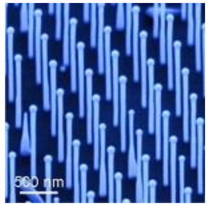
Institut des Nanotechnologies de Lyon UMR 5270

Molecular Beam Epitaxy (MBE)

Romain Bachelet

romain.bachelet@ec-lyon.fr



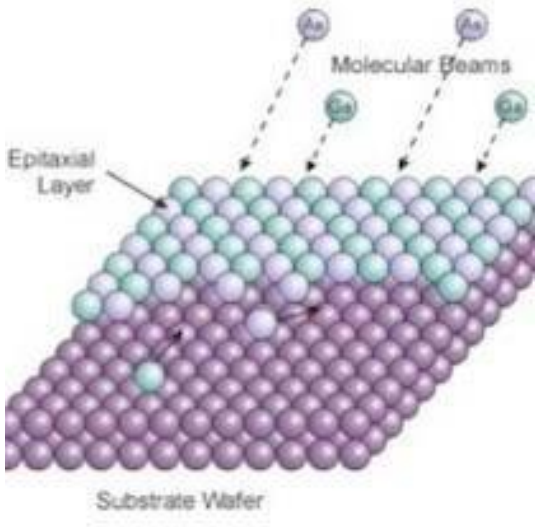
« EL NANO » thematic school, GDR NAME

June 11-16, 2023, Aussois

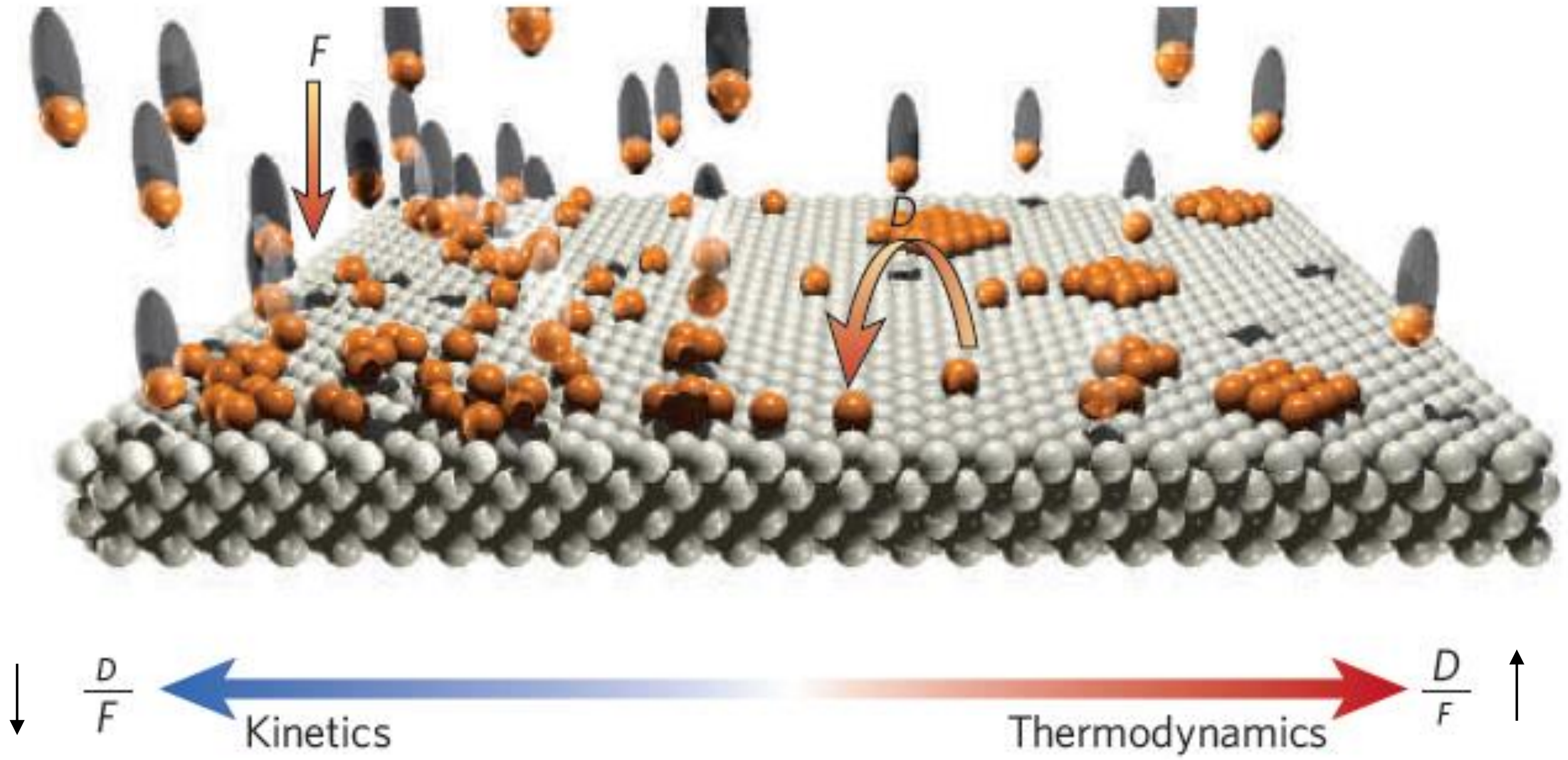
Université de Lyon · CNRS · École Centrale Lyon · INSA · Lyon 1 · CPE Lyon

Outline

1. Molecular Beam Epitaxy



Epitaxy



Atomic/molecular flux (F)

(Anisotropic) surface diffusion (D) of adatoms

Crystal nuclei & growth

Single-crystalline substrate

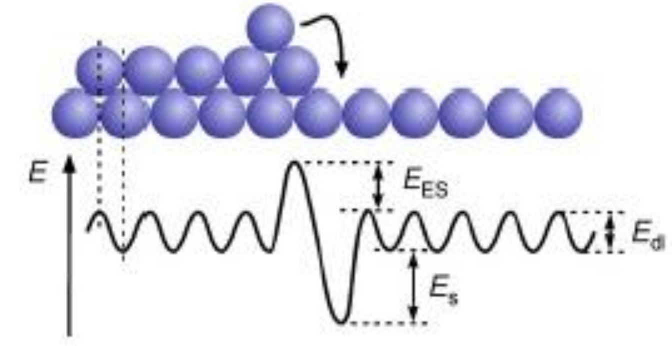
D: surface diffusion activated by $T_{substrate}$
F: atomic/molecular flux activated by T_{cell}

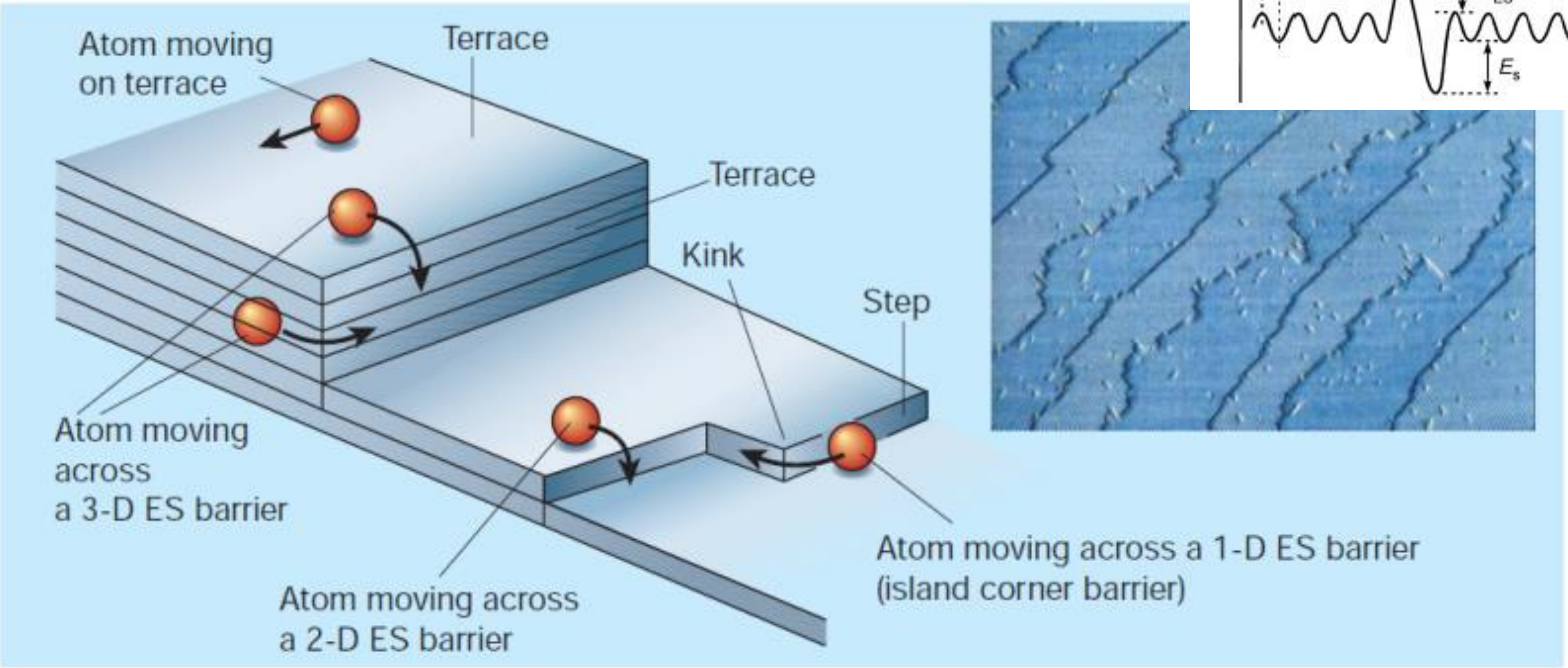
J.V. Barth *et al.*, Nature 437, 29 (2005)

➔ Different kind of nanostructures controlled by D/F

Anisotropic surface diffusion

- From atomic site to atomic site on single-crystalline substrate
- Ehrlich schwoebel (ES) energy barriers at surface steps

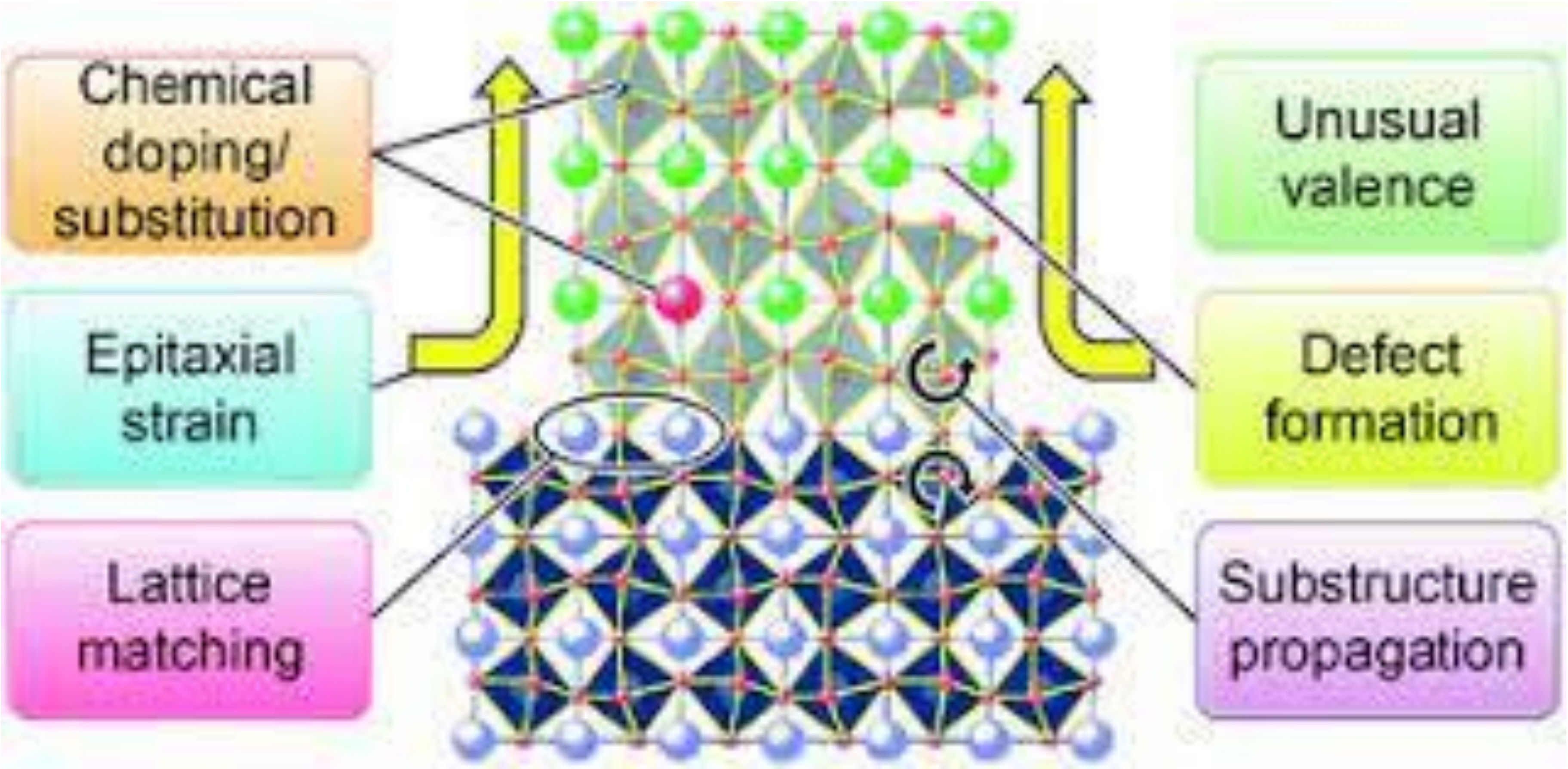




M. Lagally *et al*., Nature 417, 907 (2002)

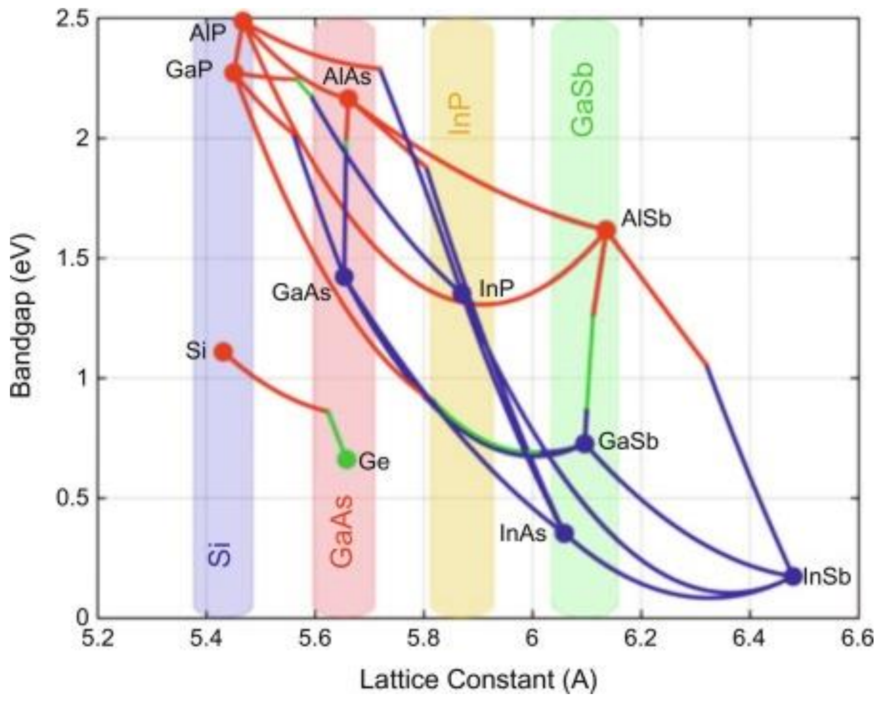
Epitaxy

➔ Both **out-of-plane** and **in-plane** preferential crystalline **orientations** imposed by the single-crystalline substrate

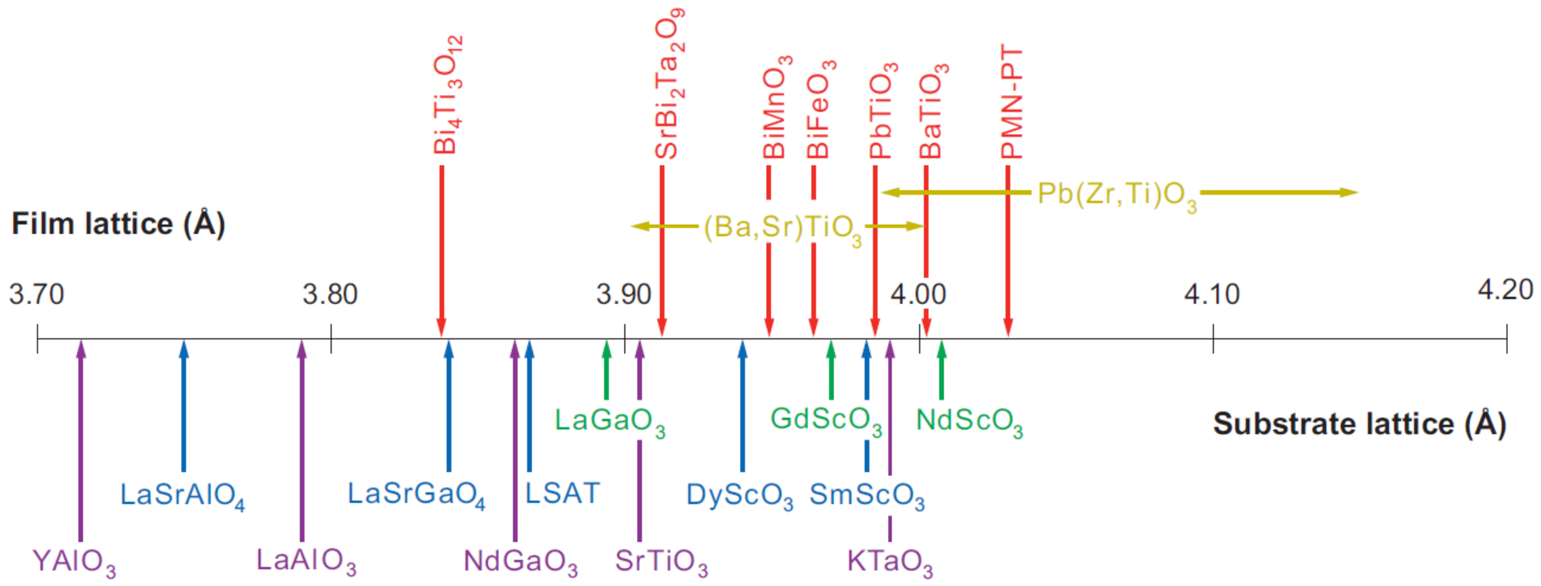


Lattice matching: choice of the substrate

Semiconductors

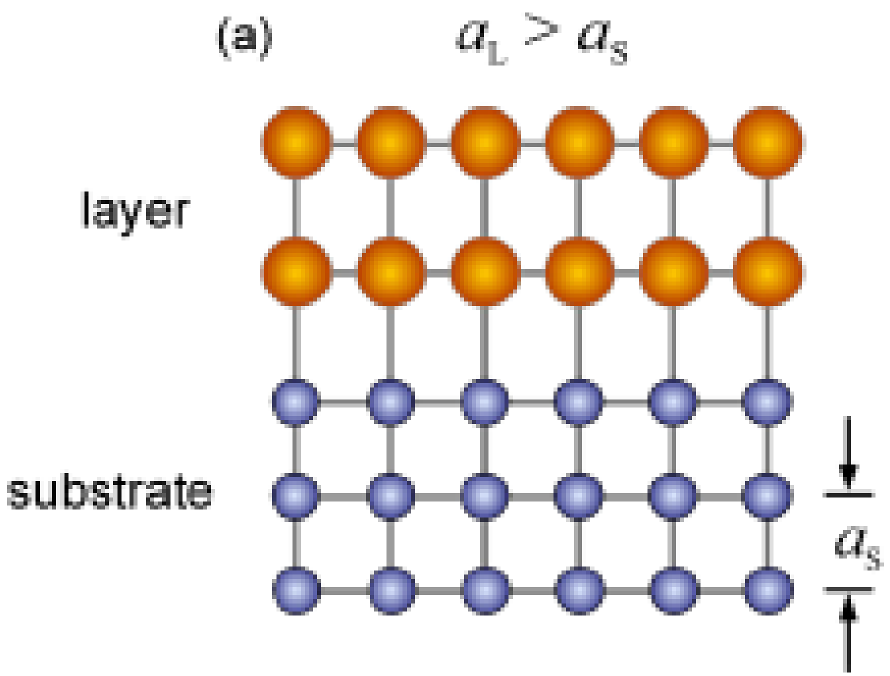


Oxides

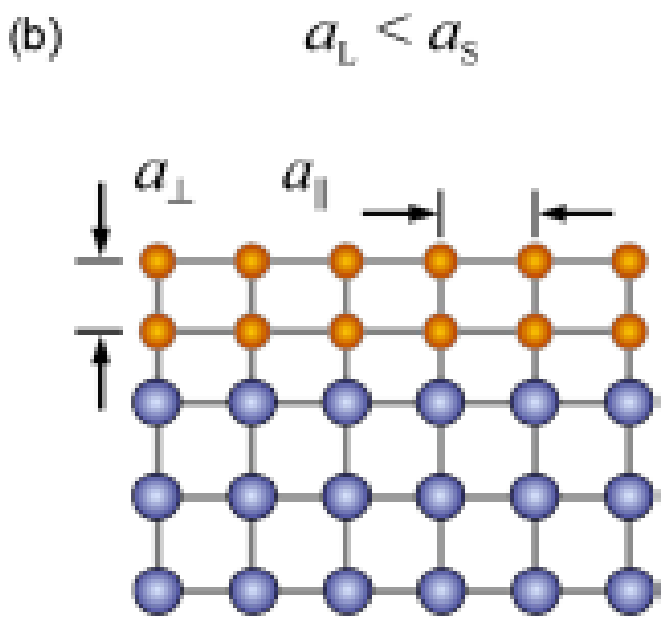


Epitaxial strain

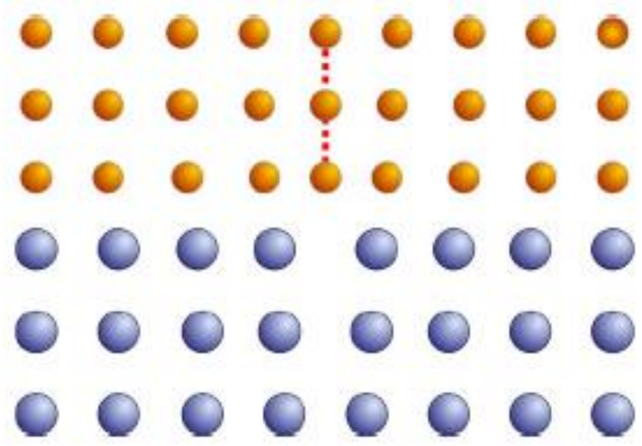
Compressive



Tensile

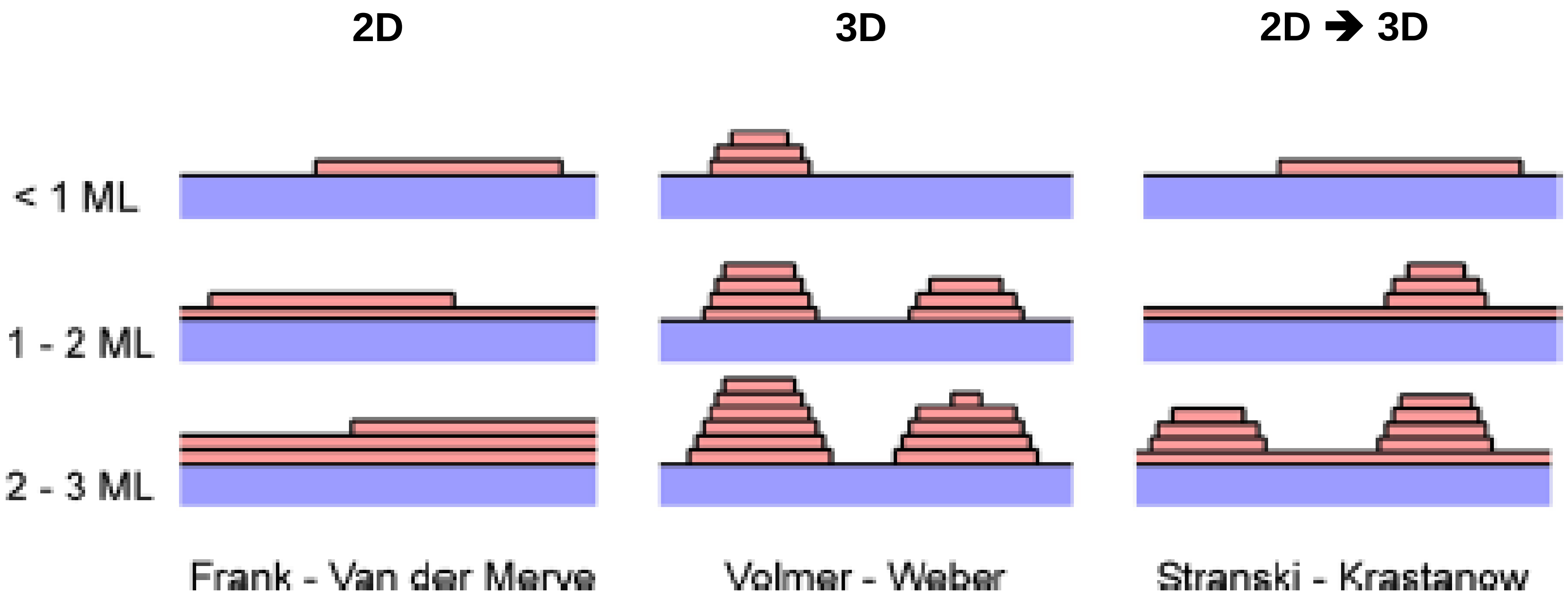


Relaxed



Udo W. Pohl, “Epitaxy of semiconductors”, Springer (2013)

