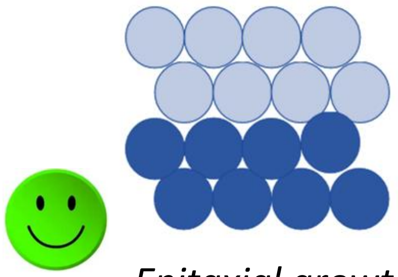
  - * High repeatability and uniformity
  - * Safe, efficient operation

Better
structural, optical, electrical… properties

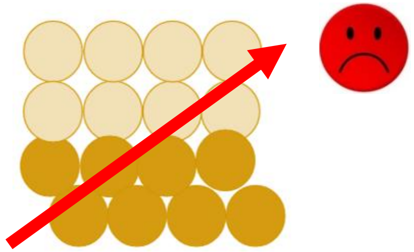
- Can create clean, fresh surface for device fabrication

Epitaxy Fundamentals – few words !

Epitaxial Growth: Deposition of a layer on substrate, a layer which matches the crystalline order of the substrate



Epitaxial growth



Ordered crystalline growth
No epitaxial growth

Massachusetts
Institute of
Technology

A common modern definition for epitaxy is "a single crystal layer that grows with a particular orientation determined by a single crystal substrate"

This definition does not require the film and substrate to be lattice matched, but they must still be similar enough to interact and have a defined relationship

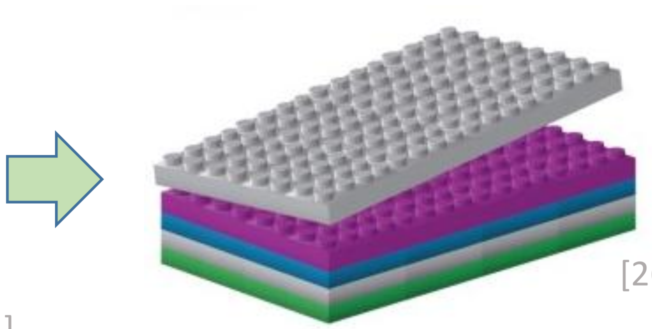
A literal definition of epitaxy would be "Any film which resembles a single crystal in its lattice structure and properties"

This definition lessens the importance of the relationship between the film and substrate. This definition would consider a single crystal layer grown on a glass (amorphous) substrate to still be epitaxial, whereas other definitions would not.

Epitaxy Fundamentals – few words !

Which epitaxial technique?

[25]



[26]

When selecting an epitaxial growth technology for a particular material system and/or device application, the choice needs to take into account:

- ✓ The basic principles of thermodynamics,
- ✓ Kinetics,
- ✓ Surface energies

…

As well as practical issues of:

- ✓ Reproducibility,
- ✓ Scalability,
- ✓ Process control,
- ✓ Instrumentation,
- ✓ Safety and capital equipment costs.

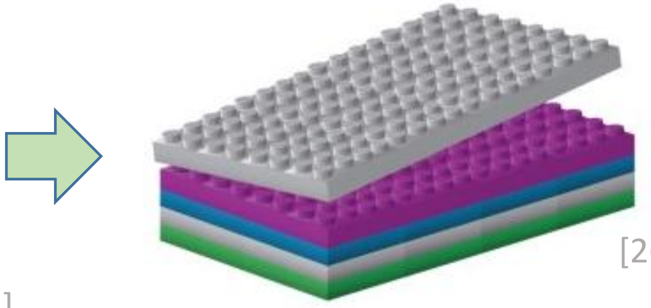
A systematic comparison of the various epitaxy techniques suggests that no single technique can satisfy the needs of all of the material/device combinations needed in

Microelectronics, Optoelectronics, Solar cells, Thermophotovoltaics, Thermoelectrics, Semiconductor electrochemical devices, Magnetic devices, Microelectromechanical systems…

Epitaxy Fundamentals – few words !

Which epitaxial technique?

[25]



[26]

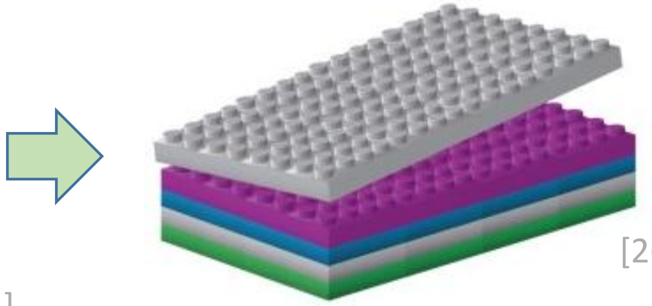
Several epitaxial techniques are used for the growth of epilayers of III-V, II-VI compound semiconductors, but also now for Oxyde and 2D-materials.

- Liquid Phase Epitaxy (LPE),
- Molecular Beam Epitaxy (MBE) and the hybrid systems
- Vapor Phase Epitaxy (VPE) and the related techniques
- Pulsed laser deposition (PLD)
- Atomic Layer Depostion (ALD)
- …

Epitaxy Fundamentals – few words !

Which epitaxial technique?

[25]



[26]

Several epitaxial techniques have been used for the growth of epilayers of III-V, II-VI **compound semiconductors**, Oxyde and 2D-materials.

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- **Vapor Phase Epitaxy (VPE) and the related techniques**
- Pulsed laser deposition (PLD)
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- …

Liquid-Phase Epitaxy (LPE)

Liquid-Phase Epitaxy (LPE)

Some history !

The first LPE systems has been developed by H. Nelson in 1963 [27]
for producing multilayer compound semiconducting structures

Since its invention, LPE has proved to be a versatile, flexible method to grow thin layers of III-V, II-VI and IV-VI compounds for material investigations and device applications.

Si, Ge, SiGe alloys, SiC, GaAs, InP, GaP, GaSb, InAs, InSb (and their ternary and quaternary alloys), GaN, ZnSe, CdHgTe, HgZnTe and HgMnTe.

Many "firsts" of electronic and optoelectronic devices were based on LPE structures.

A large technology base was established

Two important examples are:

- ✓ The GaAs/GaAlAs double-heterostructure (DH) laser diode continuous-wave lasing at room temperature [29-30].
- ✓ The continuous-wave operation of DH lasers emitting at wavelengths beyond I µm, realized in the systems InP/InGaAsP [31], GaAsSb/GaAlAsSb [32] and GaSb/GaAlAsSb [33], was first successfully achieved with LPE material.

- ➢ III–V compound semiconductor lasers [34], LEDs [35], photodiodes and solar cells [36]
- ➢ High-temperature superconductors
- ➢ Garnets, para and ferroelectrics
- ➢ Various other crystals for optics and magnetics

Liquid-Phase Epitaxy (LPE)

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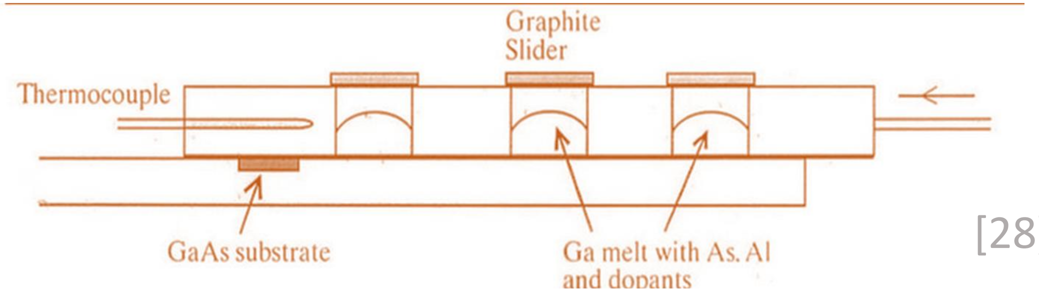
Many "firsts" of electronic and optoelectronic devices were based on LPE structures.

A large technology base was established

While, LPE does not appear in the research literature as often as MOVPE, MBE and ALE in reference to work in these systems …

… It is still used extensively in industrial applications, including III–V LEDs, particularly those based on AlGaAs and GaP alloys, where it is ideally suited to the small die areas, the high luminescence efficiencies and the relatively simple device structures needed

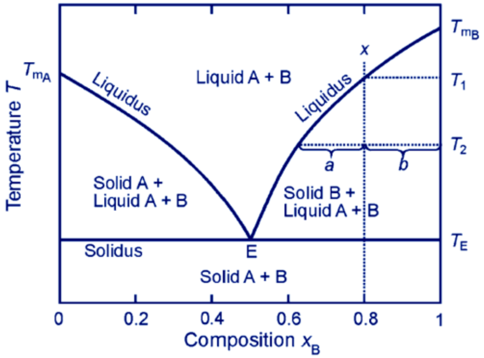
Liquid-Phase Epitaxy (LPE)



[28]

LPE is basically a high-temperature technique to grow crystal layers from a super-saturated melt (containing desired elements) onto suitable substrate.

The basis requirement is to bring the substrate and growth solution into contact while the epitaxial layers grows, and then to separate them cleanly at the end of the growth cycle.



LPE is characterized as a near-equilibrium growth process

(compare to the various vapor-phase epitaxy techniques)

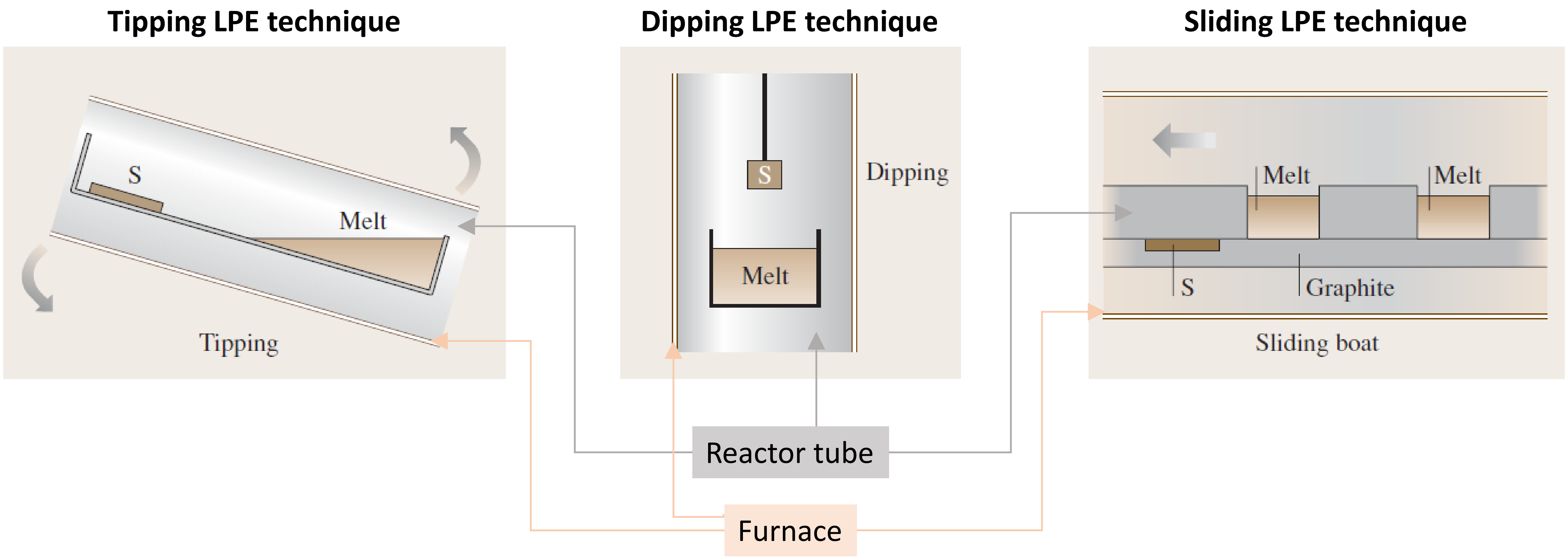
- ✓ In this technique, super-saturation necessary for deposition is achieved by reducing the temperature.
- ✓ The relationship between the temperature and solubility as predicted by the phase diagram has to be utilized in understanding the growth process.
- ✓ Besides thermodynamic consideration, there are other factors such as diffusion of constituents in the solution, nucleation and the mechanism of growth at the surface and convection as the result of temperature and compositional gradients that affect the LPE process

compare to the various vapor-phase epitaxy techniques, heat and mass transport, surface energies, interface kinetics and growth mechanisms are characteristics in LPE

