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Alexandre Arnoult, Pierre Gavras, Léo Bourdon, Guilhem Almuneau. Some selected in situ characterization tools for MBE growth and their complementarity. European Workshop on Innovative and Advanced Epitaxy, COST OPERA, Jun 2024, Vilnius (Lituanie), Lithuania. hal-04769109

HAL Id: hal-04769109

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Submitted on 6 Nov 2024

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Some selected in situ characterization tools for MBE growth and their complementarity

A. Arnoult, P. Gadras, L. Bourdon and G. Almuneau

LAAS-CNRS, Université de Toulouse, CNRS, Toulouse, France

Vilnius, 13/06/2024

- > In-situ control of growth: a global approach

- > An example structure: the growth of VCSELs

- > Focus on some tools
 - Spectral Reflectivity
 - Atomic Absorption Spectroscopy for direct flux measurement
 - Curvature

- > Complementarity
 - For alloy concentration/growth rates
 - In time scales

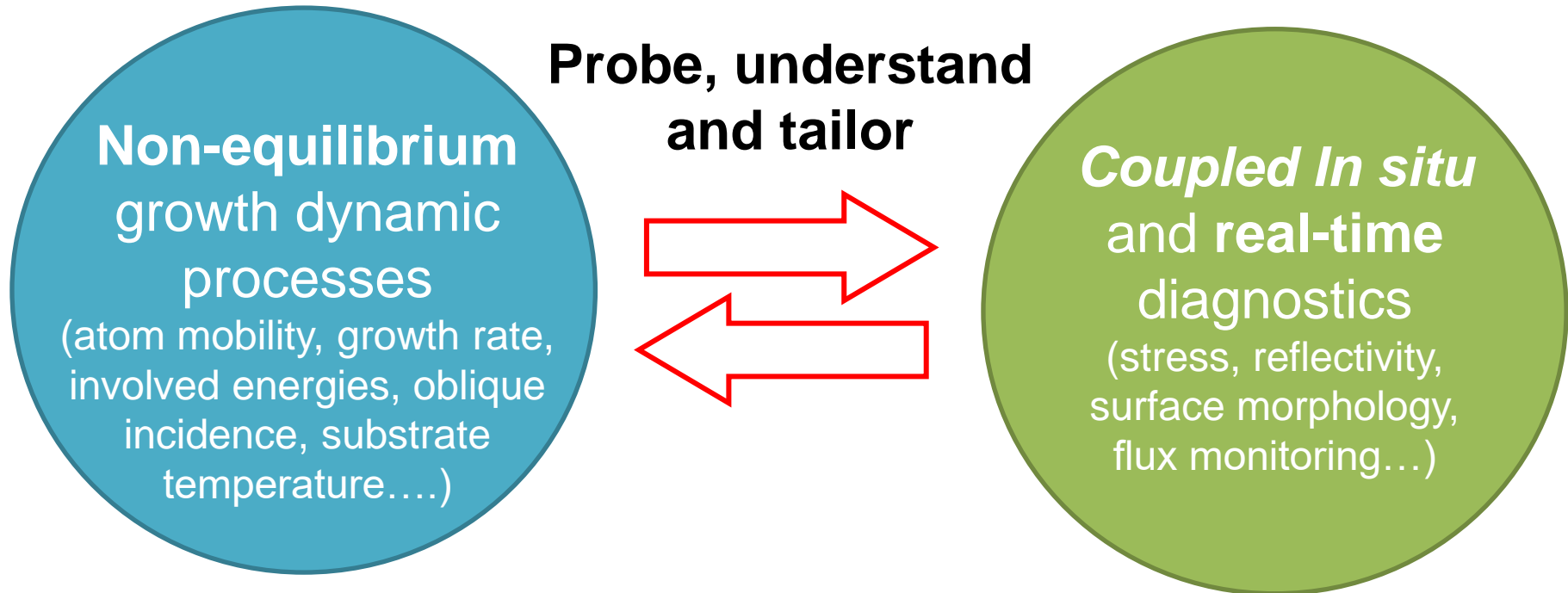
- > The case of GaAsBi growth

- > Conclusion

Non-equilibrium growth dynamic processes

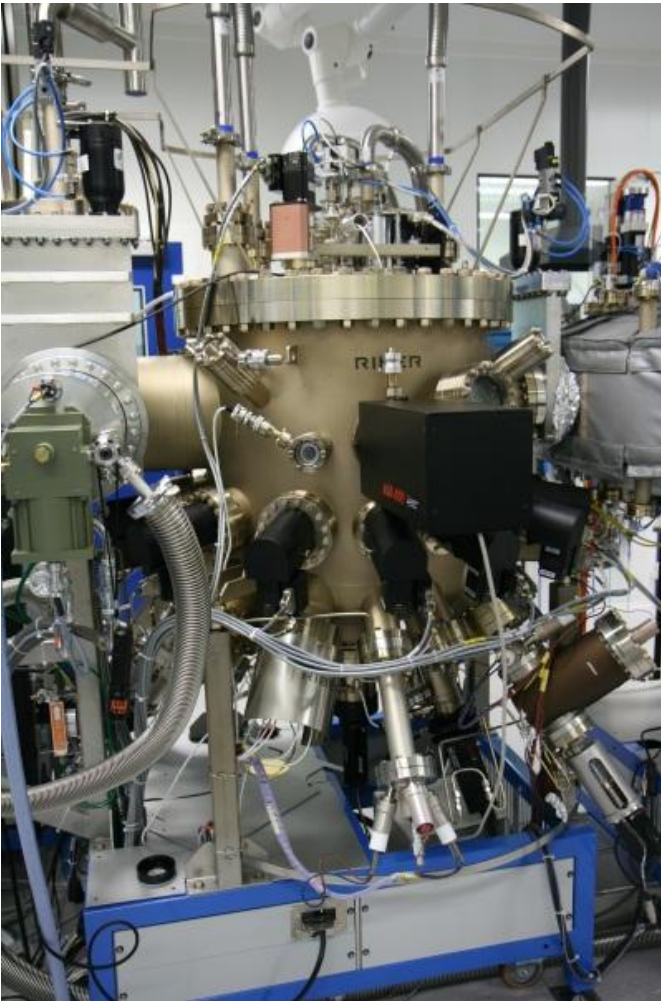
(atom mobility, growth rate,
involved energies, oblique
incidence, substrate
temperature....)

Ex-situ post-growth tools
(XRD, SEM, (HR)TEM, PL, ...)



No diagnostic tool provide a complete picture of the growth process, but coupling them in the same time base maximize their **complementarity**

A global approach: complementary tools to get a clear picture of growth processes



> **Spectral reflectivity**

- White light source
- CCD sensors



> **Temperature**

- Band-Edge Thermometry **EZ-EDGE**
- Pyrometry

> **Fluxes** (Atomic absorption Spectroscopy - OFM)

- Original tool (Patent FR1856743)

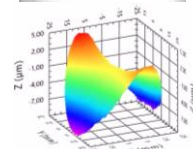
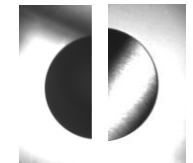
> **RHEED**: synchronised to rotation

- In-plane lattice parameter, streaks intensity

> **Roughness** (Diffuse Light Scattering)

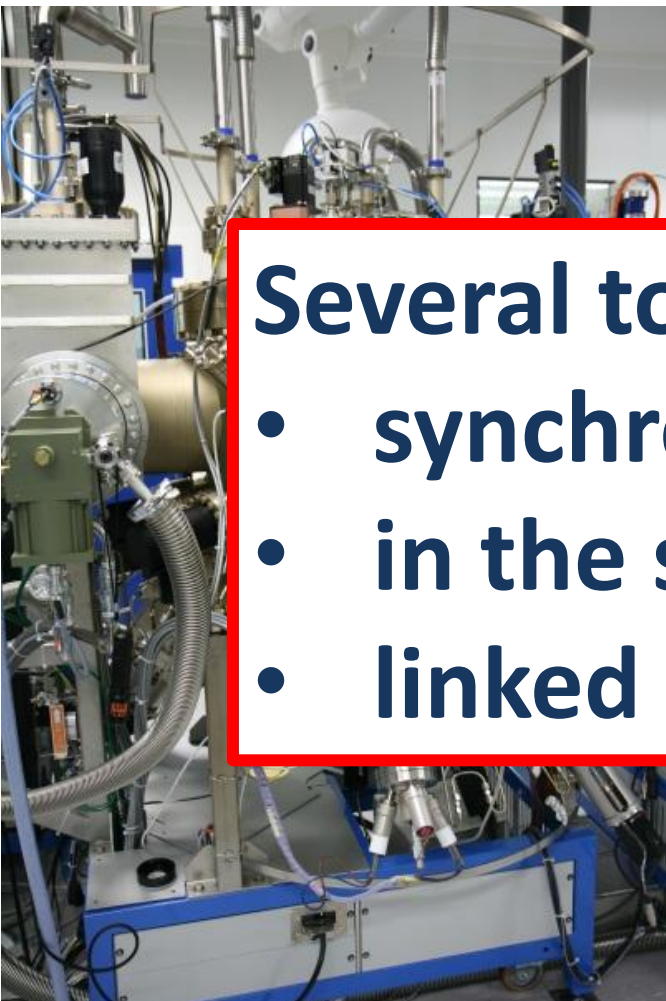
> **Curvature**

- MIC : original tool (Patent FR175461)



MBE412 - 4" III-V chamber

A global approach: complementary tools to get a clear picture of growth processes



> **Spectral reflectivity**

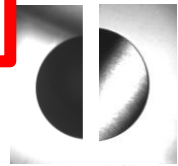
- White light source
- CCD sensors



Several tools

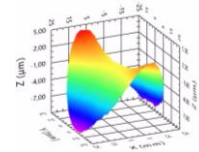
- synchronized to rotation
- in the same time base
- linked to MBE control software

> **Roughness (Diffuse Light Scattering)**

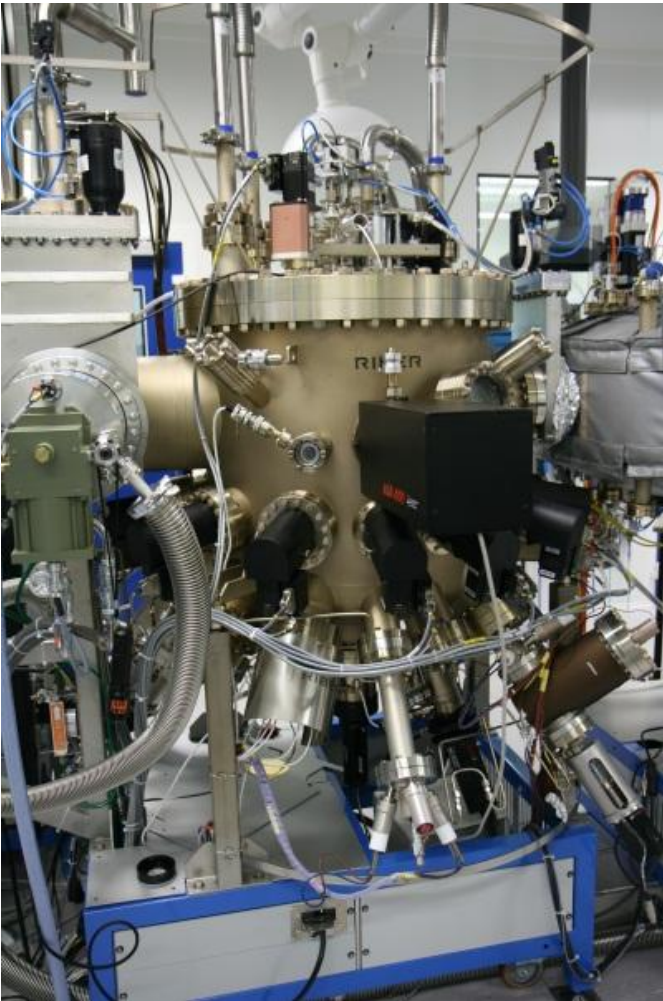


> **Curvature**

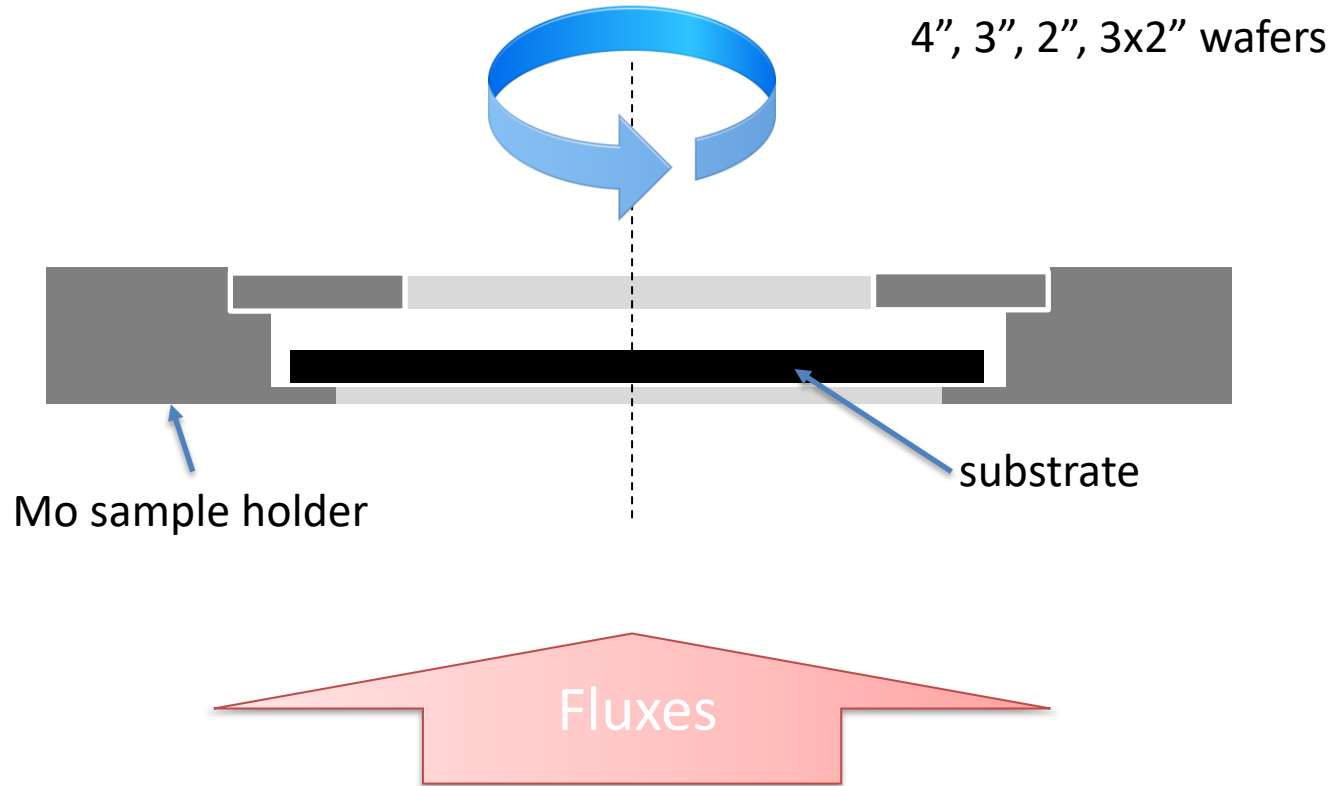
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MBE412 - 4" III-V chamber

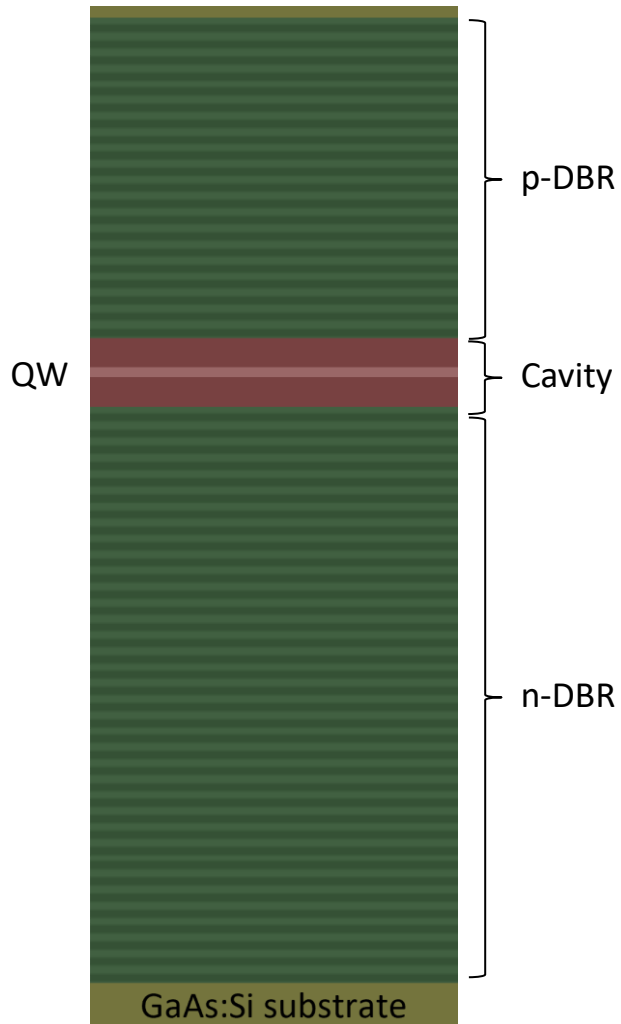


MBE412 - 4" III-V chamber

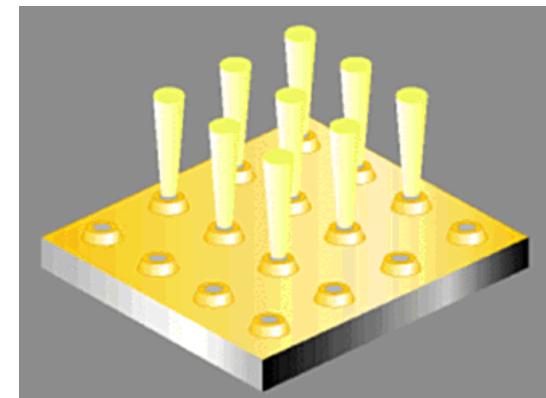
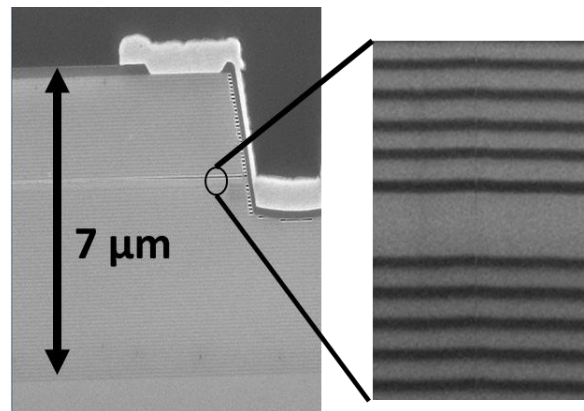