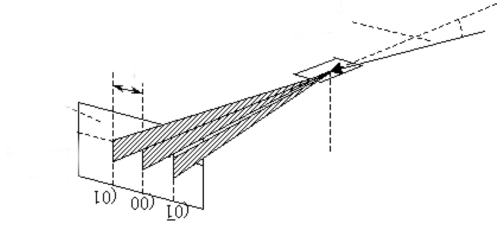
Growth modes



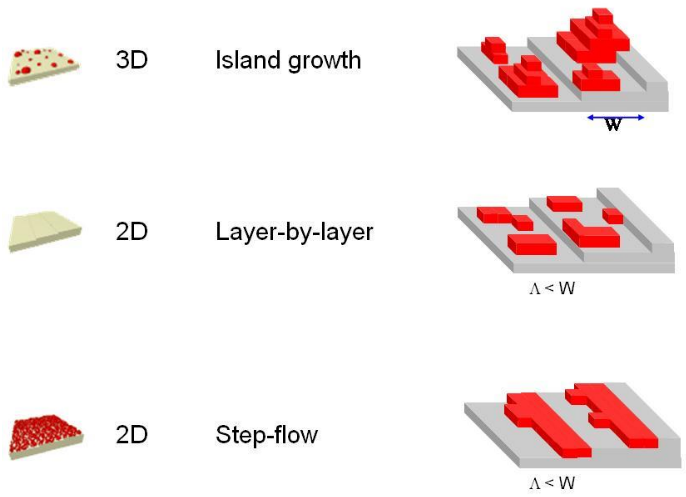
Importance of surface/interface energies, lattice mismatch/strain, D/F,…

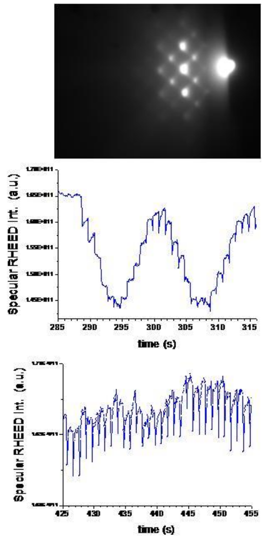
Udo W. Pohl, "Epitaxy of semiconductors", Springer (2013)

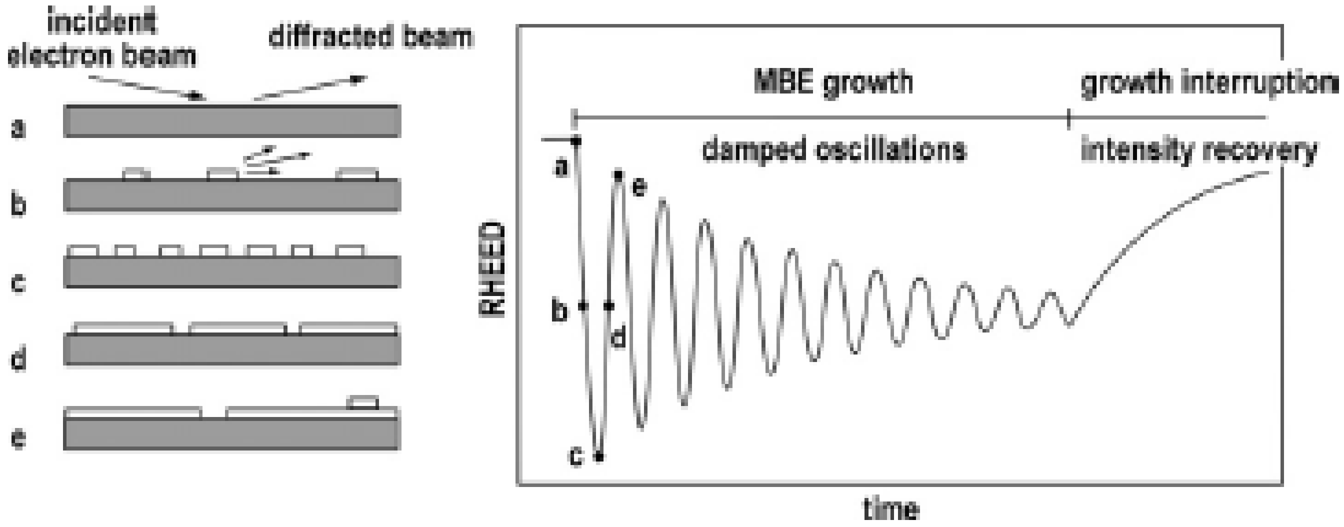
Monitoring growth modes by *in-situ* RHEED



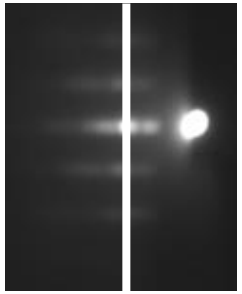
Growth modes & ad-atom diffusivities

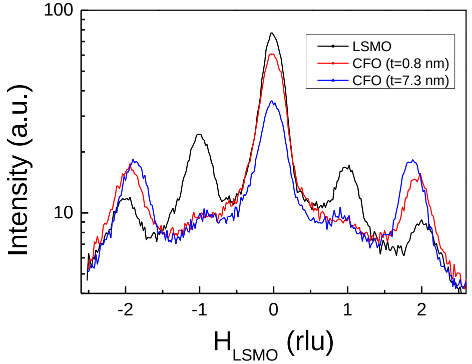


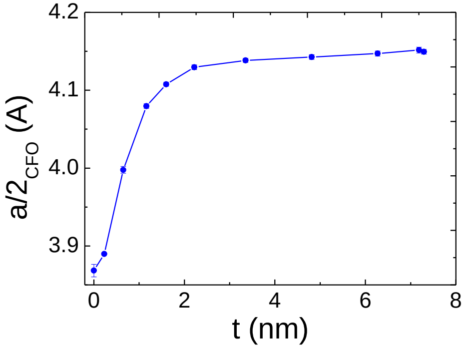


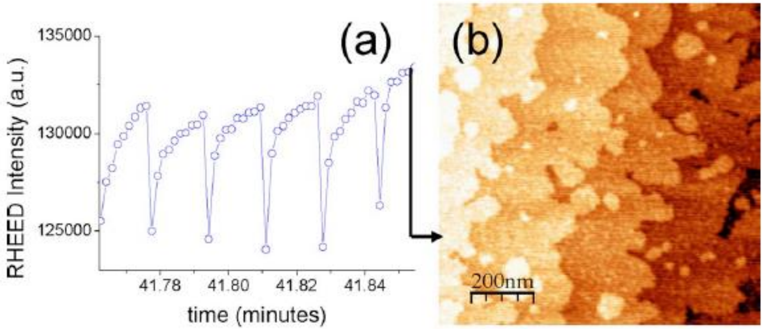


In-plane structure & strain relaxation



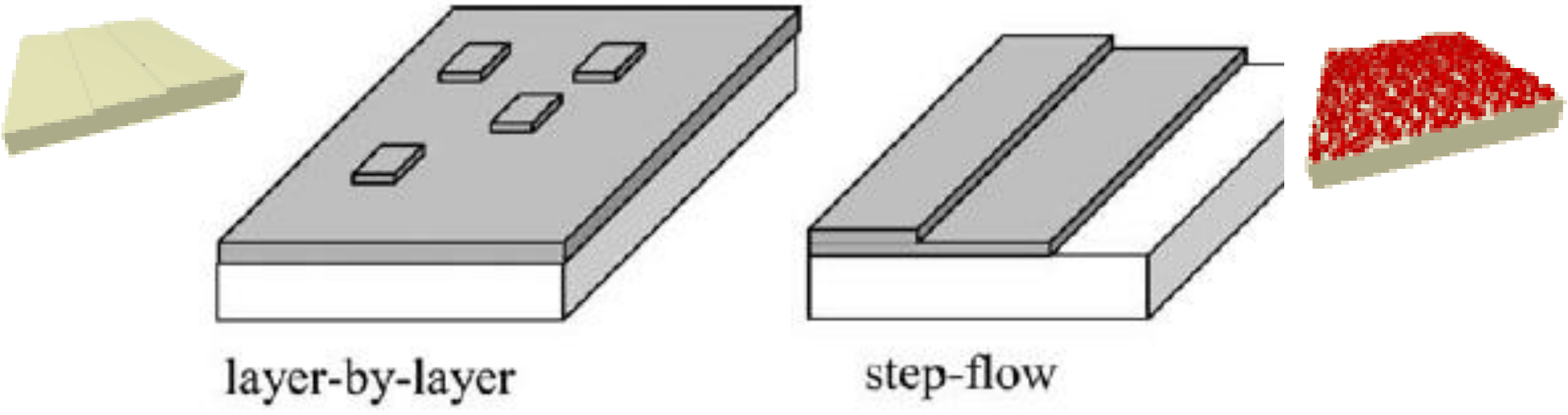


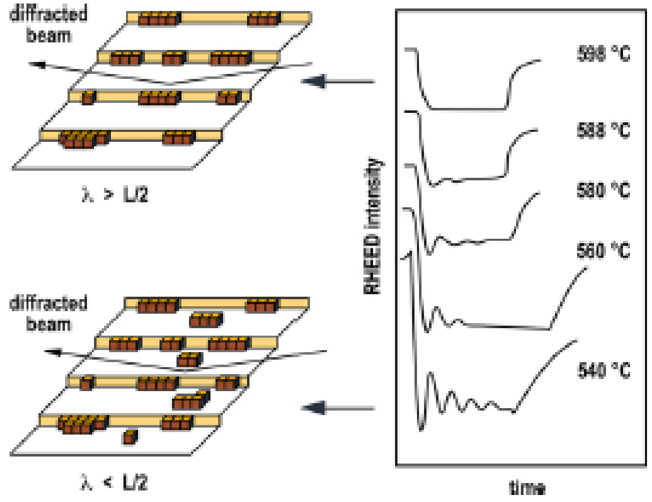




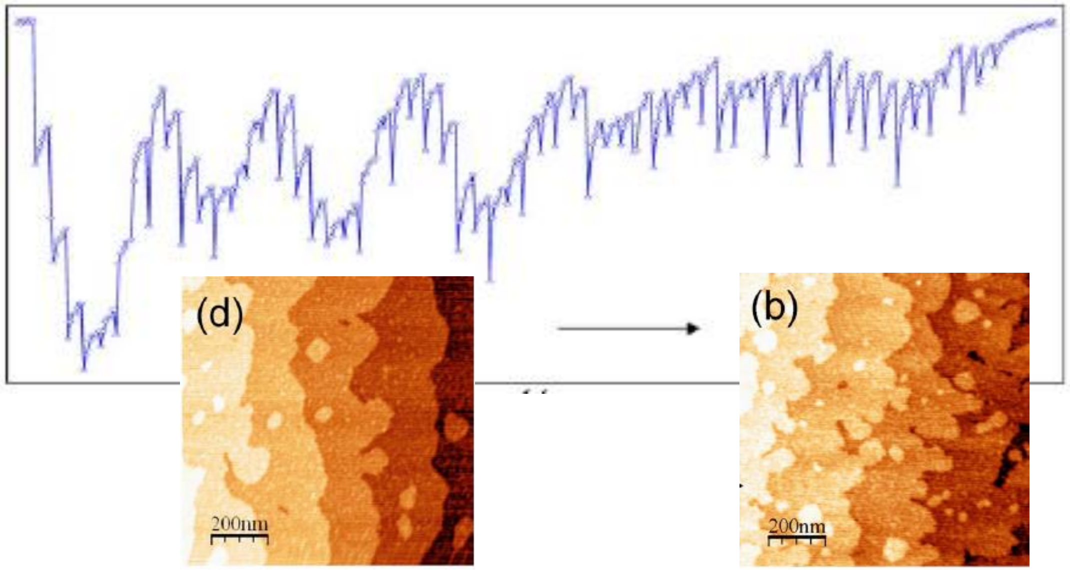
R. Bachelet *et al.*, APL (2008); N. Dix *et al.*, APL (2013)

2D growth modes





Reversible 2D growth transitions by step meandering/straightening



Key parameters:

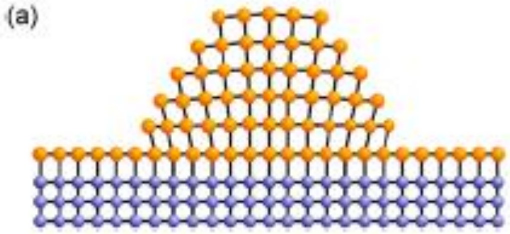
- **Λ**: mean surface diffusion length (driven by T_{growth})
- **W**: mean terrace width (given by the substrate miscut angle)

Λ < W ➔ LbL
Λ > W ➔ SF

N.P. Norton *et al*., Mater. Sci. Eng. R 43, 139 (2004); R. Bachelet *et al*., APL (2008); U.W. Pohl, “Epitaxy of SCs”, Springer (2013)

2D ➔ 3D growth

***Stranski-Krastanow** island growth of quantum dots (QDs) - by strain relaxation and/or surface/interface energy*



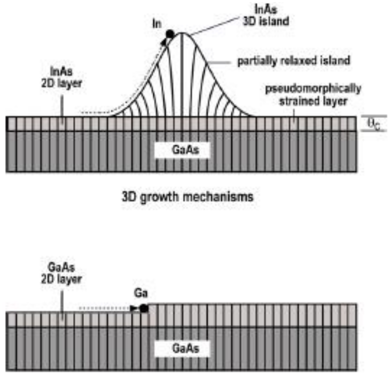
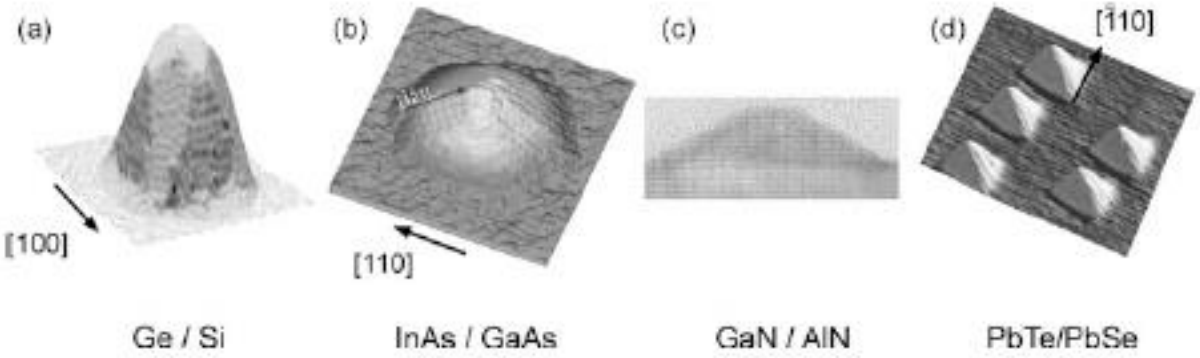
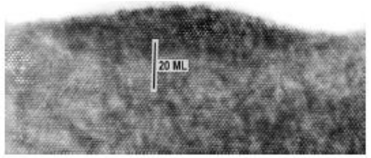
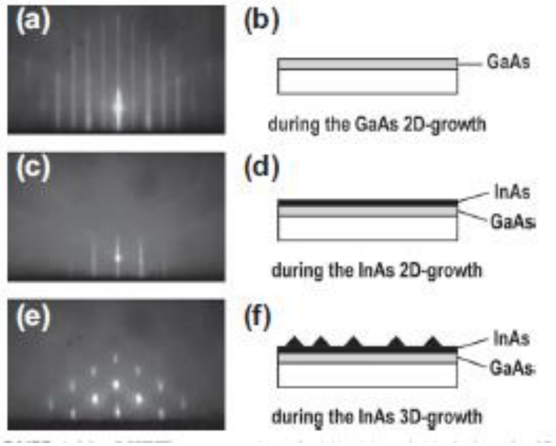


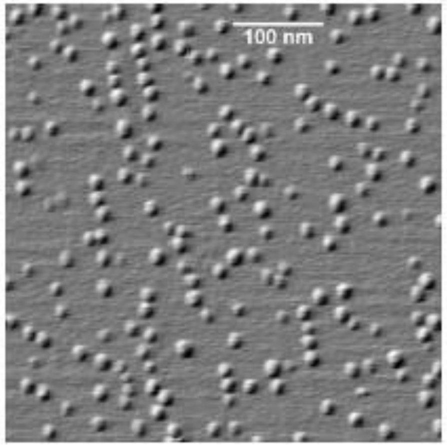
Table 5.5 Some semiconductor materials used for strain-induced, self-organized Stranski-Krastanow formation of islands

Island/matrix	Ge/Si	InAs/GaAs	GaN/AlN	PbSe/PbTe
Structure	Diamond	Zincblende	Wurtzite	Sodium chloride
Orientation	(001)	(001)	(0001)	(111)
Mismatch	−3.6 %	−7 %	−2.5 %	+5.5 %







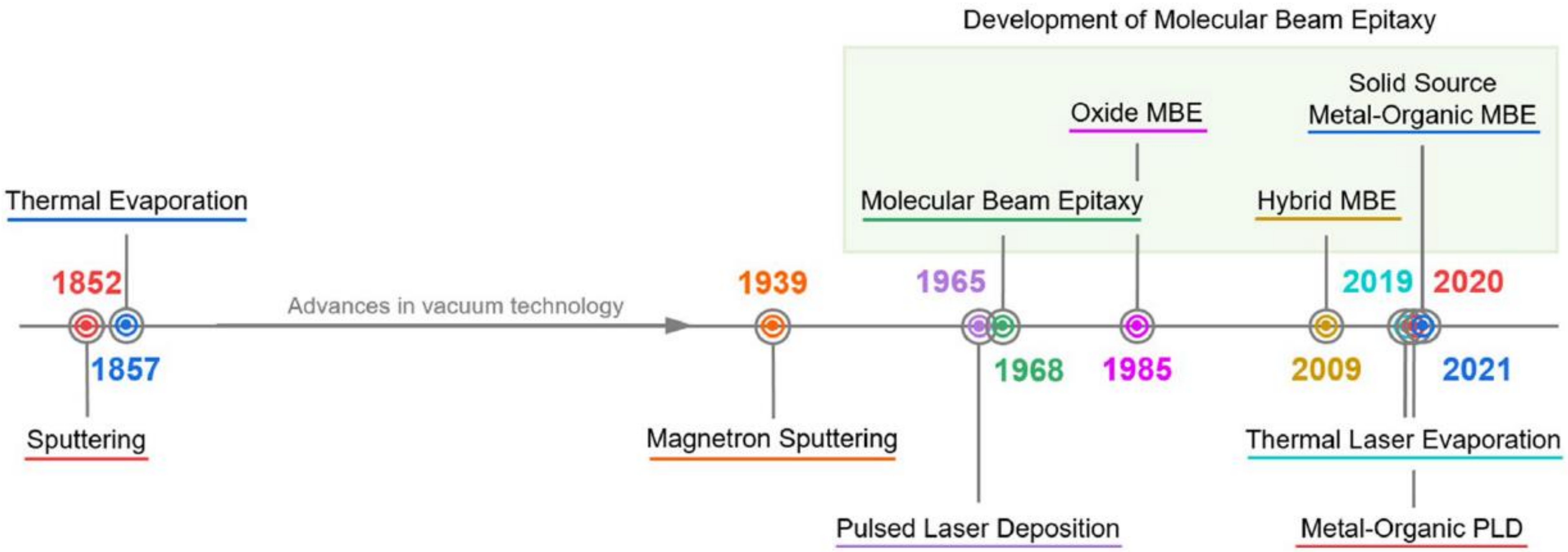


Udo W. Pohl, "Epitaxy of semiconductors", Springer (2013)

Molecular Beam Epitaxy

2. Historic background

Developments of thin film PVD elaboration techniques over time



W. Nunn *et al.*, J. Mater. Res. (2021)

MBE: key development in nanotechnology / nanoscience

MBE deserves a place in the history books

W. PATRICK MCCRAY
is at the Center for Nanotechnology in Society, University of California, Santa Barbara, California 93106, USA.

Nature Nanotechnology **2**, 260 (2007)

MBE at Bell Labs, 1978

MBE invention (Bell Labs, from the 60's):

- Few years later after R. Feynman conference "*There's plenty of room at the bottom*" (1959)
- Much before STM invention (1981)
- Key in nanoscience & nanotechnology
- Initially for III-V semiconductors

The pioneering works (from Bell Labs & IBM) in a few dates

- **1954: theory of mixed semiconductors of different bandgaps**, by *H. Kroemer*
  ➔ *Physics Nobel prize in 2000, for his work on semiconductor heterostructures*

- **1959: "*There's plenty of room at the bottom*"**, Talk by *R. Feynman* (*1965 Nobel prize in Physics*)

- **1968: 1st epitaxial GaAs layers by MBE**, paper and patent, by *John R. Arthur* (Bell Labs)
  Advances with *Alfred Y. Cho* at Bell Labs (*in-situ* RHEED)

- **1968-1973**: **superlattice as a new theoretical concept**, by *L. Esaki* & *R. Tsu* (IBM)
  1st own MBE at IBM for superlattices, by *L. Esaki & L. Chang*
  ➔ *Physics Nobel prize in 1973, for earlier work on tunneling in semiconductors*

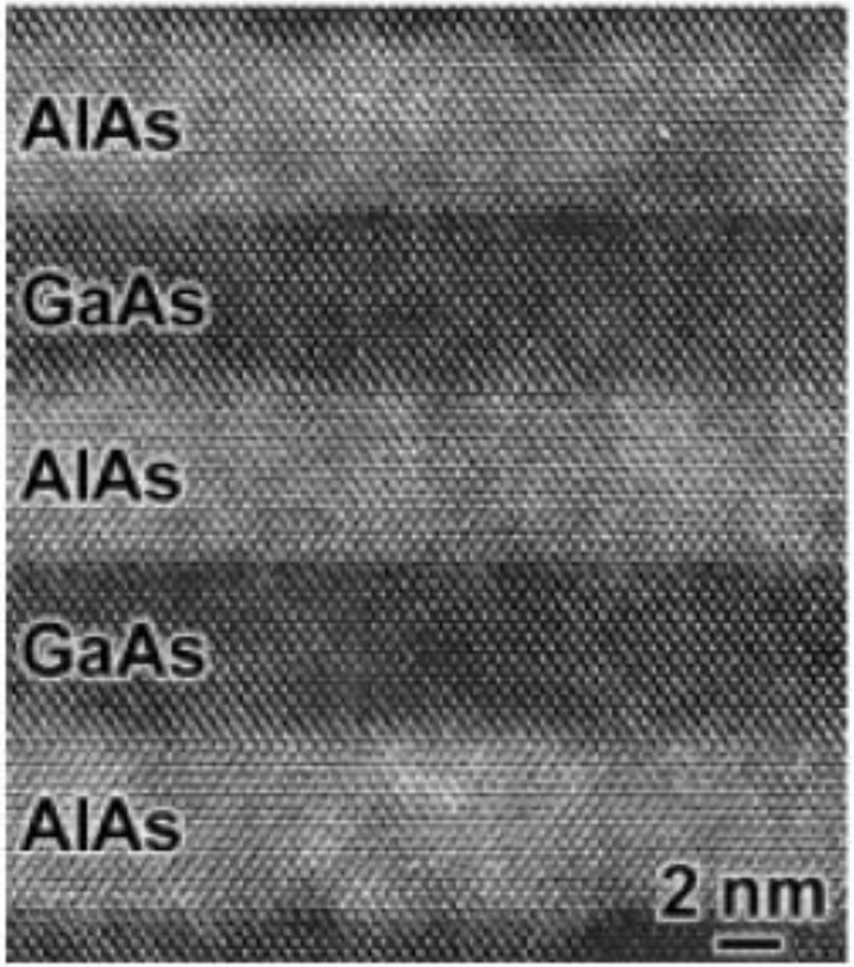
- **~1978-1981: modulation doping** (bandgap engineering), Gossard's team (Bell Labs)
  ➔ *Physics Nobel prize in 1998 (H. Störmer, D. Tsui), for the fractional quantum Hall effect*

- **~1982: 1st commercial MBE system,** from RIBER company (French, still international leader)

W.P. Mc Cray, Nature Nanotechnology **2**, 260 (2007)

From the 60's for III-V…

GaAs/AlAs SLs… to QWs (In-doped)



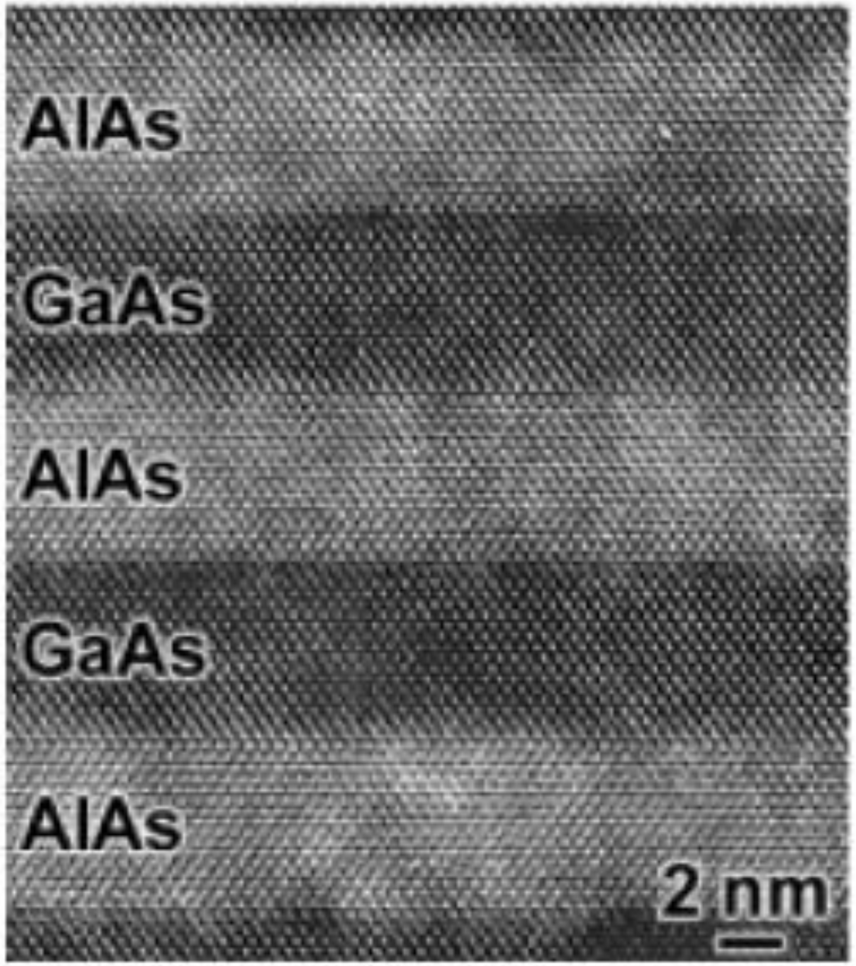
D.G. Schlom *et al.*, J. Am. Ceram. Soc. (2008)

To InGaAs/GaAs QDs…

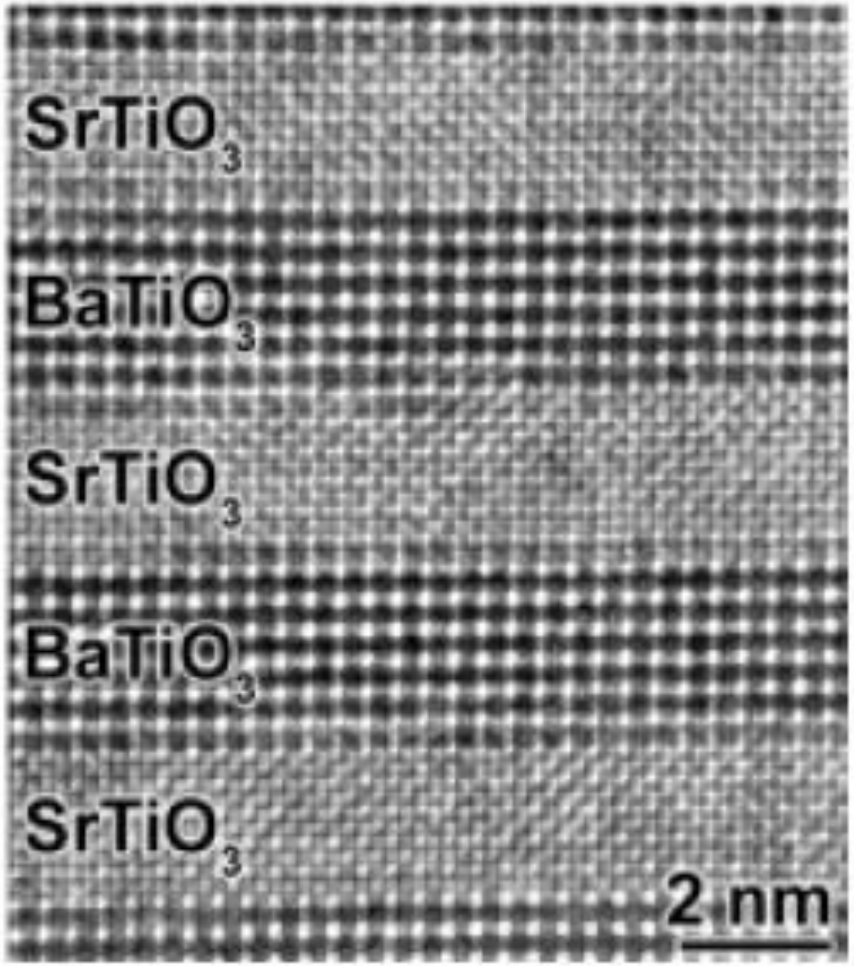
M. Henini, MBE books, Elsevier (2012)

From the 60's for III-V… to oxides since ~1985... & many more!...