Liquid-Phase Epitaxy (LPE)

3 main configurations of the LPE system

[37]



Tipping LPE technique

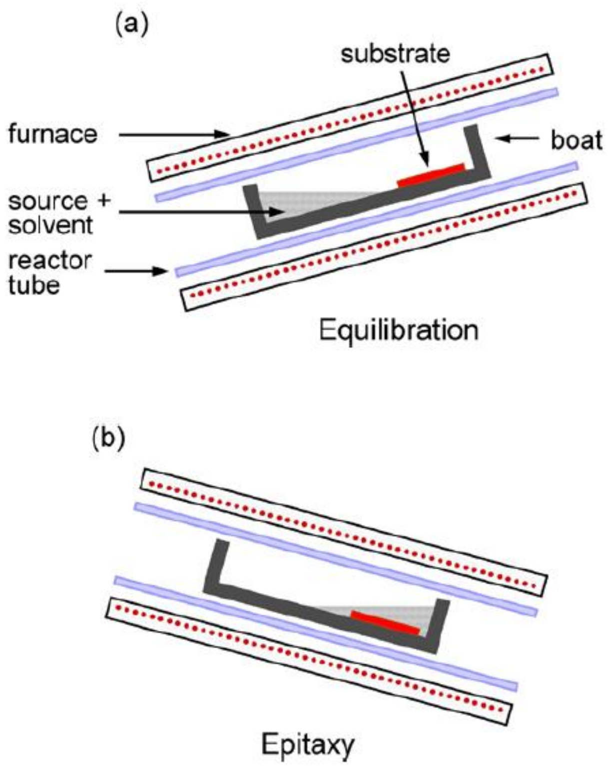
Dipping LPE technique

Sliding LPE technique

- The fused silica tube is usually within a heat pipe thermal liner in the furnace to ensure uniform temperature.
- Growth is usually carried out in an atmosphere of hydrogen.

[37-38]

Tipping LPE technique



In the tipping technique, a tipping furnace is used.

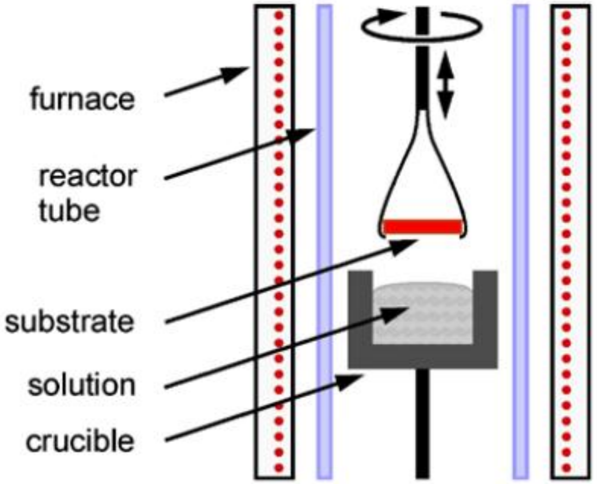
The substrate is held at the upper end of a graphite boat and the growth solution (heated to form solution) is placed at the other end. The ensemble in placed inside a reactor tube.

By tipping the substrate, the solution is brought into contact with the substrate, which is initially well clear of the solution.

The temperature is then slowly reduced and an epitaxial layer is grown on the substrate. The solution remains in contact with the substrate for the defined temperature interval and growth is terminated by tipping the furnace back to its original position.

[37-38]

Dipping LPE technique



In the dipping technique, a vertical furnace is used.

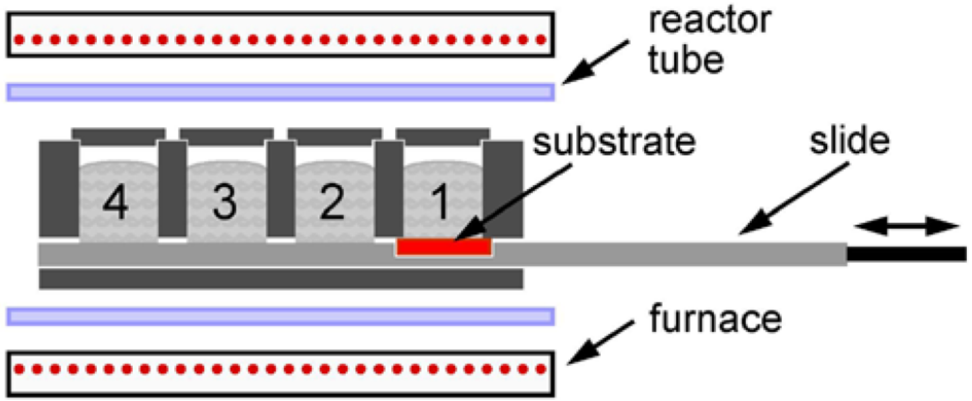
The solution is contained in a graphite or alumina crucible at the lower end of the furnace. The substrate, fixed in a movable holder is initially positioned above the solution.

At the desired temperature, growth is initiated by immersing the substrate in the solution and it is terminated by withdrawal of the substrate from the solution.

☹ Note that Tipping and Dipping techniques are relatively simple and cheap techniques, but they present the limitation to be only suitable for single-layer growth.

Sliding LPE technique

[37-38]



In the sliding technique, a horizontal furnace is used. The reactor tube contains a graphite boat with a graphite slider.

This technique has turned out to be the most popular and versatile of the three main methods. Multilayer growth is easily possible using this sliding-boat method.

The graphite barrel has the desired number of solution chambers depending on the number of layers to be grown. By motion of the barrel over the slider, the substrate is brought into contact with a solution to grow the desired layer.

This operation can easily be automated.

Liquid-Phase Epitaxy (LPE)

Advantages

- **High growth rates**
  These are typically 0.1–10µm/h, i. e. faster than in MOVPE or MBE. This feature is useful when thick layers or "virtual substrates" are required.
- **Favorable segregation of impurities into the liquid phase**.
  → lower residual or background impurities in the epitaxial layer.
- **Ability to produce very flat surfaces and excellent structural perfection**
- **Wide selection of dopants.**
  Most solid or liquid elements can be added to a melt and incorporated in the layer
- **Suppression of certain types of defects**
  In general, LPE material has lower point defects (vacancies, interstitials, antisites) than material made by other techniques.
- **Growth over a wide range of temperatures**
  Once the relevant phase diagram is established
- **Absence of highly toxic precursors or byproducts**

Limitations

- **Control of the layer thickness, alloy composition, doping, interface smoothness**
- **Difficult to grow certain combination of interest for heterostructure devices**
- **Problem of reproducibility**
- **Problem with scaling up size**

Molecular Beam Epitaxy (MBE) … *and related techniques*

Molecular Beam Epitaxy (MBE)

MBE systems has been developed by Alfred Cho and John Arthur at Bell Labs in 1968 and in the 1970s based on an original idea established by K.G. Günther in 1958 [39]

MBE has been and is used to grow a wide range of materials

Semiconductors, superconductors, metals, oxides, nitrides and organic films

There is a drive to produce structures with ever smaller dimensions, whether for higher performance devices, quantum confinement or nanotechnology

MBE is perfectly suitable !
The combination of precise growth control and in situ analysis makes MBE the preeminent technology used to meet such demands.

Al Cho (right) and Charles Radice working on the early MBE system at Bell Labs in 1970
Academia.edu

Important examples in III–V semiconductors :

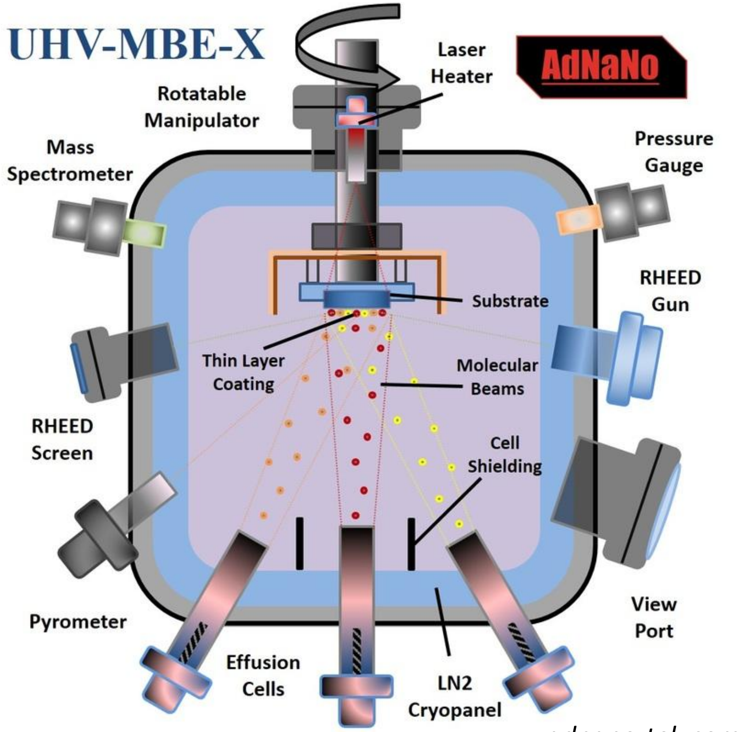
- ✓ The MBE growth of GaAs/AlGaAs superlattice in 1970 [40] and quantum wells (QWs)
- ✓ The MBE growth of quantum nanostructures (quantum wires, quantum dots, nanowires …[41]

Such low-dimensional structures form the basis for optoelectronic and microwave applications.

Molecular Beam Epitaxy (MBE)

MBE is an ultrahigh vacuum (UHV) technique to grow epitaxial thin films from molecular or atomic beams on a heated substrate.

The basis principle of MBE growth consists in atoms or clusters of atoms migrating in an UHV environment and impinge on a hot substrate surface, where they can diffuse and be incorporated to the epitaxial film.



www.adnano-tek.com

Molecular Beam Epitaxy (MBE)

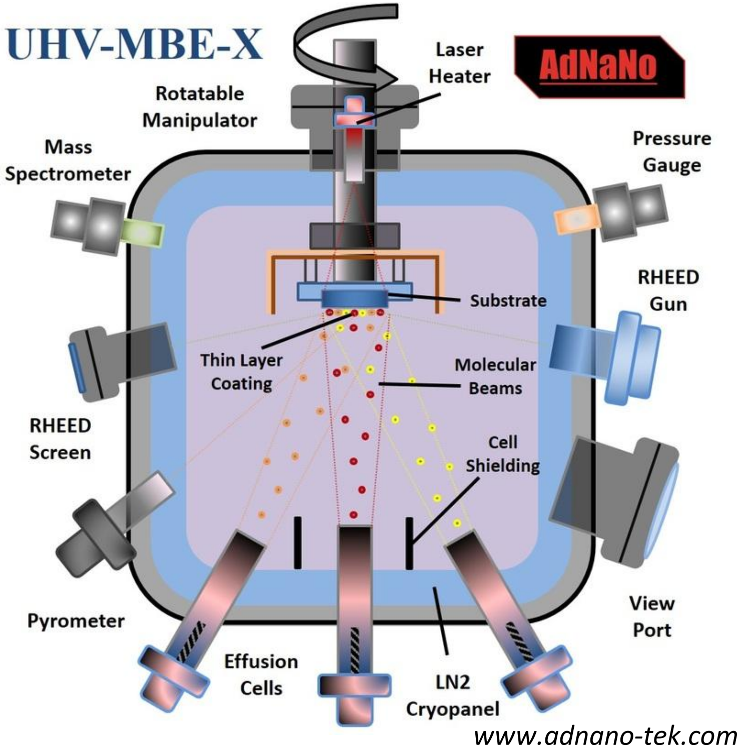
Despite the conceptual simplicity, a great technological effort is required to produce systems that yield the desired quality in terms of material purity, uniformity and interface control.