An example structure:
the growth of VCSELs

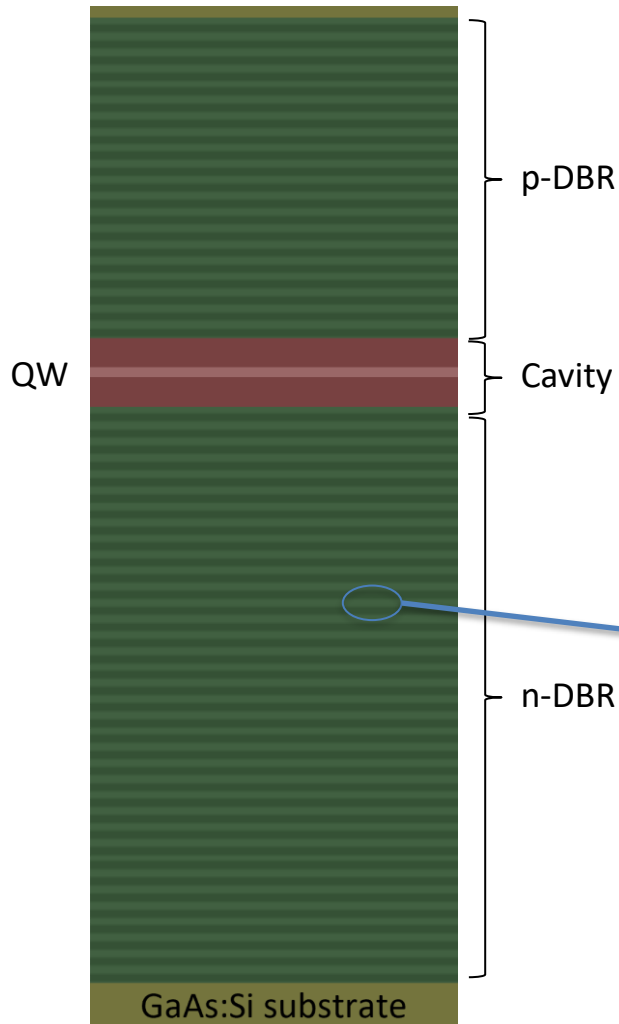
MBE growth of VCSELs



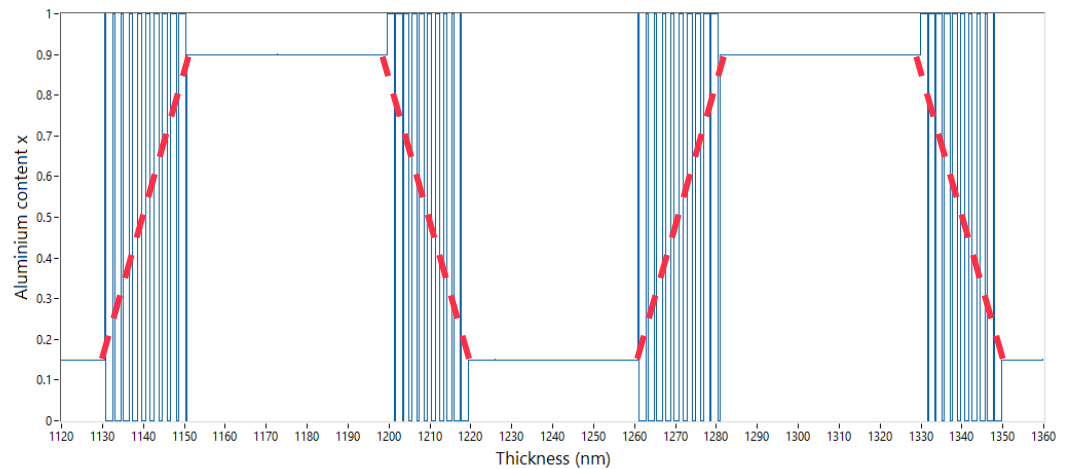
- Vertical Cavity Surface Emitting Lasers (VCSELs) are complex structures (>3000 layers, >17H growth)
- The vertical geometry permits the simultaneous processing of lasers, and the fabrication of laser matrices
- VCSELs are used in datacom, lidars, face recognition, etc...



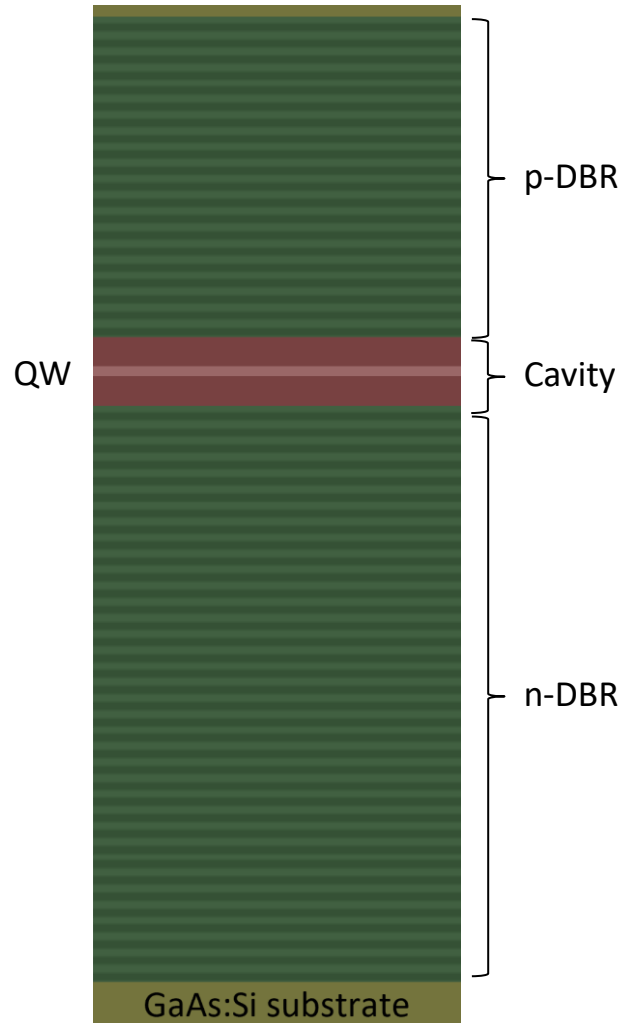
MBE growth of VCSELs



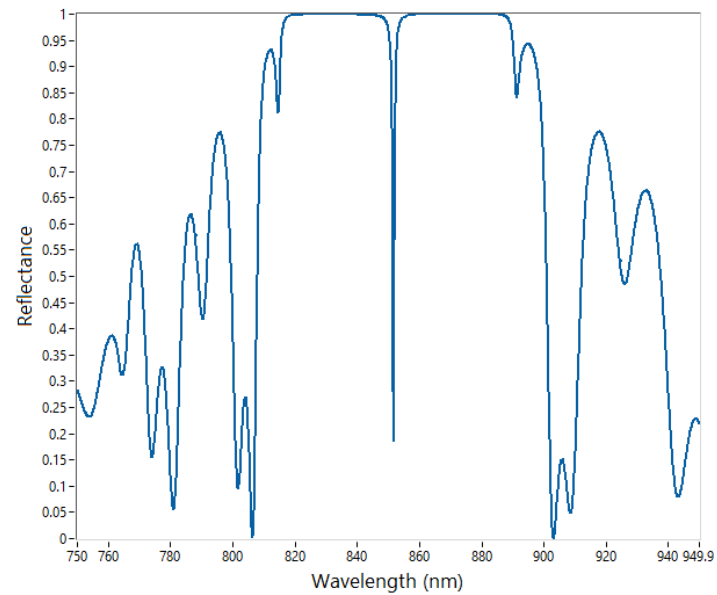
- Vertical Cavity Surface Emitting Lasers (VCSELs) are complex structures. (>3000 layers, >17H growth)
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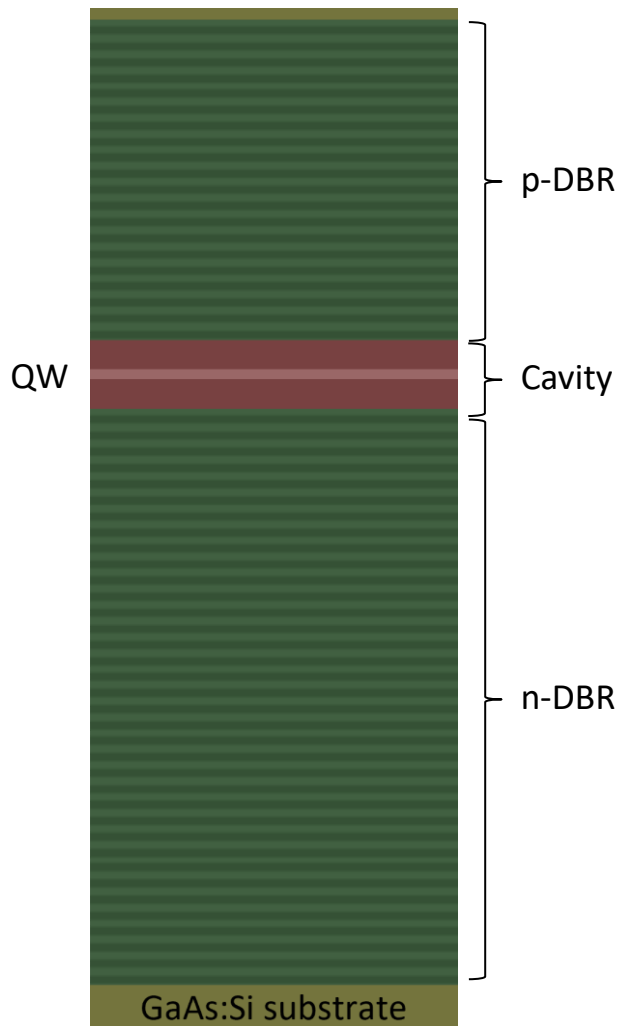
MBE growth of VCSELs