GaAs/AlAs SLs… to QWs (In-doped)

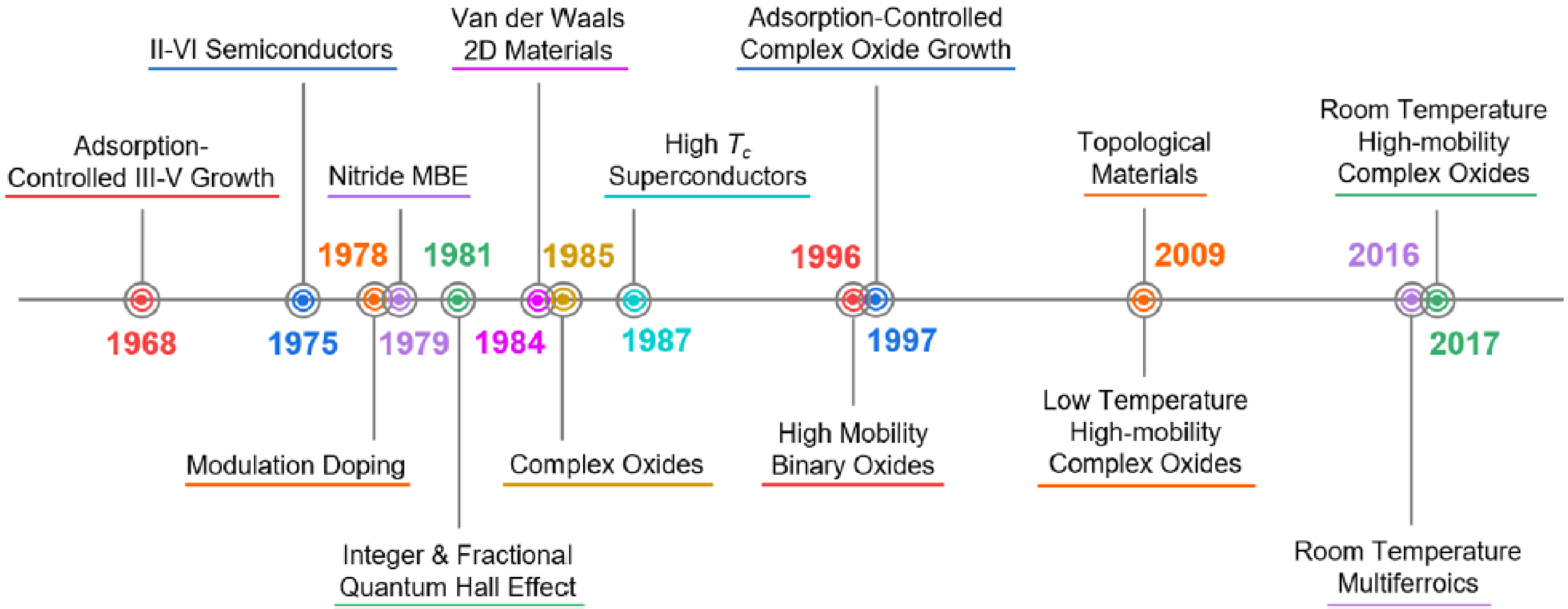


To STO/BTO SLs…



D.G. Schlom *et al*., J. Am. Ceram. Soc. (2008)

MBE developments for various materials & discoveries over time



W. Nunn *et al.*, J. Mater. Res. (2021)

Different kinds of materials developed by MBE

- **III-V** semiconductors: GaAs, AlAs, InAs, InP,… and alloys
- **II-VI** semiconductors: CdTe, ZnSe, CdS,…
- **IV-IV** semiconductors: SiGe, SiC,…
- **IV-VI** semiconductors: PbTe, PbSe, PbS,...
- **Nitrides**: GaN, AlN, BN, Si_3N_4, TiN,…
- **Oxides**: $LiNbO_3$, YBaCuO, ZnO, $SrTiO_3$, $BaTiO_3$, $BaSnO_3$,…
- **Topological** materials: Bi_2Se_3, Bi_2Te_3,…
- **2D** Van der Waals materials: MX_2 (MoS_2), III-VI (InSe), graphene-based (h-BN), Black P-like (SnS),…
- ***….

II	III	IV	V	VI		
						2 He 4.0026 Helium
	5 B 10.81 Boron	6 C 12.011 Carbon	7 N 14.007 Nitrogen	8 O 15.999 Oxygen	9 F 18.998 Fluorine	10 Ne 20.180 Neon
	13 Al 26.982 Aluminium	14 Si 28.085 Silicon	15 P 30.974 Phosphorus	16 S 32.06 Sulfur	17 Cl 35.45 Chlorine	18 Ar 39.948 Argon
30 Zn 65.38 Zinc	31 Ga 69.723 Gallium	32 Ge 72.630 Germanium	33 As 74.922 Arsenic	34 Se 78.971 Selenium	35 Br 79.904 Bromine	36 Kr 83.798 Krypton
48 Cd 112.41 Cadmium	49 In 114.82 Indium	50 Sn 118.71 Tin	51 Sb 121.76 Antimony	52 Te 127.60 Tellurium	53 I 126.90 Iodine	54 Xe 131.29 Xenon
80 Hg 200.59 Mercury	81 Tl 204.38 Thallium	82 Pb 207.2 Lead	83 Bi 208.98 Bismuth	84 Po 208.98 Polonium	85 At 209.99 Astatine	86 Rn 222.02 Radon
112 Cn 285.18 Copernicium	113 Nh 286.18 Nihonium	114 Fl 289.19 Flerovium	115 Mc 289.20 Moscovium	116 Lv 293.20 Livermorium	117 Ts 293.21 Tennessine	118 Og 294.21 Oganesson

Many applications & fundamental physics discoveries

For many kinds of applications (microelectronic field)

- **Electronic devices:** high-mobility FET, NV-memories, neuromorphic computing, power electronics,…
- **Electro-optic / photonic devices:** lasers, diodes, PV, modulators,…
- **Optical / thermal:** sensors (IR, RX), imaging tools,…
- ***…

And discoveries in nanoscience / nanomaterials / condensed-matter physics

- **Fractional Hall effect**
- **New materials: new solid solutions, 2D, topological, new multiferroic,…**
- ***…

Main MBE companies

RIBER

Bezons (95), France
https://www.riber.com/

Veeco

NY, USA
https://www.veeco.com/

DCA INSTRUMENTS

Finland
https://www.dca.fi/

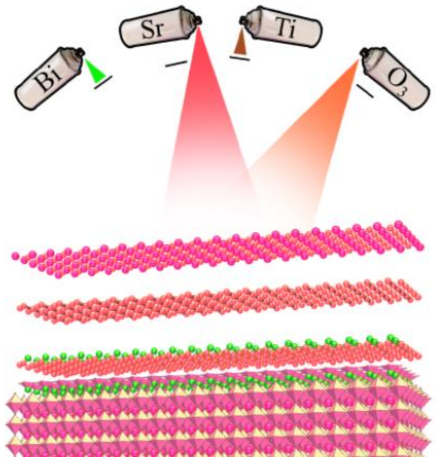
MBE KOMPONENTEN

Germany
https://www.mbe-komponenten.de/

Some French labs using MBE

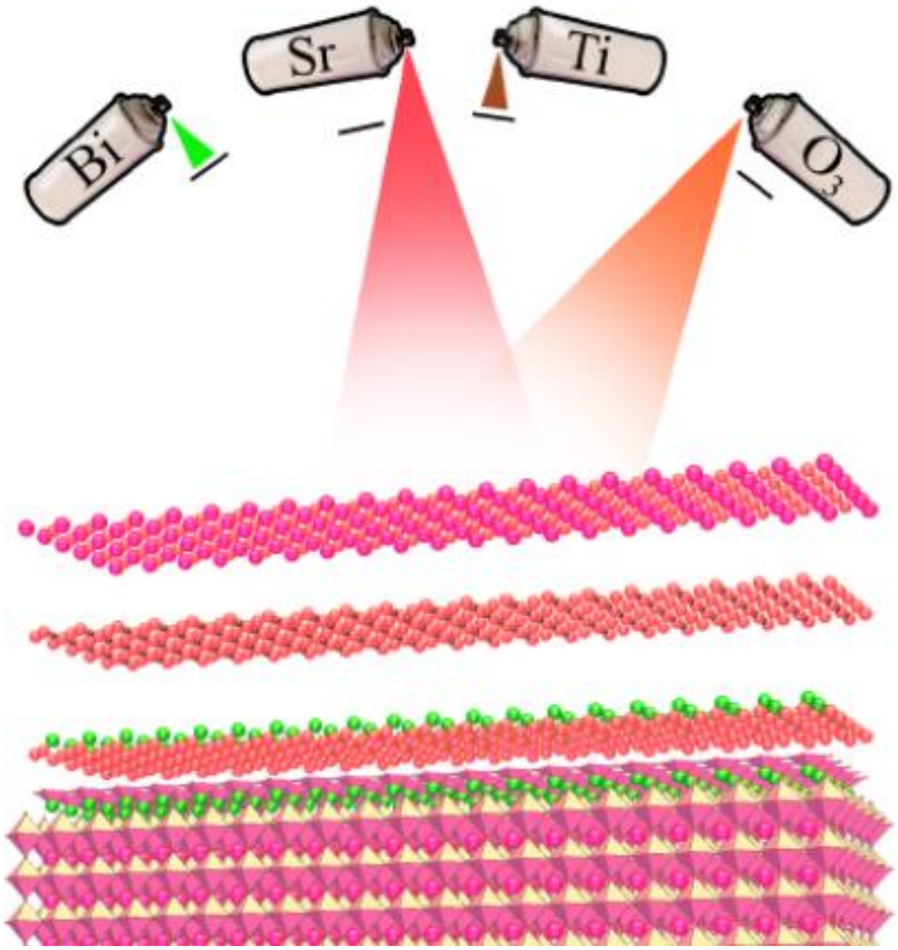
LAAS CNRS	III-V / antimonides	A. Arnoult, S. Calvez, S. Plissard,…
C2N	III-V / nitrides NWs	J.C. Harmand, A. Lemaître, M. Tchernycheva, N. Gogneau,…
CRHEA	Nitrides, (Zn,Mg)O	Y. Cordier, F. Semond, J. Zuniga-Perez,…
ies	III-V antimonides	E. Tournié,…
iemn	III-V	X. Wallart, D. Vignaud,…
im2np	SiGe,..	I. Berbezier,…
Institut foton	III-V / Si	C. Cornet,…
inl	III-V & oxides	P. Regreny, G. Saint-Girons, J. Penuelas, R. Bachelet,…

3. General principles & advantages



MBE: "*spray painting… with atoms!*"

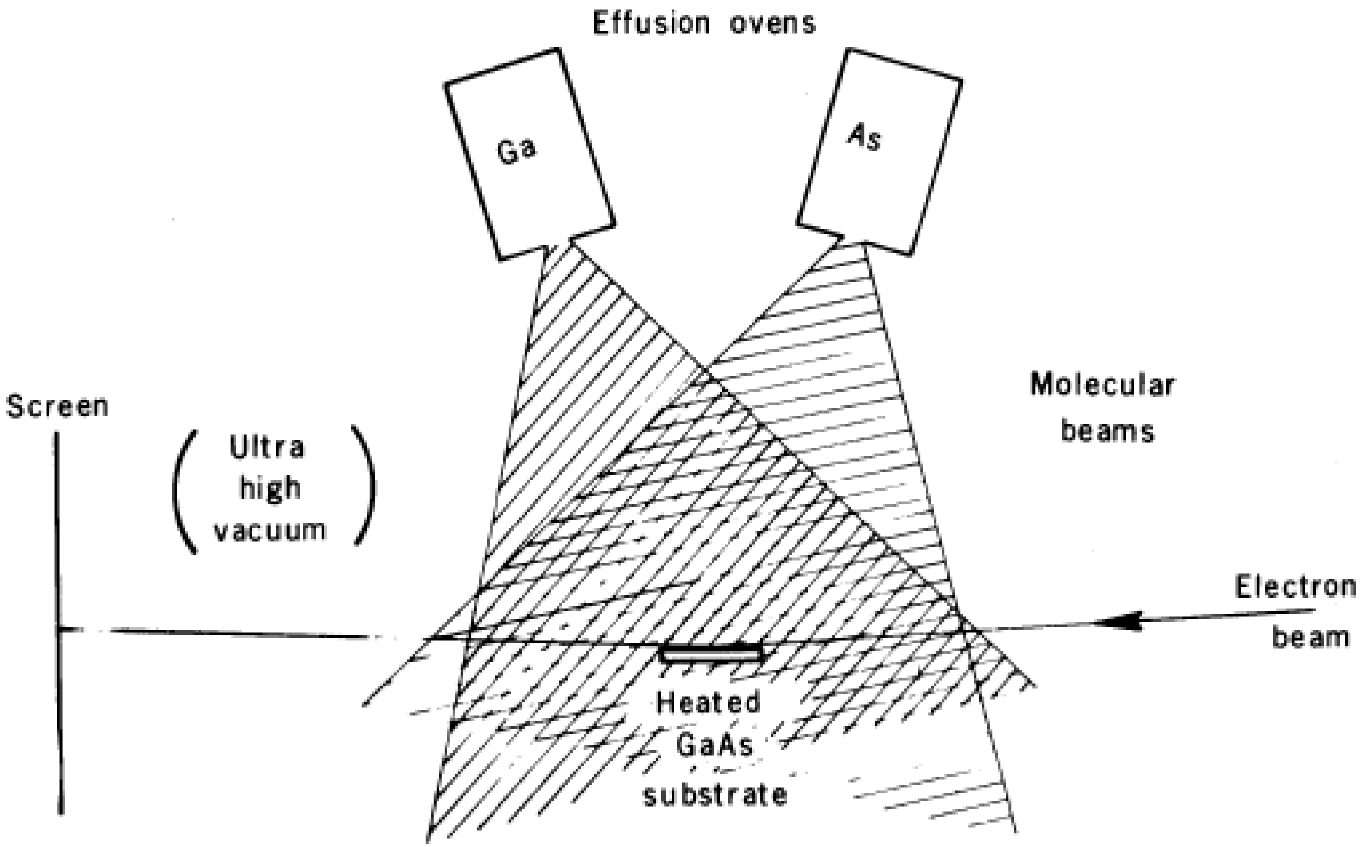
[*The New York Times, 1982*]



D.G. Schlom *et al*., J. Am. Ceram. Soc. (2008)

MBE: basic principles

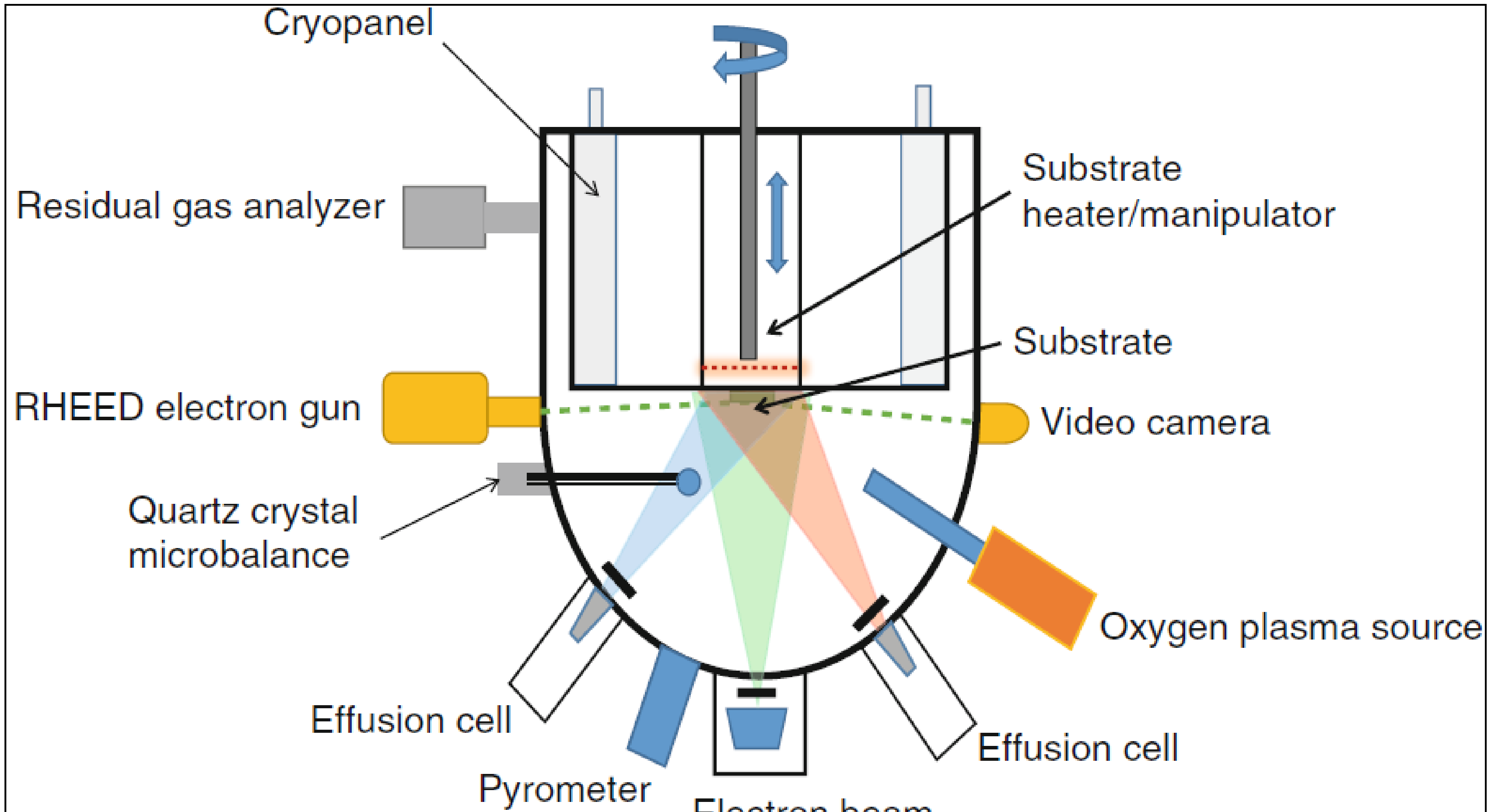
[*The New York Times, 1982*]



M.P. Panish, Science (1980)

MBE: PVD technique +

*In **UHV**, with **elemental flux**, **low flux / growth rate**, & **in-situ monitoring***



$$\phi = \phi_0 \times e^{-E/kT}$$

A.A. Demkov and A.B. Posadas, *Integration of functional oxides with semiconductors* (2014)

High purity & quality of films & heterostructures

Low Pressure (UHV)

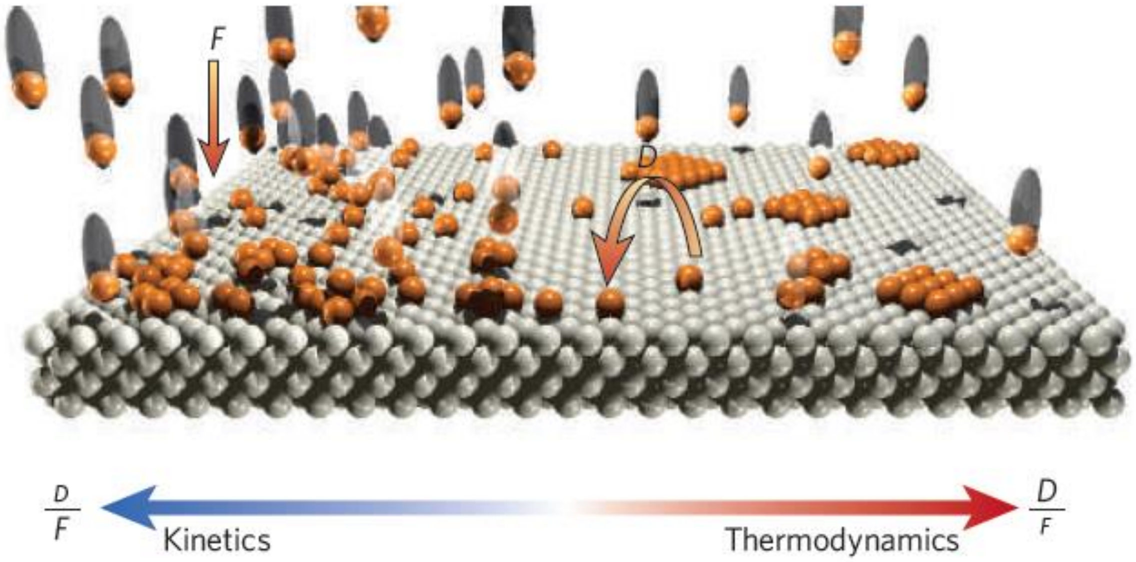
Mean free path of atoms/molecules:

$$\lambda = \frac{kT}{\sqrt{2}\pi d^2 P}$$

where k is Boltzmann constant, T is temperature, d is the kinetic diameter of atom or molecule, and P is the pressure. As

➔ >1 order of magnitude than the mean distance between gas atoms/molecules

Low growth rate (low flux & low energy)



➔ Towards thermodynamic equilibrium
➔ High crystalline/epitaxial quality

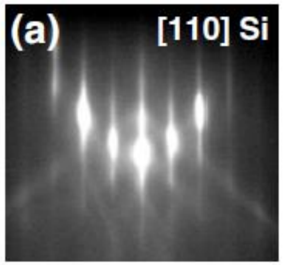
Semiconductor surface passivation ➔ Hybrid heterostructures

(*e.g.* oxides templates on SCs)

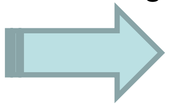
Low Pressure (UHV) + elemental sources + *in-situ* RHEED

Sr-passivated Si(001): $SrSi_2$ bonds at the surface

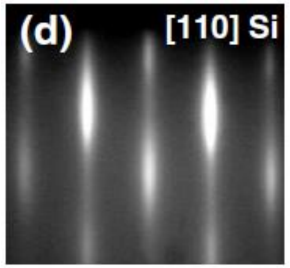
½ ML Sr/Si (2x1)

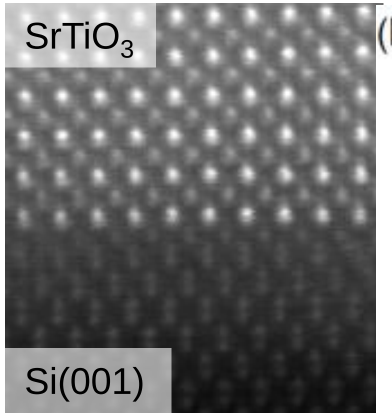


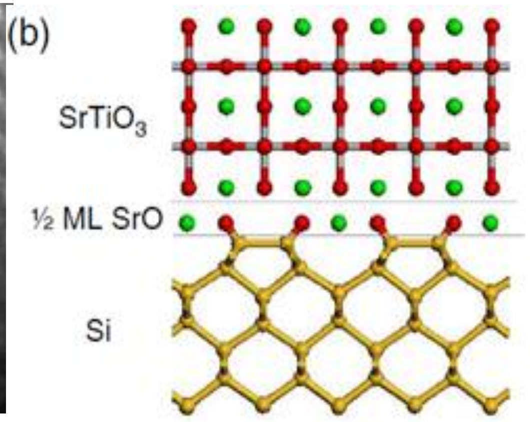
$SrTiO_3$



STO/Sr/Si (1x1)

