

Epitaxy of III-V semiconductors: some challenges and evolutions

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A French idiom

A few months ago





Bonjour Eric

L'idée de la conf est d'essayer de réunir les communautés des epitaxieurs semiconducteurs et oxydes, et **l'idée des conf plénières est de présenter et de faire découvrir l'historique et les thématiques de recherche de chacune des communautés à l'autre**. Dans ce contexte, on avait pensé à toi en tant que pilier de la communauté des epitaxieurs iii-v. On s'était dit que tu pourrais dresser un historique de l'épi des iii-v (notamment mbe bien sûr) en France: évolution des matériaux étudiés, des applications, labos impliqués, thèmes de recherche actuels, avec bien sûr un focus sur les antimoniures et leur intégration sur Si puisque c'est votre spécialité.

Outline

III-V semiconductors: properties and applications
Epitaxy of III-V semiconductors: a (personal) historical view
III-Sb based semiconductors
III-Sb grown on (001) Si substrates
Summary – Perspectives





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III-V Semiconductor structures



Hexagonal and face-centered cubic lattices are the most compact way to stack spheres.

Diamond and zinc blende structures







Diamond structure: **C, Si, Ge**

Zinc blende structure: ZnS, ZnSe GaAs, InP, GaSb,...

Two fcc lattices shifted by a/4 along the cube diagonal.

Wurtzite structure





Wurtzite structure: GaN,.... ZnS,....

Wurtzite structure:

- Two lattice parameters (a, c)
- Two hcp lattices shifted by (5/8)c

The sky map: fundamental plot



Voir Fabrice Semond, 14h45

The sky map





Large miscibility gaps for most III-V quaternary alloys: Consequences on epitaxial growth

Onabe, Jpn. J. Appl. Phys. 21, L323 (1982).

III-V semiconductors: effective masses, mobilities

	AIAs	AISb	GaN	GaAs	GaSb	InP	InAs	InSb	Si	Ge
E _g (300 K) (eV)	2.2	1.6	3.4	1.4	0.7	1.3	0.3	0.2	1.1	0.7
${\rm m_e}^*$ / ${\rm m_0}$	0.083	0.102	0.2	0.066	0.042	0.073	0.023	0.014	0.15	0.044
m _{hh} * / m ₀	0.409	0.336	0.8	0.377	0.222	0.6	0.26	0.244	0.54	0.28
μ _e (300 K) (cm². V ⁻¹ .s ⁻ ¹)			2 000	8 500	3 000	5 400	40 000	77 000	1 400	3 900
μ _h (300 K) (cm². V ⁻¹ .s ⁻ ¹)			200	400	1 000	200	500	850	450	1900

Low masses, high carrier mobilities

III-V semiconductors: applications

EVOLUTION OF COMPOUND SEMICONDUCTOR APPLICATIONS: INFLECTION POINTS

Source: Status of the Compound Semiconductor Industry report, Yole Intelligence, 2022





www.yolegroup.com | @Yole Intelligence 2023

III-V semiconductors: markets

2023-2029 compound semiconductor substrate market by application (\$M)

(Source: Status of the Compound Semiconductor Industry 2024, Yole Intelligence, January 2024)



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EPITAXY?

RECHERCHES EXPÉRIMENTALES SUR L'ÉPITAXIE OU ORIENTATION MUTUELLE

DE

CRISTAUX D'ESPÈCES DIFFÉRENTES

Par M. L. Rover

Bull. Soc. Fran. Min. 51 (1928) 7

First observation of mutual orientation of natural crystals around 1878.

Epitaxy has been developed thanks to, and for the science and technology of III-V semiconductors.

The substrate is crucial.





Liquid-Phase Epitaxy (LPE)



Principle:

Superstaurated liquid solutions contain the constitutive elements of the epitaxial material.

The substrate is is brought in contact with the baths in sequence, which drives heterogeneous nucleation on the substrate, *i.e.* epitaxy.

Peculiarity:

- A near-equilibrium growth technique.
- Rather accurate description of the growth process by thermodynamics

Liquid-Phase Epitaxy (LPE)

Advantages of LPE:

- Simple experimental set-up, rather low cost.
- High material purity.
- High growth rate (~1 μ m/min).