- The **vacuum system consists in a UHV growth chamber**, connected to a preparation chamber, where substrates are degassed prior to growth, and a load-lock module for transfer to and from air

- **To reduce the pressure and the impurity partial pressures, pumping system** composed of ion pumps, with auxiliary Ti-sublimation, and turbo-pomp or cryogenic pump **is used**, as well as **Liquid N2 cryopanels** surrounding internally both the main chamber wall and the source flange

- **The highly purified beams are thermally generated in Knudsen-type effusion cells**. Their temperatures are accurately controlled to give the thermal beams of appropriate intensity. The beam fluxes are determined by using movable nude ionization gauge placed in the substrate position

- The various cells are all placed and angled in such a way that their **beams converge without ballistics collision on the substrate** for epitaxial growth.



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- The substrate is mounted on a Mo or Ta substrate holder, fixed on the manipulator. The **manipulator** is capable of continuous azimuthal rotation around its axis to **improve wafer uniformity**.

- The heater behind the sample is designed to maximize **temperature uniformity**, which is of the order of several hundreds of degrees (depending of the grown materials and their form)

- The temperature substrate can be measured by a thermocouple in contact with the holder, by pyrometer or BandiT system

Molecular Beam Epitaxy (MBE)

In-Situ layer characterization in MBE system

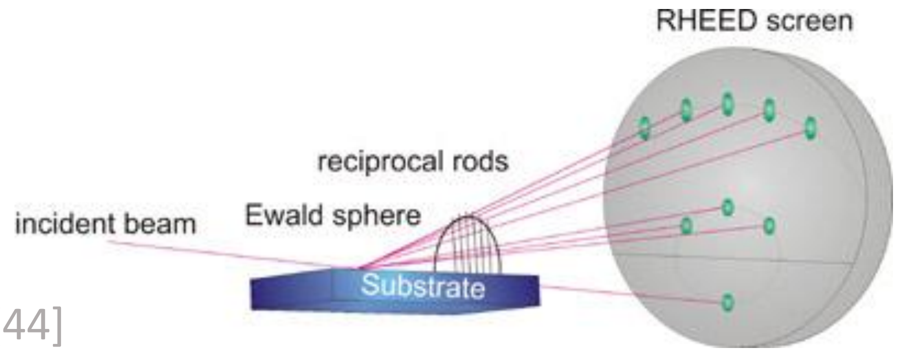
One of the first and most important of the in situ analytical techniques to be used in MBE is

Reflection High-Energy Electron Diffraction (RHEED)

RHEED provides information on surface reconstruction and quantitative measurements of growth dynamics

From an early stage [42] it was used to determine the surface structure of the clean substrate and growing layer.

⇒ **This revealed that, in general, all surfaces are reconstructed**



[44]

RHEED is basically the diffraction of the incident electrons by atoms at the surface of the sample.

A fraction of the diffracted electrons interfere constructively at specific angles and **form regular patterns on the detector**.

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[The Hybrid Molecular Beam Epitaxy Technique for Complex Oxides](https://www.youtube.com/watch?v=nvwNo-VY58Q)
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Molecular Beam Epitaxy (MBE)

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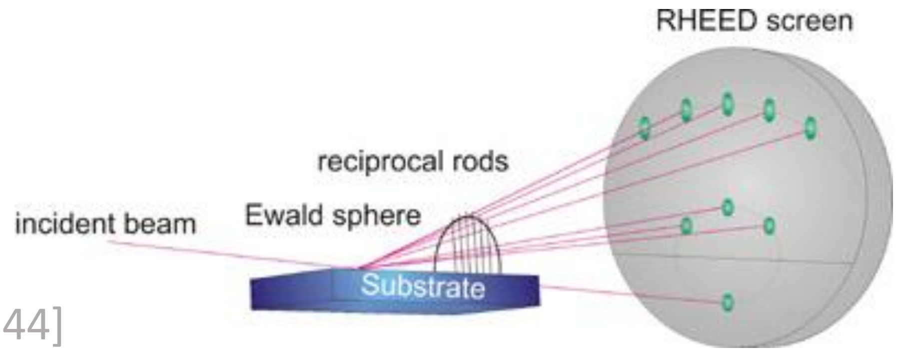

[44]

The electrons interfere according to the position of atoms on the sample surface, so the **diffraction pattern at the detector is a function of the sample surface**.

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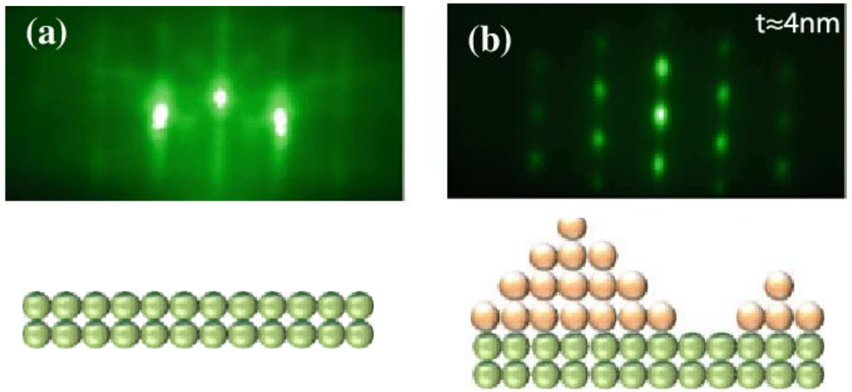

[43]

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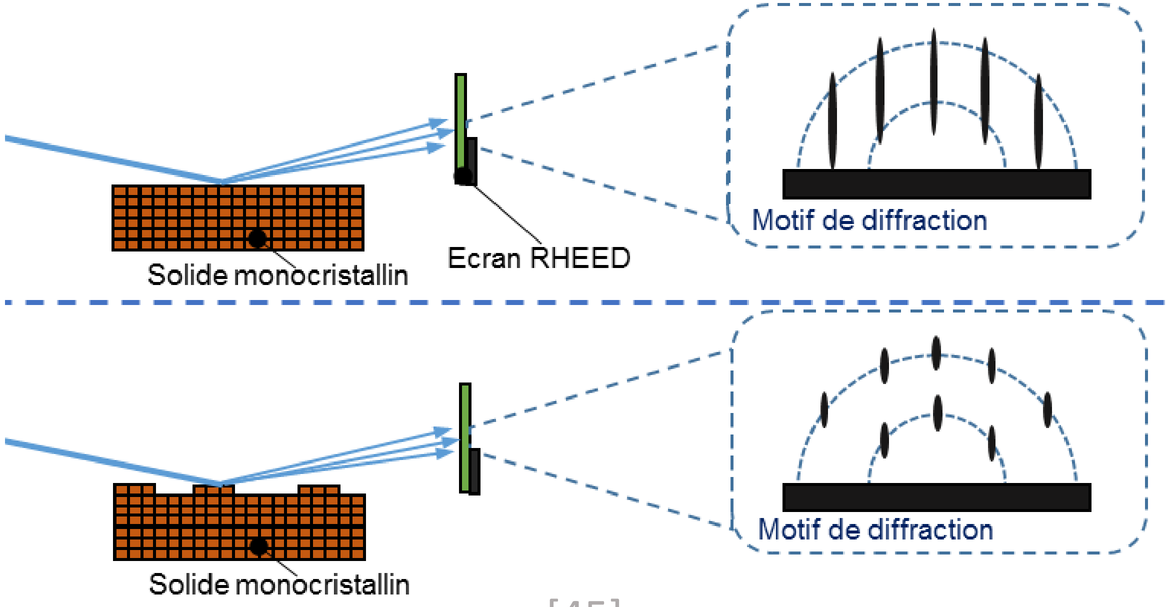
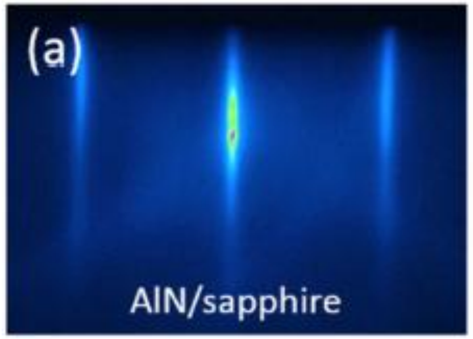
RHEED provides information on surface reconstruction and quantitative measurements of growth dynamics

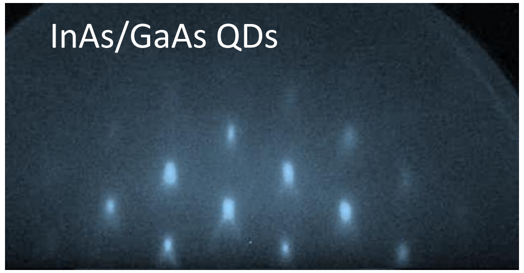
If electrons interact with the first atomic layer of a perfectly flat and ordered surface, the three-dimensional reciprocal lattice points degenerate into parallel infinite rods

If the surface is not flat, electrons will be transmitted through surface asperities and scattered in different directions, resulting in a spotty RHEED pattern



[45]





Molecular Beam Epitaxy (MBE)

Reflection High-Energy Electron Diffraction (RHEED)

RHEED provides information on surface reconstruction and quantitative measurements of growth dynamics

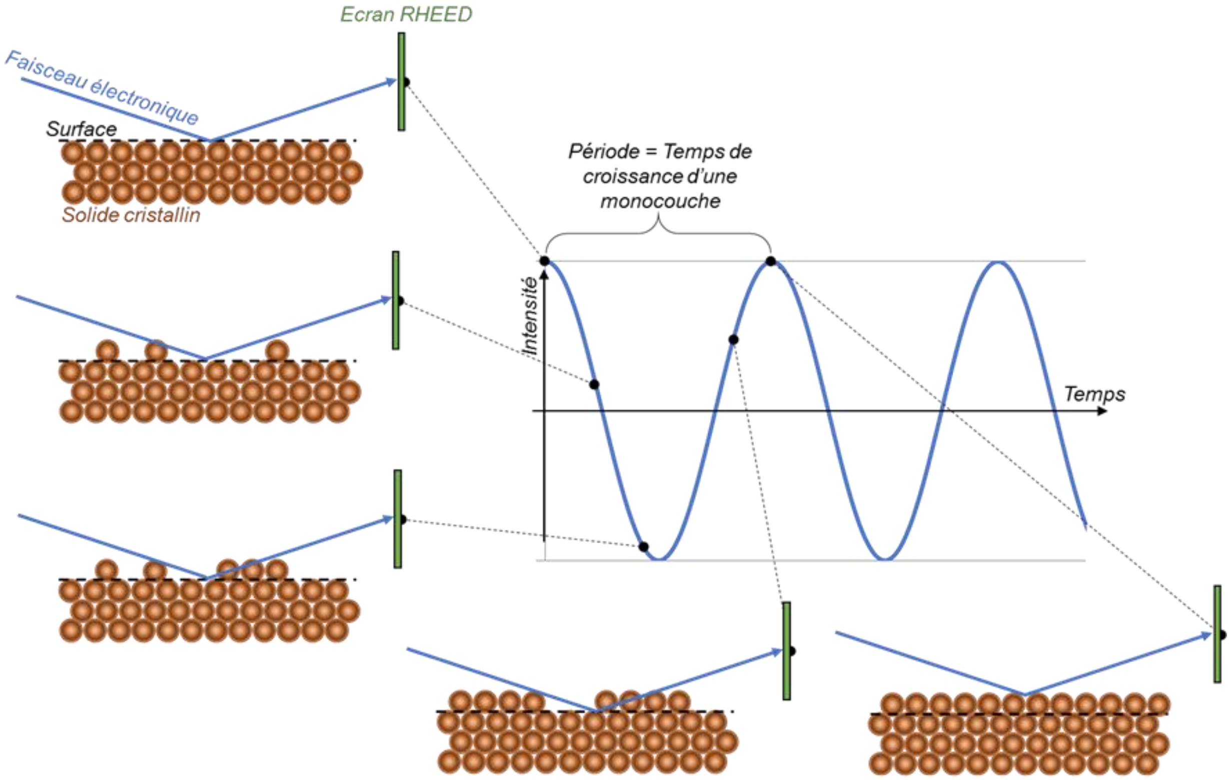
A further application of RHEED is the in situ measurement of growth rate

The principle is based on the monitoring of the specular RHEED spot intensity during the layer-by-layer growth of a 2D film [46-47]. The intensity of any diffraction feature oscillated with a period corresponding to the growth of a single monolayer.