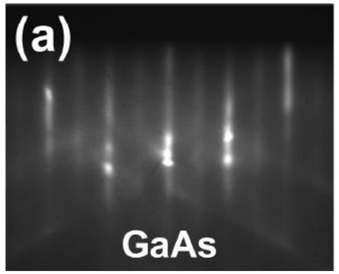


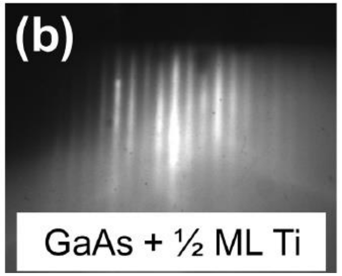


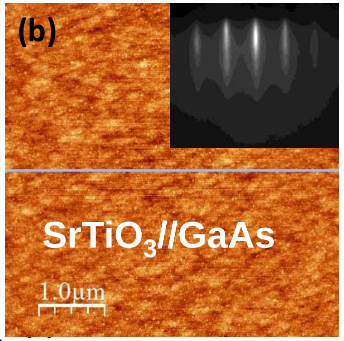


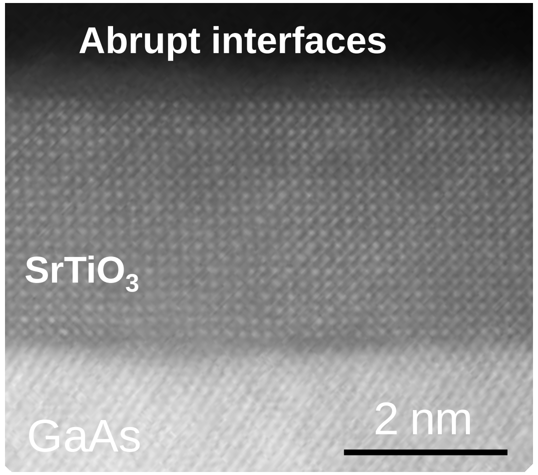
G. Niu, G. Saint-Girons *et al.*, APL (2009)
G. Saint-Girons, R. Bachelet *et al.*, Chem. Mater. (2016)

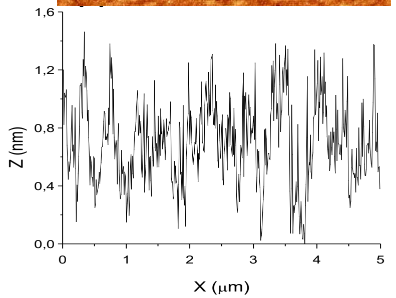
Ti-passivated As-GaAs(001)











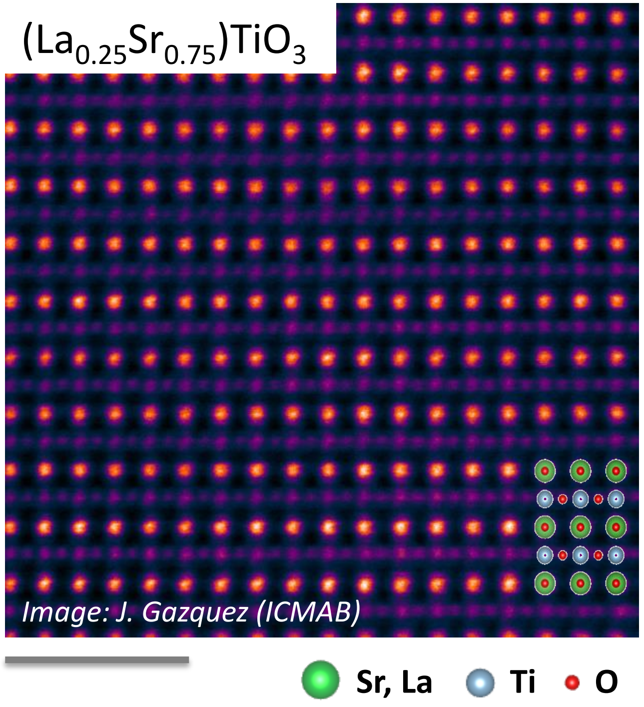
L. Louahadj *et al.*, APL (2013); *ibid*, Thin Sol. Films (2014);
B. Meunier *et al.*, J Crystal Growth (2016)

Flexibility of chemical composition: alloys, doping, combinatorial,…

Elemental sources

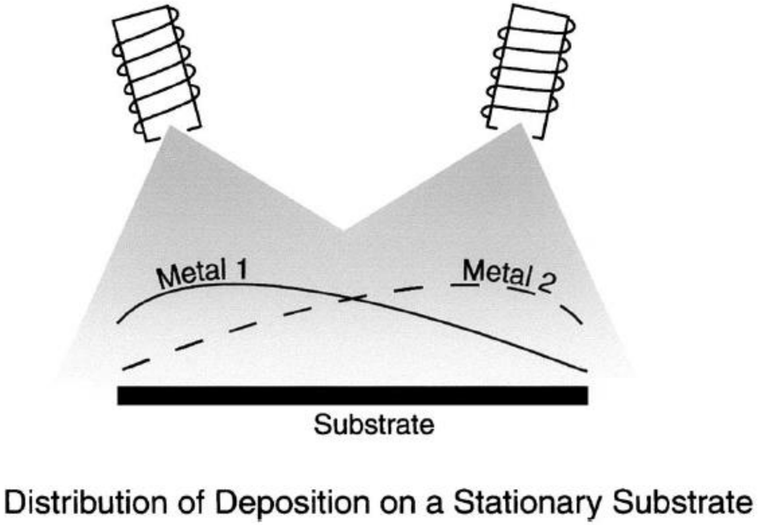
<u>Alloys or solid solutions, and doping</u>

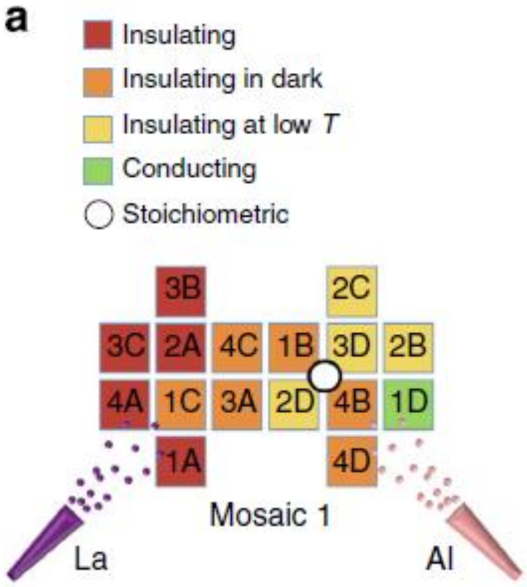
In-GaAs, Al-GaAs, In-GaN
La-$SrTiO_3$, $(Ba,Sr)TiO_3$



M. Apreutesei *et al.*, Sci. Technol. Adv. Mat. (2017)

<u>Combinatorial</u> (lateral composition gradient)

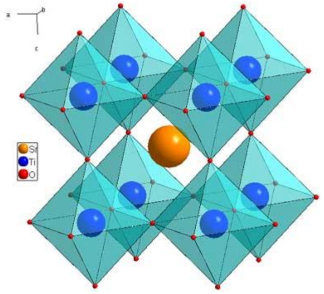




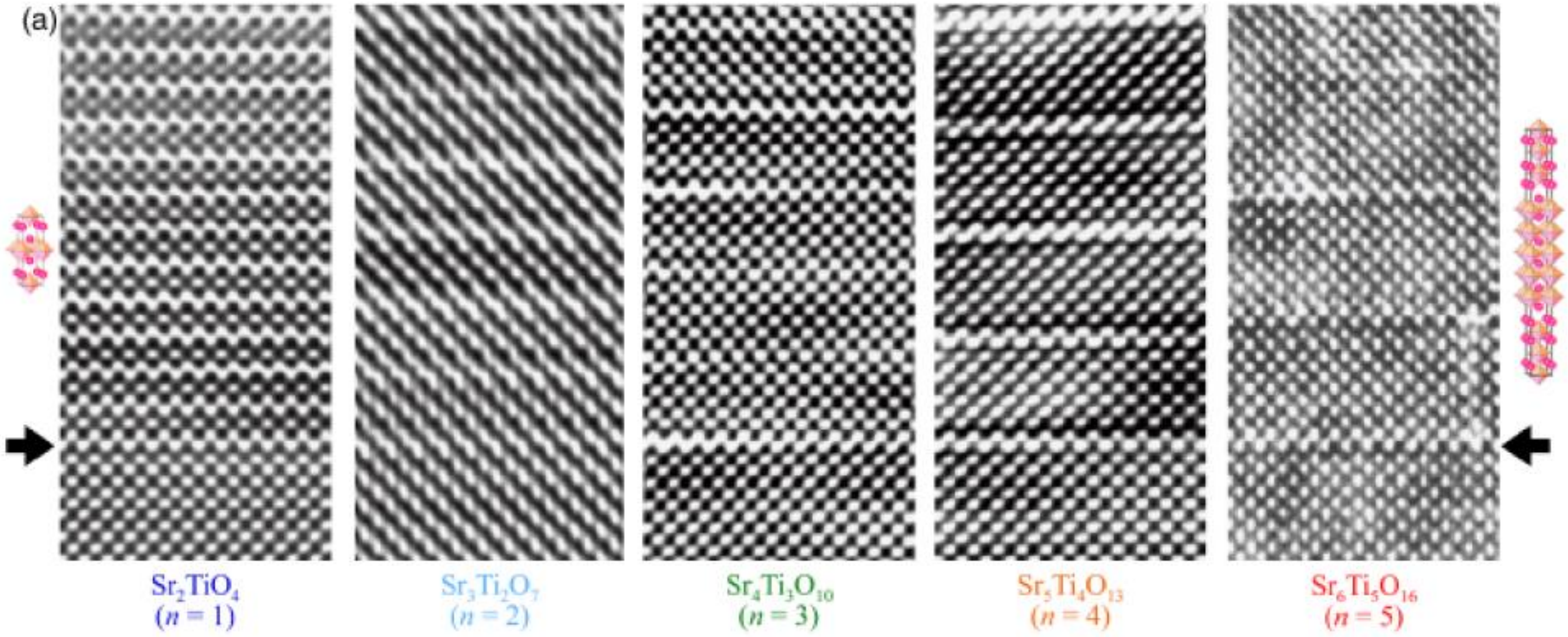
J.R. Arthur, Surface science (2002)
M.P. Warusawithana, *et al.*, Nature Com. (2013)

Flexibility of chemical composition: superstructures, phases,…

Elemental sources



$SrTiO_3$ based Ruddlesden-Popper (RP) phases = (SrO)$(SrTiO_3)_n$

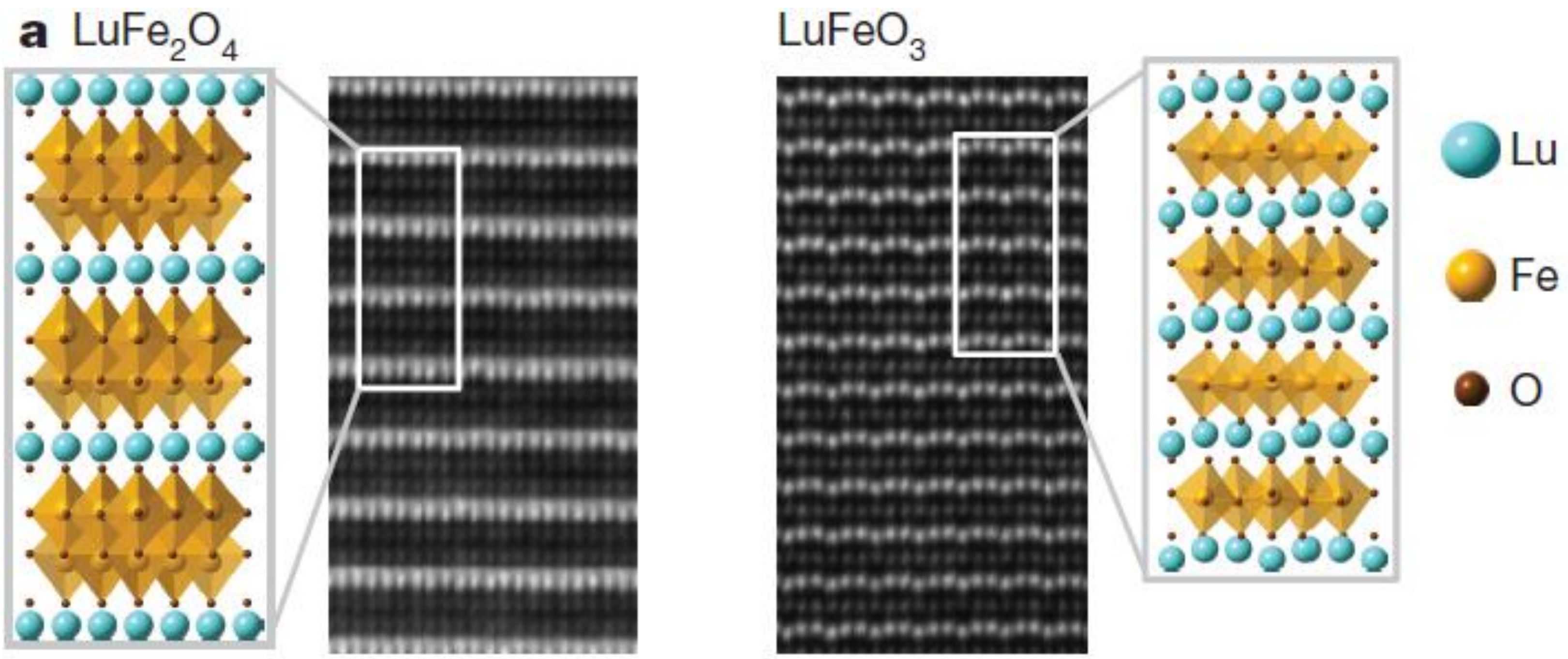


D.G. Schlom *et al.*, J. Am. Ceram. Soc. (2008)

Flexibility of chemical composition: superstructures, phases,…

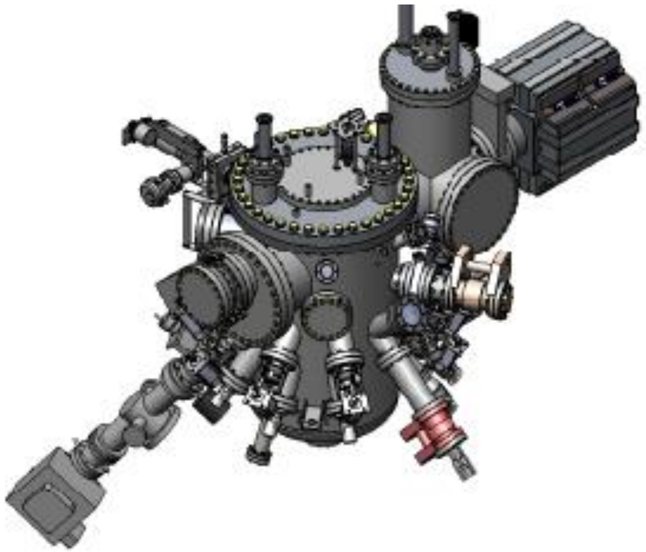
Elemental sources

Layered Lu ferrites as a new multiferroic (Schlom' group)



J.A. Mundy *et al.*, Nature (2016)

4. Technical details & challenges



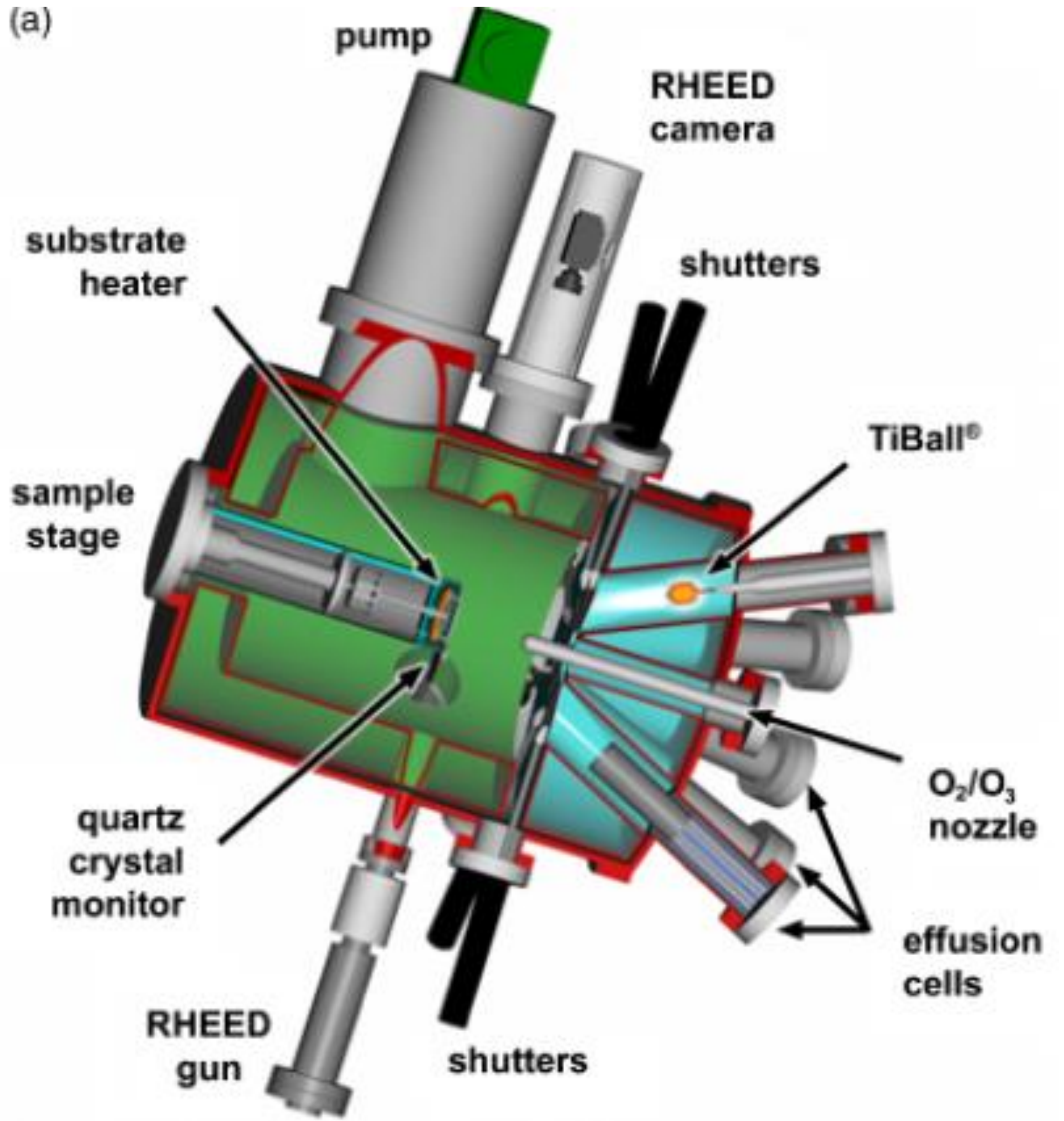
MBE chamber - main technical elements

Main parts

- Effusion cells / sources
- Flux control / measurements
- Pumping / P(atm) control
- Growth monitoring (RHEED)

Main challenge

- Stoichiometry control



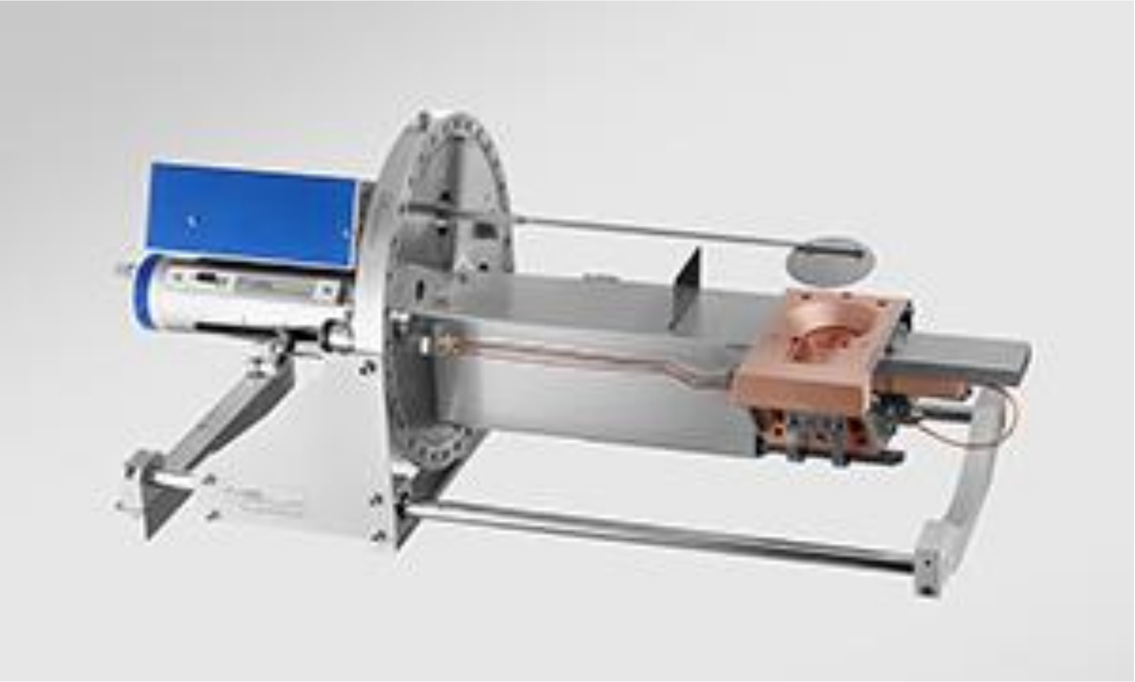
D.G. Schlom *et al.*, J. Am. Ceram. Soc. (2008)

Effusion cells / sources

Knudsen effusion cell

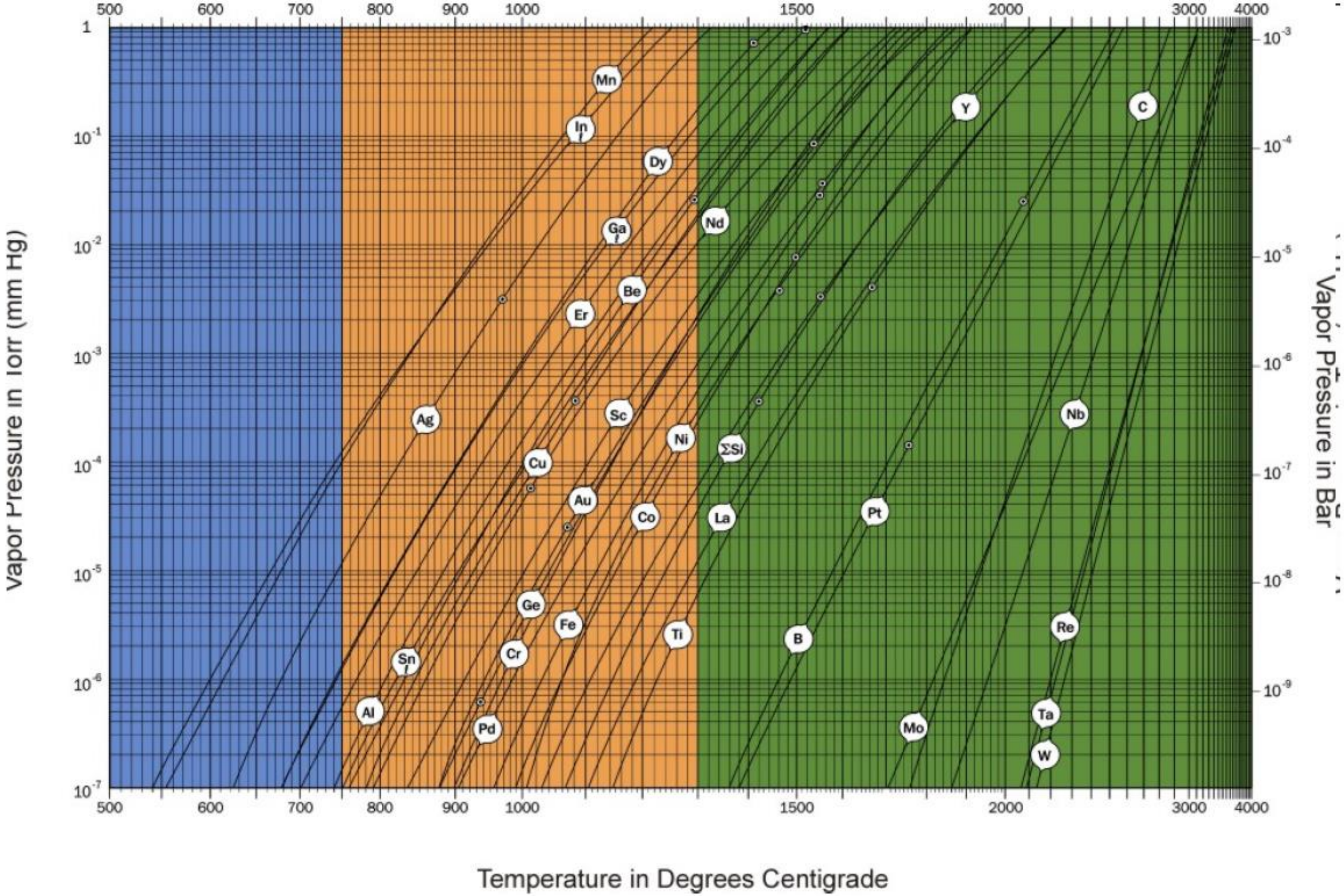
Different cells for different T ranges (LT, MT, HT)
Different cells for different kinds of elements (e.g. As)
Different crucibles depending of the element reactivity

E-beam evaporator



For refractory (or too reactive) elements

Vapor pressure *vs* T of the elements

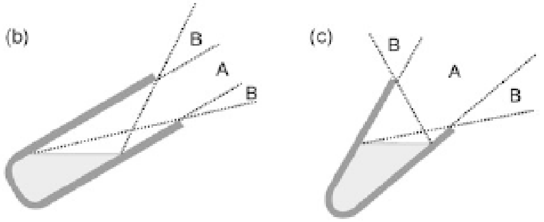


Effusion cells / sources

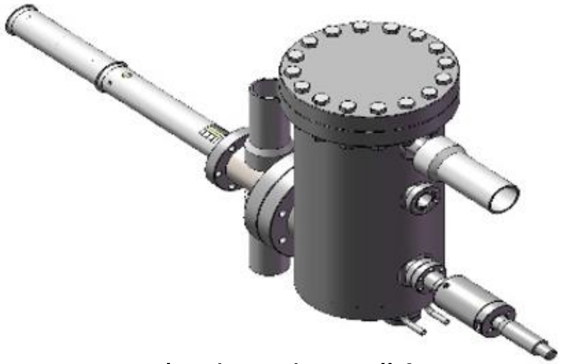
Main challenges

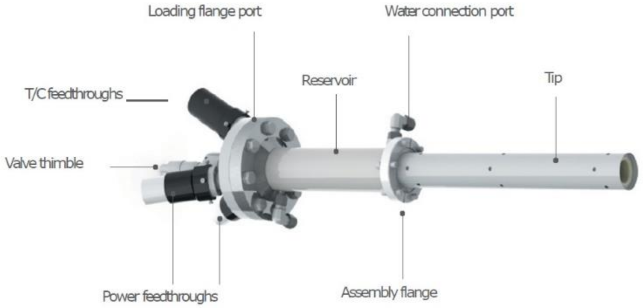
- Flux stability/reproducibility ➔ cell robustness, inert source materials?, *in-situ* flux measurements?,…

- Lateral chemical homogeneity ➔ large cells, conical cells/crucibles,…

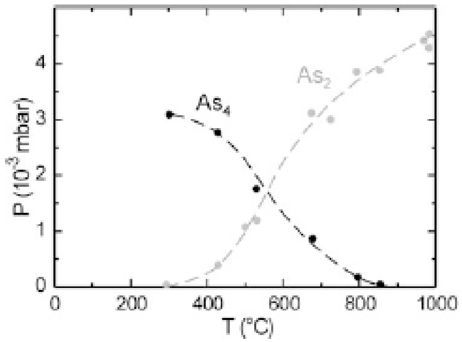


- Refractory / volatile / “sticky” / toxic elements ➔ specific cells/crucibles (crackers, RF plasma, valved,...)