Disadvantages of LPE:

- Thermodynamics equilibrium: low flexibility (but results can be predicted).
- Reproducibility issues.
- High growth rate: difficult to control interfaces and thickness accurately, not adapted to the growth of nanostructures.

Applications:

- Very much used in the 80s for opto-devices, inc. in the industry.
- Still used for particular applications/materials:
 - CdHgTe infrared photodetectors
 - •

Vapor Phase Epitaxy (VPE)



Principle:

The elements are transported by carrier gases.

Reactions occur near the substrate zone to form the compound.

Ex:

- Ga (I) + HCl (g) \rightarrow GaCl (g) + $\frac{1}{2}$ H₂ (g)
- GaCl(g) + NH_3 (g) \rightarrow GaN (s) + HCl (g) + H_2 (g)

See Yamina André for more details

Vapor Phase Epitaxy (VPE)

Advantages of VPE:

- Simple, versatile: epitaxy or polycristal deposition, depending on the substrate.
- High material purity.
- High growth rate (>>1 μm/min).
- Possibility of *in situ* etching + re-growth.

Disadvantages of VPE:

- Deposition everywhere in the reactor (parasitic reactions).
- Thermodynamics equilibrium: low flexibility (but results can be predicted).
- High growth rate: difficult to control interfaces and thickness accurately.

Applications:

- LEDs
- Very thick layers (quasi substrates, periodic polar orientation for non linear optics)
- Nanowires

See Yamina André for more details

Metal-Organic Vapor Phase Epitaxy (MOVPE)



Principle:

Sources are organo-metallic compounds or hydrides containing the elements of the layer.

They are transported to the substrate zone by a carrier gas.

The reaction occurs near the substrate which is the only zone at high temperature.

ex: $(CH_3)_3$ Ga (g) + AsH₃(g) \rightarrow GaAs (s) + 3 CH₄ (g)

Metal-organic vapor phase epitaxy (MOVPE)

US and German patents in the early 60s.

First papers in the UK in the late 60s from CVD users.

Also known as:

- Metal-Organic Chemical Vapor Deposition (MOCVD)
- Organo-Metallic Vapor Phase Epitaxy (OMVPE)
- Organo-Metallic Chemical Vapor Deposition (OMCVD)

MOVPE/OMVPE better reflects the real nature of the technique: **epitaxy**.

Metal-organic vapor phase epitaxy (MOVPE)

Advantages of MOVPE:

- Non-equilibrium technique: high flexibility.
- Adjustable growth rate: $0.05 0.5 \,\mu$ m/min.
- Accurate control of thicknesses, down to a fewMLs.
- Easy control of alloy composition by gas flux control.
- Easy maintenance.
- Well suited to the growth of materials containing volatile species (P, S,..).
- Chemistry: good selectivity.

Disadvantages of MOVPE:

- Difficult *in situ* control
- \Rightarrow New reactor geometries
- Toxic gases (AsH₃, PH₃,..) \Rightarrow New group-V molecules
- Complex, expensive equipment.

Applications:

- GaN LEDs,
- Lasers (GaAs pump lasers, InP telecom lasers)

Group-V decomposition



- Pyrolysis within narrow T range ($\Delta T = 50 100 \text{ K}$)
- Group-III OM helps the pyrolysis of group-Vs
- 2 paths of decomposition:
 - in gas phase (homogeneous reaction)
 - at surface (heterogeneous reaction)

 $Ga(CH_3)_3 + AsH_3 \rightarrow GaAs + 3CH_4 \uparrow$.

Note that the actual chemistry is not well known:

 $Ga(CH_3)_3 \rightarrow Ga(CH_3)_2 + CH_3 \rightarrow GaCH_3 + 2CH_3 \rightarrow Ga + 3CH_3.$

Pb: C incorporation is a serious problem in MOVPE













AIXTRON CCS or planetary reactors





Molecular Beam Epitaxy (MBE)



Principle:

Evaporation of the elements constituting the epitaxial layer from ultra-pure source material.

UHV: mean free path larger than the cell-substrate distance: reaction on the substrate surface.

3-temperature principle: for III-Vs: $T_v < T_s < T_{III}$: no group-V accumulation

Growth rates are governed by the group-III cell temperatures, that must be controlled to \pm 0.5 °C.