When a ML is completed, the roughness of the surface is reaching a minimum, implying its larger reflectance. Hence, the specular RHEED spot intensity reaches a local maximum.

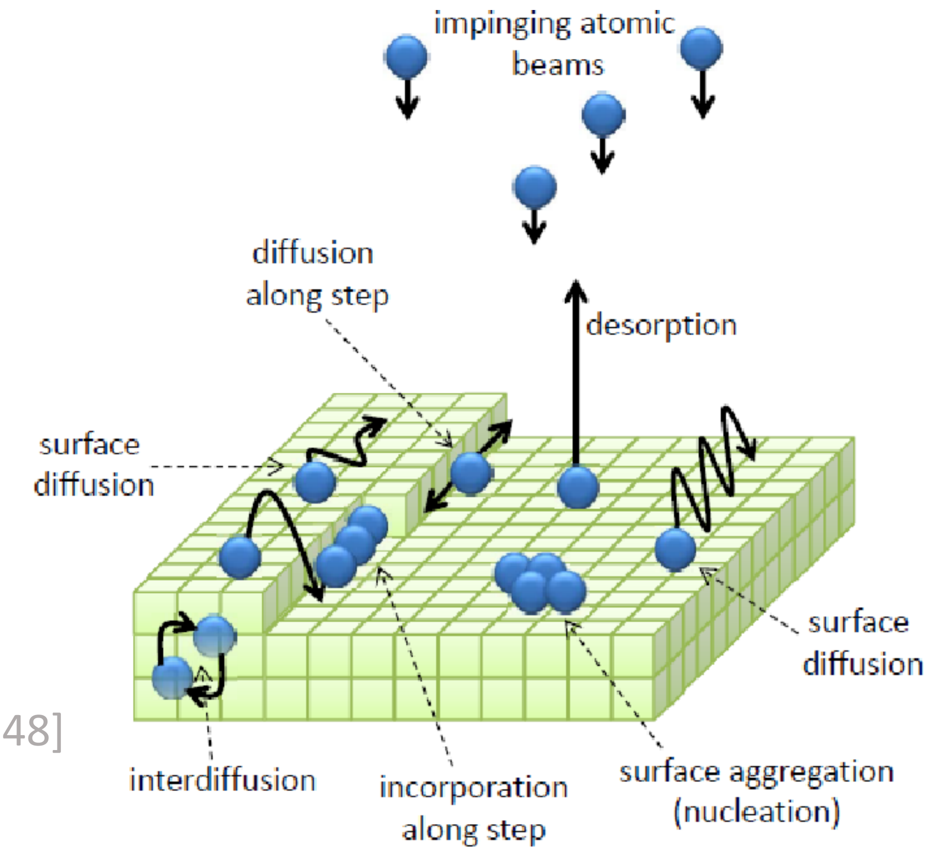
When a ML is half completed, the several islands constituting the uncompleted layer increase the surface roughness, implying a more pronounced scattering of the impinging electrons. This results in a minimum of the specular spot intensity.

Therefore, during one complete RHEED oscillation, one ML has been grown. **By counting the number of oscillations in the unit of time, the effective 2D growth rate can be determined**.



[48]

When beams condense on the clean and heated wafer, they are free to move until finding appropriate position in the crystal lattice to bond

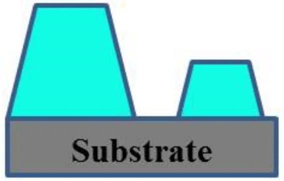


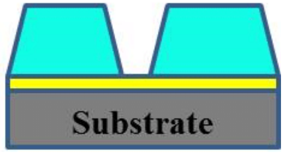
[48]

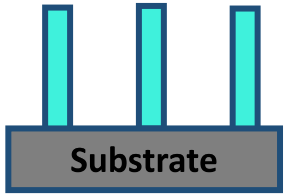
- Atoms arriving at the substrate surface may undergo **absorption** to the surface, **surface migration**, **incorporation** into the crystal lattice, and **thermal desorption.**
- The growth is principally governed by Kinetics
- The competing pathways dominating the growth will depend strongly on the temperature of the substrate:
  - At a low temperature, atoms will stick where they land without arranging properly, leading to poor crystal quality.
  - At a high temperature, atoms will desorb (re-evaporate) from the surface too readily, leading to low growth rates and poor crystal quality.
  - In the appropriate intermediate temperature range, the atoms will have sufficient energy to move to the proper position on the surface and be incorporated into the growing crystal.

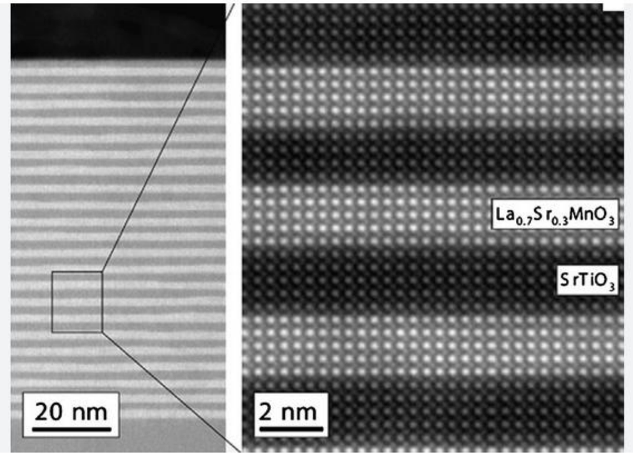
Molecular Beam Epitaxy (MBE)

Link to the material under growing and the underlying layer
Link to the growth parameters

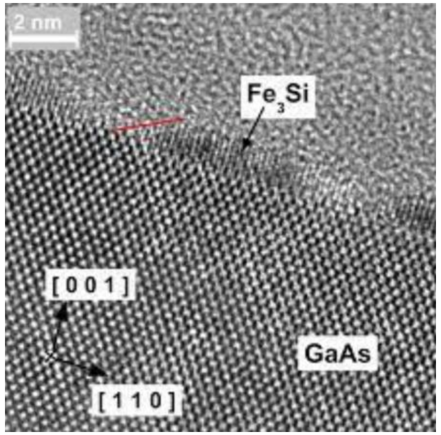




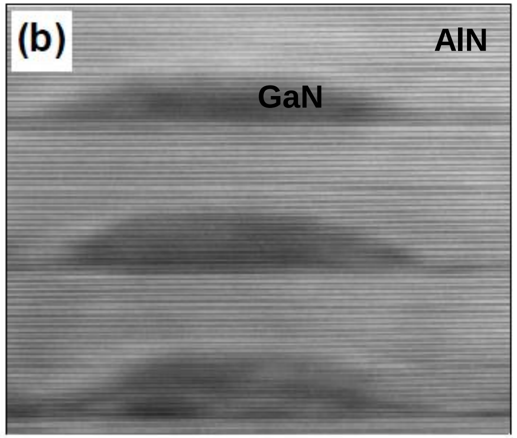




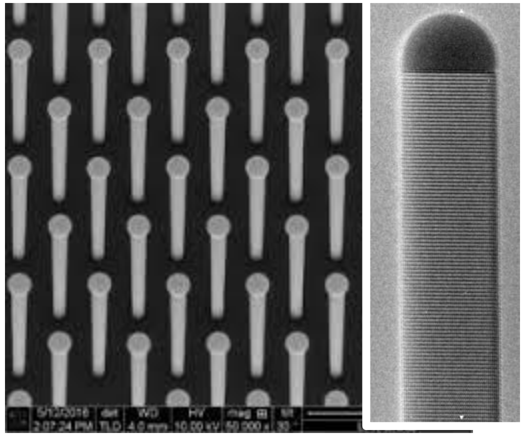
DOI: 10.1016/j.crhy.2016.08.009



Lattice matched Volmer-Weber growth of Fe_3Si on GaAs(001)
https://ar5iv.labs.arxiv.org/html/1907.05076



N. Gogneau et al. @CEA-Grenoble

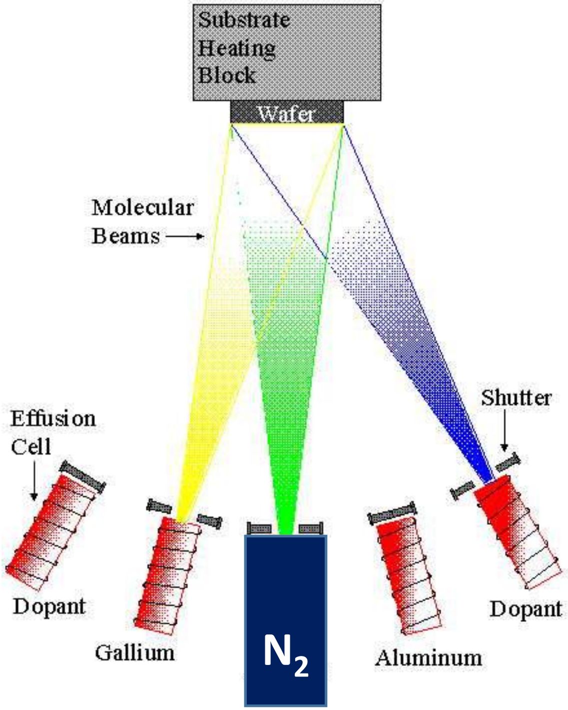


@C2N/Paris-Saclay

Sometime, the growth mode are affected by the configuration of the MBE machine

Molecular Beam Epitaxy (MBE)

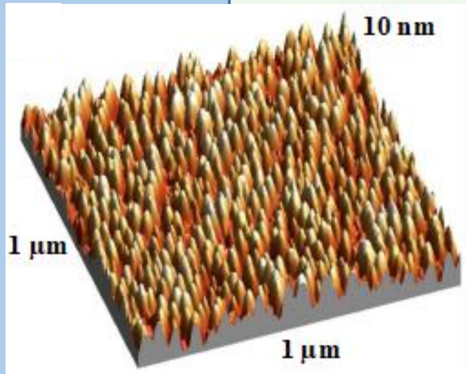
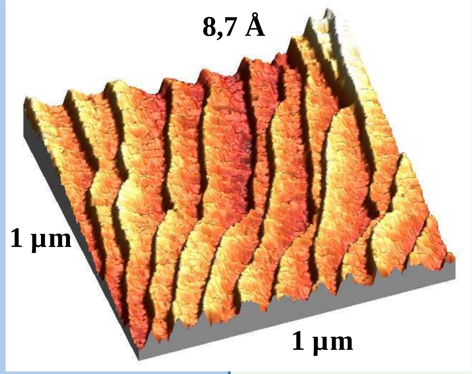
<u>For GaN growth by MBE system</u>, III elements and dopant are contained into effusion cells, while N2 source is different



N_2 Plasma or NH_3 source

GaN grown on AlN layer

Opposite growth mode according to the used N2 source

N_2 Plasma		**NH_3 source**
N-rich conditions		*Ga-rich conditions*
Ga-rich conditions		*N-rich conditions*

Molecular Beam Epitaxy (MBE)

Advantages	Limitations
❖ High-quality (low defect, high uniformity) semiconductor crystals and other materials	❖ Deposition rates require proportionally better vacuum to achieve low impurity levels
❖ Low deposition rate (typically less than 1ML/s or 1µm/h)	❖ Quite slow epitaxial growth technique
❖ Precise control of the thicknesses *Possibility of growing multilayered structures including super-lattices with ML thickness control and abrupt interfaces*	❖ Frequent shutdowns are required to replenish the source materials and opening the UHV apparatus.
❖ Ultimate control over the nanostructure properties such as their size, aspect ratio, doping level	❖ Expensive and complicated systems
❖ In-situ characterization	
❖ Versatile technique for growing elemental and compound semiconductors.	