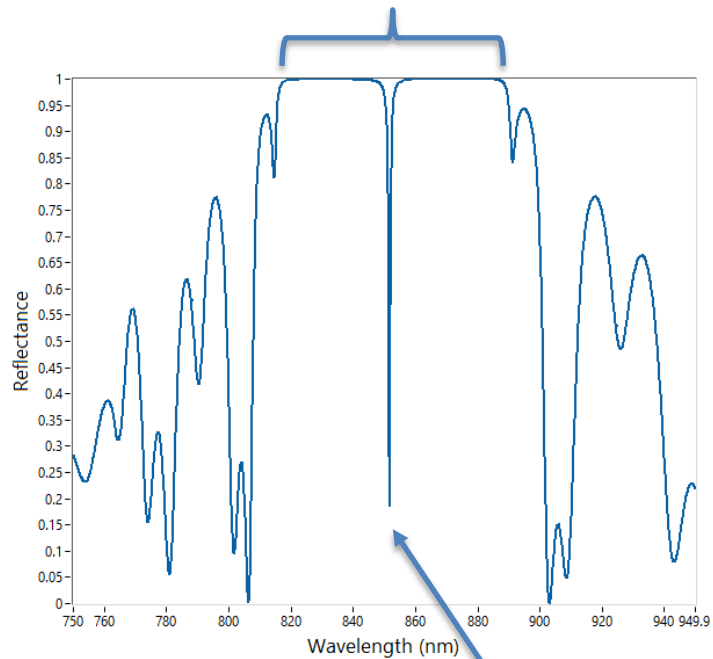
Reflectance spectrum of a VCSEL at RT



MBE growth of VCSELs

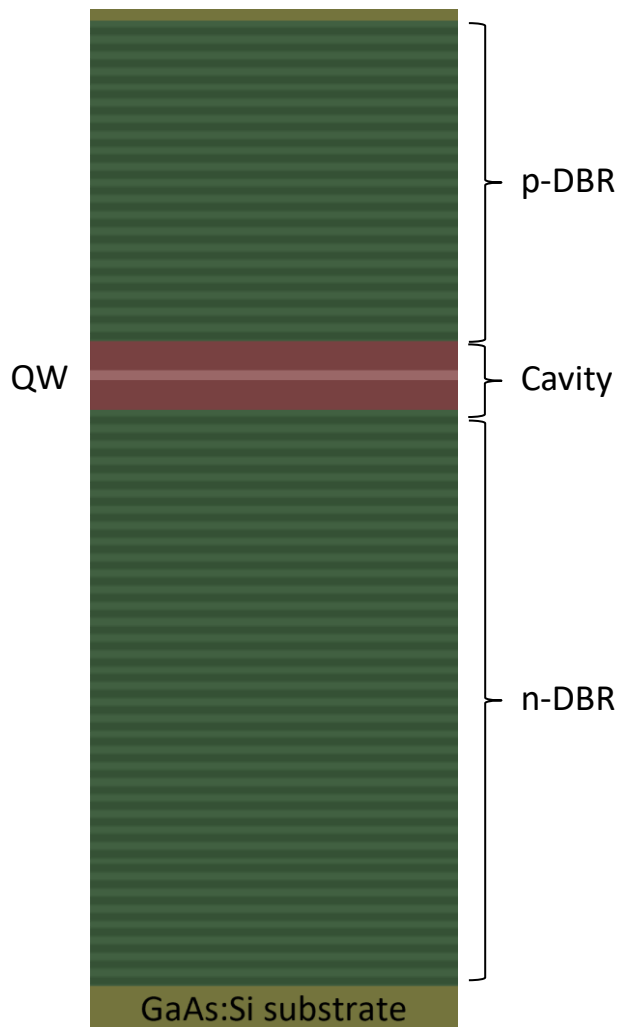


Reflectance spectrum of a VCSEL at RT
High reflectivity plateau

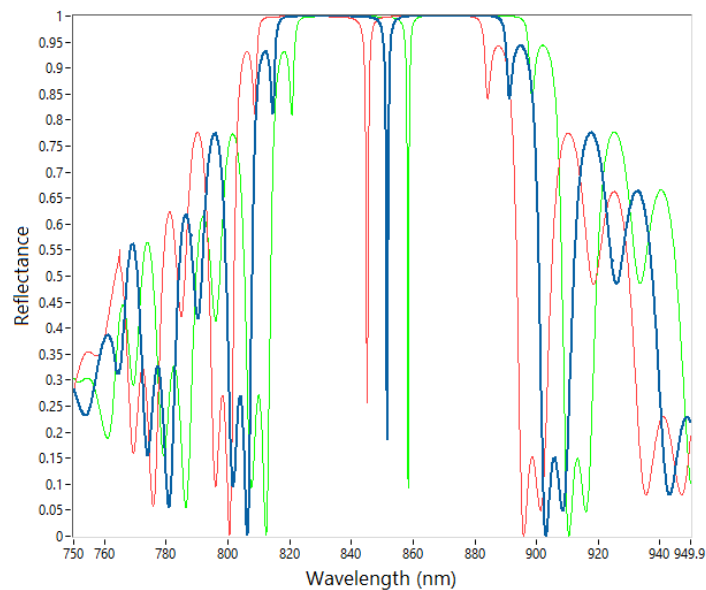


Fabry Perot dip

MBE growth of VCSELs



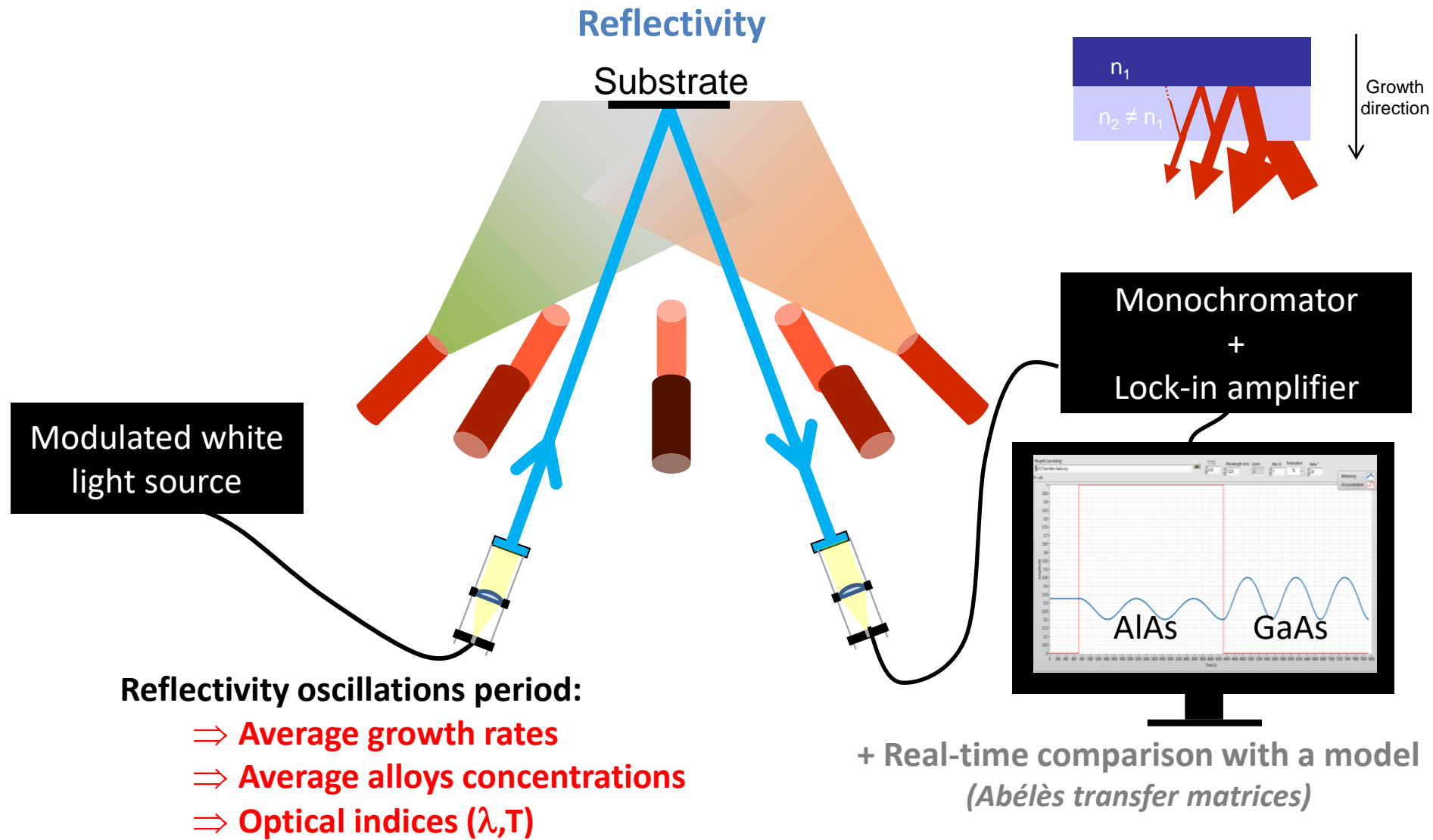
Reflectance spectrum of a VCSEL at RT



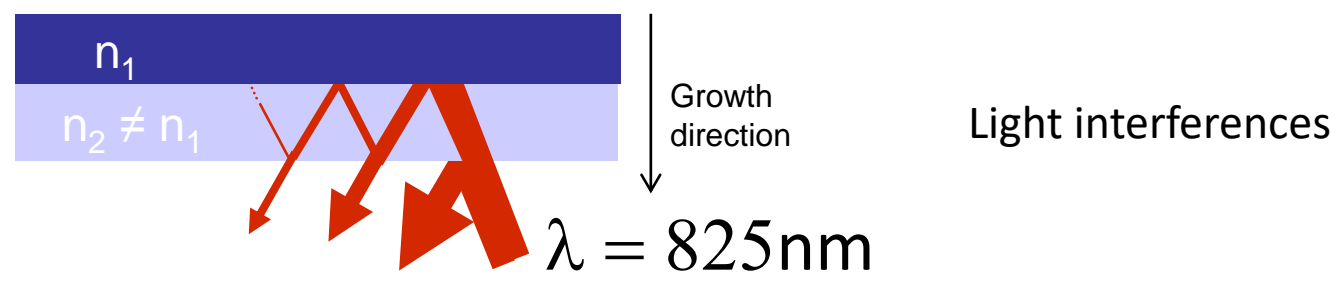
$\pm 1\%$ flux variation $\rightarrow \pm 6\text{nm}$ wavelength variation

In-situ characterization tools: *Spectral reflectivity*

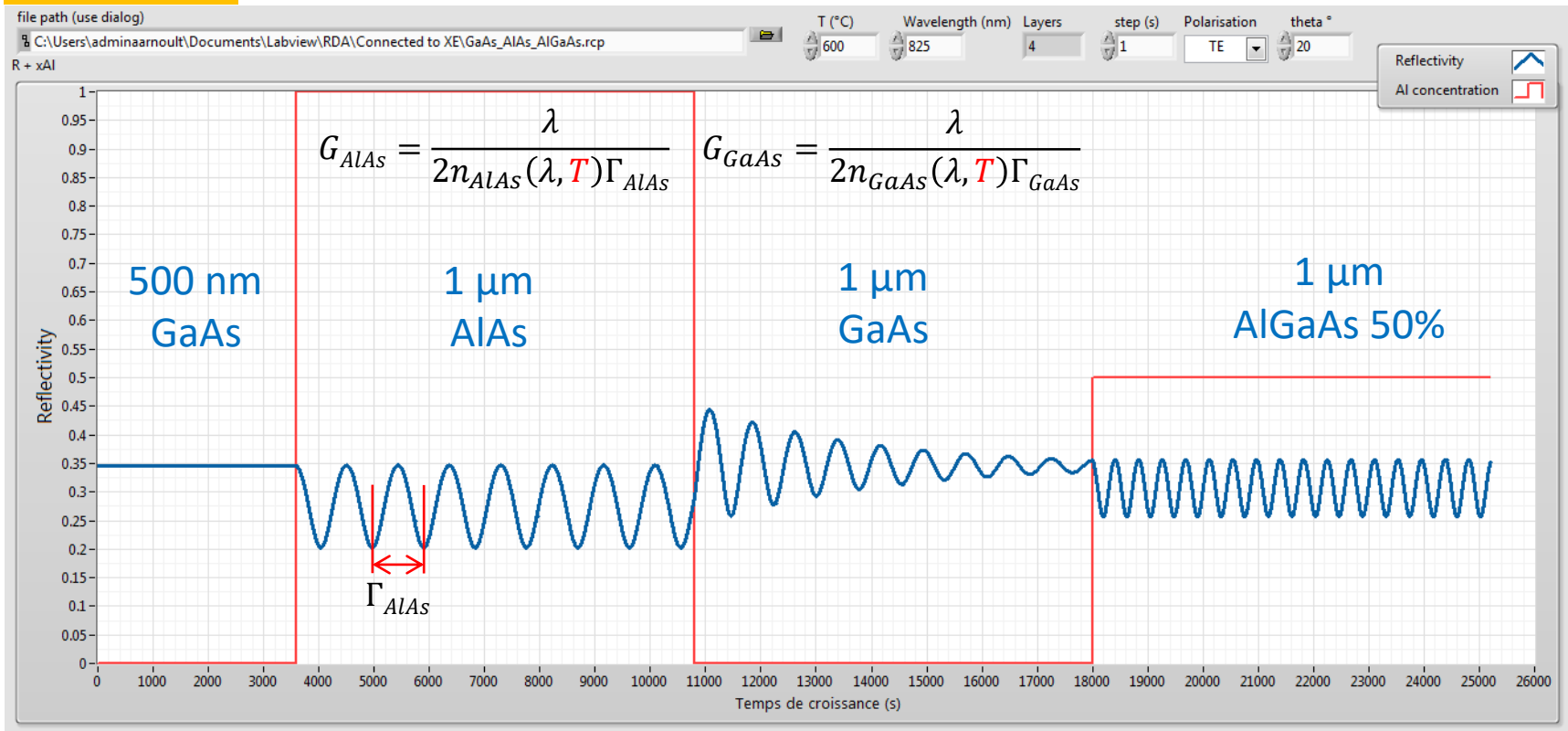
In situ characterization tools in MBE: Reflectivity



In situ characterization tools in MBE: Reflectivity

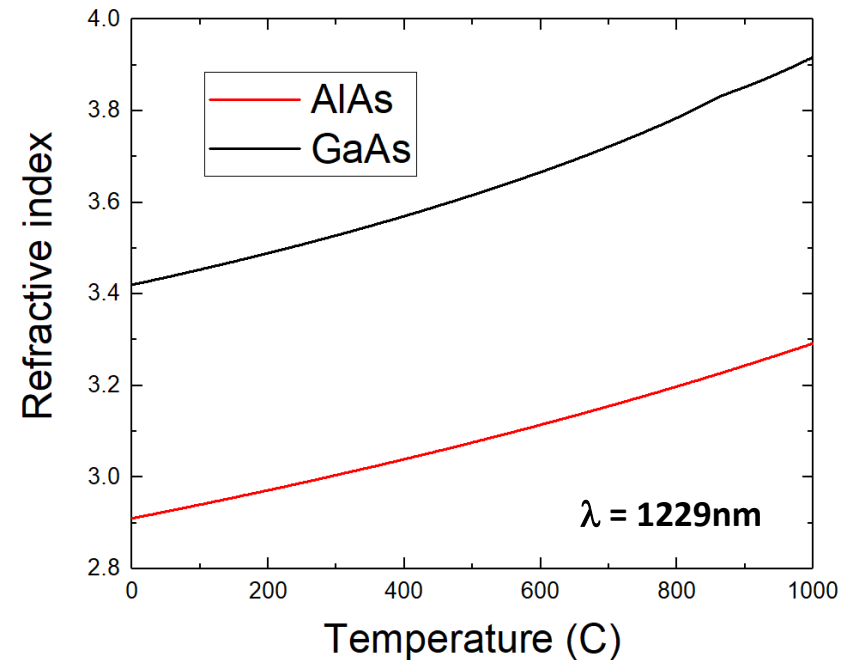
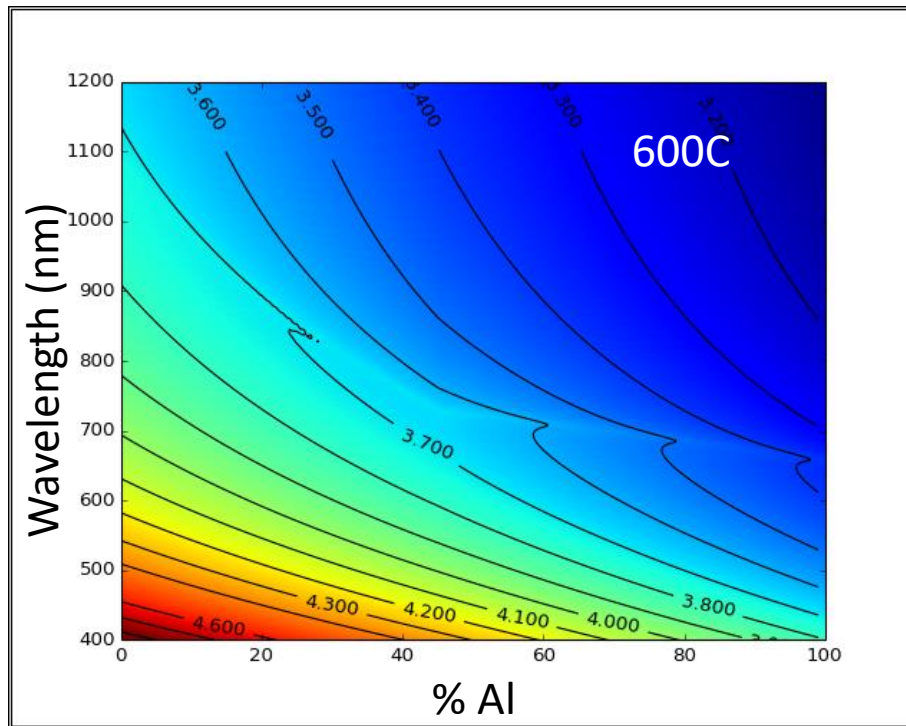


Reflectivity



In situ characterization tools in MBE: Reflectivity

- Optical index evolution with Al concentration and temperature



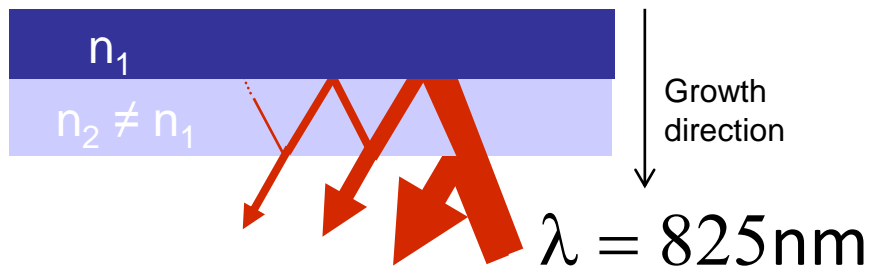
Données :

M.A.A. Afromovitz, *Solid State Commun. (USA)*, **15**, pp59-63 (1974)

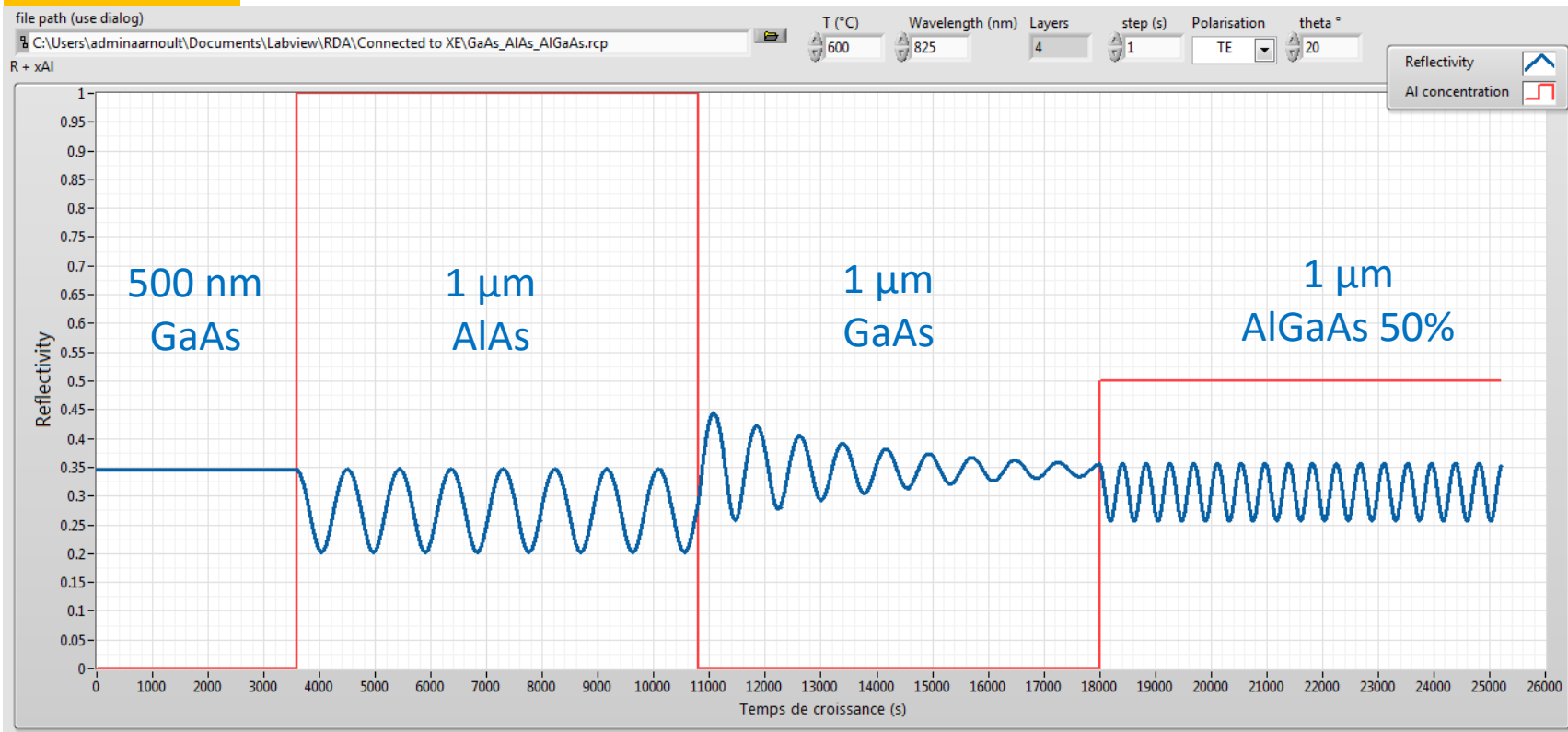
K.P. O'Donnell, *Appl. Phys. Lett.* **58**, 2924 (1991)

