

## **Epitaxy of III-V semiconductors: some challenges and evolutions**

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universitaire de France



#### **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**



### **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**



**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 | CYole 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. ROYER

**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  $(-1 \mu m/min)$ .

#### **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
	- $\bullet$  …………………

### **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) +  $\frac{1}{2}$  H<sub>2</sub> (g)
- GaCl(g) +  $NH_3$  (g)  $\rightarrow$  GaN (s) + HCl (g) + H<sub>2</sub> (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) + **As**H<sub>3</sub>(g)  $\rightarrow$  GaAs (s) + 3 CH<sub>4</sub> (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:

- o **Metal-Organic Chemical Vapor Deposition (MOCVD)**
- o Organo-Metallic Vapor Phase Epitaxy (OMVPE)
- o 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  $(AsH_3, PH_3, ...)$  $\Rightarrow$  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 ( $\Delta T = 50 100$  K)
- Group-III OM helps the pyrolysis of group-Vs
- 2 paths of decomposition:
	- o in gas phase (homogeneous reaction)
	- o **at surface (heterogeneous reaction)**

 $Ga(CH_3)$ <sub>3</sub> + AsH<sub>3</sub>  $\rightarrow$  GaAs + 3CH<sub>4</sub> $\uparrow$ .

Note that the actual chemistry is not well known:

 $Ga(CH_3)$ <sub>3</sub>  $\rightarrow$   $Ga(CH_3)$ <sub>2</sub> + CH<sub>3</sub>  $\rightarrow$  GaCH<sub>3</sub> + 2CH<sub>3</sub>  $\rightarrow$  Ga + 3CH<sub>3</sub>.

#### 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:  $<< 1 \mu m/h$
- 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<sub>s</sub>. The system was in a reactor under **primary vacuum**.

Günther demonstrated that the growth of III-V layers is possible when  $T_v < T_s < T_{\text{III}}$  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''







### **Riber MBE production systems**





### **Veeco MBE production systems**

**Dual GEN200 system**



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

### MBE production **Riber MBE production systems**

# $\blacksquare$ Intelli $\epsilon$ P/

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





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#### **The antimonides**



The semiconductors based on GaSb, InAs, AlSb, InSb and their alloys: AlGaAsSb, GaInAsSb, AlGaInAsSb… *Generally grown on GaSb or InAs substrates*

<sup>42</sup> **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:**
	- *Lattice matching is an issue*

#### **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** 44 **InAs/GaSb**

#### **No common atom InAs/GaSb SLs**



• **A tool to adjust the lattice parameter and the electronic properties**

### **The antimondes: epitaxy**

- III-Sb compounds and heterostructures:
	- "Low temperature" materials:  $T_m(lnSb) = 515 °C$ ,  $T_m(GaSb) = 712 °C$  (GaAs: 1238 °C) o 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! ( $\sim$ 400 €/2 inch wafer)
- Doping properties:
	- Residual GaSb always p-type in the 10<sup>16</sup> cm<sup>-3</sup> 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  $\circledcirc$
- Large band offsets  $\odot$
- Type I to type III alignments  $\heartsuit$
- Low effective masses  $\circledcirc$
- Two group-V elements  $\circledcirc$   $\circledcirc$   $\circledcirc$
- No common atom interfaces  $\circledcirc$   $\circledcirc$   $\circledcirc$
- Complex (quat-/pent-anary) alloys <sup>8</sup>
- Large mismatch range  $(-8\% / +7\%)$
- Conductive substrates (8)



#### III-Sbs are well adapted to:

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

#### **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**

• GaP: 0.3 %

• **GaSb: 12 %**

• **Ge: 4 %**

 $a_{layer} - a_{Si}$  $a_{\Sigma i}$ 

> • **GaAs: 4 %** • **InP: 7 %**

### **Antiphase domains and antiphase boundaries**

Zinc blende = polar



### **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

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

On going collaboration with:



#### **Integration on a Si photonic circuit**



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

#### **CHALLENGES:**

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

- $\cdot$  ~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**









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**Thank you!!** 58