Valved cracker cell for As



Valved cell for corrosive elements



Flux measurements

Main Possibilities

- Ionization Bayard-Alpert (BA) gauge — not *in-operando*, lack of accuracy, element-dependent
- Quartz Crystal Microbalance (QCM) — not *in-operando*, lack of accuracy (sensible to radiations, vibrations)
- Mass spectrometer — not *in-operando*, impossible to distinguish some different elements
- e- Impact Emission Spectroscopy (EIES) — not *in-operando*, lack of accuracy, small signals

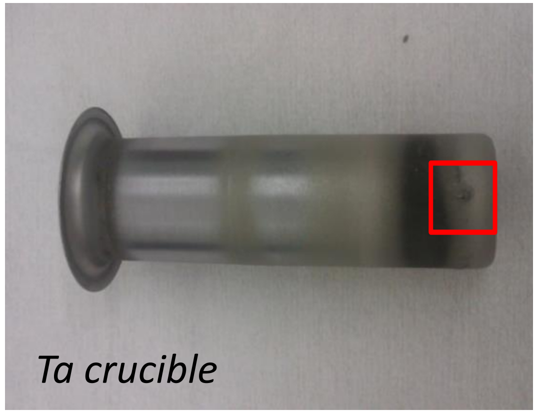
Main challenge

- Need of ***in-operando*** (accurate) flux measurements

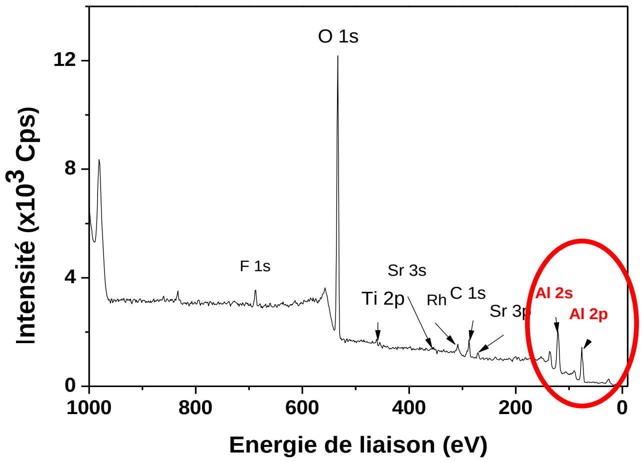
Evaporation of refractory (& reactive) elements: *e.g.* Ti under $P(O_2)$

Ti: point de fusion 1668°C, point d'ébullition 3287°C ➔ Température d'évaporation = **1550°C pour un flux 3.10^{-9} Torr** sous UHV

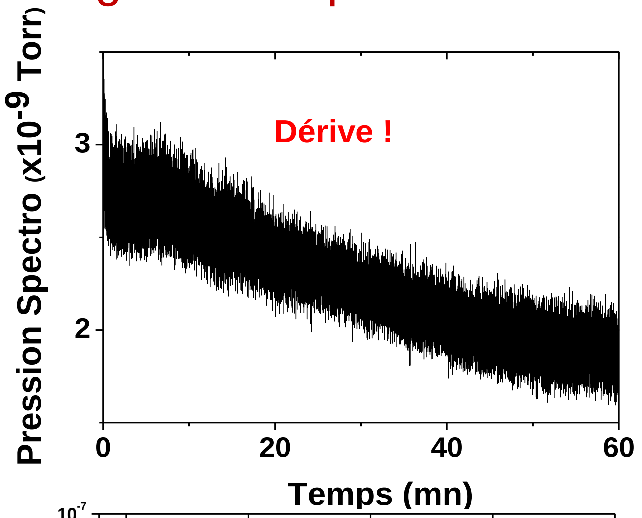
Reaction with standard crucibles

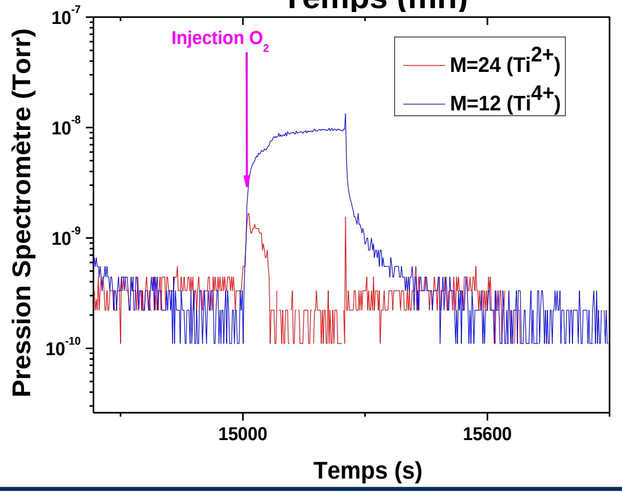


Liner Al_2O_3 ➔ evaporation of Al_2O_3 and not Ti!...



E-beam evaporation: drift & regulation impossible under $P(O_2)$





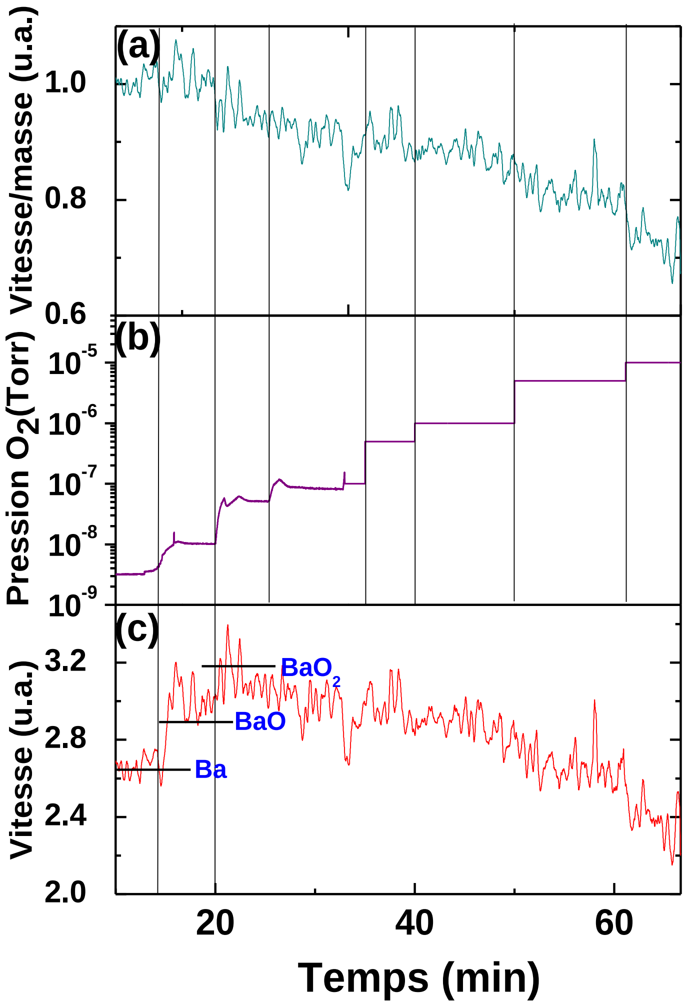
Special inert/stable crucibles for Ti

W crucibles OK!
But limited T in MHT standard cells

HT DCA cells OK!
up to 2000°C with special crucible!
But not accurate or impossible flux measurements!…

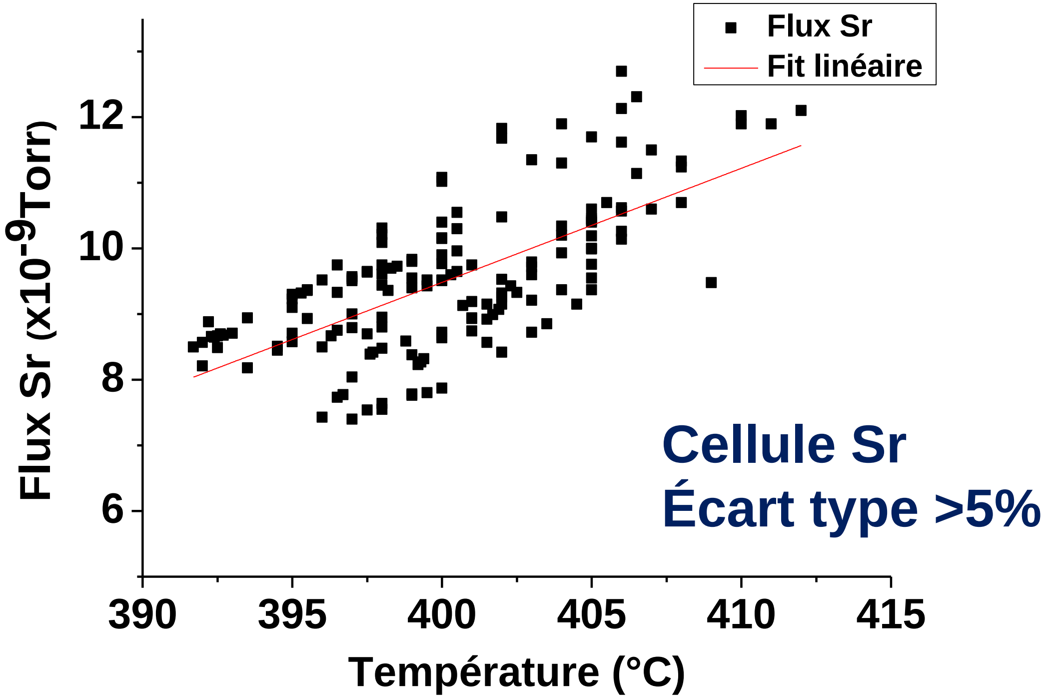
Flux drift & low accuracy of small flux measurements

Flux drift due to oxidation of the metallic sources during growth!...



➔ Growth at $P(O_2) \leq 10^{-7}$ Torr or differential pumping

Low accuracy of tiny flux measurements



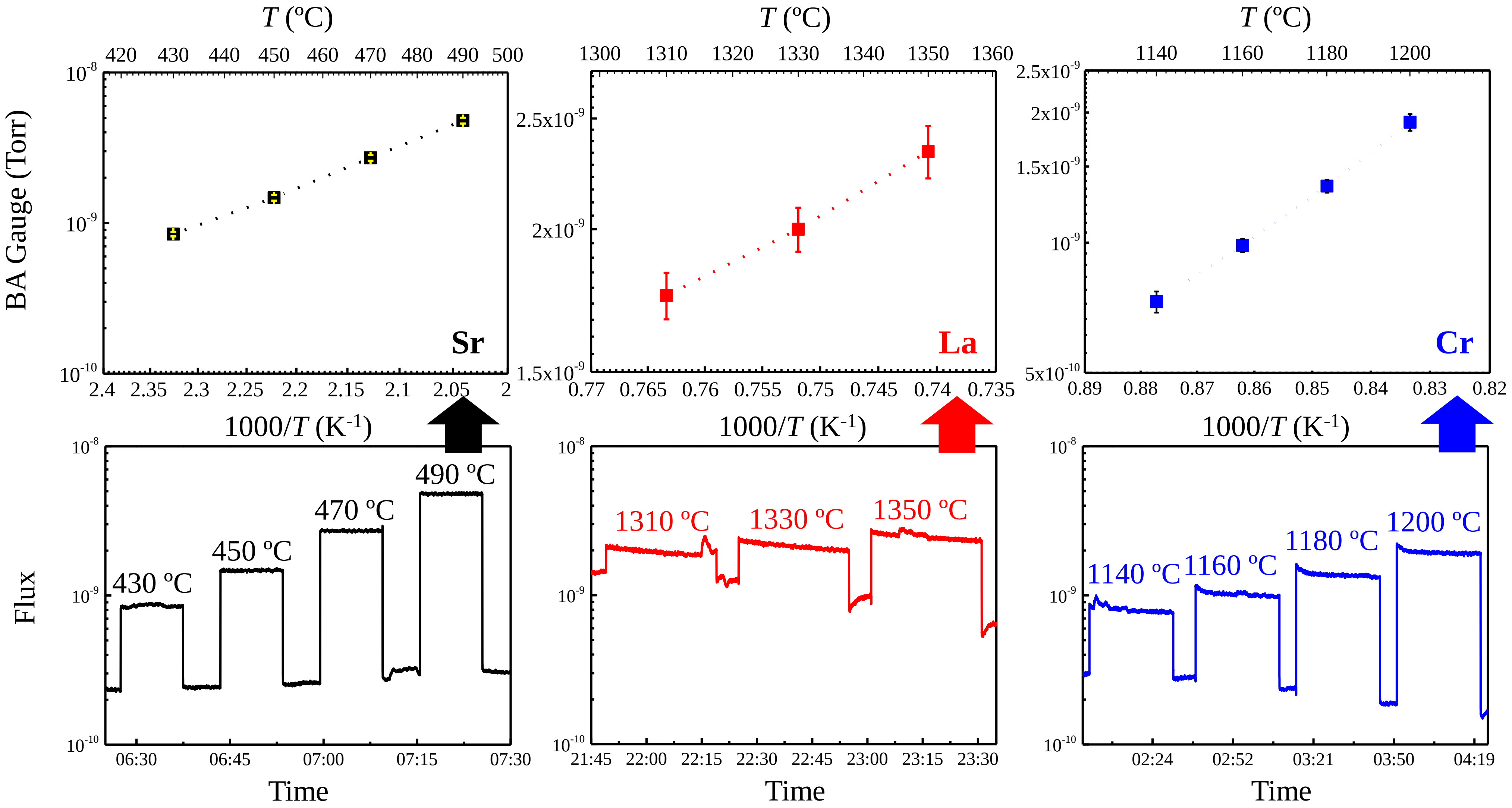
➔ Automatization of measurement sequences

L. Louahadj, PhD Thesis, ECL (2014)

Flux measurements under UHV

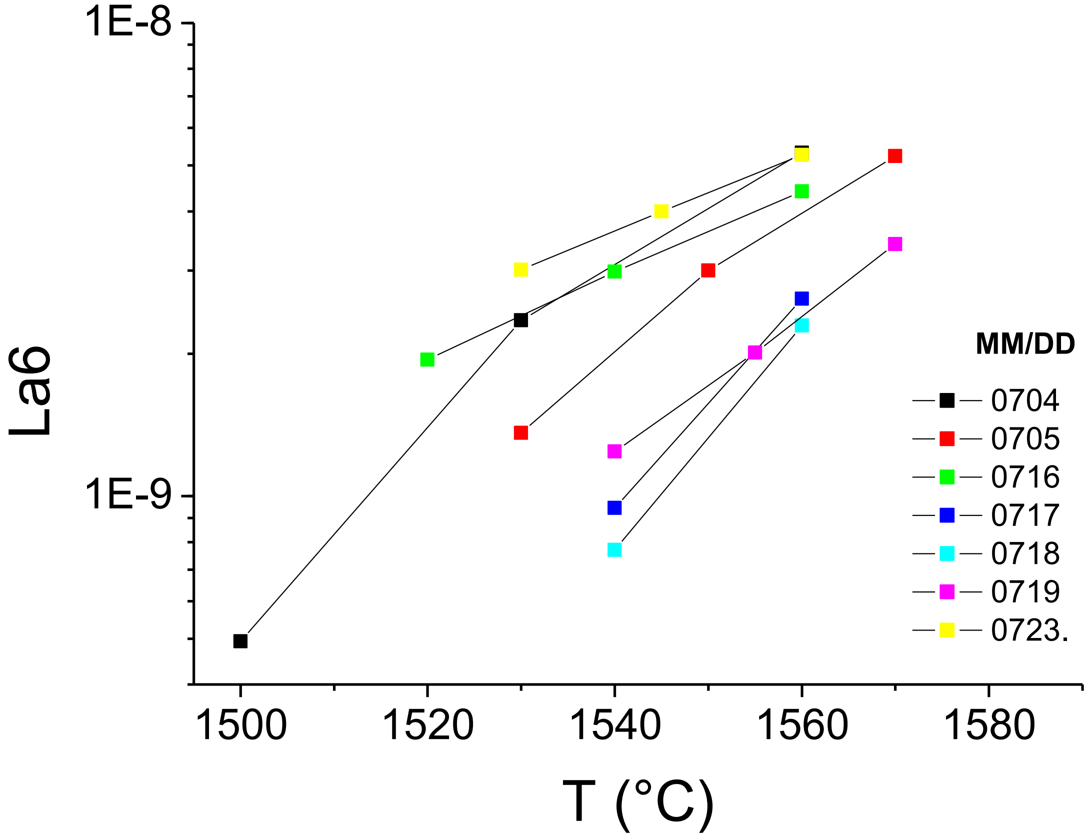
➔ Uncertainty within ~5%

$$\phi = \phi_0 \times e^{-E/kT}$$



D. Han, PhD Thesis, ECL (2020)

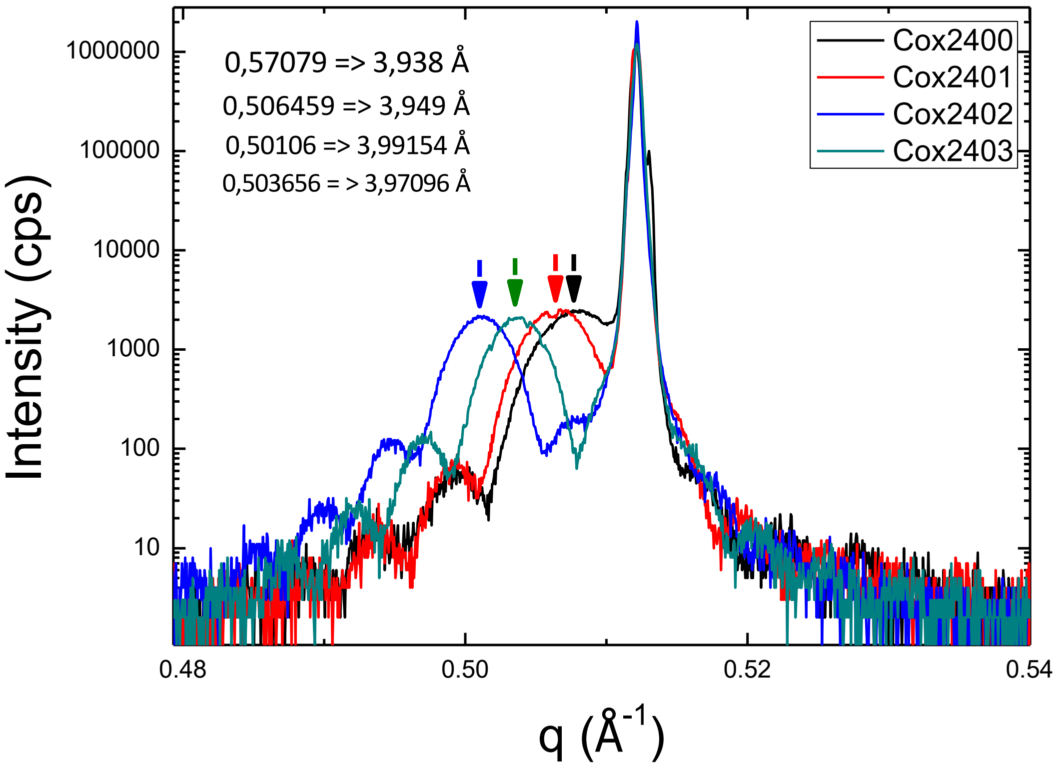
Lack of accuracy/reproducibility in solid-source oxide MBE



4 $SrTiO_3$ films, same day, same conditions:

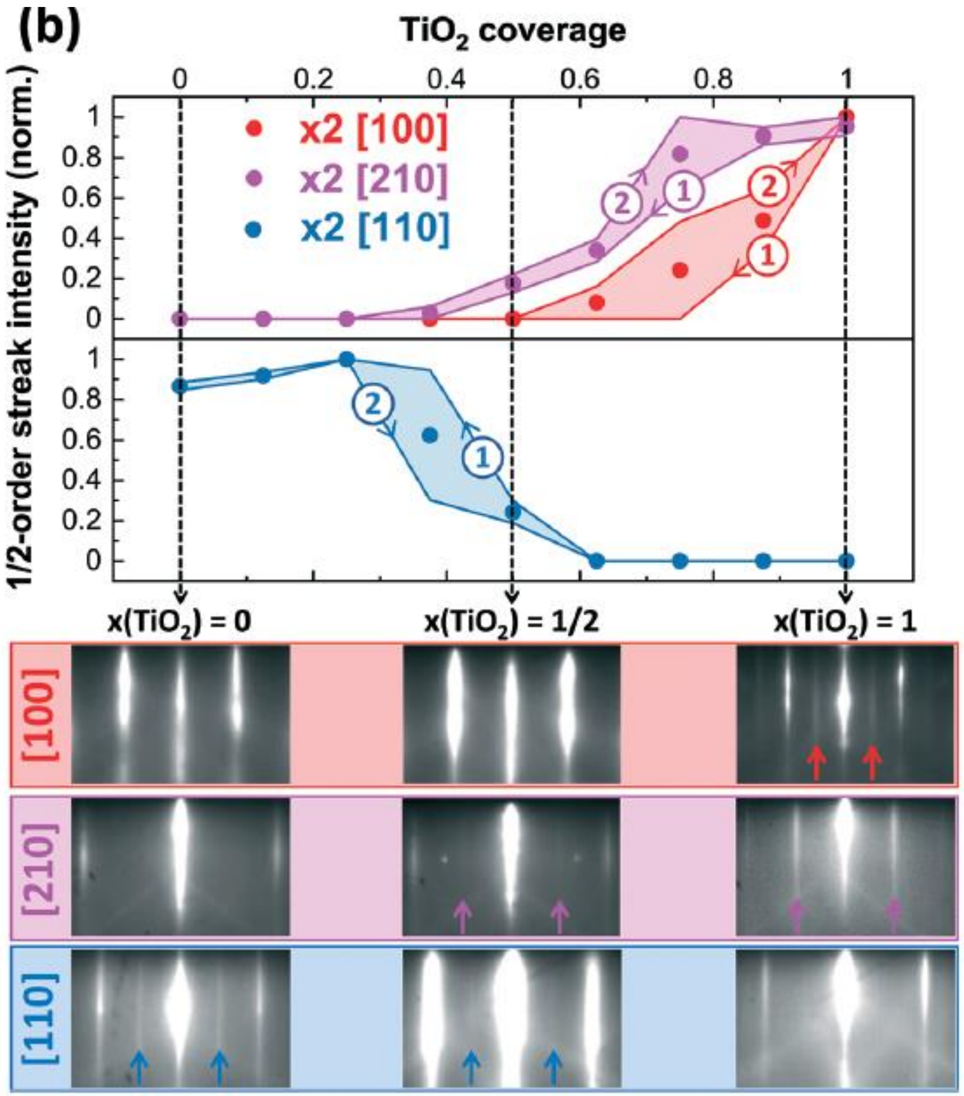
T = 700°C; $P(O_2)$ = 1 10^{-7} Torr

Ti7 = 1949,5°C ; Sr3 = 538,3°C

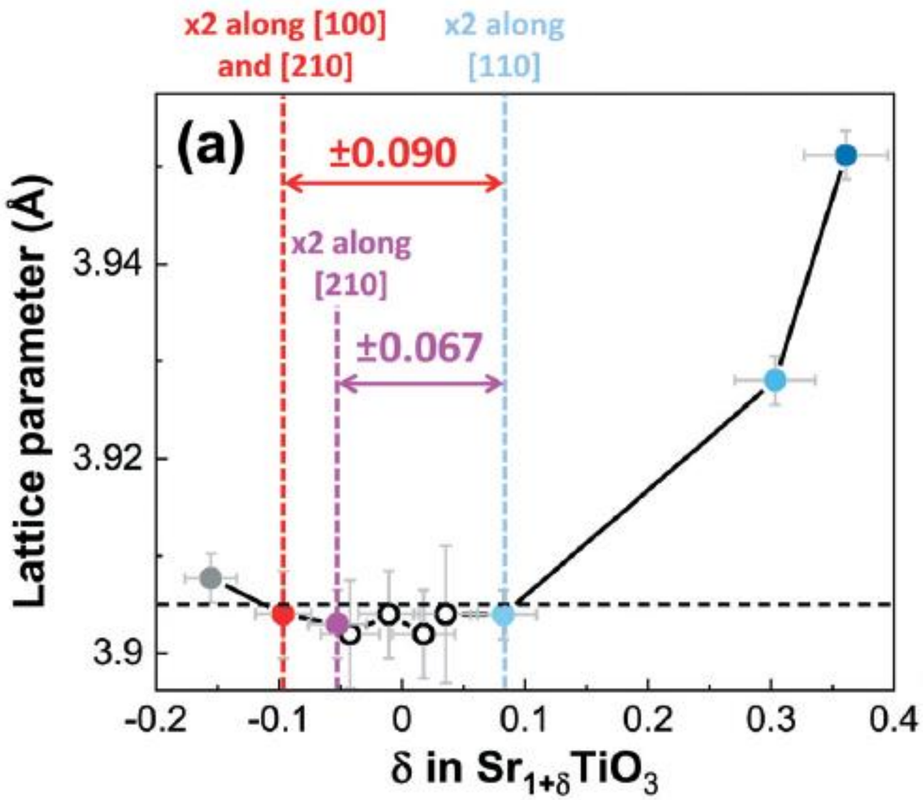


D. Han, PhD Thesis, ECL (2020); M. d'Esperonnat (2019-2022)

RHEED-assisted *in-situ* control of stoichiometry



➔ uncertainty/errors in composition (~ 5%)