➔ **n evolves with T**
Need to know precisely T

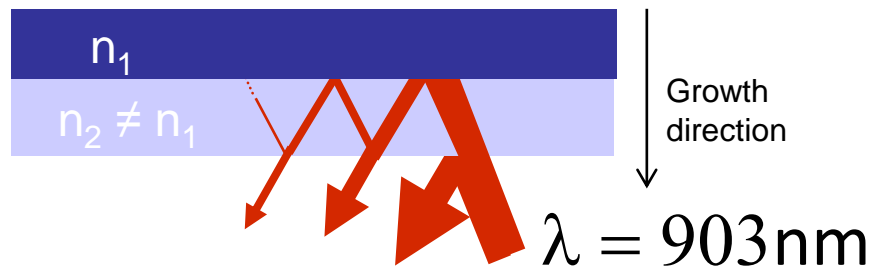
In situ characterization tools in MBE: Reflectivity



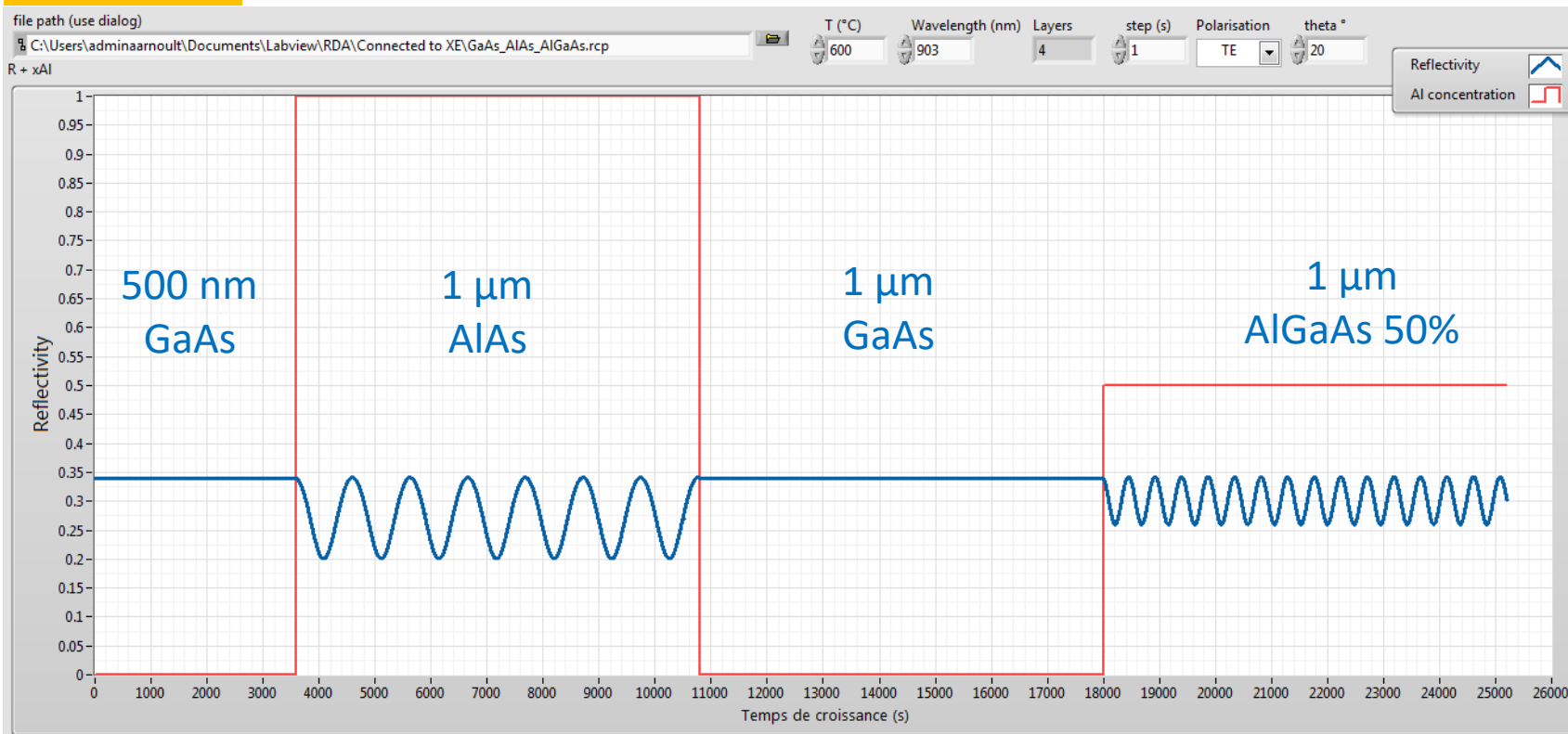
Reflectivity



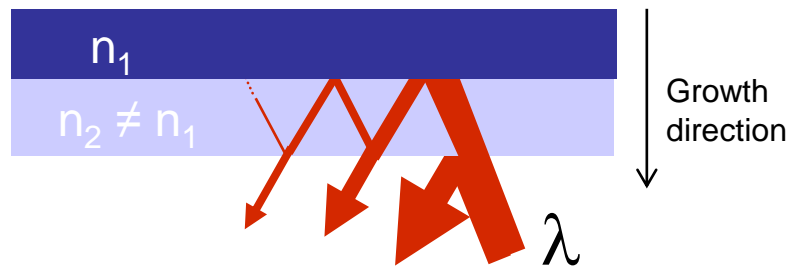
In situ characterization tools in MBE: Reflectivity



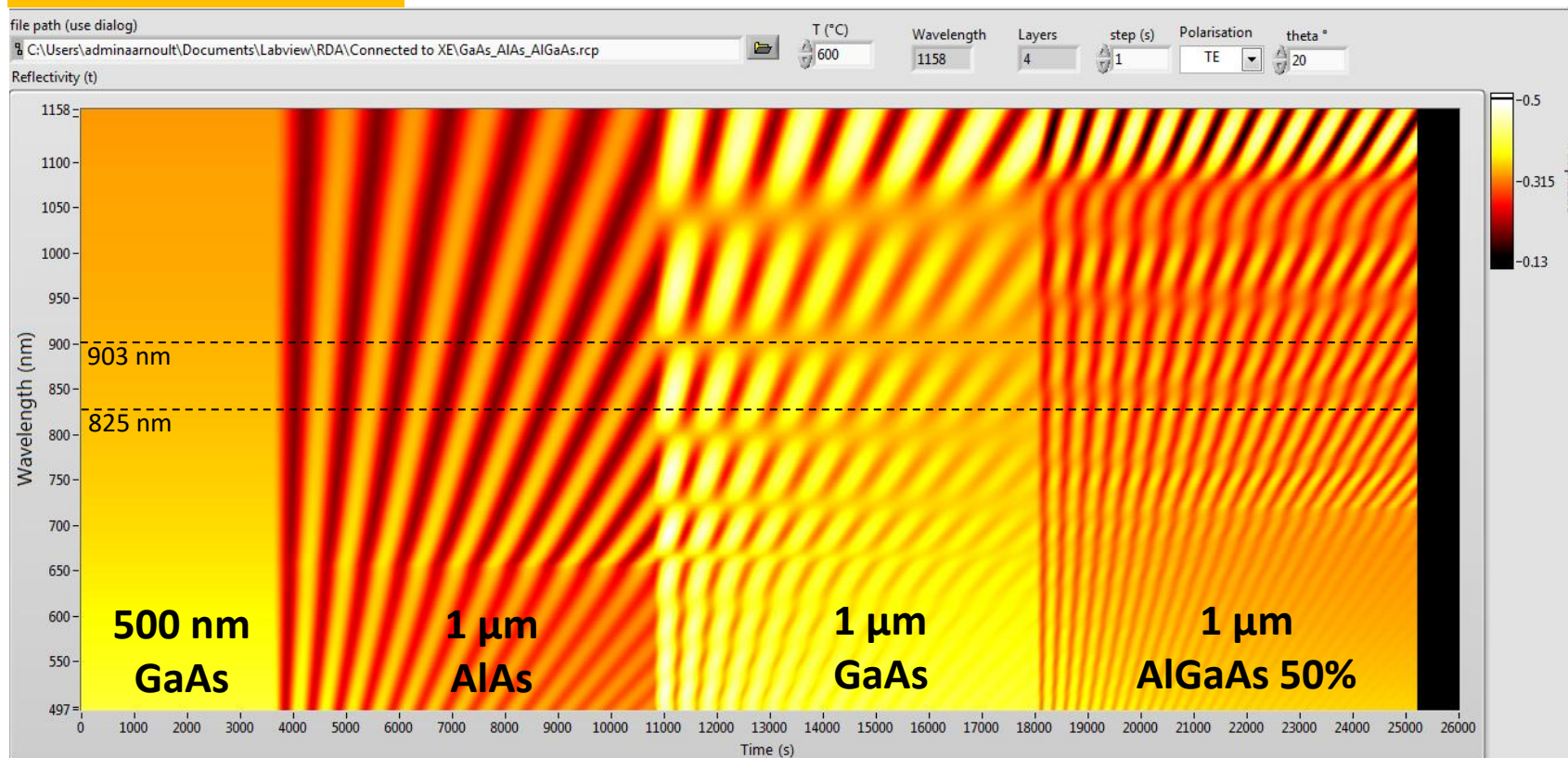
Reflectivity



In situ characterization tools in MBE: Reflectivity

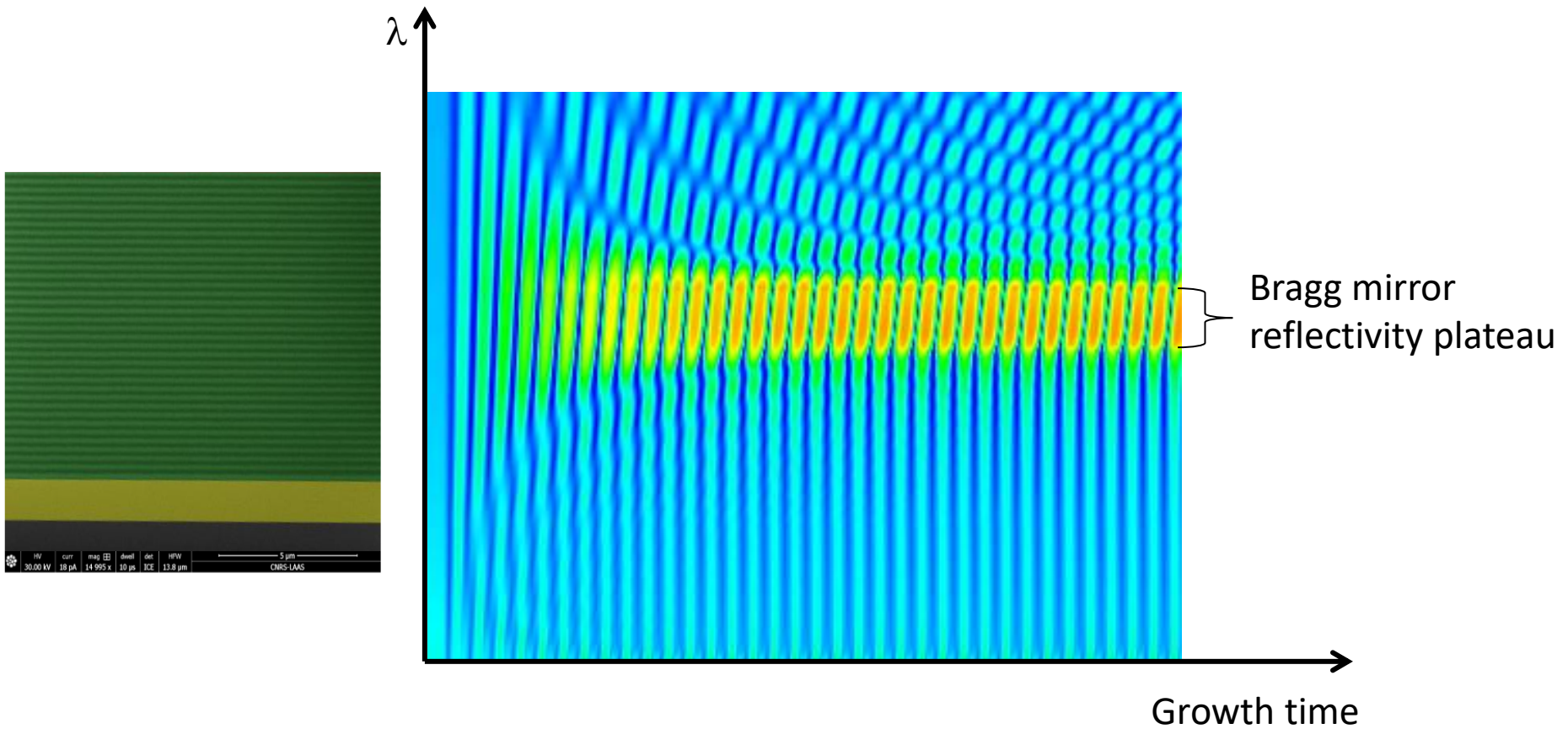


Spectral Reflectivity



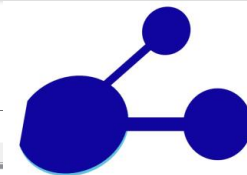
In situ characterization tools in MBE: Reflectivity