Molecular beam epitaxy (MBE)

Advantages of MBE:

- Far-from-equilibrium technique: high flexibility.
- Low-temperature growth.
- Low growth rate: << 1 μ m/h
- Accurate control of thicknesses, down to a fraction of ML.
- Easy control of group-III alloy composition by cell-temperature control.
- **UHV:** high material purity and *in situ* real-time characterization techniques.

Disadvantages of MBE:

- Difficult control of group-V alloy compositions (competition between group-V species)
- Not well suited to materials containing volatile elements (P, S,..)
- Temperatures have to be regulated to \pm 0.5 °C
- Physical mechanisms: low/no selectivity
- UHV
- Complex, expensive equipment.

Applications:

- GaAs HEMTs
- III-Sb-based opto devices

Combined techniques (MBE + VPE)

Aim: Combining the main advantages of two techniques:

- MBE UHV: *in situ* control, high purity, high interface control
- MOVPE: selective growth, volatile elements.

Principle: some of the individual elements are introduced as gases into an MBE-like reactor. Working pressure is then intermediate between MBE and MOVPE ($\sim 10^{-5}$ Torr).

Gas-source MBE (**GS-MBE**): group-V gas sources + elemental group III sources Metal-organic molecular-beam epitaxy (**MOMBE**): metal-organic group III + group-V gas sources

Applications:

InP telecom lasers

Molecular beam epitaxy (MBE)

Historical perspective

The principle has been demonstrated by Günther (Siemens) in the late 50s. He used an As crucible at a temperature T_V to impose a sufficient overpressure on the substrate, and a Ga crucible at temperature T_{III} . Fluxes were aiming toward a **polycristalline substrate** at temperature T_s . The system was in a reactor under **primary vacuum**.

Günther demonstrated that the growth of III-V layers is possible when $T_v < T_s < T_{III}$ and T_s , the substrate temperature, is high enough to evaporate excess As.

Still, Günther didn't get good results because he had polycristalline substrates and the vacuum was not good enough.

In the late 60s-70s, vacuum technology and cryogeny had made a lot of progress.

J. Arthur and A. Cho (Bell Labs) revisited the 3-temperatures technique. They achieved good crystal quality of epilayers grown on GaAs **single crystals** in a **ultra-high vacuum (UHV)** reactor ($10^{-10} - 10^{-11}$ Torr). Ga and As fluxes were obtained by heating up liquid Ga and solid As in dedicated crucibles.

MBE was born

The invention of MBE by Al Cho



Al Cho, IC-MBE 2018, Shanghai



The equipment





Early MBE systems





Recent MBE lab



Batches of samples can be grown, which allows systematic investigations

Riber MBE production systems



1x200mm 1x150mm 3x4''

4x200mm 9x150mm 14x4''

1x200mm 4x150mm 9x4''





Riber MBE production systems





Veeco MBE production systems

Dual GEN200 system



7 x 3inch, 4 x100mm, 1x6inch, 1x200mm

Riber MBE production systems

Intelli*EPI*

USA MBE pure player – 100% RIBER 2x MBE 49 - 9x MBE 6000 - 1x MBE 8000 GaAs-, InP-, GaSb-based products III-V –on-Si

Opto. Devices (APD, EEL, VCSEL, QWIP, QCL)



USA both MOCVD and MBE player 1x MBE 6000 7x V100 – 4x V150



USA MBE player 1x MBE 6000 3x V100 – 3x V150 Singapore company

Singapore MBE player – 100% RIBER 6x MBE 6000

Chineese

company

China MBE player 9x MBE 6000 HEMT, PHEMT, MHEMT, HBT



USA MBE player

2x MBE 6000 Nitrides for microelectronics applications



And many more



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The antimonides



The semiconductors based on GaSb, InAs, AISb, InSb and their alloys: AIGaAsSb, GaInAsSb, AIGaInAsSb... Generally grown on GaSb or InAs substrates

Sb-based materials: narrow bandgap semiconductors

The antimonides



• Large bandgap range :

0.1 – 1.6 eV

- Band gap engineering
- Various band alignments: Type I, Type II, Type III
- Large band offsets:

 $\Delta E_{c} = 0 - 1.5 \text{ eV}$ $\Delta E_{v} = 0 - 0.5 \text{ eV}$

- ***** Band offset engineering
- Large lattice parameter range:
 - **The set of the set of**

The antimonides: interfaces

Some material combinations exhibit no-common atom interfaces:

- GaSb / InAs
- AlSb / InAs



 \Rightarrow Interface engineering



TEM image : Anne Ponchet, CEMES, Toulouse



TEM: E. Luna, PDI-Berlin

InAs/AlSb

InAs/GaSb

No common atom InAs/GaSb SLs



The antimondes: epitaxy

- III-Sb compounds and heterostructures:
 - "Low temperature" materials: $T_m(InSb) = 515 \degree C$, $T_m(GaSb) = 712 \degree C$ (GaAs: 1238 °C) \circ low growth temperature : 400 °C < T_g < 520 °C
 - Unstable/metastable compounds,
 - High-Al content in many devices.
- Molecular-beam epitaxy (MBE) is the preferred (only?) growth technique for optoelectronic devices.
 - Lack of MOVPE developments: catching up?
- GaSb and InAs substrates:
 - Always conductive,
 - 2 to 4 inch, 5 inch under development,
 - Few producers of high-quality substrates: high price! (~400 €/2 inch wafer)
- Doping properties:
 - Residual GaSb always *p*-type in the 10¹⁶ cm⁻³ range: native defects,
 - Si = *p*-type dopant in III-Sb compounds,
 - Te = preferred *n*-type dopant,
 - Be = typical *p*-type dopant.

The antimonides

- Unrivaled band gap range
- Large band offsets
- Type I to type III alignments
- Low effective masses
- Two group-V elements 🙂 🙂 😕
- No common atom interfaces 🙂 😕 😕
- Complex (quat-/pent-anary) alloys
- Large mismatch range (-8% / +7 %)
- Conductive substrates



III-Sbs are well adapted to:

- high frequency, low power devices
- opto devices operating the IR, particularly mid- and far- IR

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III-Sb-based IR devices







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A number of mismatches:

- Surface energies: Volmer-Weber (3D) growth mode of III-Vs on Si
- Lattice parameter: dislocations (cannot be avoided!)
- Thermal expansion coefficient: cracks (when the III-V thickness > 7 10 μm)
- Crystal structure: polar vs non polar: anti-phase domains and boundaries

Epitaxy generally results in high threading-defect density

Antiphase domains and antiphase boundaries



Voltage (V)

GaSb on Si

Key to eliminate APBs in III-Vs grown on on-axis group-IV substrates: Substrate surface organization with parallel steps

III-V growth anisotropy: the antiphase domain is buried by the main domain

See Charles Cornet, tomorrow, 10h45



Early GaSb on Si layer

On going collaboration with:

See J.-B. Rodriguez, today, 11h50 ; A. Gilbert, tomorrow, 11h30



Integration on a Si photonic circuit



Integrated sensors need photonic integrated circuits: preliminary step = laser on patterned Si wafers + passive waveguides

CHALLENGES:

- Processing Si photonic platform without damaging the Si substrate
- Epitaxial growth on a patterned Si platform
- Etched-facet mirrors of the laser: smooth (to preserve laser performance) and vertical (to promote light coupling)
- > Complex laser integration process : air gap between laser and waveguide unavoidable + WGs should be carefully protected
- Divergence of the laser emission 60°



Light transmitted through the waveguide!

ICLs and QCLs perform similarly to their native counterpart: tolerant to dislocations (see Maëva Fagot, Friday, 9h15)

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Epitaxy of III-V semiconductors

- ~50 years of development.
- MOVPE and MBE mature for production (for some materials).
- Large activity in France, inc. in the industry.
- New research activity toward the hybridation of different technologies :
 - III-V and Si(Ge)
 - III-V and II-VI
 - III-V and metals?
 - III-V and oxydes?



III-Sb MBE at U. Montpellier



Jean-Baptiste RODRIGUEZ CNRS



Laurent CERUTTI U. Montpellier

+ many PhD students!! Currently:

- Audrey Gilbert
- Maëva Fagot
- Milan Silvestre









OPTAPHI Optical Sensing using Advanced Photo-Induced Effects

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