Molecular Beam Epitaxy (MBE) … and related techniques

A hybrid of MOCVD & MBE that exploited the advantages of both the techniques

Gas source MBE (GSMBE)

The use of cracked arsine and phosphine for the epitaxial growth of GaAs, InP, GaInAsP, has been investigated in first by M. B. Panish in 1980 [51]

The use of cracker cells allow producing controllable fluxes of the dimers As2 and P2, giving improved control of the As:P ratio and thus growing high-quality III-V semiconductors [52]

Metalorganic MBE (MOMBE)

This system uses cracked V-elements & gaseous Group III sources

In 1985, N. Putz has demonstrated the growth of GaAs into a modified commercial system using TMGa and cracked arsine [53]

Chemical Beam Epitaxy (CBE)

The use of alkyl sources of both Group III and Group V elements was demonstrated in 1984 by W.T. Tsang [54] to grow device-quality GaAs, InGaAs and InP from.

The use of Group V alkyls, which had much poorer purity than the hydrides, was undertaken for safety reasons [55]

Material quality was improved when cracked arsine and phosphine were used [56]

Vapor Phase Epitaxy (VPE) … *and related techniques*

Vapor Phase Epitaxy (VPE) and related techniques

Some history !

The technique of MOCVD was first introduced by H.M. Manasevit and W.I. Simpson [57] *in the late 1960s for the deposition of compound semiconductors from the vapor phase*

The near-equilibrium techniques such as LPE were not suitable for nucleation onto a surface chemically very different to the compound being deposited. **The combinations of an alkyl organometallic for the Group III element and a hydride for the Group V element, allow the deposition of films (such as GaAs in 1969) onto a variety of different surfaces**.

In the late of 1960s, the technique of MOCVD was born. **But it wasn't until the late 1980s that MOCVD became a production technique** of any significance. This success depended on the **improvement of the impurity of the organometallic precursors and hydrides**.

Vol. 116, No. 12 J. Electrochem. Soc.: SOLID STATE SCIENCE December 1969

The ingots were polycrystalline because of the severe

during synthesis. Considerably more

for single crystal

2. S. E. Blum and R. J. Chicotka, *ibid.*, **115**, 298 (1968).

3. S. E. Blum, R. J. Chicotka

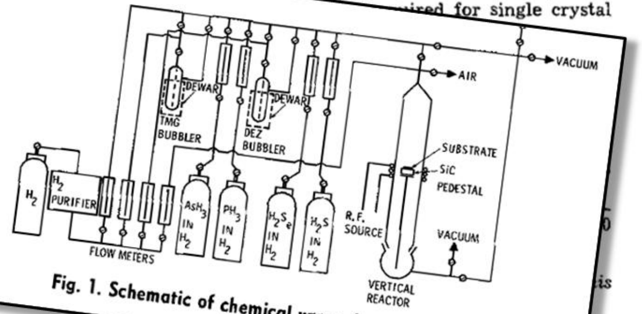


Fig. 1. Schematic of chemical vapor deposition apparatus

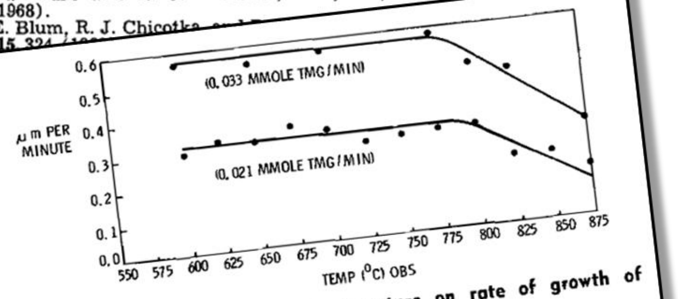


Fig. 10. Effect of substrate temperature on rate of growth of (111) GaAs on (0001) Al_2O_3.

The Use of Metal-Organics in the Preparation of Semiconductor Materials

I. Epitaxial Gallium-V Compounds

H. M. Manasevit and W. I. Simpson

Autonetics Division of North American Rockwell Corporation, Anaheim, California

ABSTRACT

Single-crystal GaAs, GaP, $GaAs_{1-x}P_x$ and $GaAs_{1-x}Sb_x$ films have been grown on GaAs and a number of insulating substrates by the decomposition of alkyl-gallium compounds in the presence of arsine, phosphine, arsine-phosphine, and arsine-stibine mixtures. Both triethylgallium and trimethylgallium have been used successfully in the preparation of GaAs. This process makes compound semiconductor film growth compatible with methods used for the growth of elemental semiconductors and eliminates many of the difficulties inherent in multitemperature-zone processes.

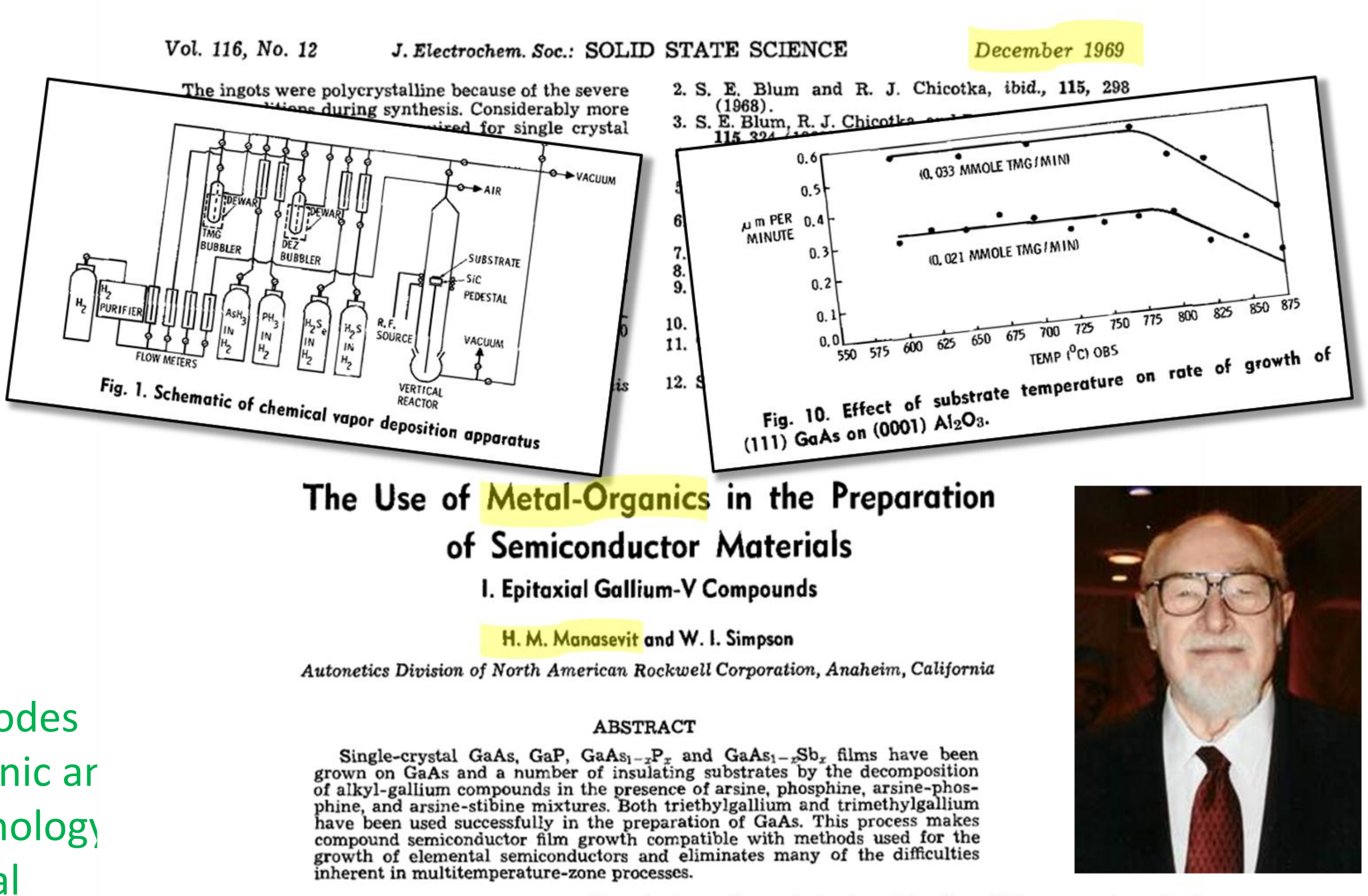
North American Aviation (Rockwell International) Science Center

The technique of MOCVD was first introduced by H.M. Manasevit and W.I. Simpson [57] *in the late 1960s for the deposition of compound semiconductors from the vapor phase*

VPE technique are today used to grow a wire range of materials and devices

III-V semiconductors (GaAs and InP based materials), III-Nitrides, Antimonides, II–VI semiconductors, Sulfides and Selenides (ZnS, ZnSe…), Group II-Oxides (ZnO…) …

MOCVD is used in manufacturing light-emit-ting diodes (LEDs), lasers, transistors, solar cells and other electronic ar optoelectronic devices, and is the key enabling technolog for future markets with high growth potential



Vol. 116, No. 12 J. Electrochem. Soc.: SOLID STATE SCIENCE December 1969

The ingots were polycrystalline because of the severe

2. S. E. Blum and R. J. Chicotka, ibid., 115, 298 (1968).

Fig. 1. Schematic of chemical vapor deposition apparatus

Fig. 10. Effect of substrate temperature on rate of growth of (111) GaAs on (0001) Al_2O_3.

The Use of Metal-Organics in the Preparation of Semiconductor Materials

I. Epitaxial Gallium-V Compounds

H. M. Manasevit and W. I. Simpson

Autonetics Division of North American Rockwell Corporation, Anaheim, California

ABSTRACT

Single-crystal GaAs, GaP, $GaAs_{1-x}P_x$ and $GaAs_{1-x}Sb_x$ films have been grown on GaAs and a number of insulating substrates by the decomposition of alkyl-gallium compounds in the presence of arsine, phosphine, arsine-phosphine, and arsine-stibine mixtures. Both triethylgallium and trimethylgallium have been used successfully in the preparation of GaAs. This process makes compound semiconductor film growth compatible with methods used for the growth of elemental semiconductors and eliminates many of the difficulties inherent in multitemperature-zone processes.

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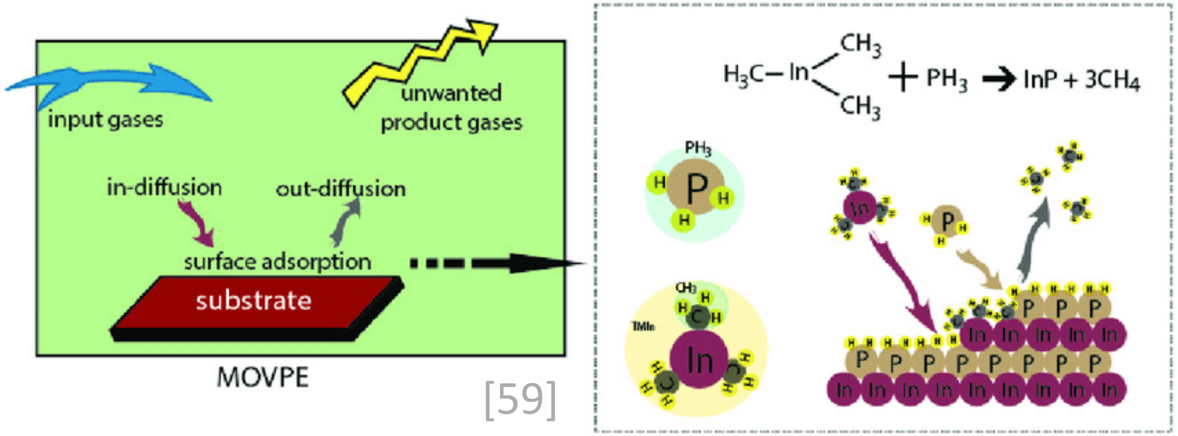
Vapor Phase Epitaxy (VPE) and related techniques

Metalorganic Chemical Vapor Deposition (MOCVD)
Metalorganic vapor phase epitaxy (MOVPE)
Organometallic vapor phase epitaxy (OMVPE)