Spectral reflectivity during the growth of a Bragg mirror

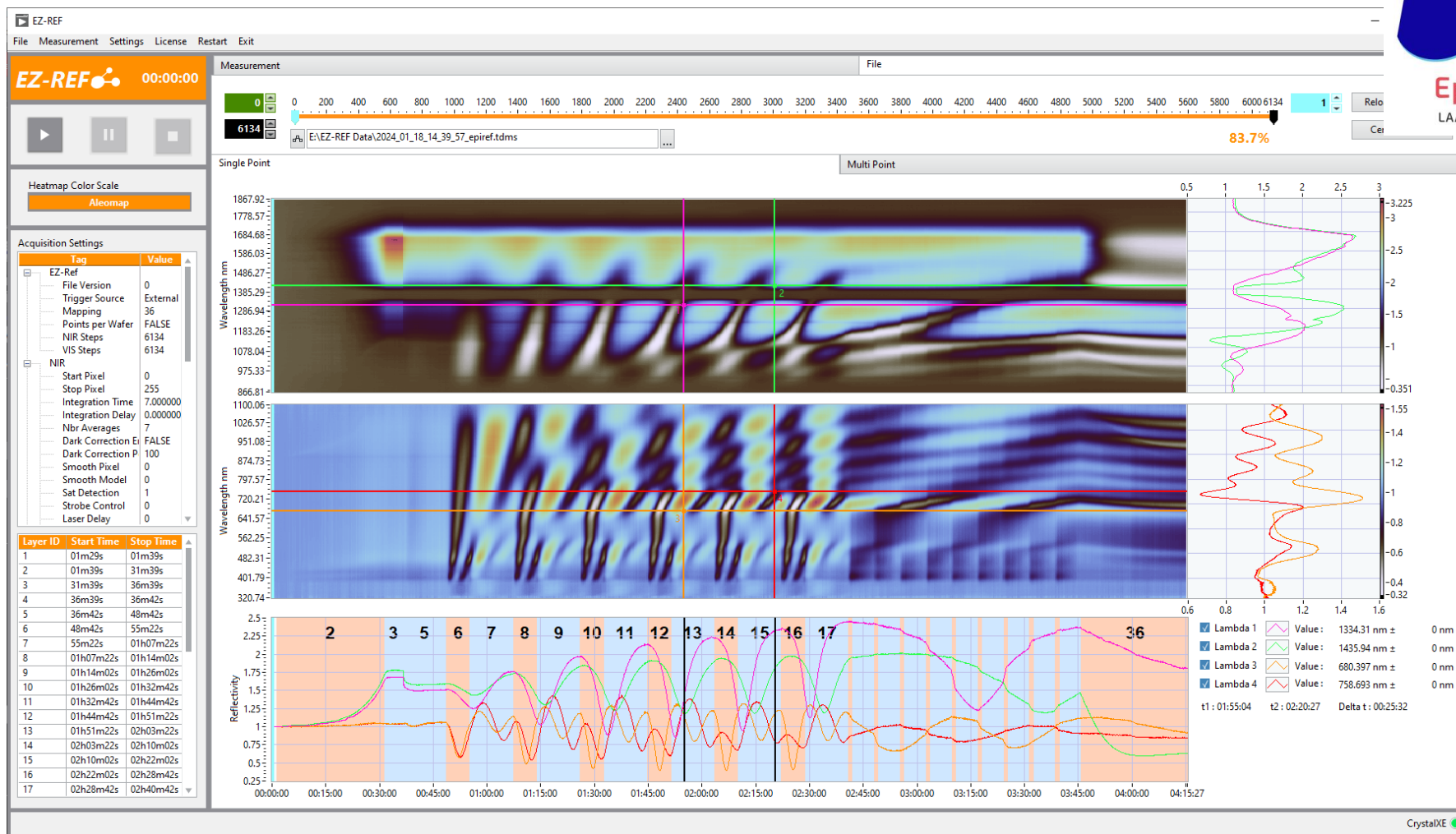


In situ characterization tools in MBE: Reflectivity

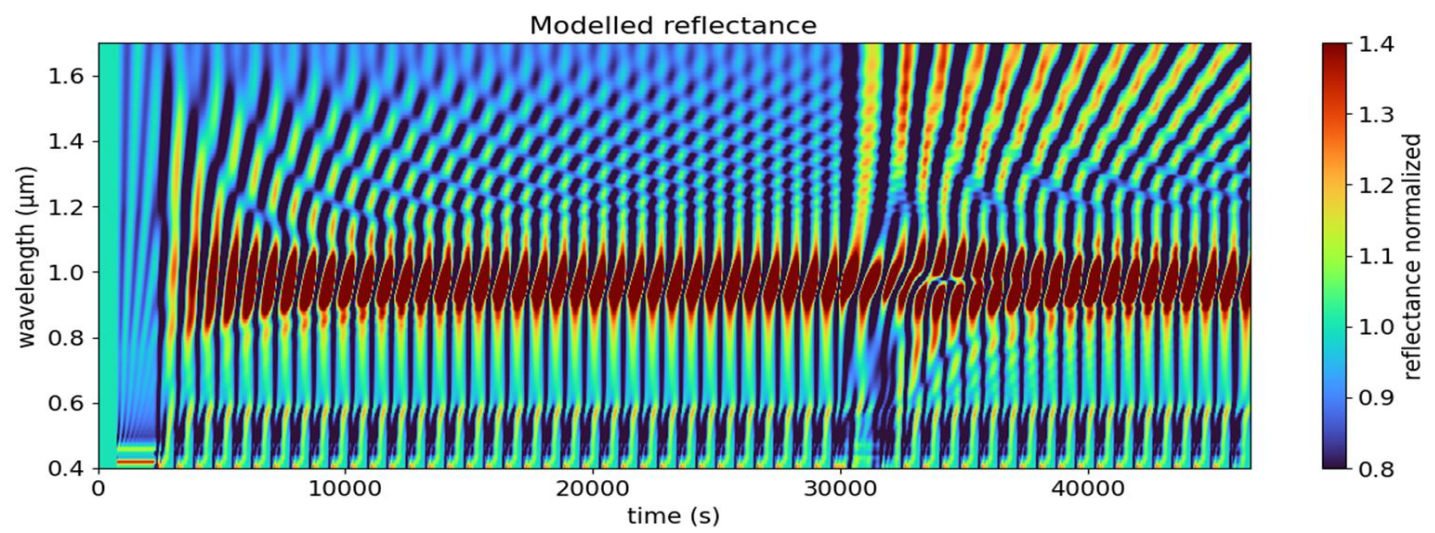
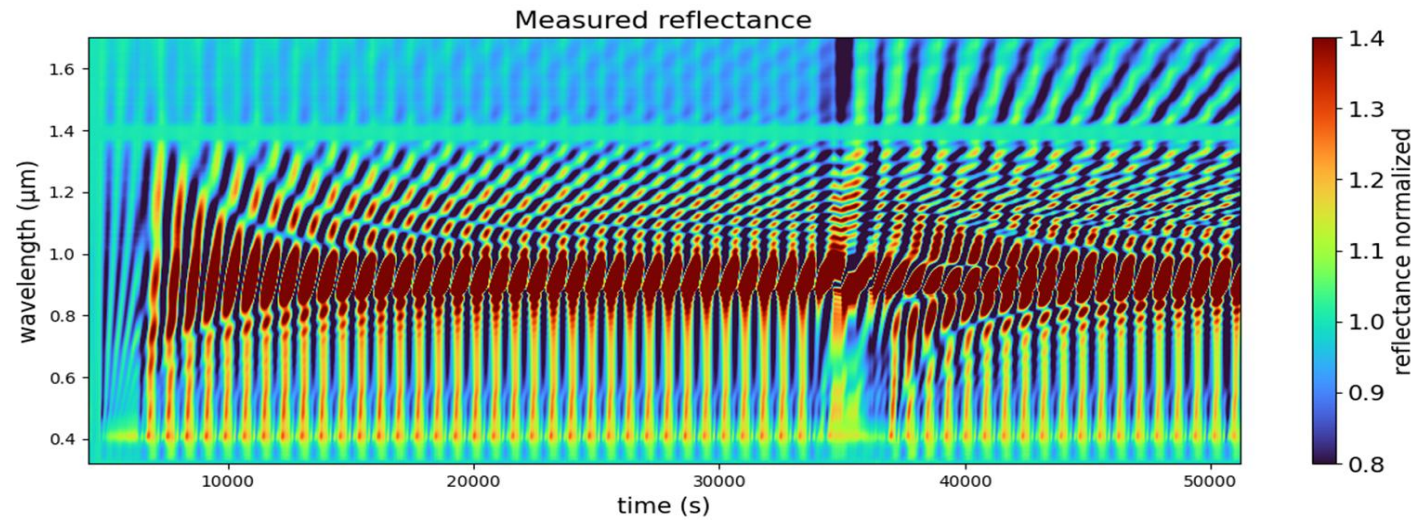
EZ-REF software developed within EpiCentre joint lab



EpiCentre
LAAS CNRS - RIBER



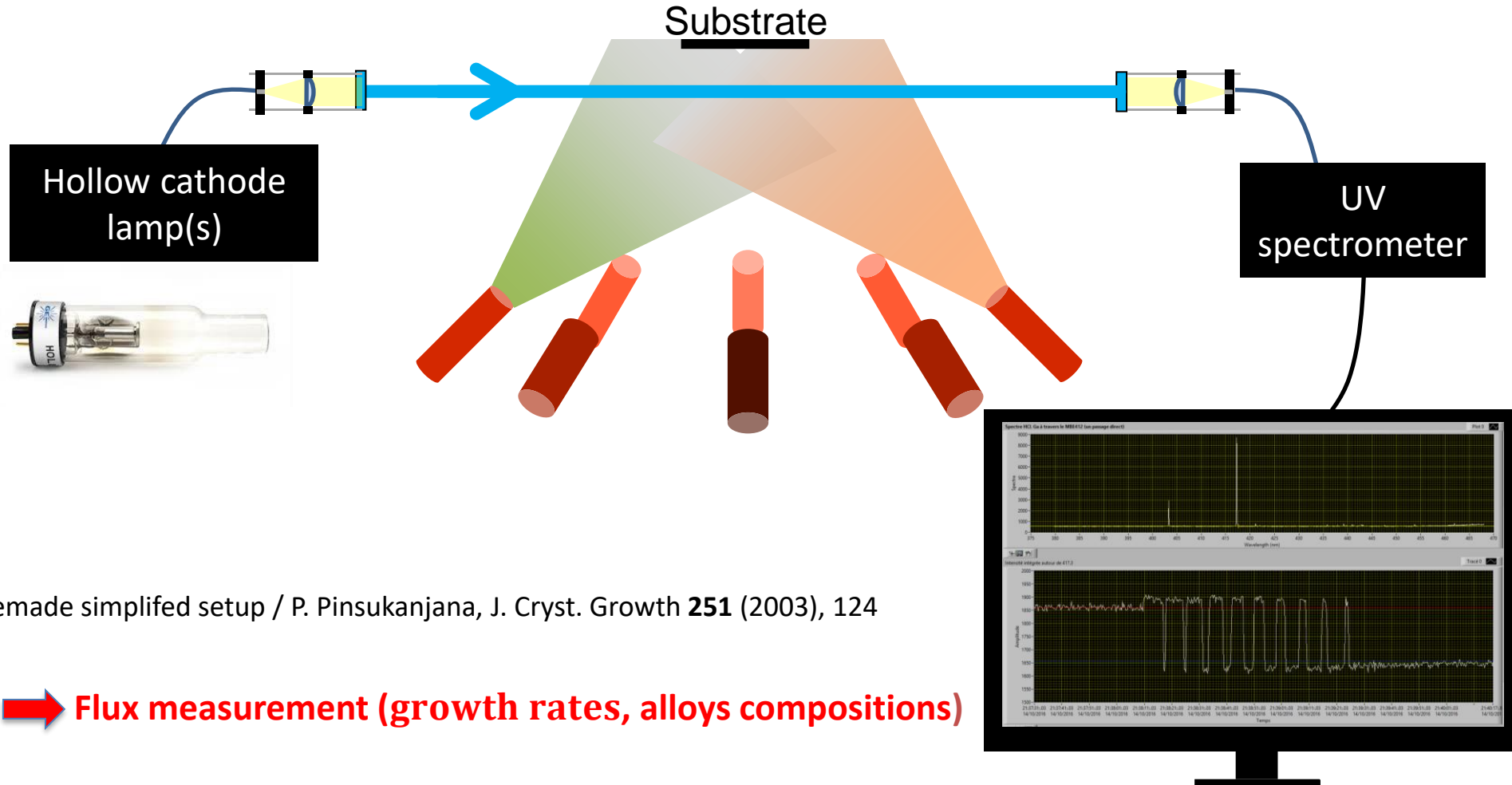
In situ characterization tools in MBE: Reflectivity



In-situ characterization tools: *Atomic Absorption*

In situ characterization tools in MBE: Atomic Absorption

Atomic absorption measurement of fluxes

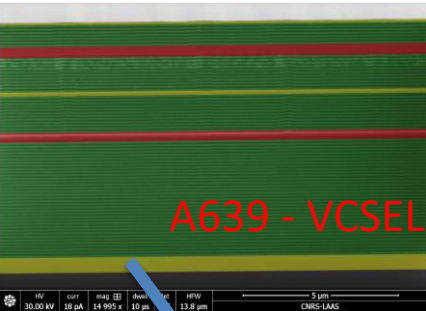


Homemade simplified setup / P. Pinsukanjana, J. Cryst. Growth **251** (2003), 124

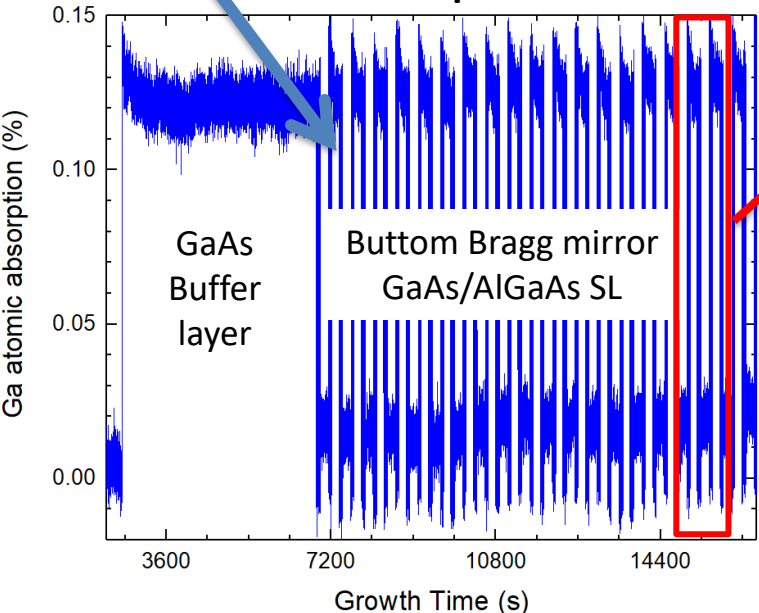
➔ Flux measurement (growth rates, alloys compositions)

In situ characterization tools in MBE: Atomic Absorption

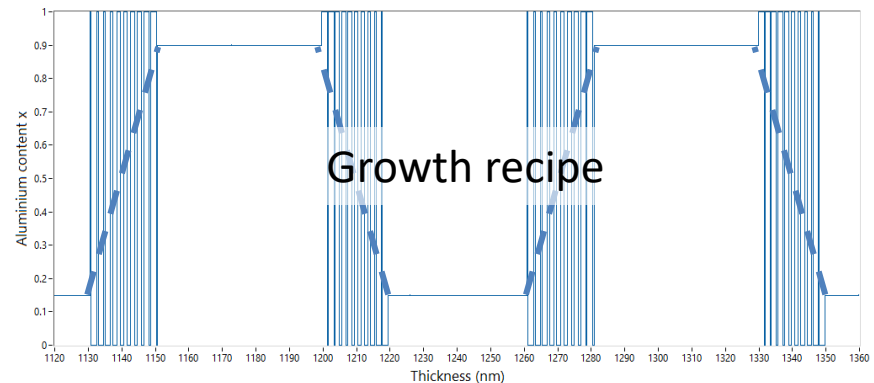
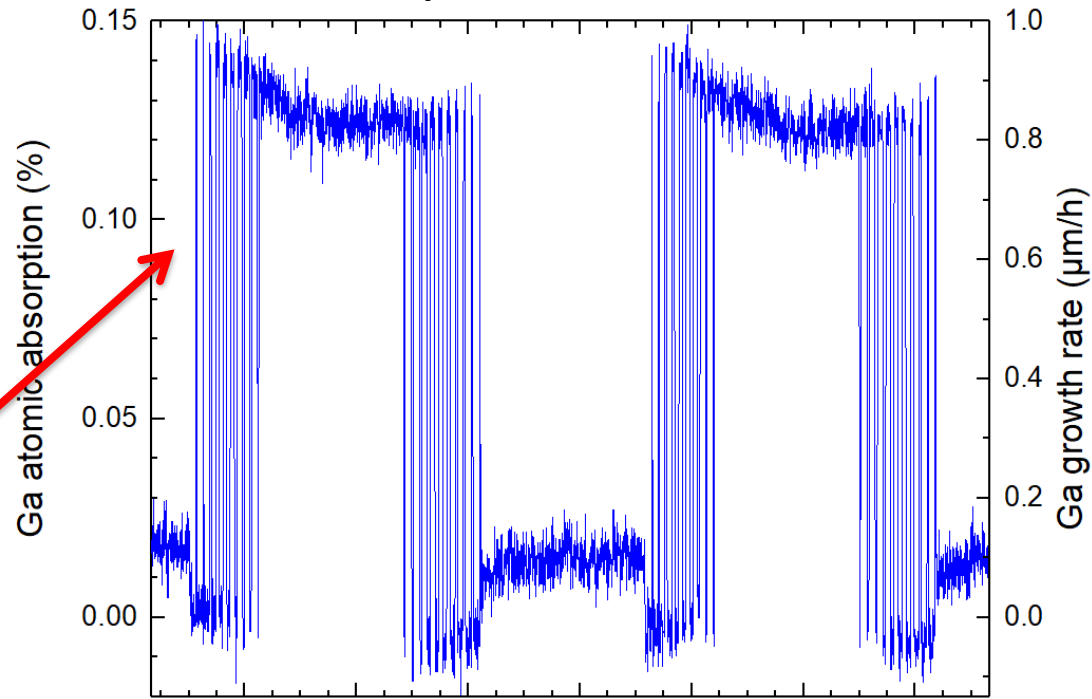
▪ SEM cross section