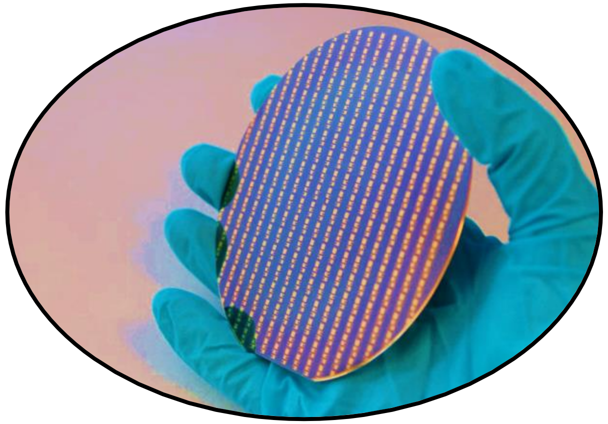
M.R.P. Ghaleh *et al.*, CrystEngComm (2019)

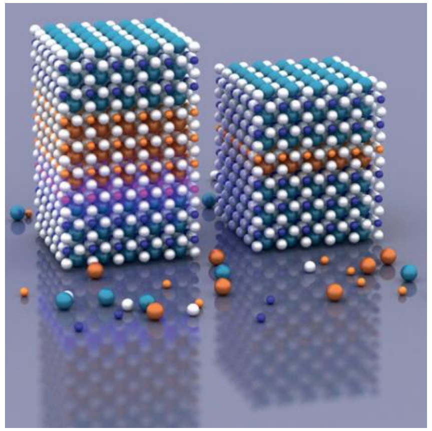
➔ **Towards new/enhanced flux measurement methods**

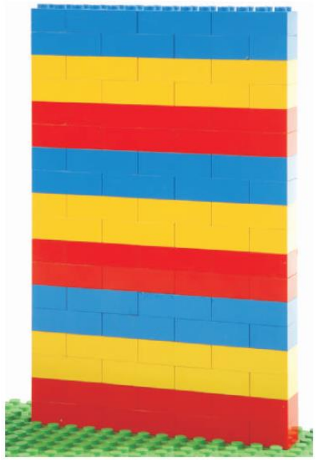
& cell differential pumping to lower source oxidation

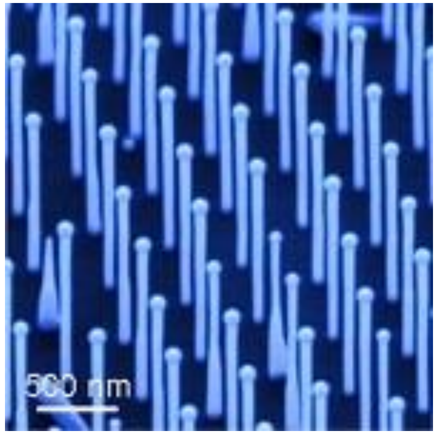
5. Some examples of heterostructures from INL

- *Oxide films (2D)*
- *III-V nanowires (1D)*









Pole Epitaxy at INL-Nanolyon

nanolyon

UHV linear cluster

2 III-V MBE
1 oxide MBE
1 ECR/ALD
1 sputtering (mutlisources)

1 XPS

1 new oxide MBE (2023)

ÉCOLE CENTRALE LYON

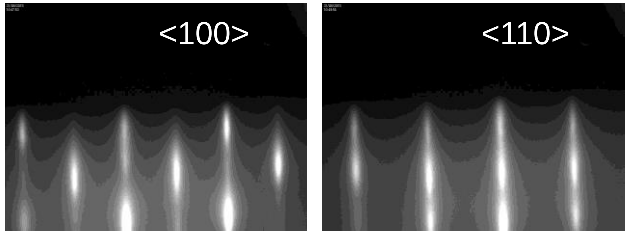
inl

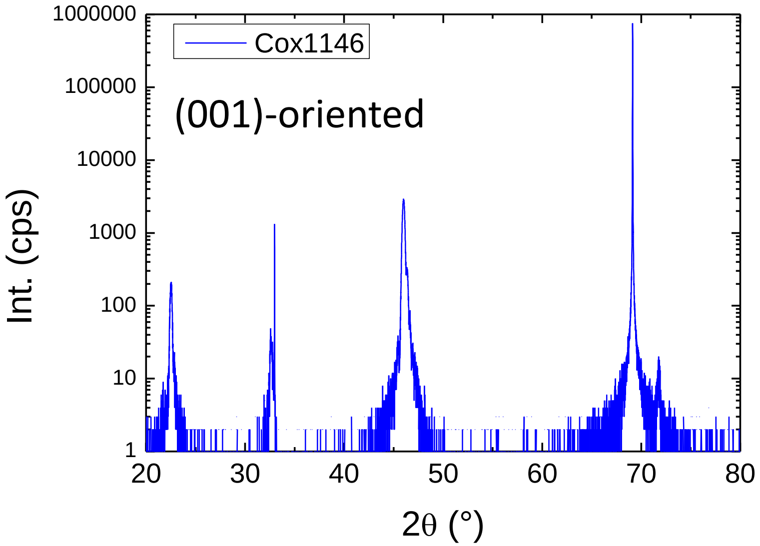
Epitaxial oxides on semiconductors

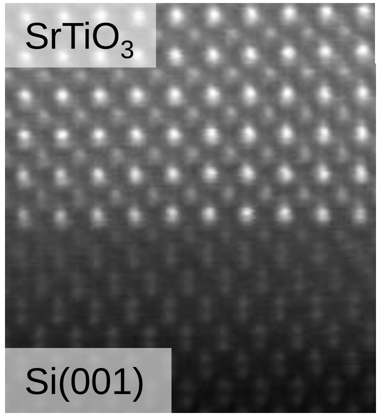
Epitaxial oxide buffer layers on semiconductors

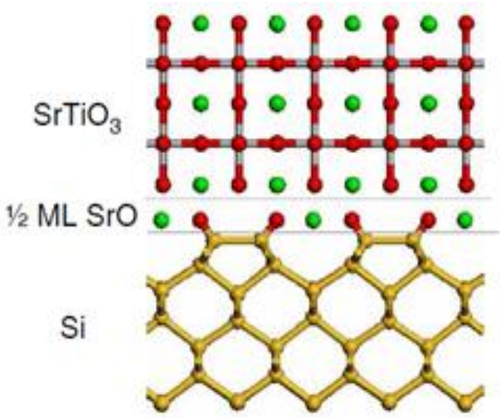
$SrTiO_3$/Si(001)

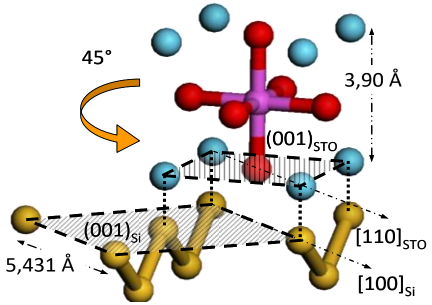
≥ 40 nm 2 inch. STO/Si with state-of-the-art structural qualities











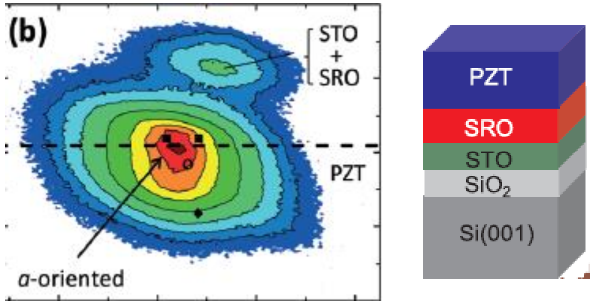
G. Saint-Girons, R. Bachelet *et al.*, Chem. Mater. (2016)

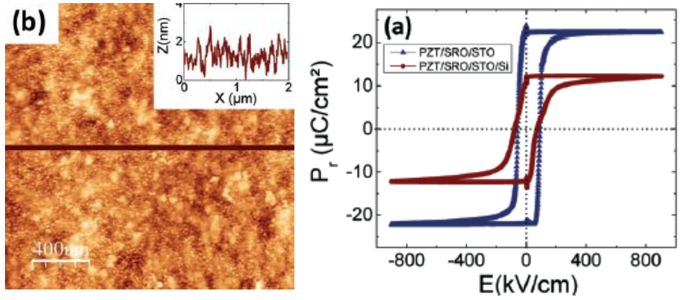
Epitaxial oxide buffer layers on semiconductors

$SrTiO_3$/Si(001): ideal pseudo-substrate for the integration of many materials!

Functional ABO_3 (001)

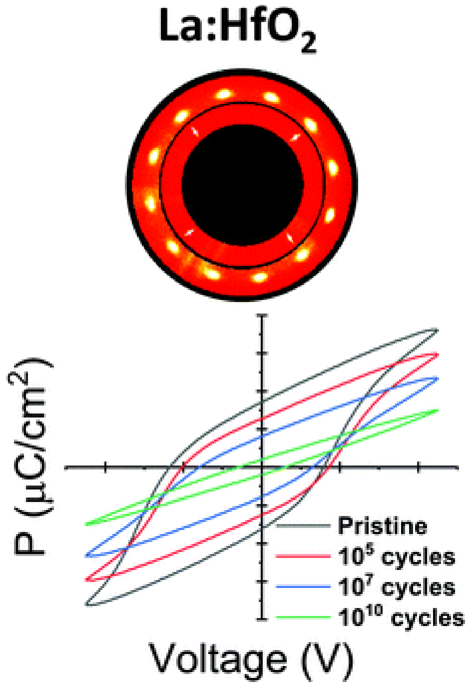
Ferro-/Pyro-/Piezo-electrics, Thermoelectrics, Ferromagnetics,…





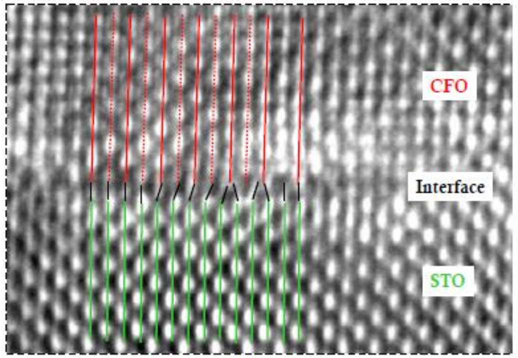
R. Moalla *et al.*, CrystEngComm (2016); *ibid*, Nano Energy (2017); A. Gomez et al., Small (2017); J.M. Vila-Fungueirino *et al.*, Sci. Technol. Adv. Mater. (2018);…

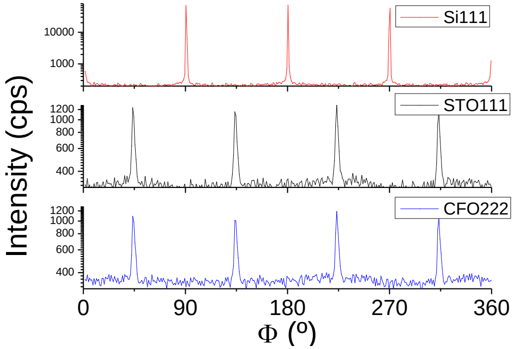
Ferroelectric $(Hf,Zr)O_2$ (111)



T. Song *et al.*, ACS Appl. Electron. Mater. (2020, 2021); *ibid*, J. Mater. Chem. C (2021);…

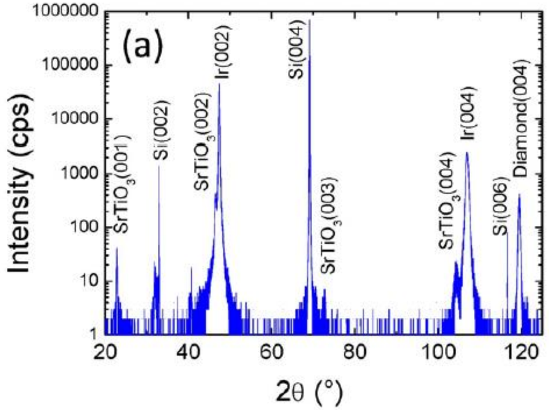
Ferromagnetic AB_2O_4 (001)

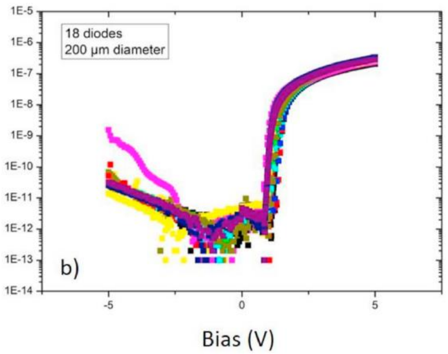




P. De Coux *et al.*, PhD thesis; N. Dix et al., APL (2013)

Semiconducting Diamond (001)



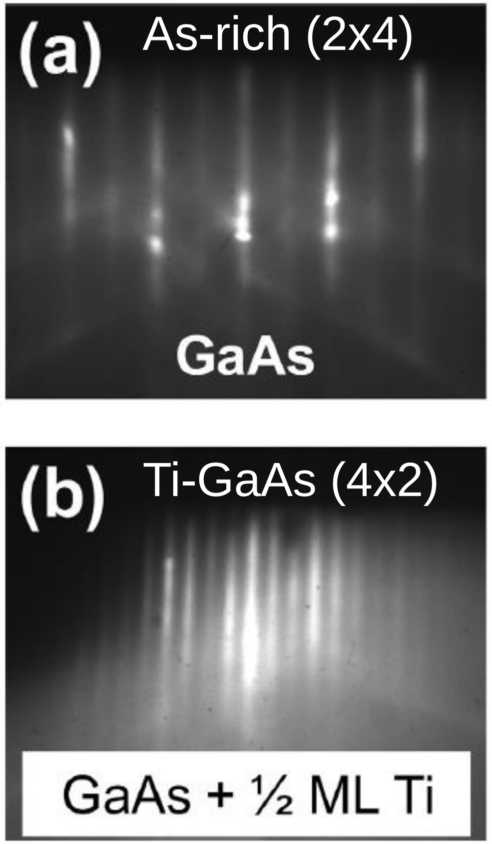


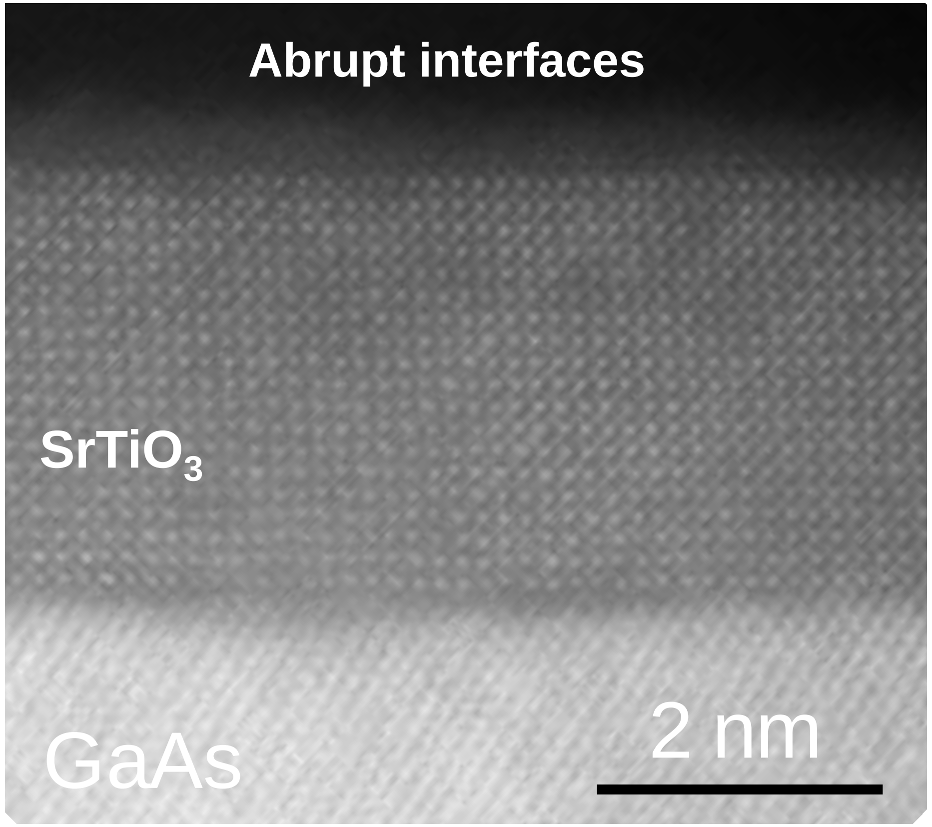
K.H Lee *et al.*, Diam. Related Mater. (2016); J.C. Arnault *et al.*, Diam. Related Mater. (2020)

Epitaxial oxide buffer layers on semiconductors

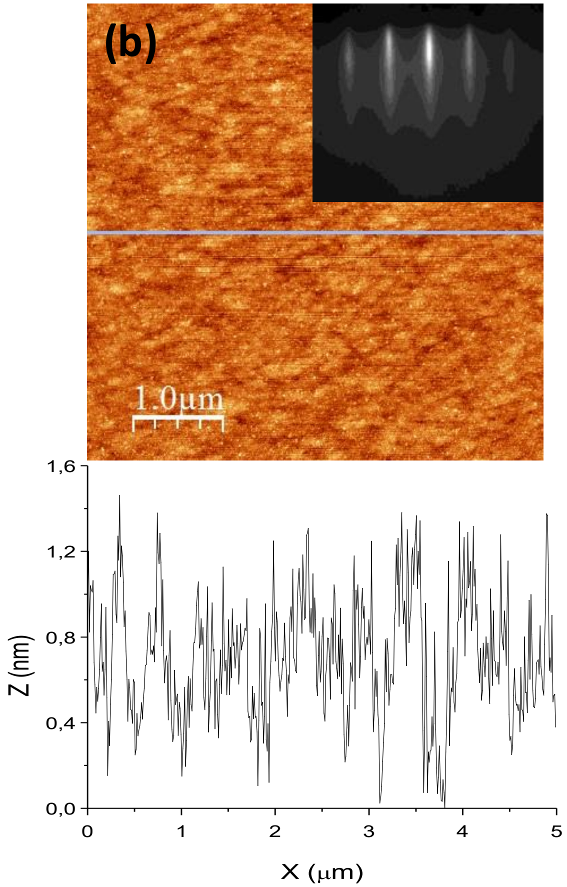
$SrTiO_3$/GaAs(001)

As-terminated surface passivation by Ti (1/2 ML) at ~400°C
First STO layers grown partially amorphous at low temperature
Complete crystallization during annealing around 450°C in UHV





Flat surface

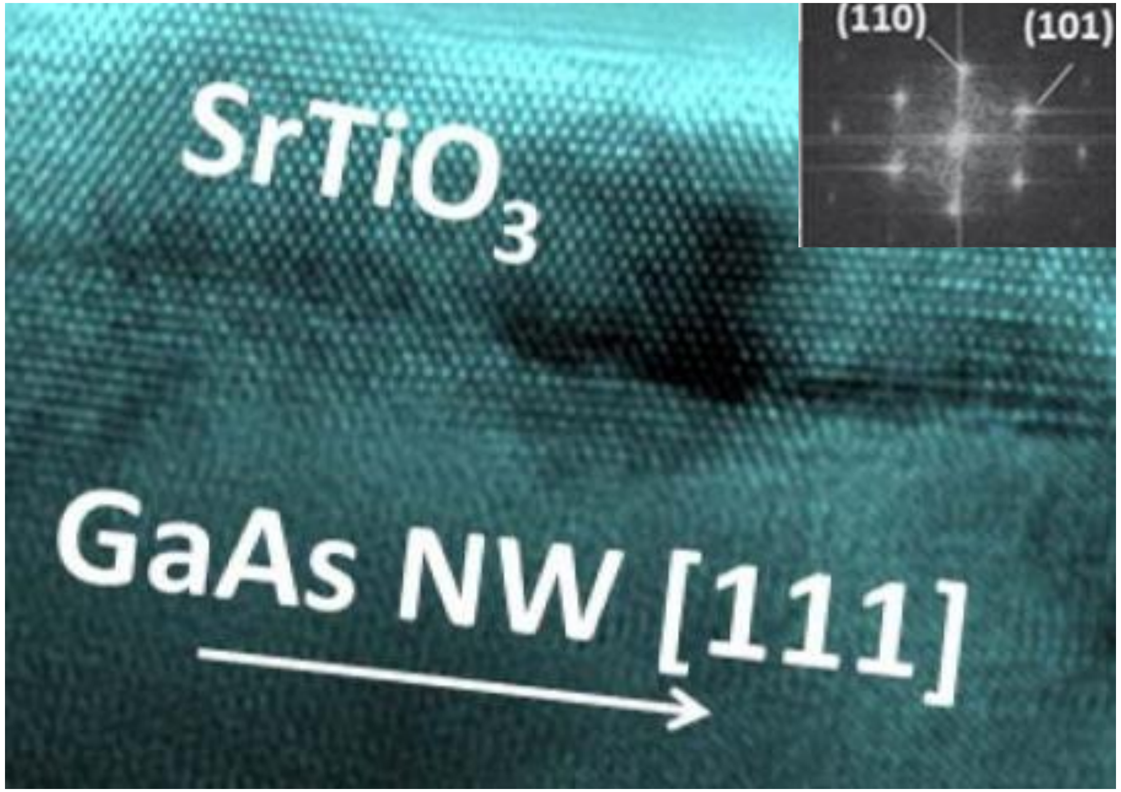


L. Louahadj *et al.*, APL (2013); *ibid*, Thin Sol. Films (2014); B. Meunier *et al.*, J Crystal Growth (2016)

Epitaxial oxide buffer layers on semiconductors

$SrTiO_3$/GaAs(001) core-shell nanowires

Epitaxial $SrTiO_3$ shell!



➔ **Piezo/flexo-phototronics**
➔ **Water splitting**

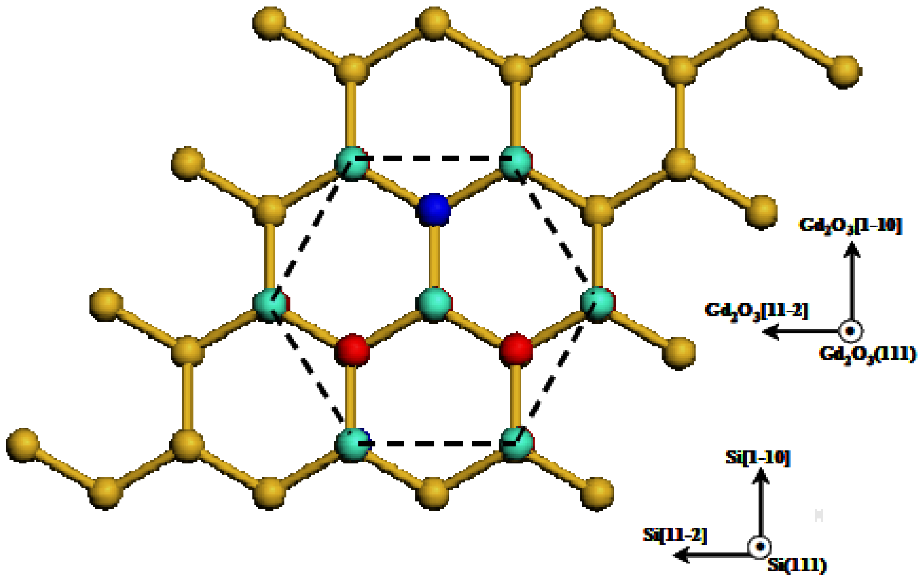
X. Guan *et al.*, Nano Letters (2016); Projects of J. Penuelas, INL

Epitaxial oxide buffer layers on semiconductors

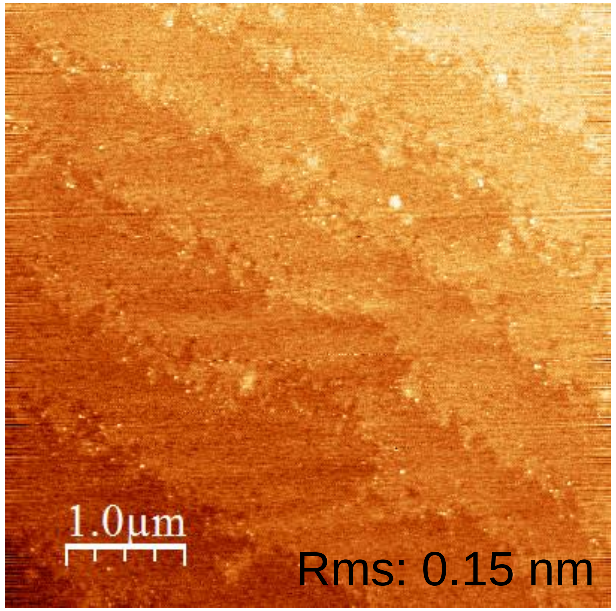
Gd_2O_3/Si(111)

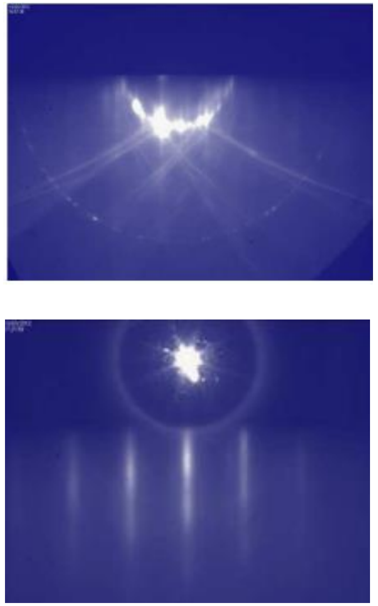
a_{Gd2O3} ~ 5.41 Å *vs* a_{Si} = 5.4309 Å ➔ ***f* = +0.39% structural mismatch**