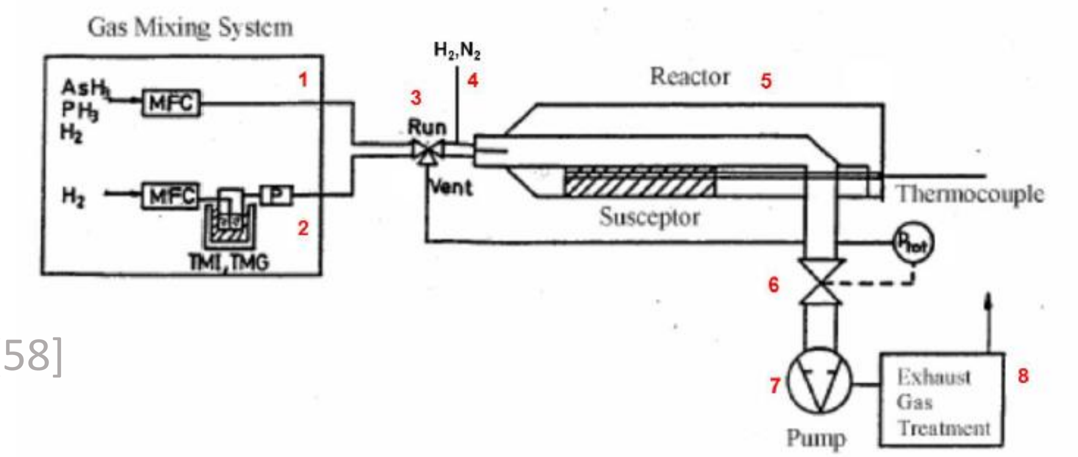
All of these variants of the name found in the literature can be, in most cases, used interchangeably

The basis principle of MOVPE (MOCVD, OMVPE) relies on transport of precursor molecules (usually metalorganic + hydride) in a cold wall reactor where they will be decomposed, will react and grow on a heated substrate.



[59]

The operating pressure is between 103 Pa and atmospheric pressure, but for reasons of uniformity, low pressures are preferred



[58]

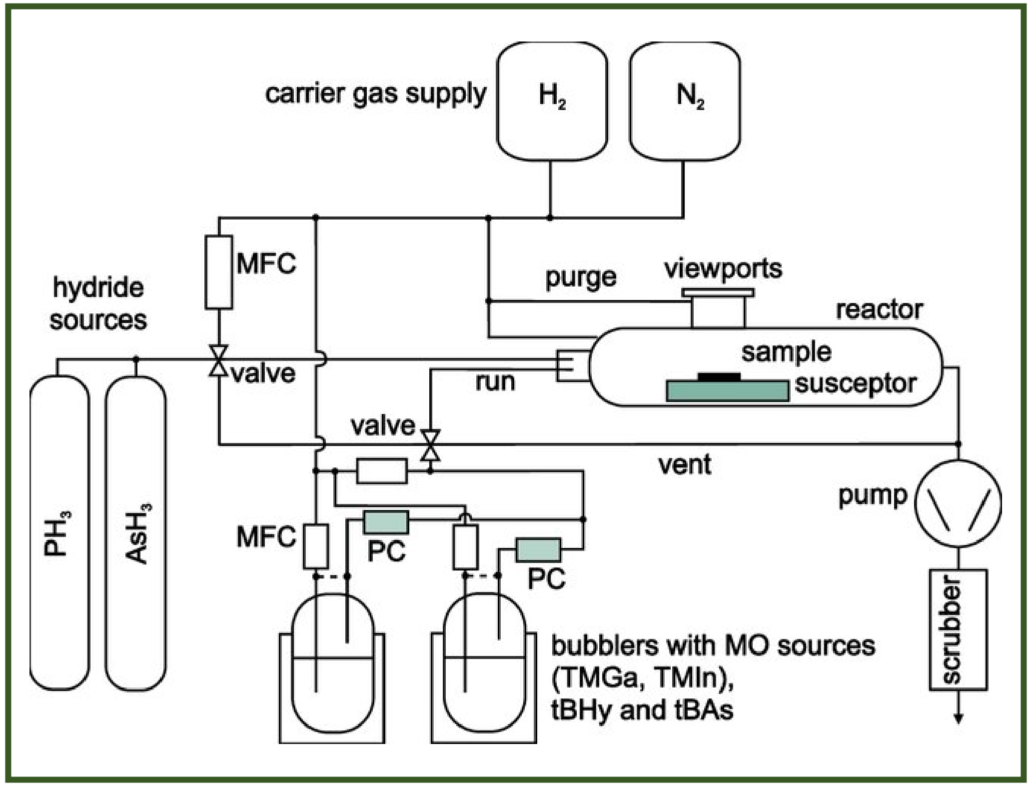
In few words, MOVPE system consist of

- Gas mixing cabinet
- Reactor
- Pump and scrubber system

MO-Vapor Phase Epitaxy (VPE)

Gas cabinet

- Gas handling system mainly includes the sources (precursors and other necessary gases), and the gas mixing system.
- Its purpose is to deliver into the growth chamber precisely metered amounts of reactants. Mass flow controllers (MFC) are used to accurately and reliably measure and control the molar flow rates of gases.



[60]

- Hydride sources (Ph_3, AsH_3, NH_3, SiH_4…) are stored in pressurized cylinders and their molar mass flow rates are precisely controlled by MFC
- MO precursors are stored in the stainless-steel cylinders called bubblers. The carrier gases (N_2 or H_2) flows into the bubbler to transport MO precursor. The exact amount of materials is controlled with the MFC as well as the pressure controller and temperature controllers (thermal bath of the bubbler)

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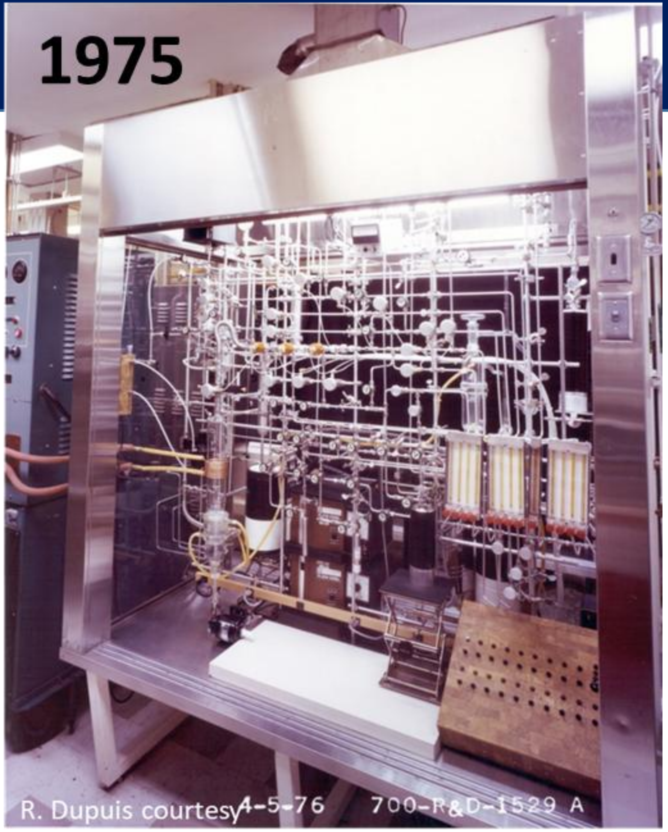
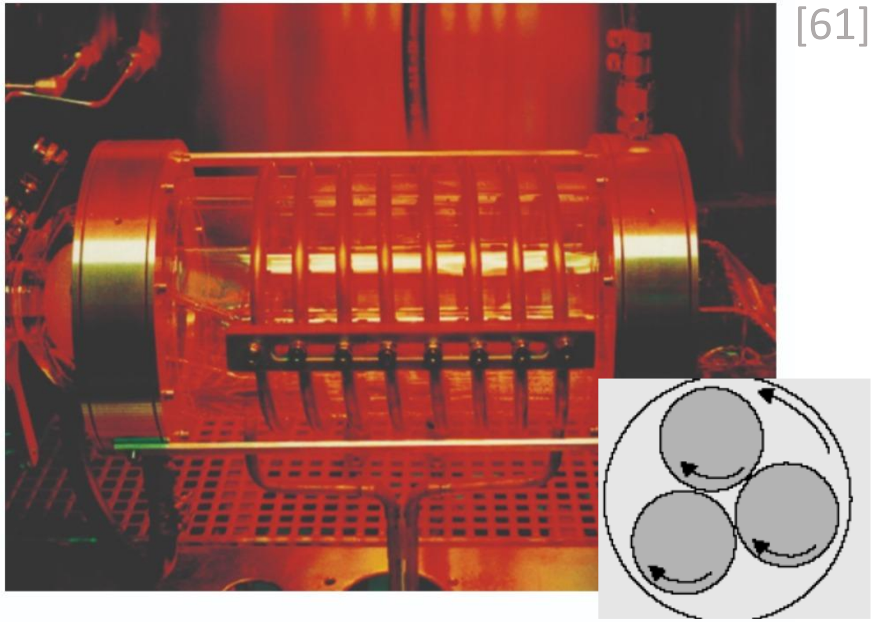


R. Dupuis courtesy

MO-Vapor Phase Epitaxy (VPE)

VPE reactor

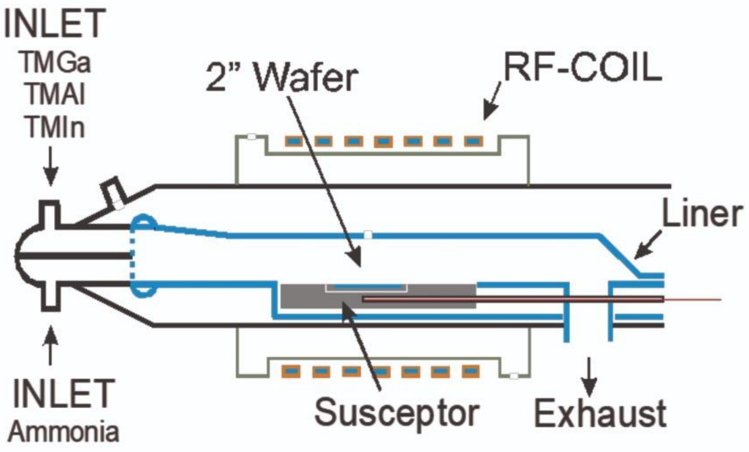
- The reactor is the growth chamber where reactant gases are combined at elevated temperatures to cause a chemical interaction, resulting in the deposition of materials on the substrate.
- This chamber is composed by reactor walls, liner, a graphite susceptor, gas injection units, and temperature control units.
- The reactor walls are usually made from stainless steel or quartz, two materials that do not react with the used chemicals. The walls can be water-cooled or gas-cooled to minimize reaction and deposition onto these surfaces.



[61]

Horizontal reactor geometry

- The reactor is made from quarts and the heat is supplied using radio frequency (RF) coils around the chamber.
- The precursor arrives horizontally with respect to the substrate surface.
- The substrates are under rotation for uniformity
- Quite large gas velocity, which ensure very rapid changes in the gas phase composition
- Most suitable for researchers than for industrial world since it is difficult to scale this design up to accommodate large volume production



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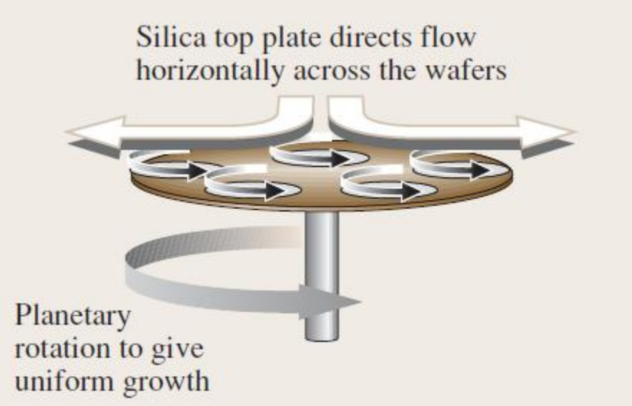
Vertical reactor geometry

- The reactor is made from stainless steel and the heat is supplied using three sets of coils (Tungsten Rhenium) located below the susceptor.