▪ In situ atomic absorption of Ga

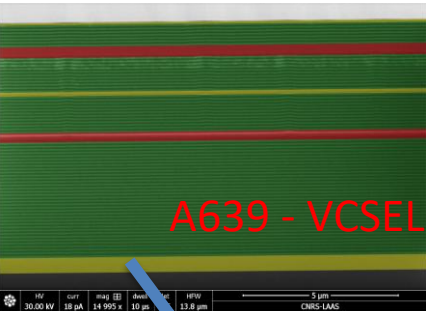


▪ In situ atomic absorption of Ga

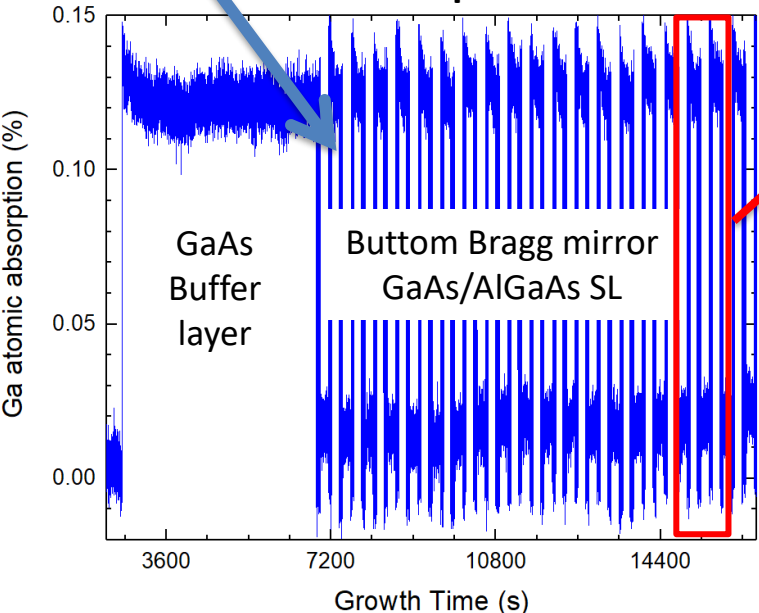


In situ characterization tools in MBE: Atomic Absorption

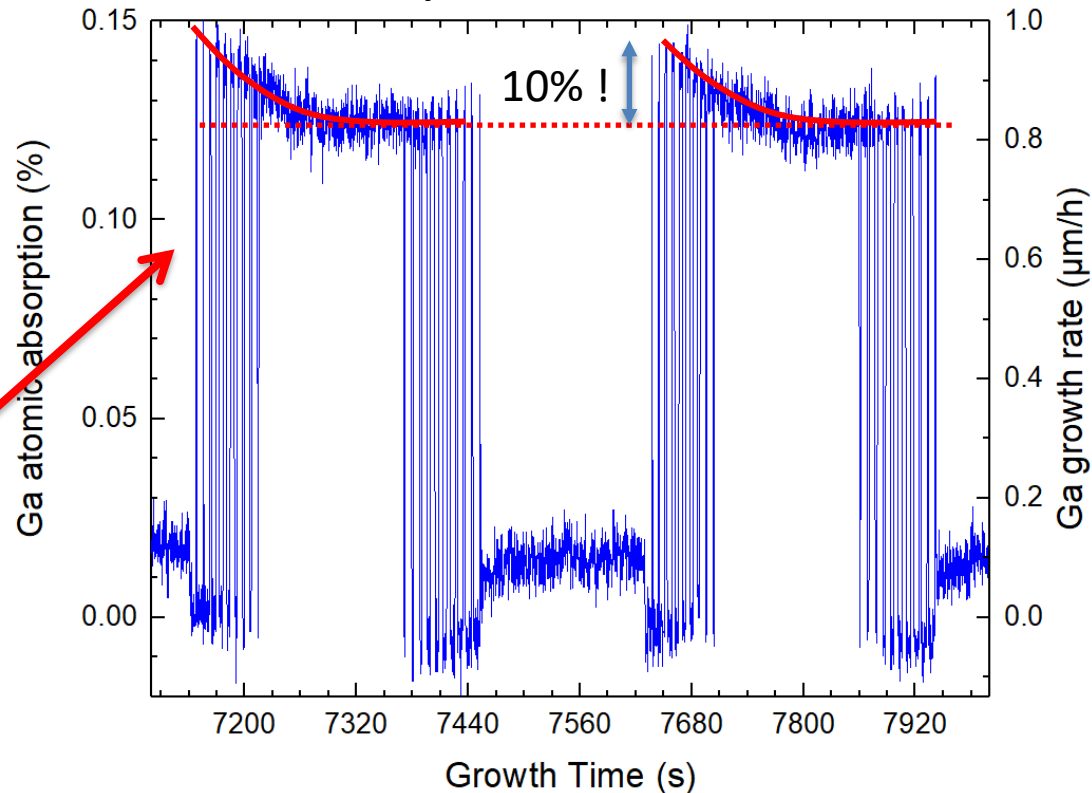
▪ SEM cross section



▪ In situ atomic absorption of Ga



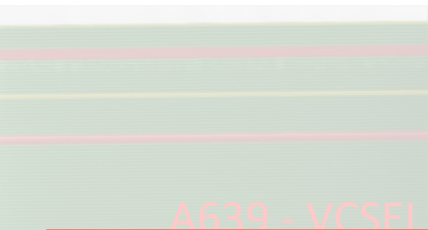
▪ In situ atomic absorption of Ga



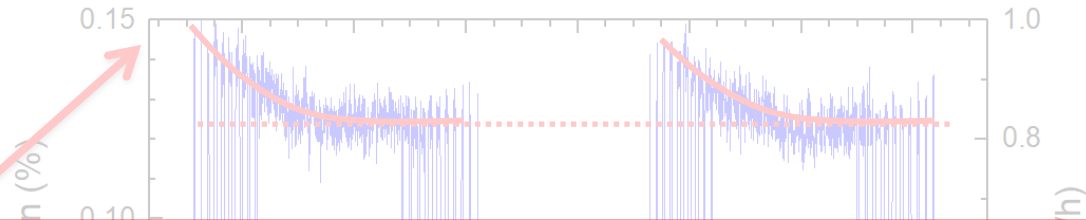
➔ Evidence of a systematic error:
flux transients of the Ga cell

In situ characterization tools in MBE: Atomic Absorption

▪ SEM cross section



▪ In situ atomic absorption of Ga



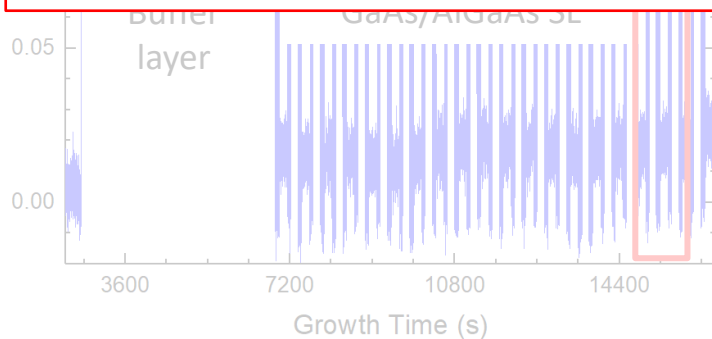
Result : 10% flux variations in some layers

Maximum tolerable error <1% on the whole wafer (100 mm diameter)

Atomic absorption allows for

- errors identification
- real-time corrections

Ga atomic absorption (%)



**Evidence of a systematic error:
flux transients of the Ga cell**

In-situ characterization tools: *Curvature*

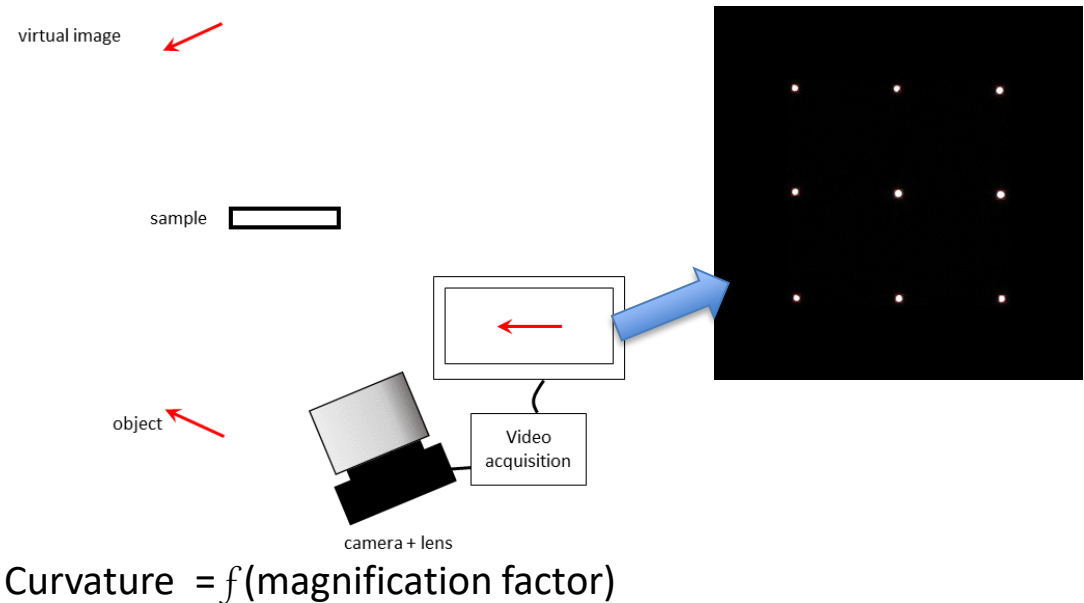
In situ characterization tools in MBE: Curvature

Virtual image magnification analysis: **MIC** (Magnification Inferred Curvature) measures the magnification factor of a virtual image created by a surface (i.e. a wafer)



Highly stable and alignment-free measurements

High rate capability (100FPS)



RIBER
EZ-CURVE

Arnoult, A., Colin, J. Magnification inferred curvature for real-time curvature monitoring. *Sci Rep* **11**, 9393, 2021
<https://doi.org/10.1038/s41598-021-88722-6>

Curvature and stress are linked

> Usually, **three stress components** are distinguished:

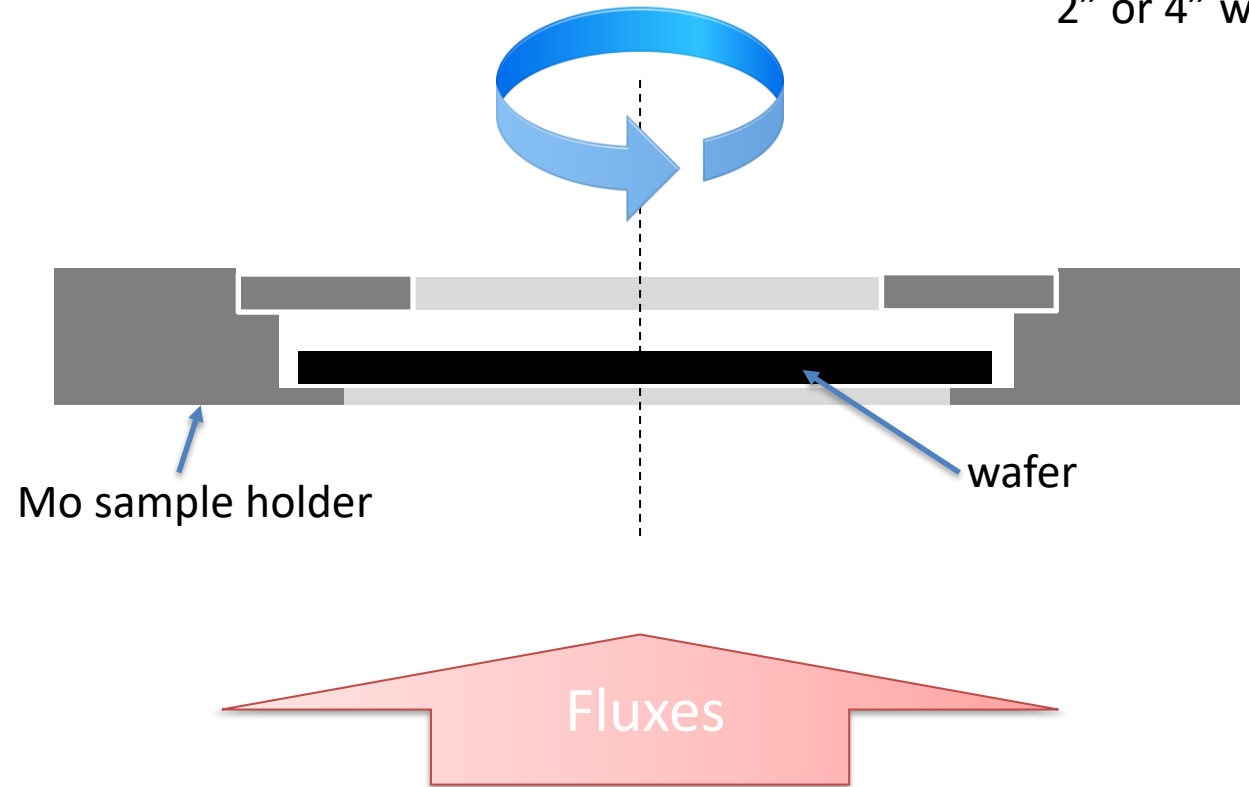
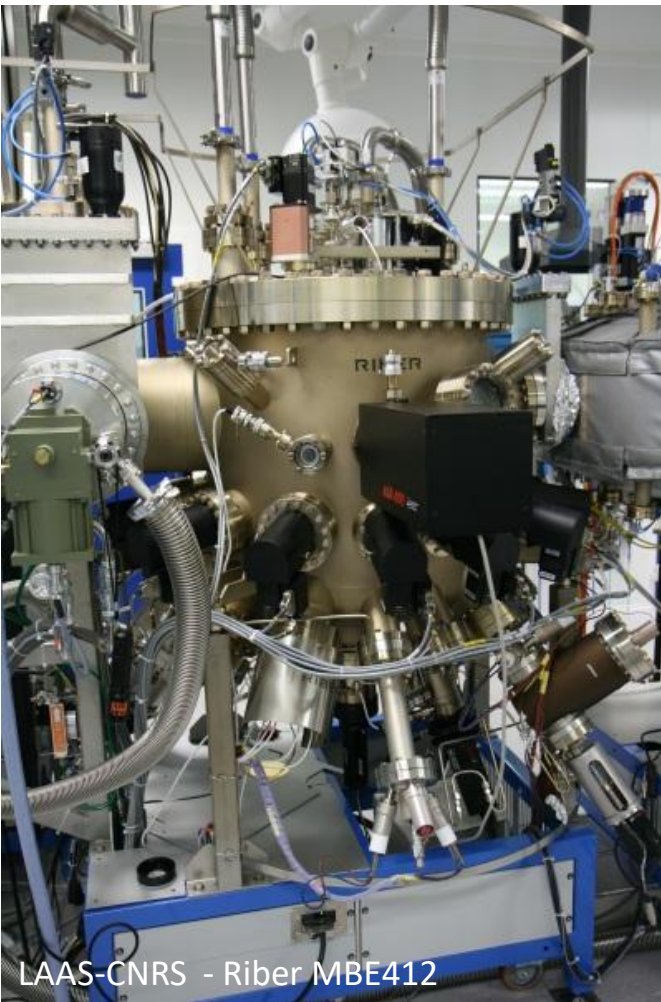
 **1. Extrinsic stress**

- Induced by external factors: external loading, exposure to environment, ...

Stress/Curvvature and crystal growth

Extrinsic stress

2" or 4" wafers



Wafer free to expand in holder \Rightarrow no extrinsic stress here

LAAS-CNRS - Ribier MBE412

Curvature and stress are linked

> Usually, **three stress components** are distinguished:

1. Extrinsic stress

- Induced by external factors: mechanical loading, exposure to environment, ...

No extrinsic stress here

2. Intrinsic stress

- Stress source introduced during the MBE process : lattice mismatch, growth mode, relaxation, surface and/or interface stress, incorporation or desorption of impurities, phase transformations...



Curvature and stress are linked

> Usually, **three stress components** are distinguished:

1. Extrinsic stress

- Induced by external factors: mechanical loading, exposure to environment, ...

No extrinsic stress here

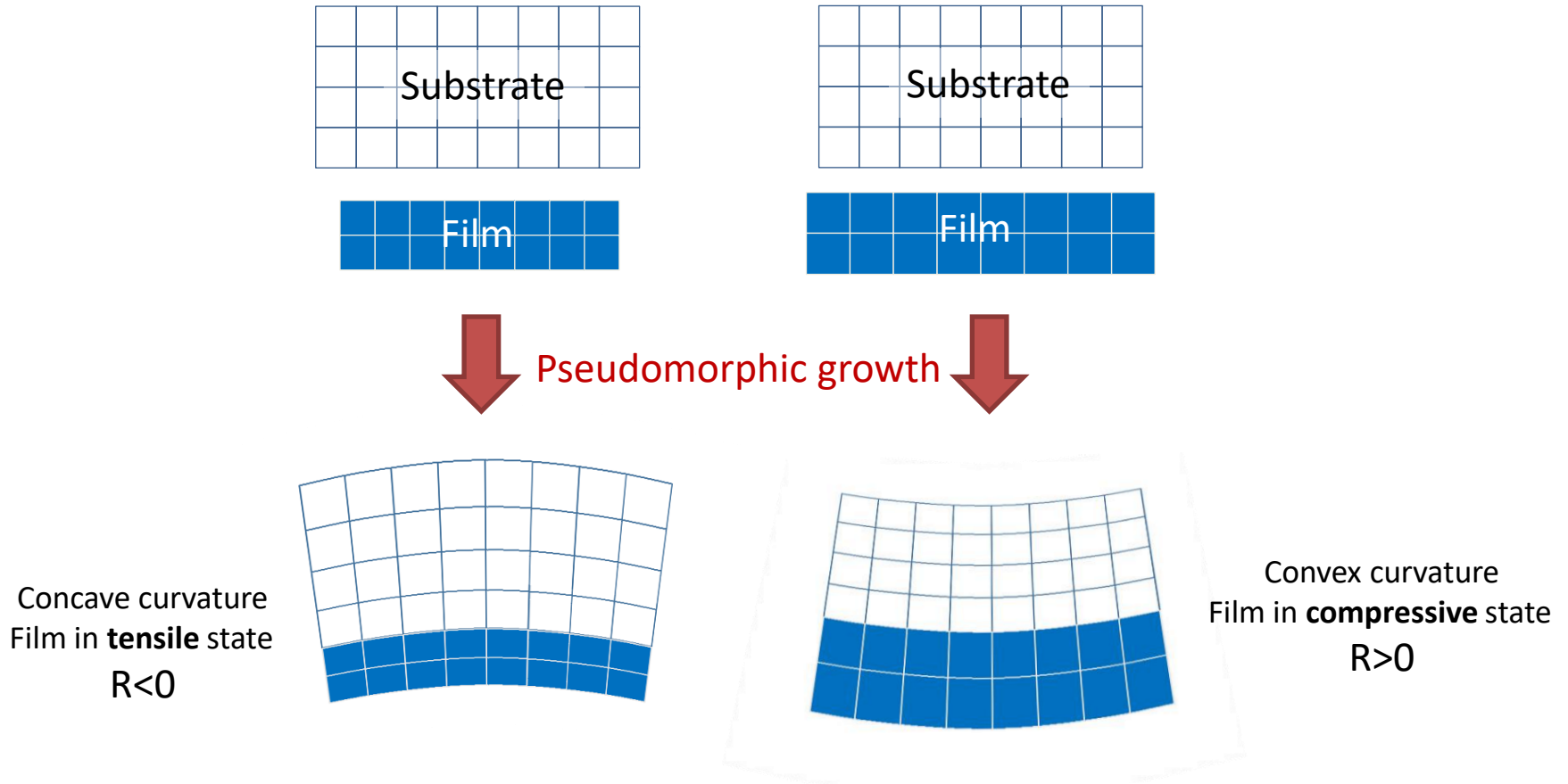
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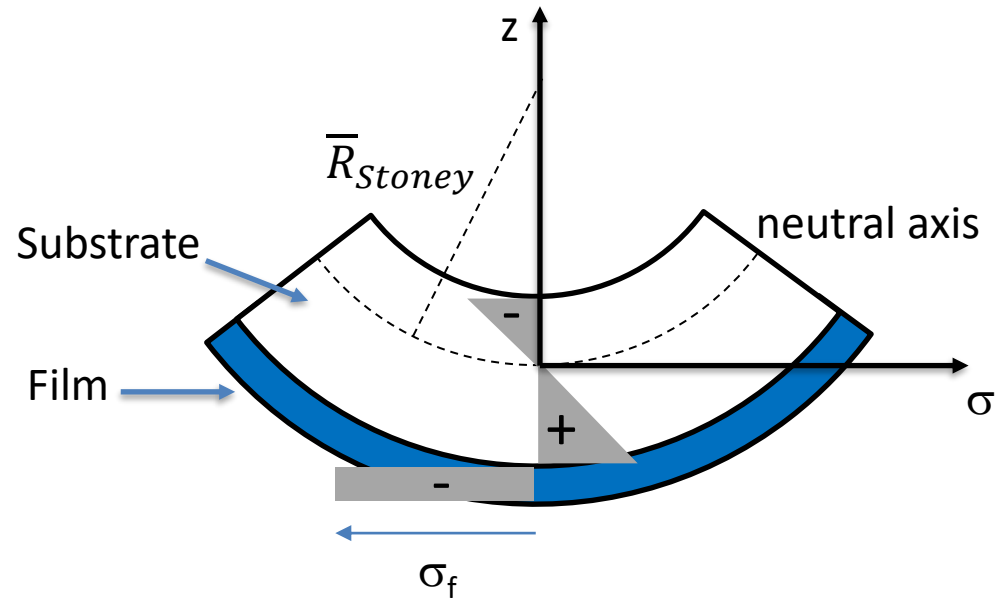
In situ characterization tools in MBE: Curvature

Why thin films are usually in a stressed state?