Coincidence site lattice



Atomically flat surface





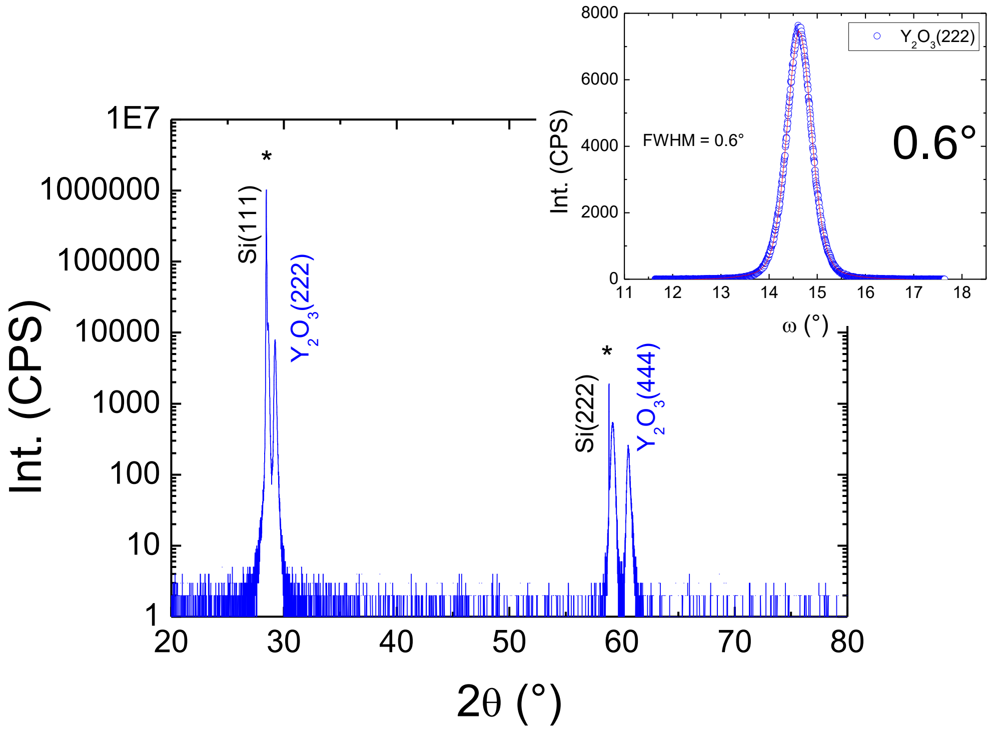
D. Ferrah *et al.*, J. Crystal Growth (2015)

Epitaxial oxide buffer layers on semiconductors

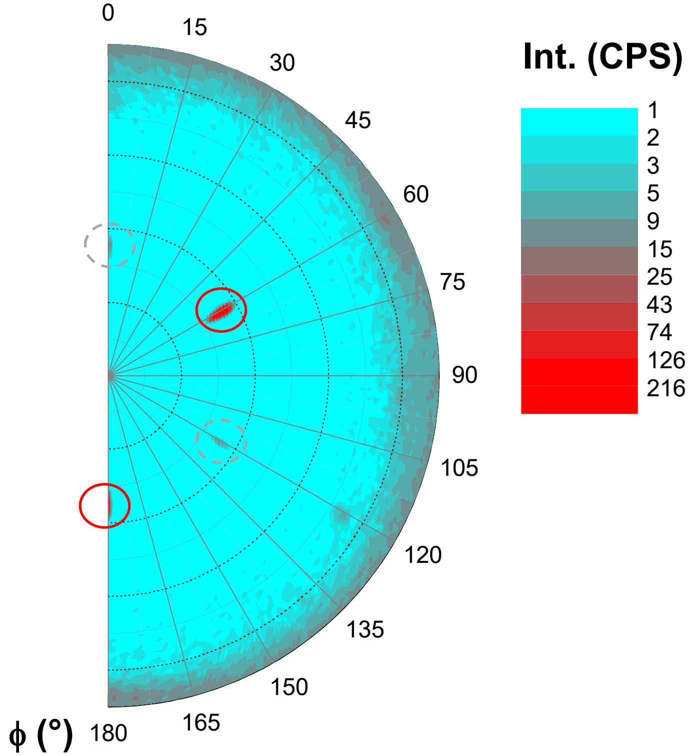
Integration of Eu-doped Y_2O_3 on Gd_2O_3/Si(111) by CVD

$a_{Y2O3}/2 \sim 5.316$ Å *vs* $a_{Gd2O3} \sim 5.41$ Å ➔ ***f*** **= +1.77% structural mismatch**

(111)-oriented **Low mosaicity**



Single in-plane domain



➔ **Quantum technologies**

N. Harada *et al.*, J. Appl. Phys. (2020); *ibid*, to be published; Collab. A. Tallaire, IRCP

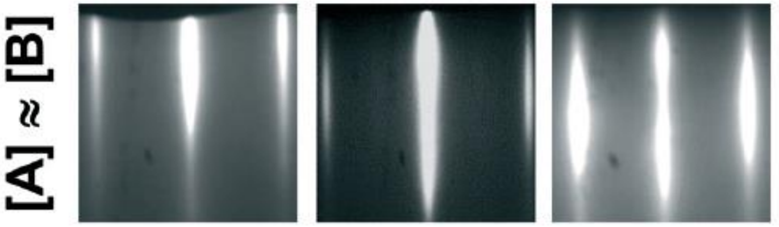
Solid solutions

Solid solutions

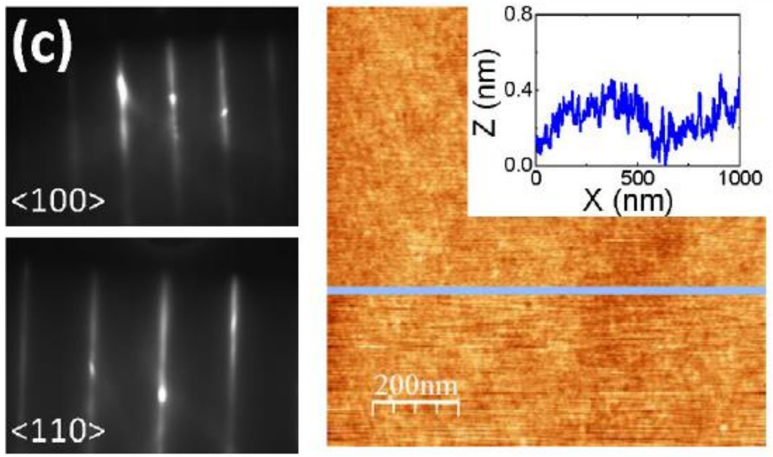
N-type La-doped $SrTiO_3$ = $(Sr_{1-x}La_xTiO_3)$

Since ~2015 (H2020 TIPS)

RHEED-assisted control of composition

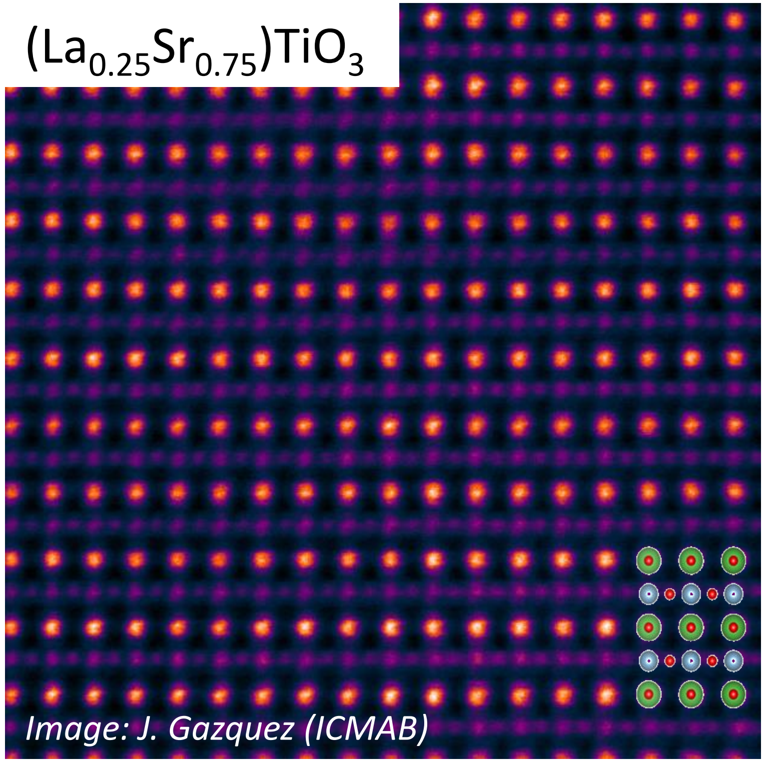


M.R.P. Ghaleh *et al.*, CrystEngComm (2019)



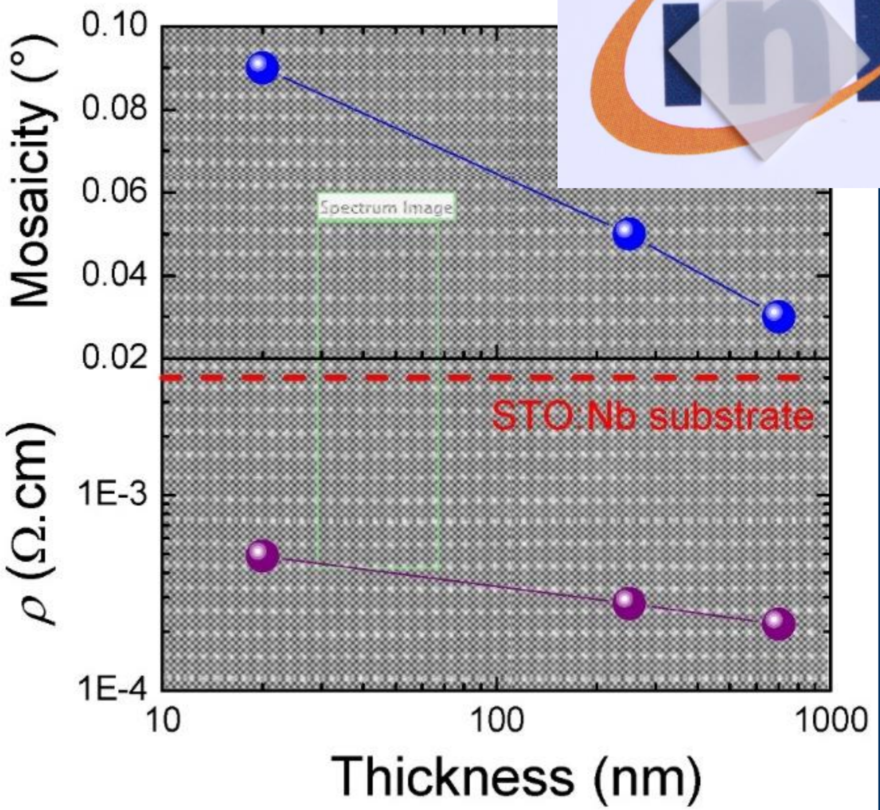
➔ Atomically flat 700 nm thick epitaxial film!

Single-crystal quality



Sr, La   Ti   O

Very low mosaicity



Low resistivity & "high" transparency

M. Apreutesei *et al.*, Sci. Technol. Adv. Mat. (2017)

➔ **TCO applications**

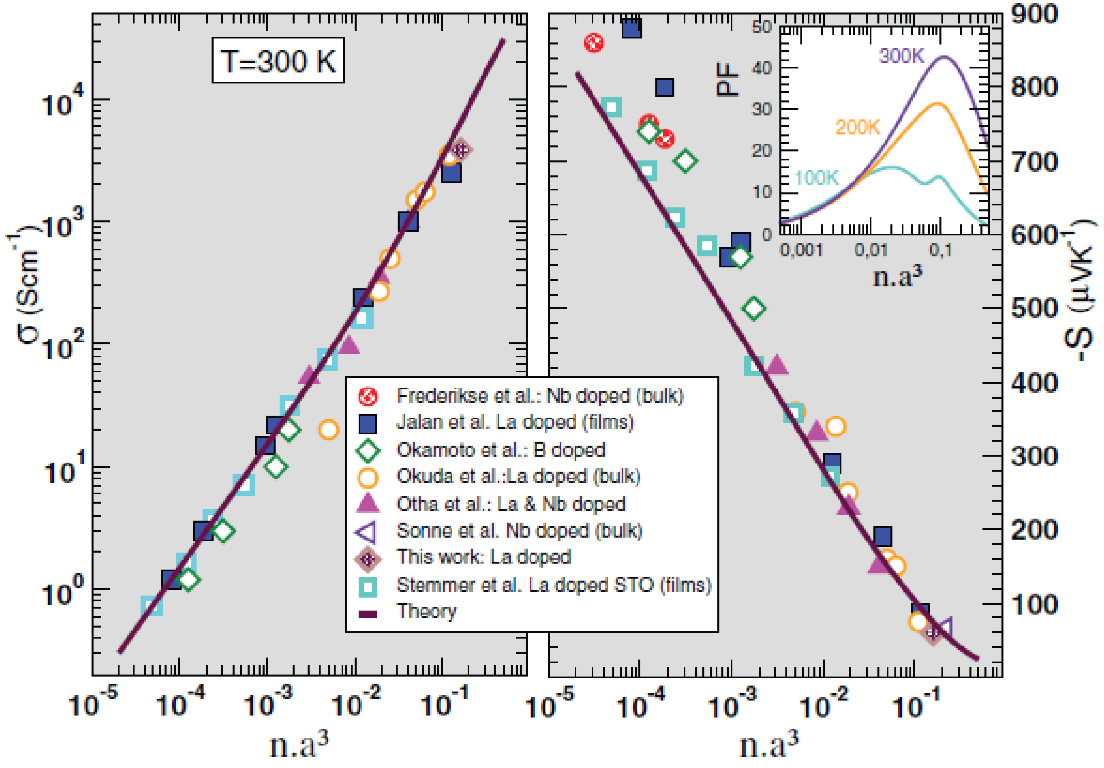
Solid solutions

N-type La-doped $SrTiO_3$ = ($Sr_{1-x}La_xTiO_3$)

Since ~2015 (H2020 TIPS)

Tunable electronic, thermoelectric and optical properties!

➔ **Good thermoelectric material**



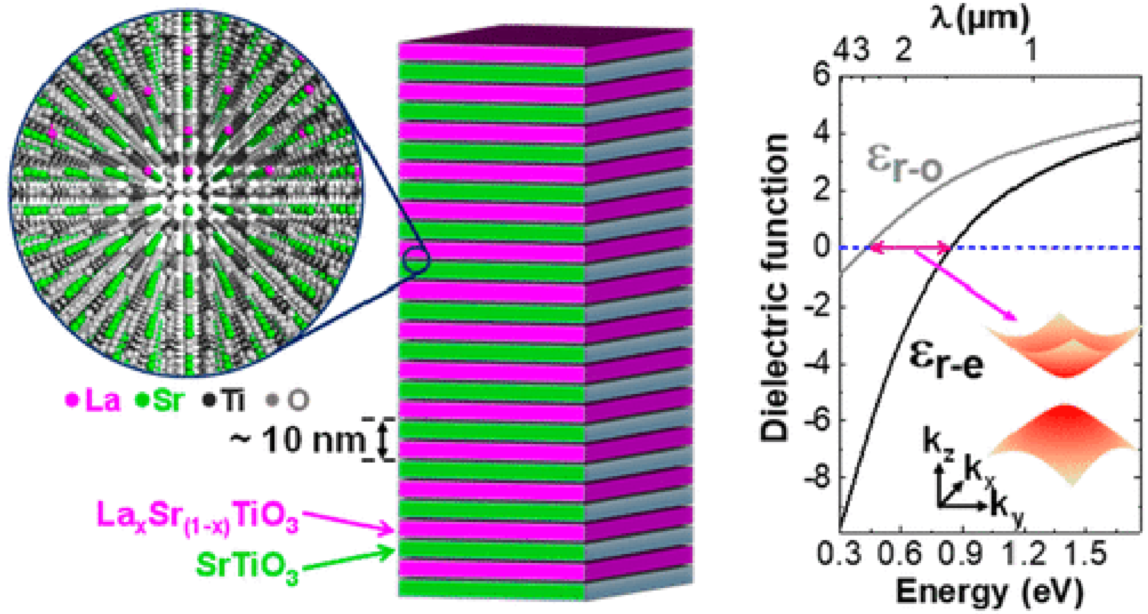
G. Bouzerar *et al.*, EPL (2017)

$PF_{300K} = S^2\sigma$

$\sim 40\ \mu W \cdot cm^{-1} \cdot K^{-2}$

$\approx PF(Bi_2Te_3)$

➔ **Good plasmonic & hyperbolic metamaterial in the NIR range**



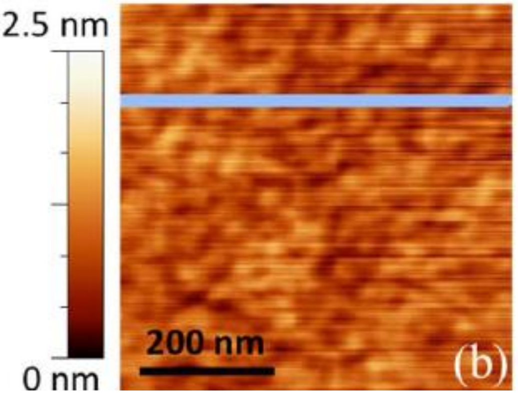
M. Bouras *et al.*, ACS Photonics (2019)

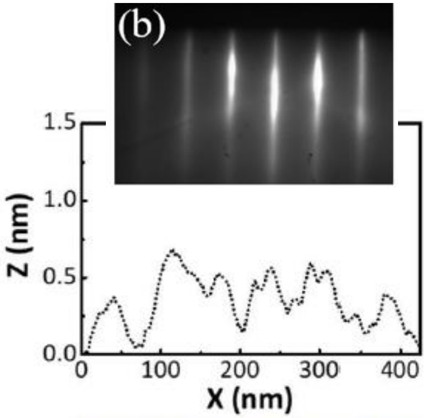
Solid solutions

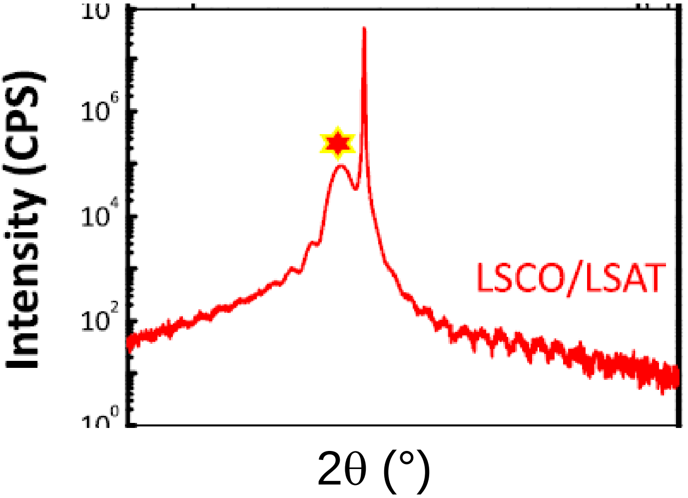
P-type Sr-doped $LaCrO_3$ = $(La_{1-x}Sr_xCrO_3)$

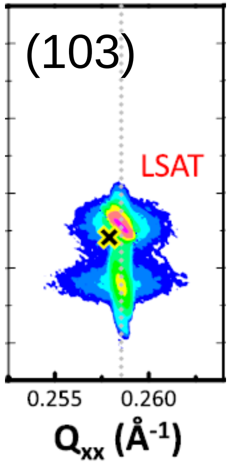
Since ~2017 (ANR MITO)

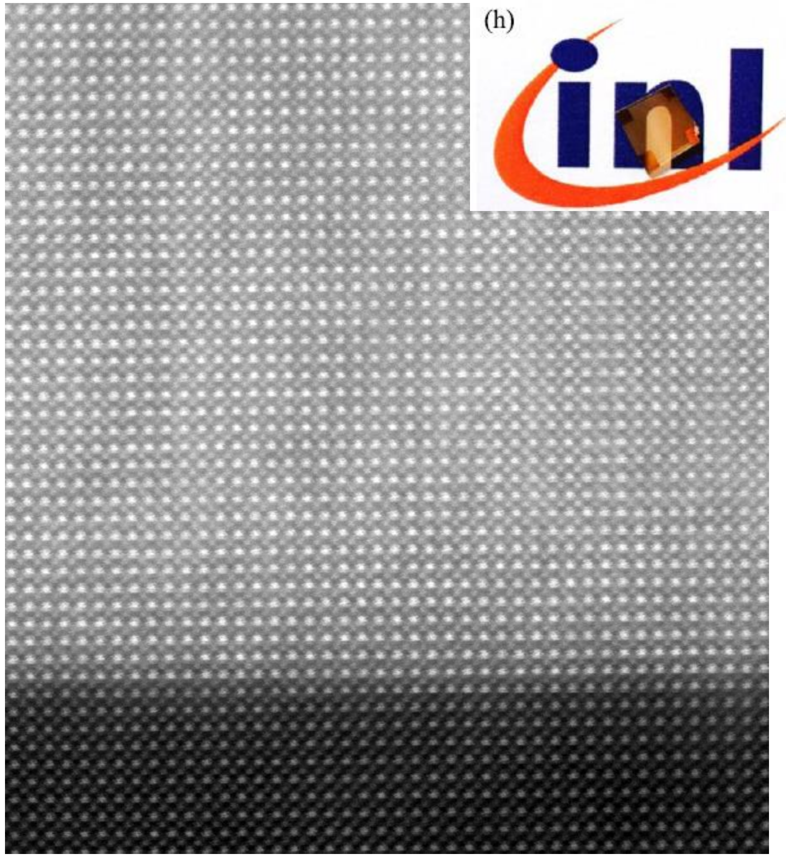
State-of-the-art structural & physical qualities



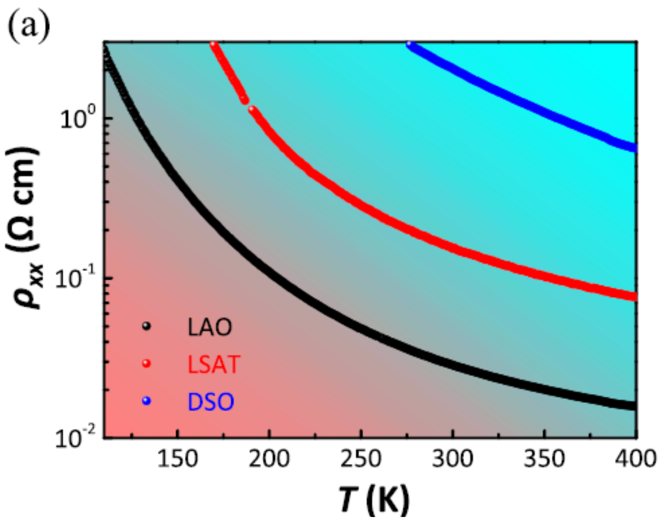


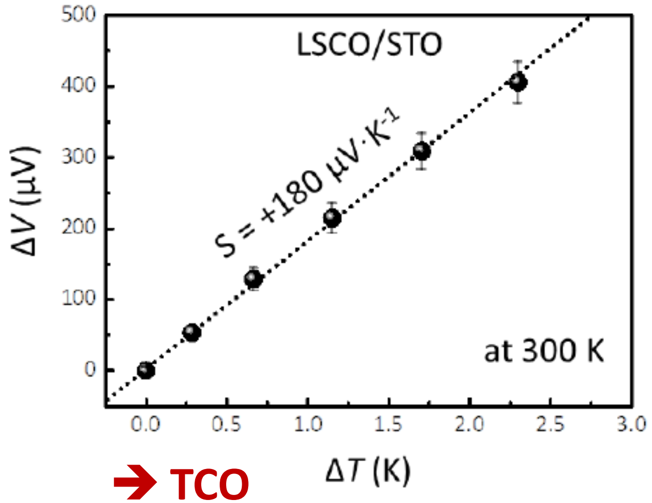






TEM: C. Furgeaud (INL) & M. Bugnet (MATEIS)





➔ **TCO**

➔ **Thermoelectricity**

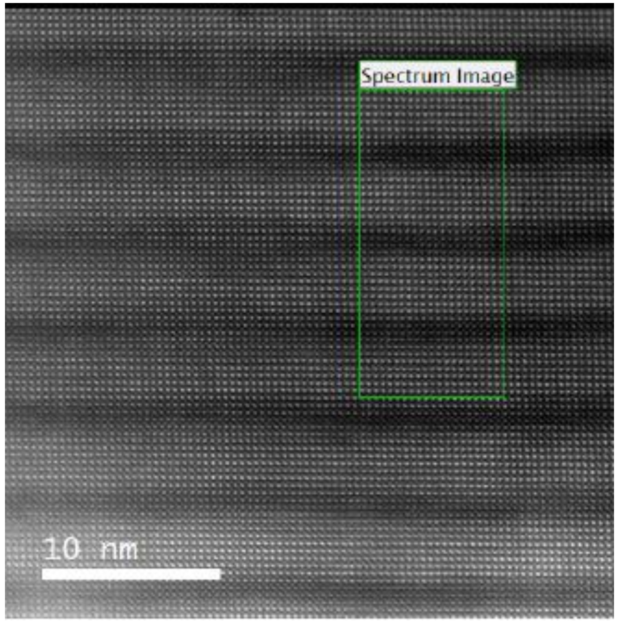
D. Han *et al.*, JVSTA (2019); JAP (2019); ACS Appl. Electron. Mater. (2021)