MO-Vapor Phase Epitaxy (VPE)

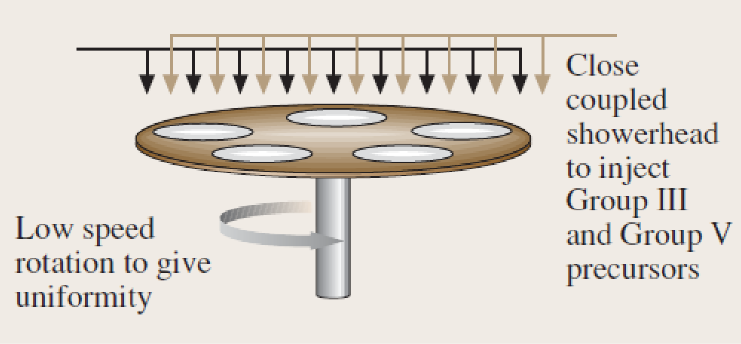
Vertical reactor geometry - Planetary technology [62, 37]

based on the principle of horizontal laminar flow. The gases enter the deposition chamber through a special gas inlet located in the center of the reactor



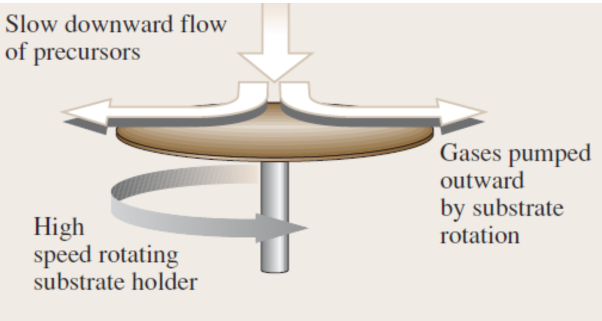
Vertical reactor geometry - Showerhead technology [62, 37]

based on the principle of vertically introduction of chemicals over the entire surface area of deposition, the showerhead being close to the substrates.



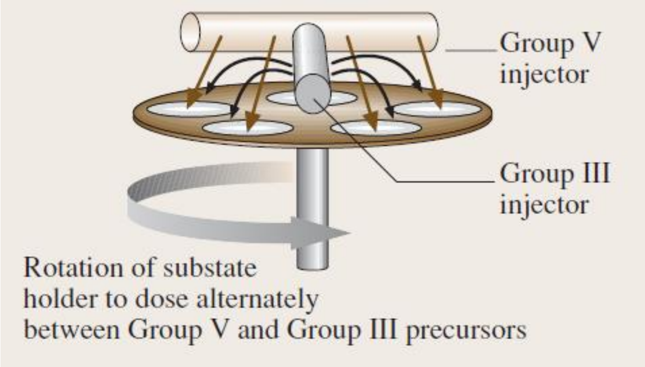
Vertical reactor geometry – Turbo-disk technology [63, 37]

based on a vertical introduction of the precursors with the rotation speeds up to 2000 rpm to create a lateral flow of the precursor gases above the substrate.



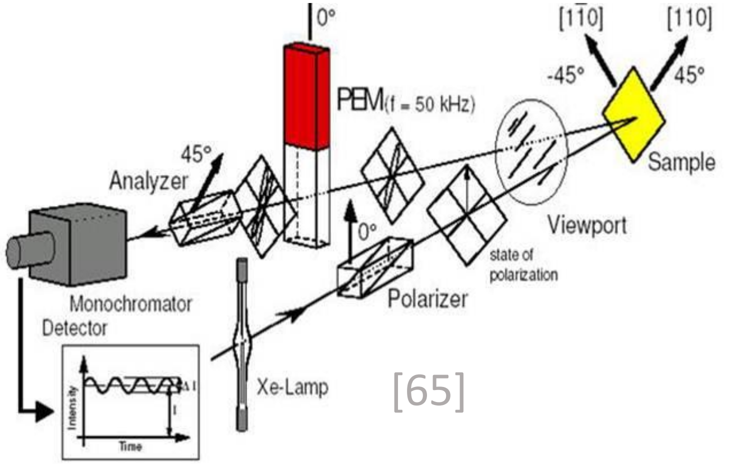
Vertical reactor geometry – Vector flow reactor technology [37]

based on separately introduction of the Group III and Group V precursors over a rotating susceptor offering an alternately dosing the surface with Group III and Group V precursors to grow the film from atomic layers



In-Situ layer characterization in MOPVE system

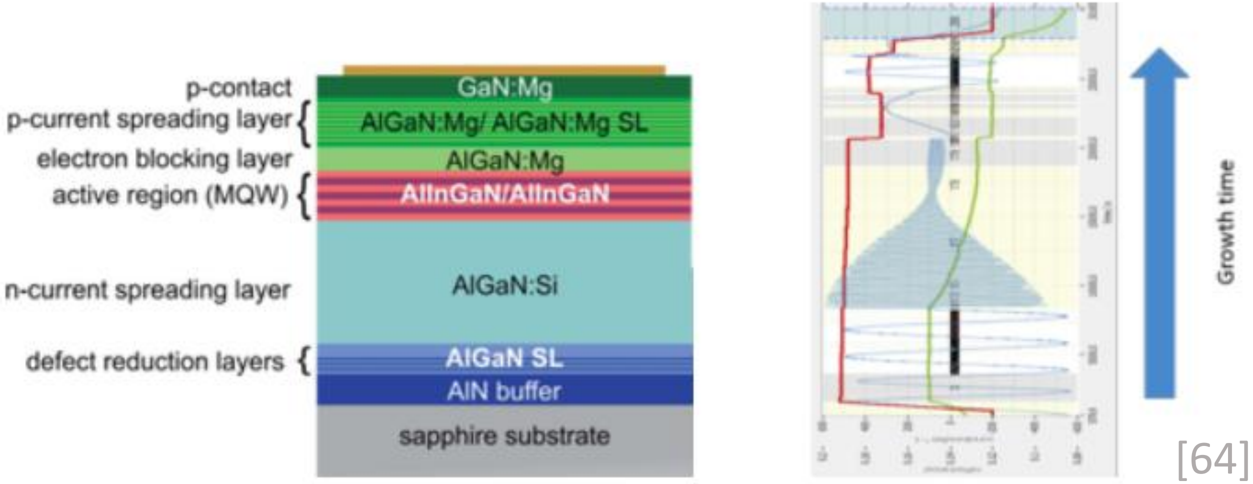
Due to high vacuum in a MBE growth chamber, it was possible to implement in-situ characterization methods, such as RHEED.
MOCVD during long time did not have a comparable useful control method due to the gas atmosphere in the MOCVD reactor.



[65]

Reflectance Anisotropy Spectroscopy (RAS), also known as Reflectance Difference Spectroscopy (RDS) is appeared few tens years ago, which allows to observe microscopic phenomena on the surface [64]

- RAS monitors the properties of surfaces, interfaces and doping-induced surface electric fields, which makes it a unique optical in-situ technique.
- RAS uses the difference in the reflectance for the light polarized along two axes (x and y) of the crystal under investigation.
- The method allows for determination of layer thickness, growth rate and composition through reflectance analysis.

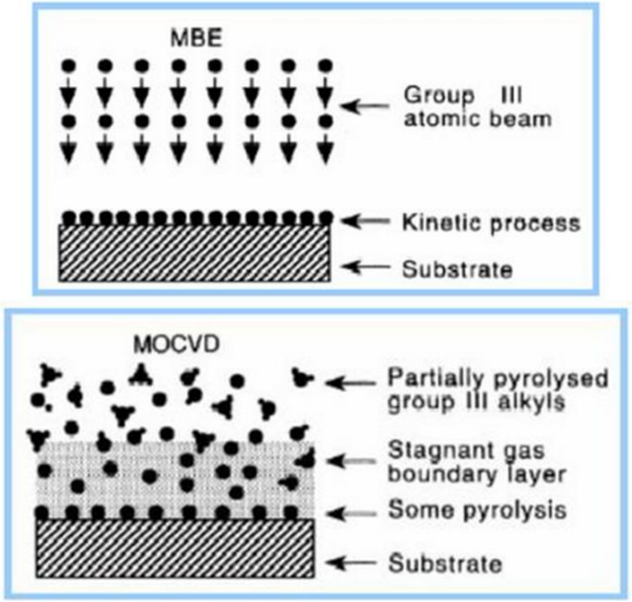


[64]

Fig. 1: State-of-the art UV-LED design according to “Chip designs for high efficiency III-nitride based ultraviolet light emitting diodes”, N. L. Ploch, PhD thesis, Technical University of Berlin 2015

MO-Vapor Phase Epitaxy (VPE)

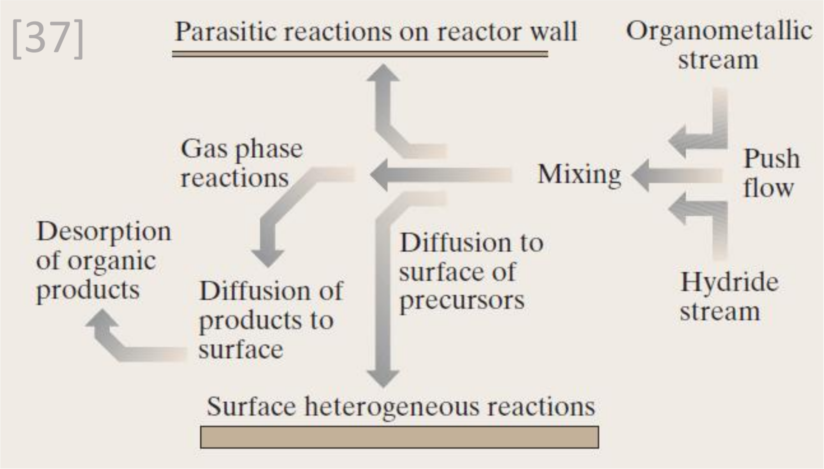
MOCVD growth process



[28]

- MBE : reactions occur only at the substrate
- MOVPE : parasitic reaction can occur and species decomposition partly occurs before reactant species reach the substrate
- MOVPE = A more complex kinetic reaction process in comparison with MBE

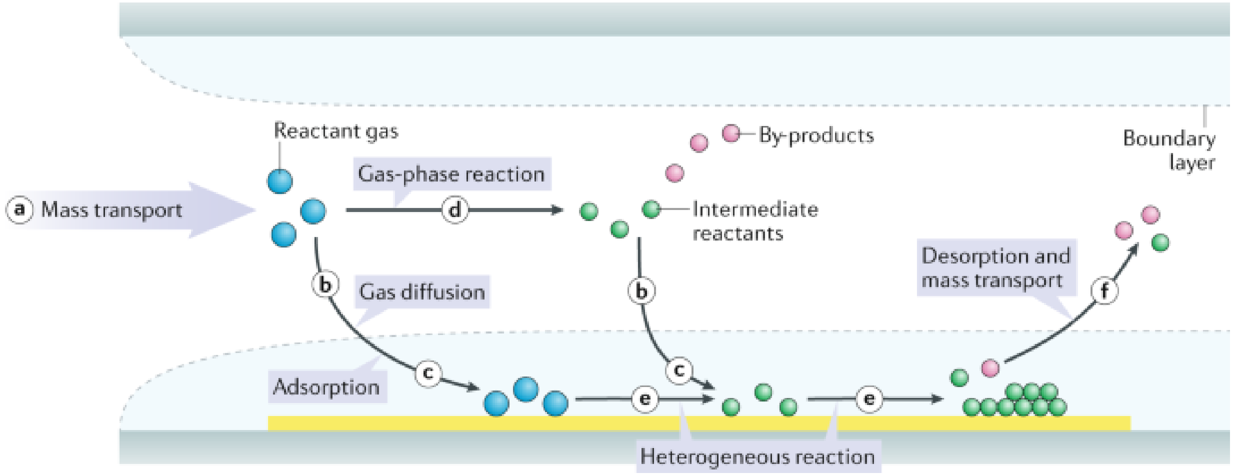
MO-Vapor Phase Epitaxy (VPE)



Precursors (MO for Group III source and hydride for the Group V source) are mixed outside and then introduced into the reaction chamber through injector directed onto a hot substrate.