The stress in the film leads to a bending of the system “film+substrate”

In situ characterization tools in MBE: Curvature



h_f = film thickness
 M_s = substrate biaxial modulus
 h_s = substrate thickness
 σ_f = stress in the film

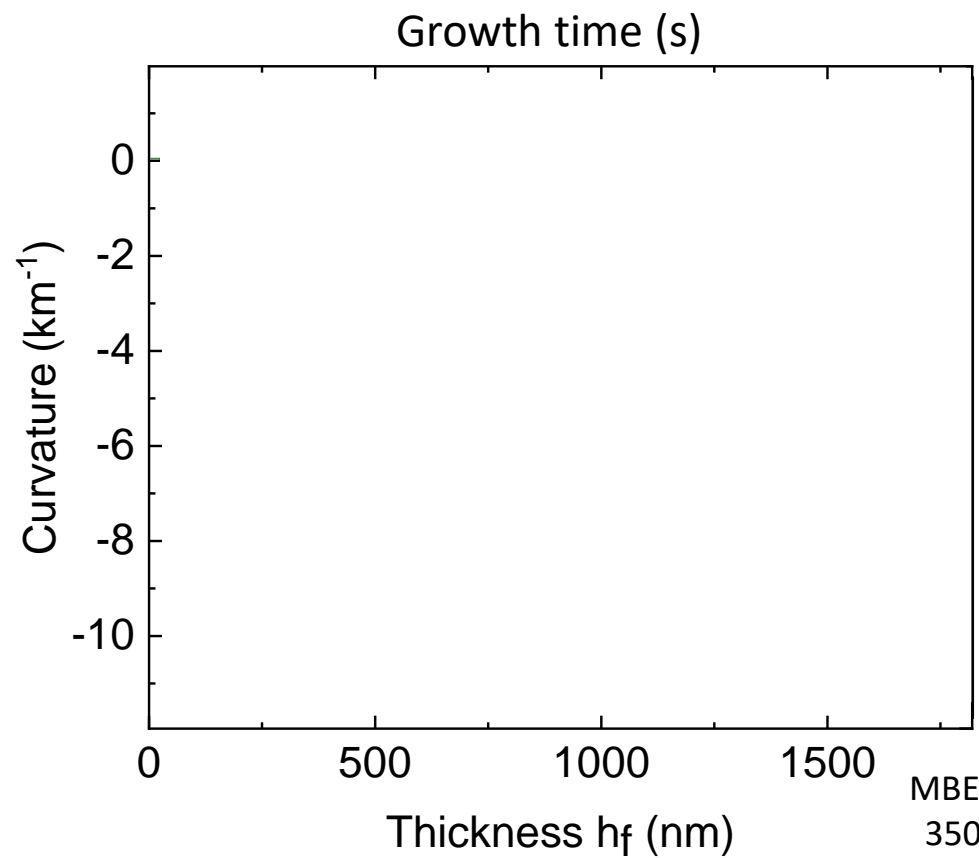
- > Satisfying equilibrium conditions ($\Sigma F = 0$ and $\Sigma M = 0$) leads to the **Stoney equation**

$$\kappa = \frac{1}{\bar{R}_{Stoney}} \cong \frac{6\bar{\sigma}_f h_f}{M_s h_s^2} \quad \text{with } M_s = \frac{E}{1-\nu}$$

G.G. Stoney, The tensions of metallic films deposited by electrolysis, Proc. R. Soc. Land. A82 (1909) 172-175

Curvature/Stress and MBE growth

Intrinsic stress

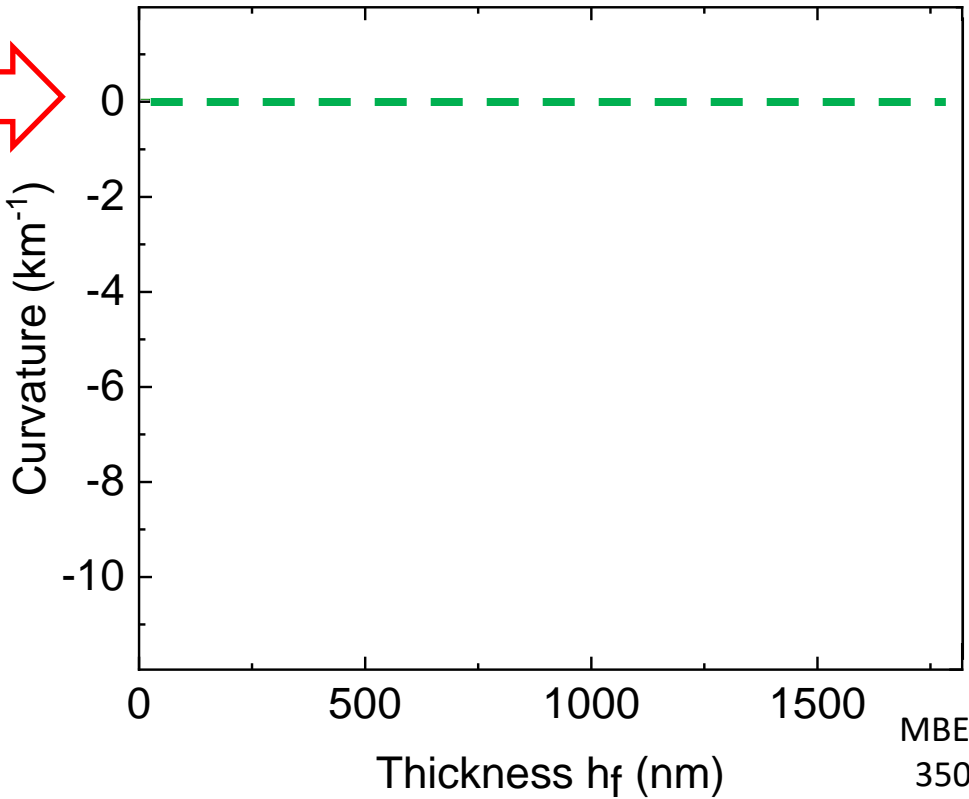


MBE growth of GaAs/AlGaAs on a rotating 350 μm -thick (001) GaAs wafer at 600°C

Curvature/Stress and MBE growth

Intrinsic stress

Zero curvature = initial state
(relative curvature changes)

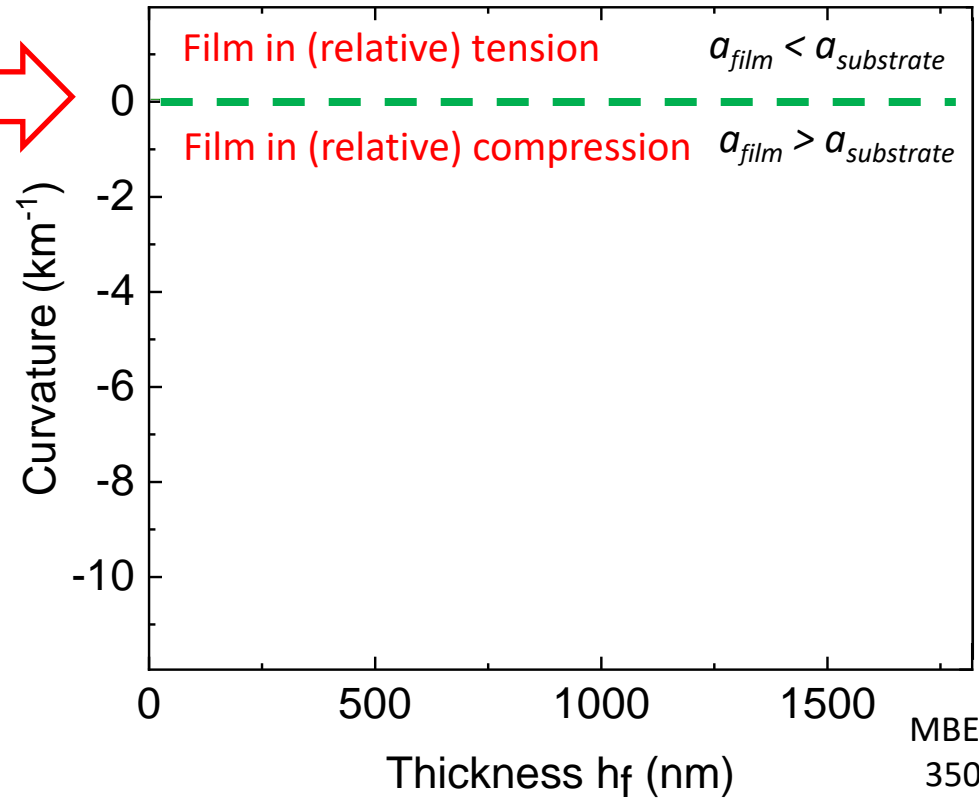


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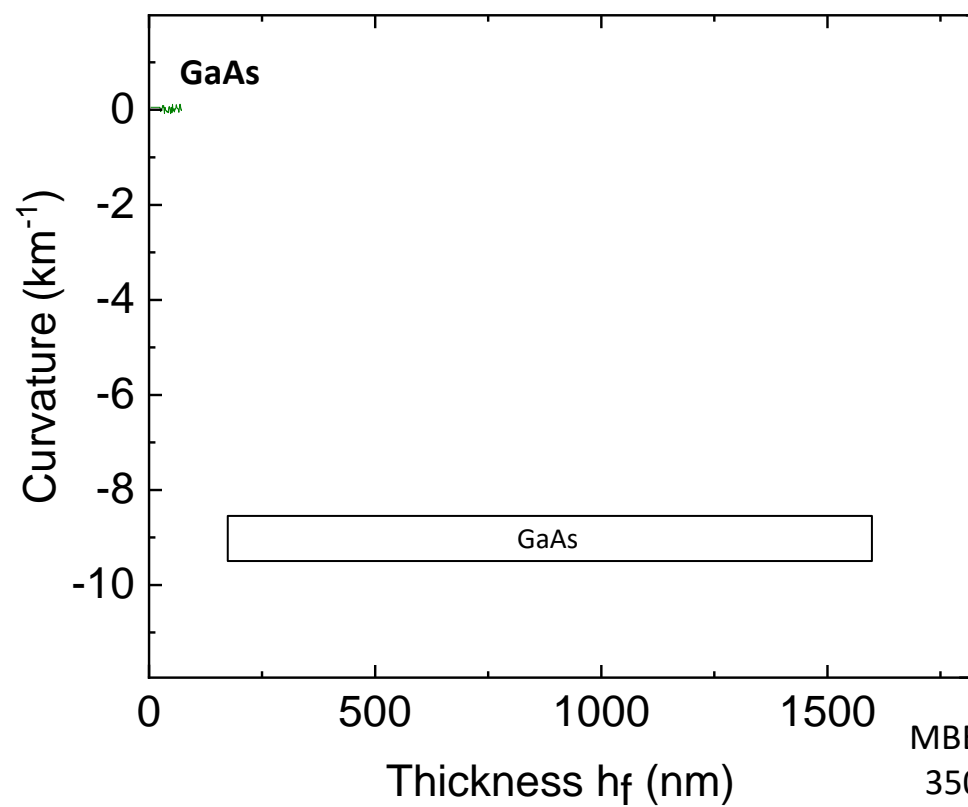
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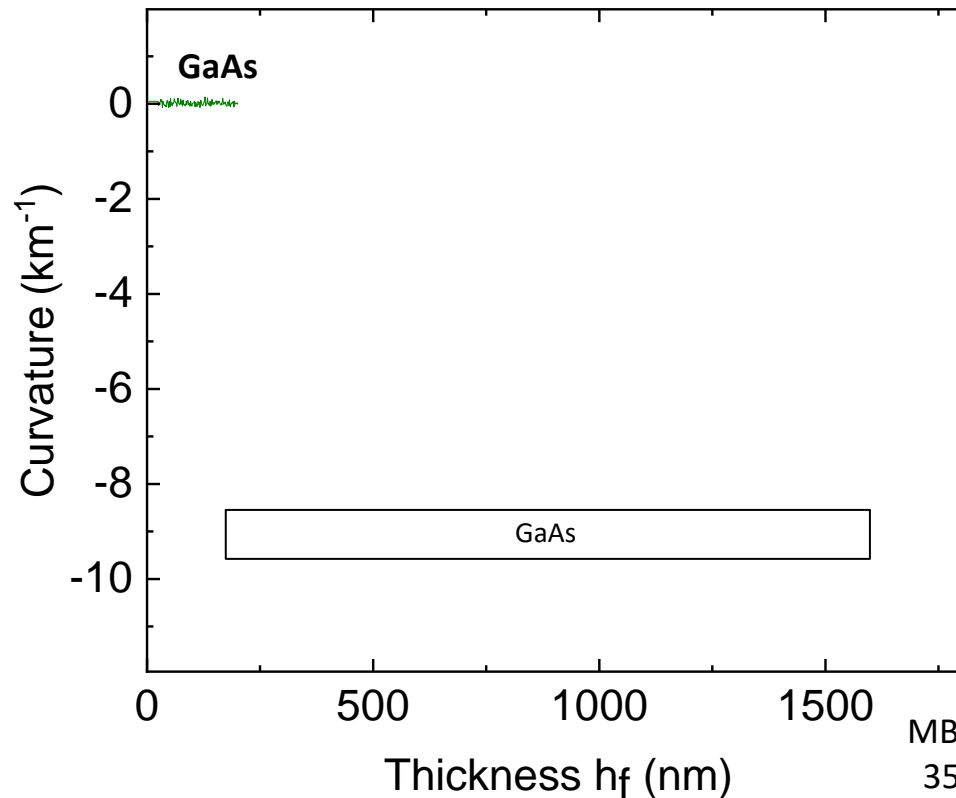
Intrinsic stress



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Curvature/Stress and MBE growth