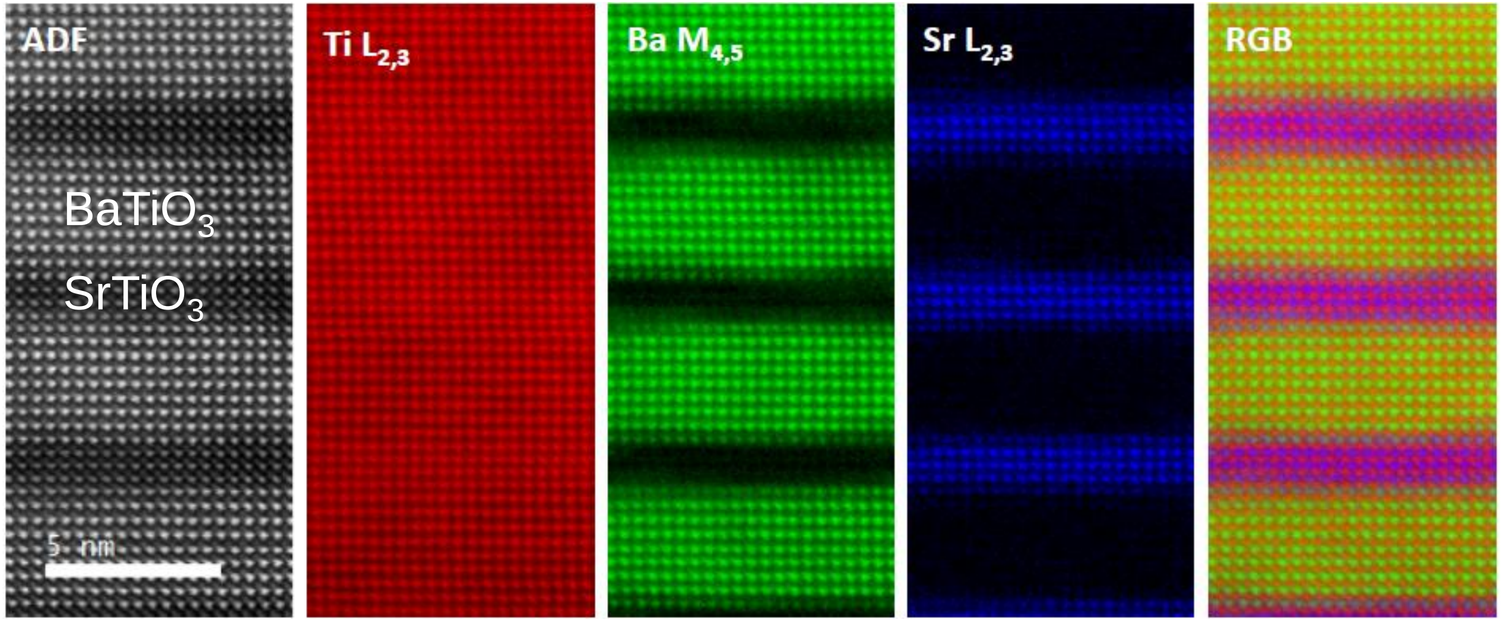
Ultimate superlattices / Phases

Ultimate superlattices / Phases

$[(BaTiO_3)_n/(SrTiO_3)_m]$ SL on $SrTiO_3$/Si(001)

Here n = 7 and m =3

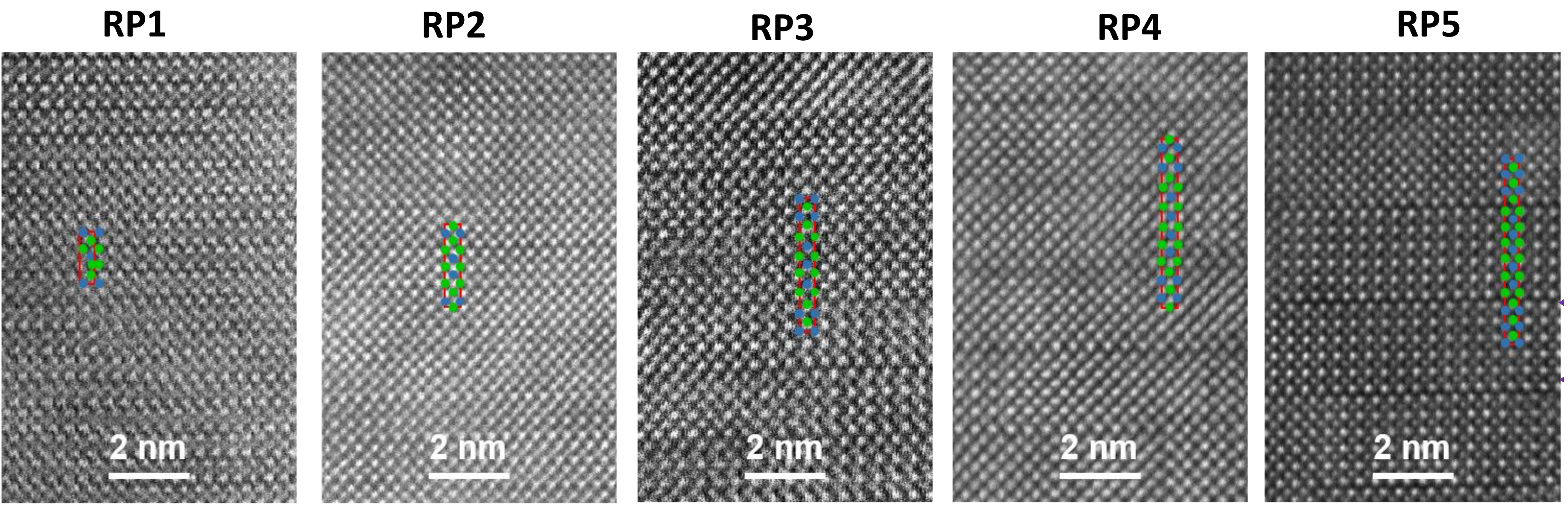


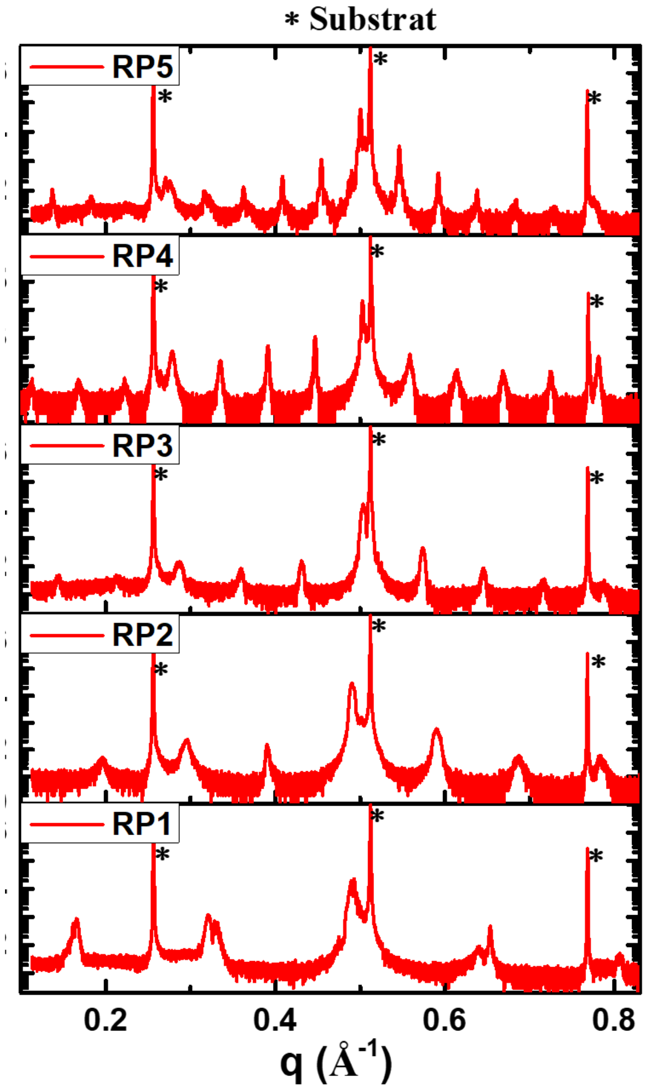


R. Moalla *et al.*, PhD Thesis (2016); Collab. STEM: M. Bugnet, MATEIS

Ultimate superlattices / Phases

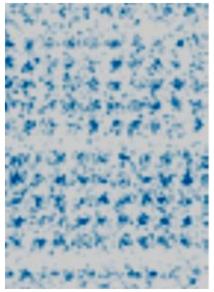
Ruddlesden-Popper (RP) phases of $SrTiO_3$ = $Sr_{n+1}Ti_nO_{3n+1}$ (n = 1-5)





= [SrO/$(SrTiO_3)_n$] SL ➔ strongly anisotropic structures

EDX
Ti map



Towards new original phases / metamaterials "on demand"!...

➔ *e.g.* [AO/$(A'BO_3)_n$], eventually with partial cationic substitution!...

➔ Or Magnéli or other phases ?...

➔ **Optoelectronics & thermoelectricity**

M. Bouras, PhD Thesis ECL (2019); Collab. TEM: L. Largeau, C2N

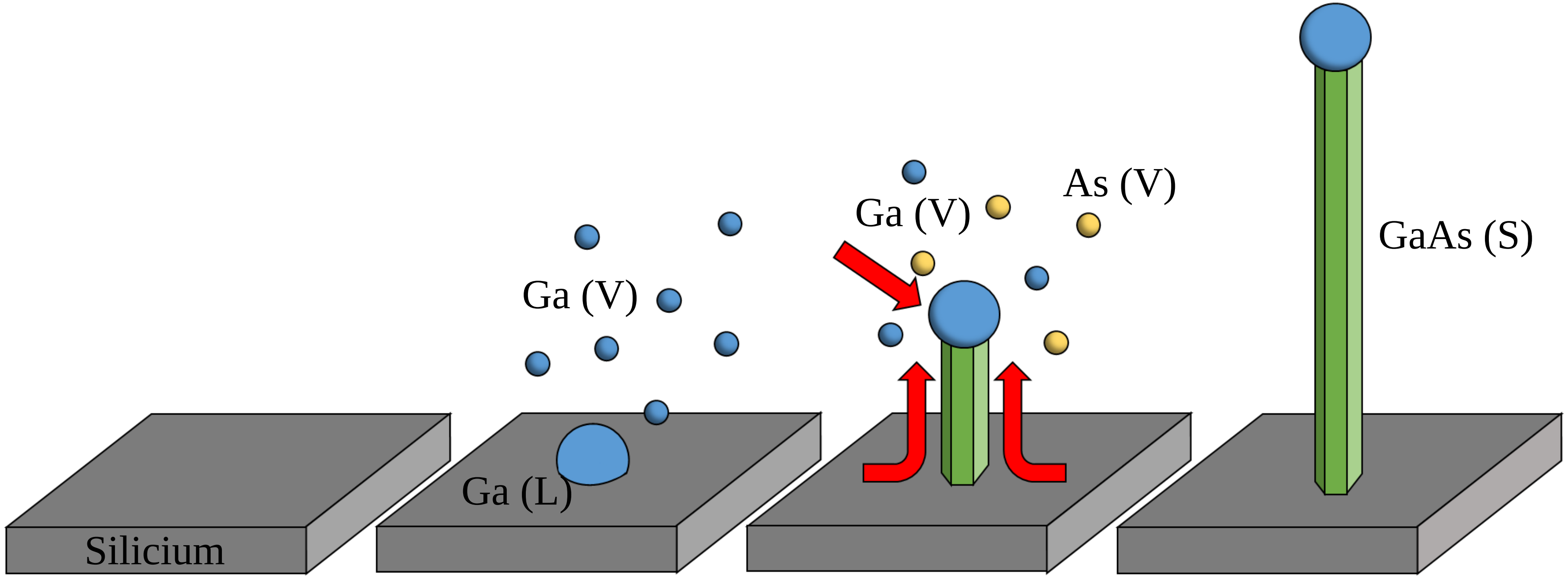
III-V nanowires

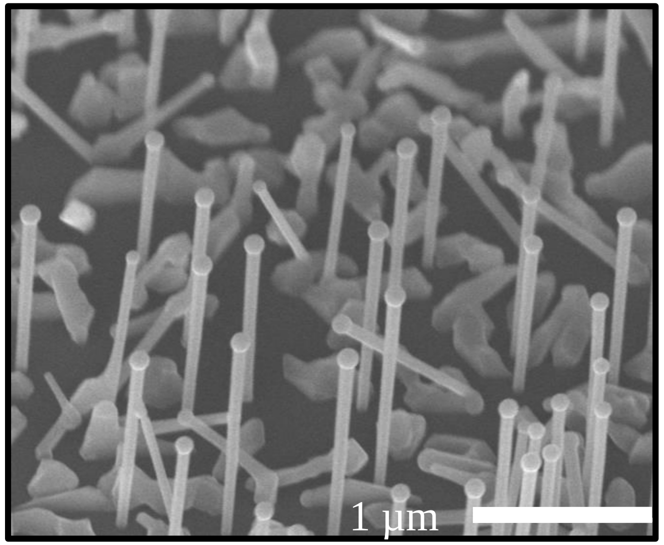
VLS growth

La croissance d'émetteurs nanofils à base de GaAs – MBE et VLS

- Croissance des nanofils par **épitaxie par jets moléculaires** (MBE)
  - Mécanismes de croissance **Vapeur – Liquide – Solide** (VLS)

    R. S. Wagner and W. C. Ellis, Appl. Phys. Lett. 4, 89 (1964)
    A. Fontcuberta i Morral et al., Appl. Phys. Lett. 92, 063112 (2008)





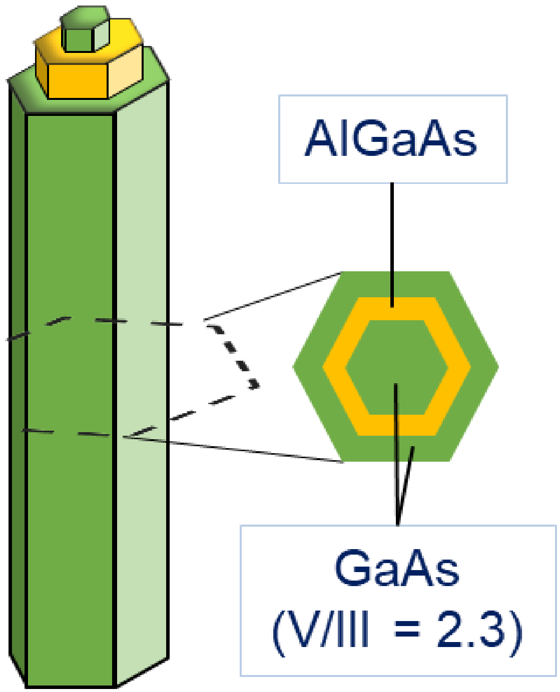
From H.G. Glories PhD defense (2023), supervisor: J. Penuelas

La croissance d'émetteurs nanofils à base de GaAs – Hétérostructures

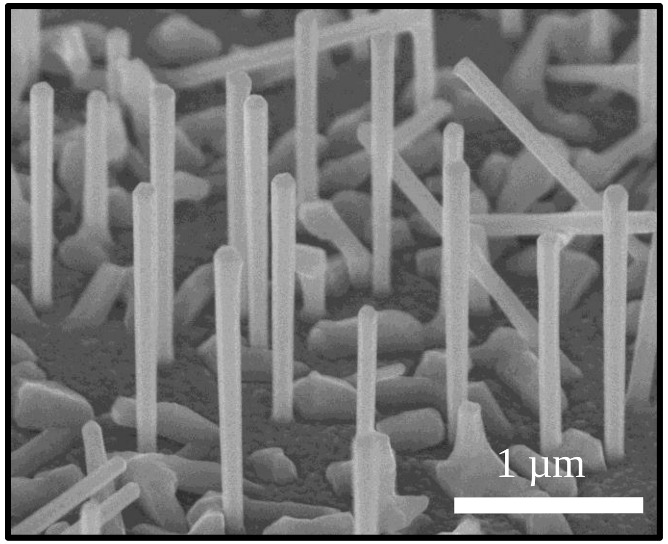
- Hétérostructure **cœur/coquille**

GaAs/AlGaAs/GaAs

20 nm AlGaAs
5 nm de GaAs

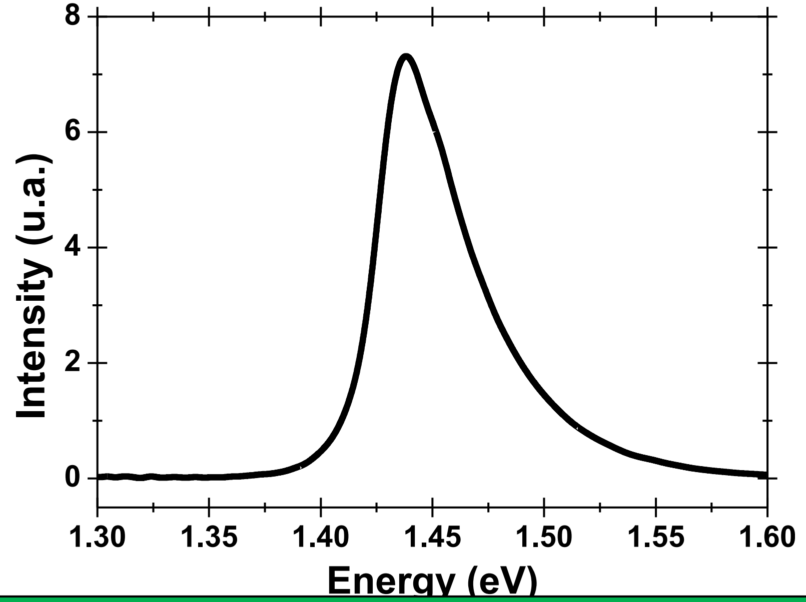


L = 2,05 ± 0,05 µm
D = 120 ± 8 nm
d = 2,2 NFs/µm²



E_g(GaAs)= 1,43 eV
$E_g(Al_{0,3}Ga_{0,7}As)$= 1,66 eV

E_{PL}(NFs)= 1,44 eV

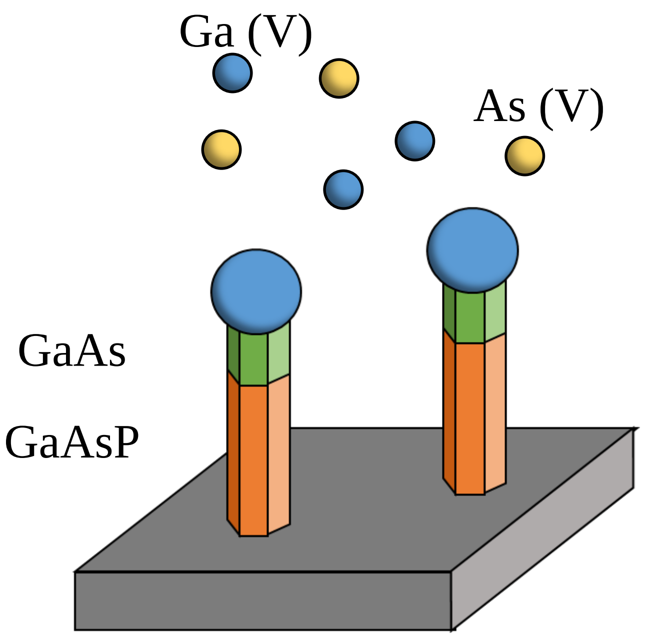


- Coquille de **passivation** :
  - ✓ **Evite l'oxydation** du cœur
  - ✓ **Confinement** des porteurs dans le cœur

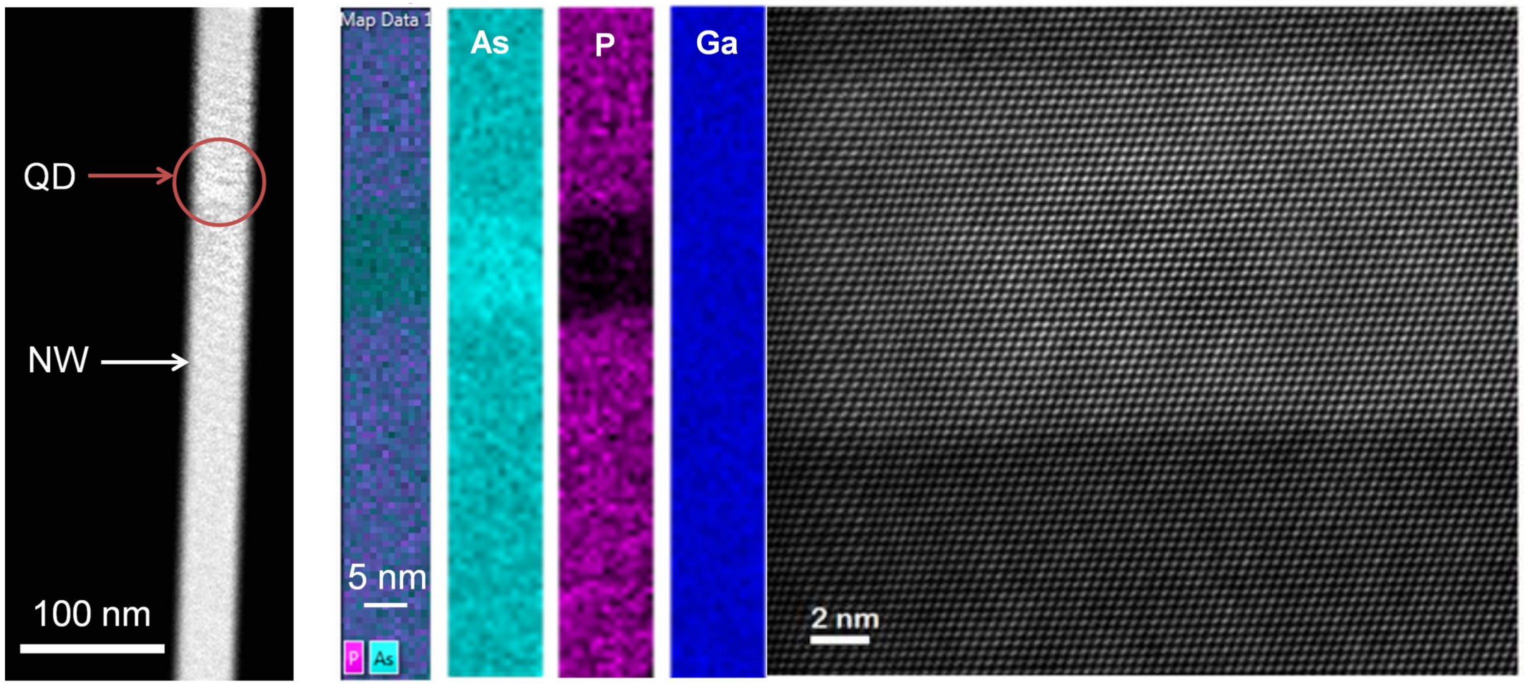
- ❖ Couche de passivation epitaxiée
- ❖ Excellent contrôle de la morphologie
- ❖ Echantillons homogènes en densité
- ❖ Résultats reproductibles
- ❖ Croissance optimisée

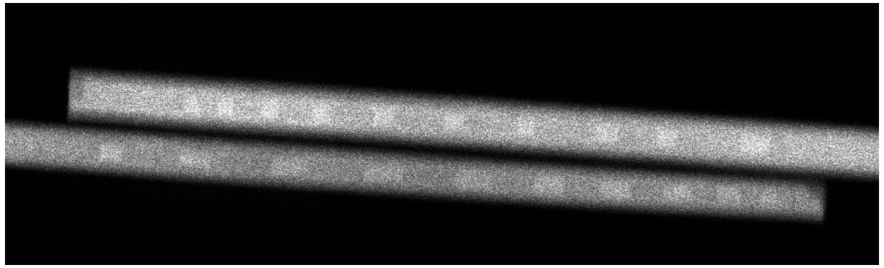
La croissance d'émetteurs nanofils à base de GaAs – Hétérostructures

- Hétérostructure à **boîte quantique**
  - **Sans interruption** de croissance



$E_g(GaAs_{0,6}P_{0,4})$= 1,9 eV
$E_g(GaAs)$= 1,43 eV





A. Jaffal, P. Regreny, N. Chauvin, **M. Gendry**

Conclusions & perspectives

MBE: ideal tool for high-quality epitaxial heterostructures and nanostructures of various materials
Integration on semiconductors, solid solutions (alloys and doping), ultimate SLs (beyond QWs), termination-controlled interfaces (polar & field effects), QDs, III-V / III-N nanowires, core-shell structures,…

Challenges to overcome!:
- Avoiding metallic source reaction / flux drifts ➔ differential pumping
- Flux monitoring and composition control!... ➔ new measurement/growth methods
- Good oxidation/nitruration/.. during growth! ➔ ozone, plasma sources (atomic O, N,..), crackers,…

Perspectives:
- *In-operando* (flux) monitoring / characterizations (structural & physical properties)
- New solid solutions / materials
- Ultimate SLs, original phases and metamaterials…
- Machine learning for smart growth with the desired properties ➔ Dreamed MBE!...

References

Books

“Materials Fundamentals of Molecular Beam Epitaxy”
Jeffrey Y. Tsao, Academic Press (1993)

“*Molecular Beam Epitaxy - From research to mass production*”
Edited by Mohamed Henini, Elsevier (2012)

“*Molecular Beam Epitaxy: an overview*”
P. Frigeri, L. Seravalli, G. Trevisi, and S. Franchi, Elsevier (2011)

“Epitaxy of semiconductors – Introduction to physical principles”
Udo W. Pohl, Springer (2013)

“*Integration of functional oxides with semiconductors*”
Alexander A. Demkov and Agham B. Posadas, Springer (2014)

Reviews / Key articles

M.B. Panish, Science 208, 916 (1980)
John R Arthur, Surface Science 500, 189 (2002): *molecular beam epitaxy*
W. Patrick Mc Cray, Nature Nanotechnology (2007)
D.G. Schlom et al., J. Am. Ceram. Soc. (2008)

Conferences / Networks

GDR MatEpi

Journées plénières de lancement 3-6 juillet 2023, Jussieu, Paris
https://matepi2023.sciencesconf.org/

MBE conferences

International Conference on MBE (each 2 years)
Next ICMBE in 2024

European conference on MBE (each two years)
Next EuroMBE in 2025

Acknowledgements

Main colleagues of the team “Functional Materials & Nanostructures” of INL, & Pole Epitaxy” of Nanolyon platform

Guillaume Saint-Girons, *DR CNRS (oxides)*

José Penuelas, *MCF ECL (III-V / Ge nanowires)*

Philippe Regreny, *IR CNRS (Resp. Pole Epitaxy, III-V)*

Claude Botella, *IE CNRS (Softs & electronic)*

Jean-Baptiste Goure, *T CNRS (maintenance)*

PhD students & post-docs

Oxides: L. Louahadj (2011-2014), R. Moalla (2013-2016), B. Meunier (2013-2016), M. Apreutesei (2015-2016), M. Bouras (2016-2019), D. Han (2017-2020), M. d’Esperonnat (2019-2023)
III-V: X. Guan (2013-2016), T. Dursap (2018-2021), H.G. Glories (2019-2023), J. Dudko (2021-2024)

Collaborators

ICMAB — list cea tech — C2N — CETHIL UMR 5008 — iLM Institut Lumière Matière — ies — IRCP — Mateis — LOMA UMR5798 Laboratoire Ondes et Matière d'Aquitaine

& Fundings…

ANR (Projet financé par l'ANR - Project funded by the ANR) — China Scholarship Council — CNRS INSIS — Horizon 2020 (Le programme de recherche et d'innovation de l'Union Européenne) — TIPS — La Région Auvergne-Rhône-Alpes

inl