The reaction of the precursors to yield the III–V compound on the substrate occur:

- in the hot vapor above the surface
- on the hot surface



[66]

→ InP MOCVD growth under V-element excess. The growth rate of InP is thus driven by the incorporation rate (IR) of the In active species, which depends on the attachment rate and on the diffusion lengths of the species [67]

MO-Vapor Phase Epitaxy (VPE)

Gas entering the reactor is heated and undergoes pyrolysis

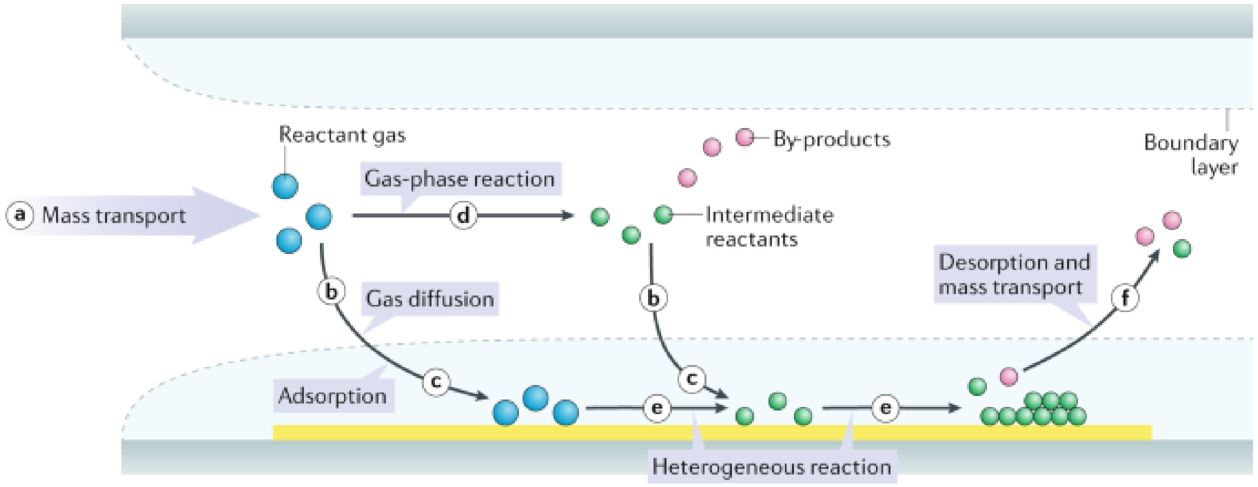
The pyrolysis reaction leading to the atomic In consists of three consecutive homolythis fission steps [60-70].

In the gas phase

$$(CH_3)_3In \rightarrow (CH_3)_2In + CH_3 \ (1)$$
$$(CH_3)_2In \rightarrow CH_3In + CH_3 \ (2)$$

According to kinetic studies, reactions (1) and (2) occur almost simultaneously yielding MMIn as intermediate reactant.

MMIn diffuses through a boundary layer forms at the interface of the solid substrate and the gas-phase



[66]

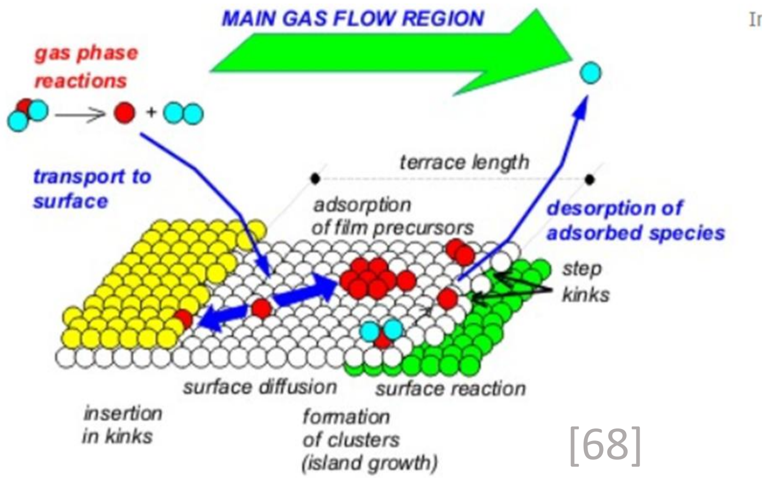
At the surface

$$CH_3In \rightarrow In + CH_3 \ (3)$$

At temperature higher than 480°C (that is the case in our growth conditions), reaction (3) proceeds yielding atomic In as the final reaction product.

In atoms then migrate to the appropriate lattice site and deposit epitaxially by associating with a group V atom that was derived from the thermal decomposition of the hydrides.

The growth rate here is usually limited by the diffusion rate of the group III elements through the boundary layer and on the surface.



[68]

MO-Vapor Phase Epitaxy (VPE)

Advantages	Limitations
❖ High grown layer quality ❖ Faster growth rate than MBE, can be a few µ/h. ❖ Large variety of materials, precursors, gases ❖ Growth with good thickness deposition control, sharp interfaces ❖ Doping uniformity and reproducibility ❖ Growth a medium pressure, no UHV system. ❖ Economically advantageous (multi-wafer capability)	❖ Low (very low) vapor pressures of used materials *Difficult to transport via gases* ❖ No abruptable process (as MBE) due to gas flow issues ❖ Use of toxic and corrosive gases ❖ High growth temperatures ❖ Carbon contamination and possible hydrogen(carrier gas) incorporation

Vapor Phase Epitaxy (VPE) and related techniques

Hydride vapor phase epitaxy - HVPE: an alternative technique

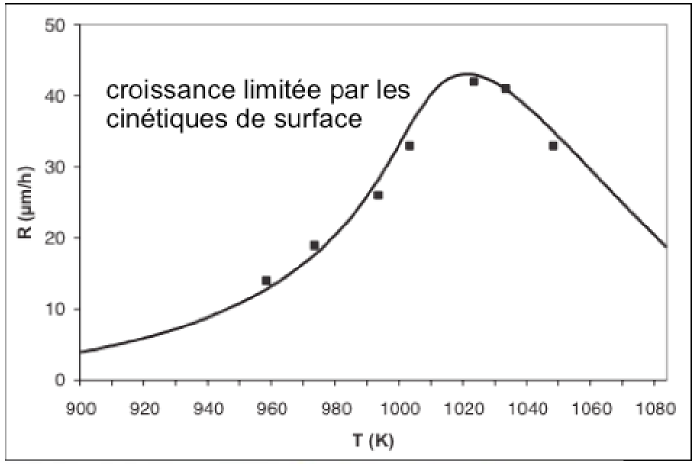
HVPE is the only III-V and III-N semiconductor crystal growth process working close to equilibrium controlled by the super-saturation of reactants at the substrate surface

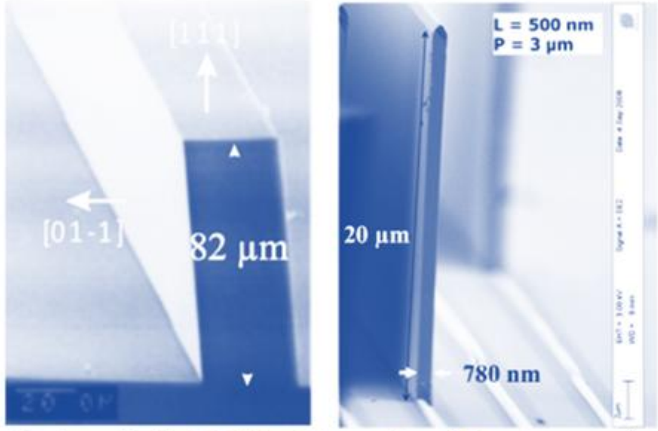
HVPE implements high mass inputs of hydride VH3 and NH3, and chlorinated III-Cl gas precursors of which decomposition frequency is fast.

Because of the fast precursor decomposition, there is no kinetic delay, then inducing a fast growth rate of the solid
The variation of growth rate as a function of temperature shows the typical bell curve, related to growth controlled by thermodynamics and surface kinetics.

High growth anisotropy towards the controlled shaping of structures

The growth rate can be modulated by simply varying the mass input rate of the reactants. It is then possible to fully take advantage of the growth anisotropy of III-(V,N) crystals with a wide range of condensation rates, from 3 to more than 100 µm/h as a function of the temperature, the vapor phase composition, for each face of the crystals.





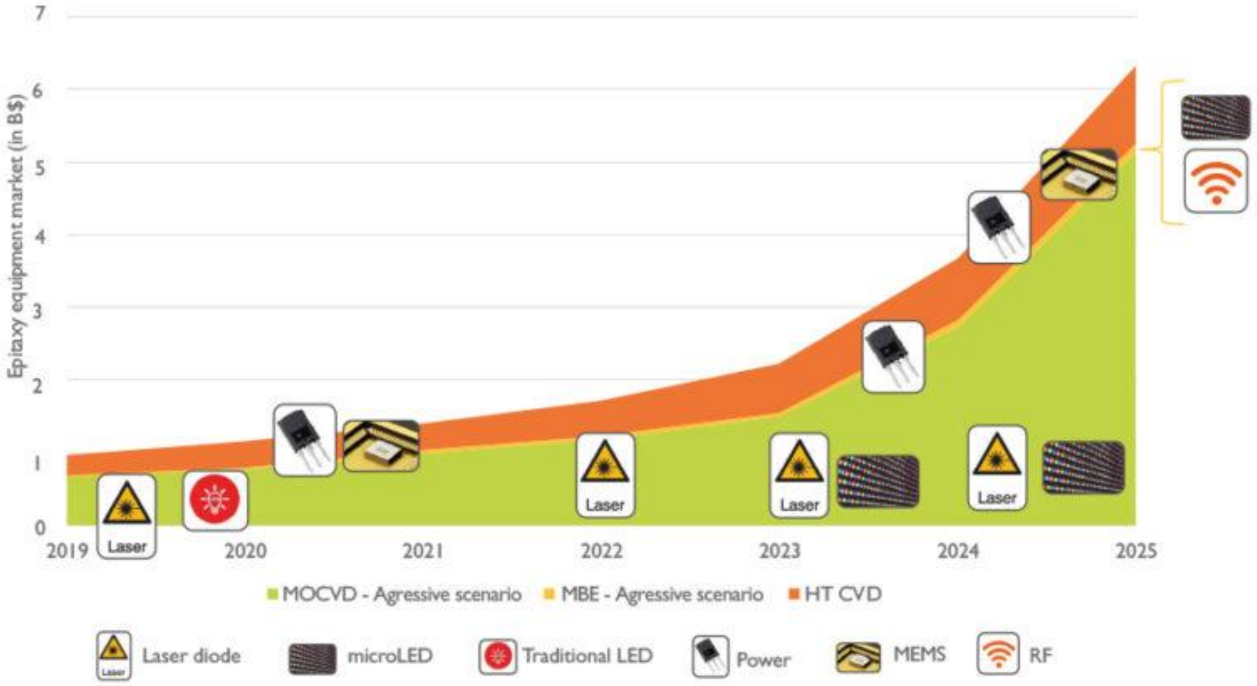
[71]

GaAs: *(left)* [-211]-stripe after 30 min-growth on GaAs(111)A - *(right)* [1-10]-stripe after 15 min-growth on GaAs(001)

Epitaxy Fundamentals – Towards applications

Current applications and industrial activities

“The epitaxy growth equipment market for “More than Moore” devices was worth close to US$990 million in 2019 and is expected to reach more than US$6 billion by 2025 in the aggressive scenario” as announced by Yole Development (Yole).



Epitaxy equipment market for More than Moore devices: 2019-2025 breakdown by technology

(Source: Epitaxy Growth Equipment for More Than Moore Devices Technology and Market Trends 2020, Yole Développement, January 2020)

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Thank You !