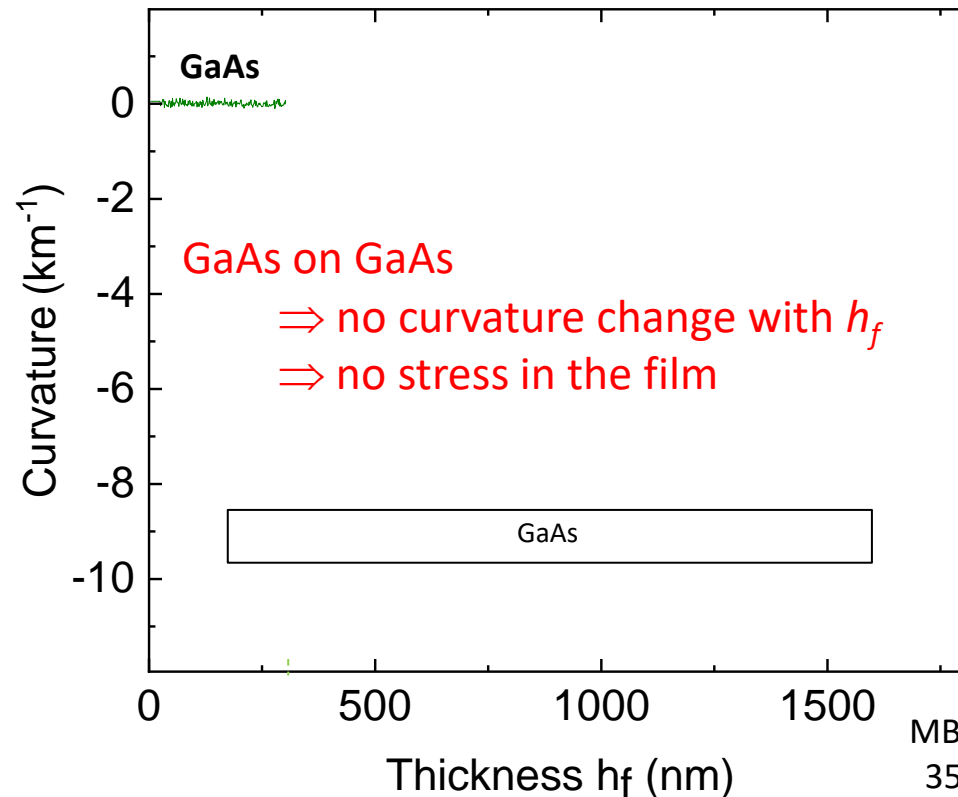
Intrinsic stress



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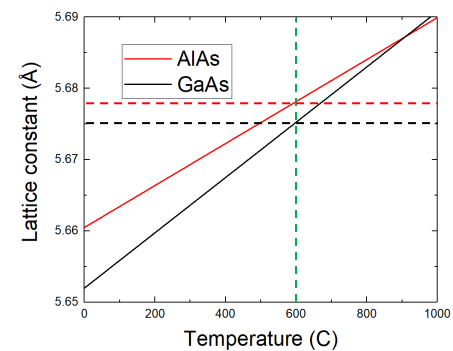
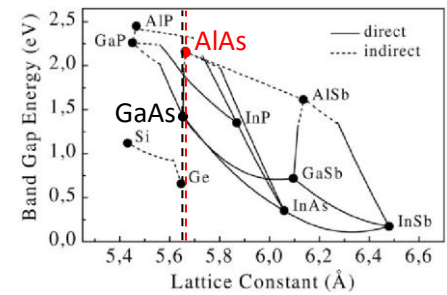
Intrinsic stress



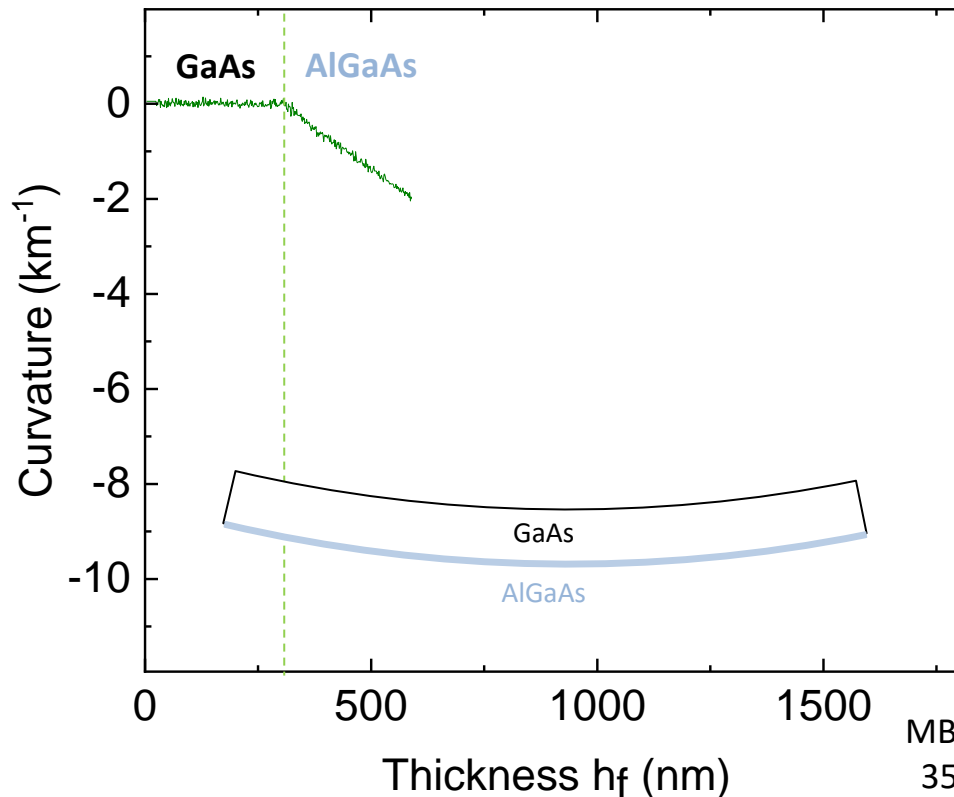
MBE growth of GaAs/AlGaAs on a rotating 350 μm -thick (001) GaAs wafer at 600°C

Curvature/Stress and MBE growth

Intrinsic stress



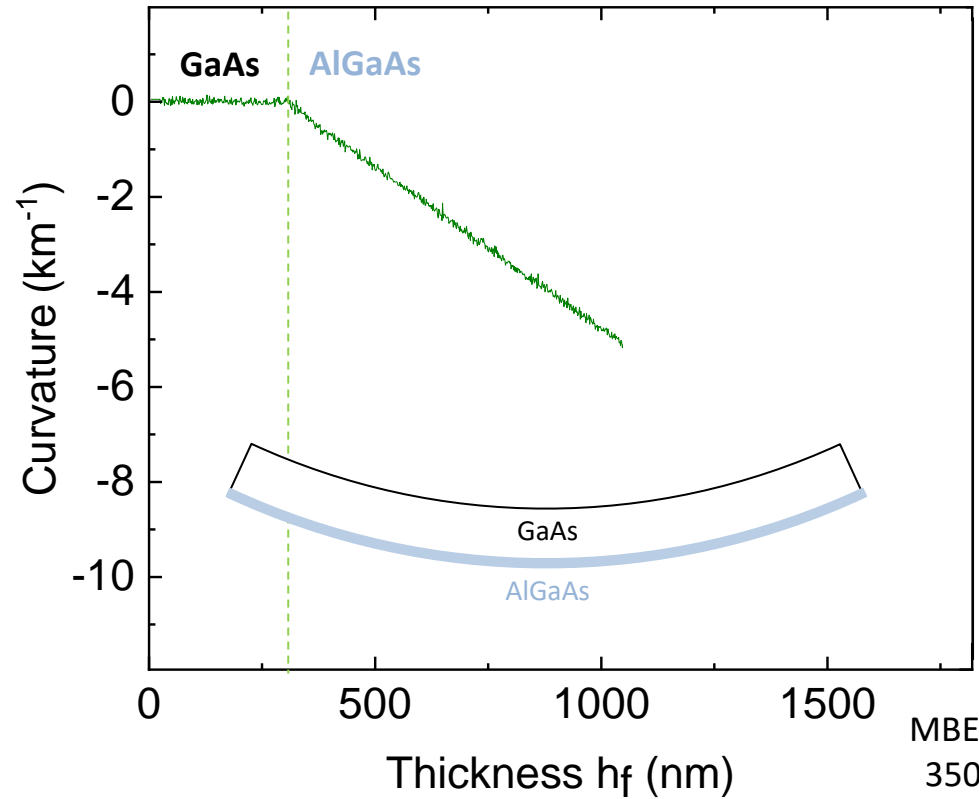
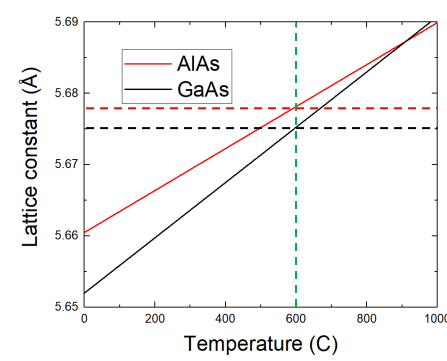
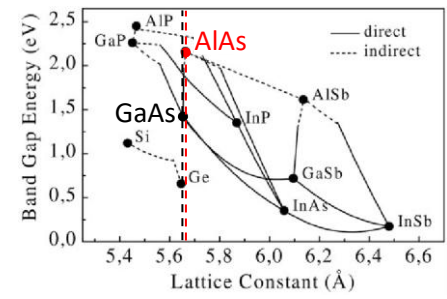
M. Ettenberg, R. J. Paff, J. Appl. Phys., **41**, no.10, pp.3926-3927 (1970)



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Curvature/Stress and MBE growth

Intrinsic stress

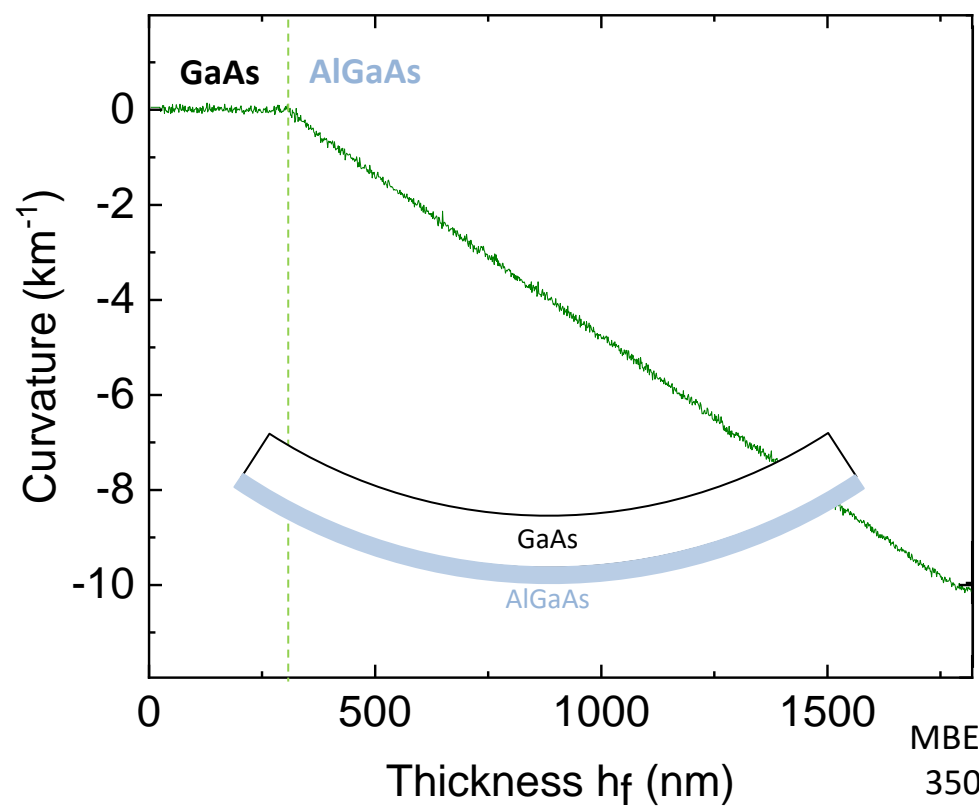
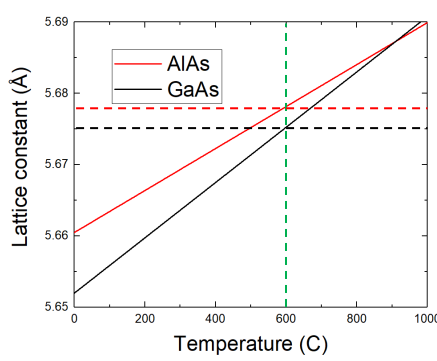
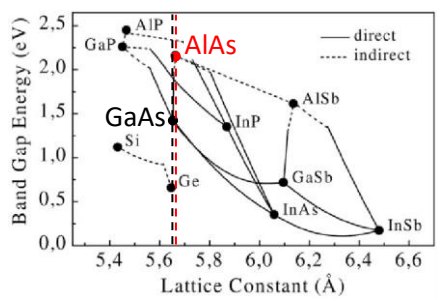


MBE growth of GaAs/AlGaAs on a rotating 350 μm -thick (001) GaAs wafer at 600°C

M. Ettenberg, R. J. Paff, *J. Appl. Phys.*, **41**, no.10, pp.3926-3927 (1970)

Curvature/Stress and MBE growth

Intrinsic stress

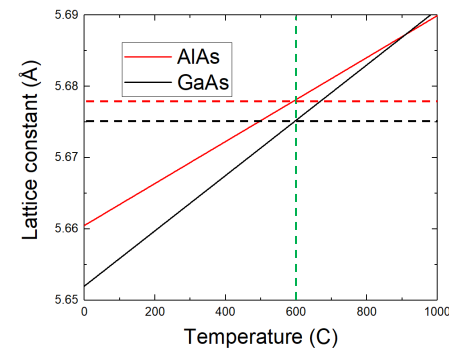
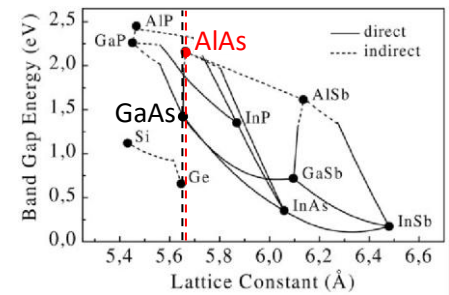


MBE growth of GaAs/AlGaAs on a rotating 350 μm -thick (001) GaAs wafer at 600°C

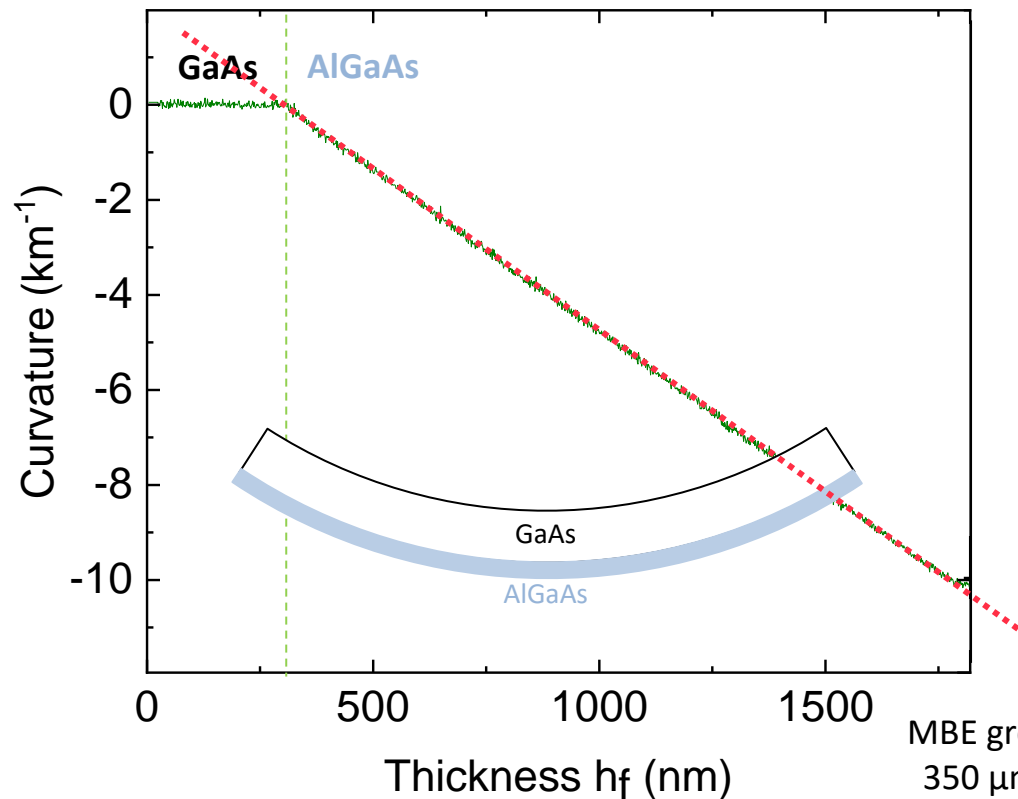
M. Ettenberg, R. J. Paff, J. Appl. Phys., 41, no.10, pp.3926-3927 (1970)

Curvature/Stress and MBE growth

Intrinsic stress



M. Ettenberg, R. J. Paff, *J. Appl. Phys.*, **41**, no.10, pp.3926-3927 (1970)



MBE growth of GaAs/AlGaAs on a rotating 350 μm -thick (001) GaAs wafer at 600°C

Curvature/Stress and MBE growth

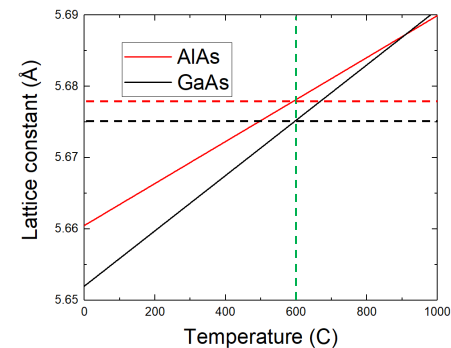
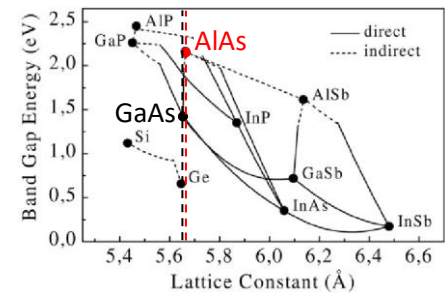
Intrinsic stress

Curvature
(m^{-1})

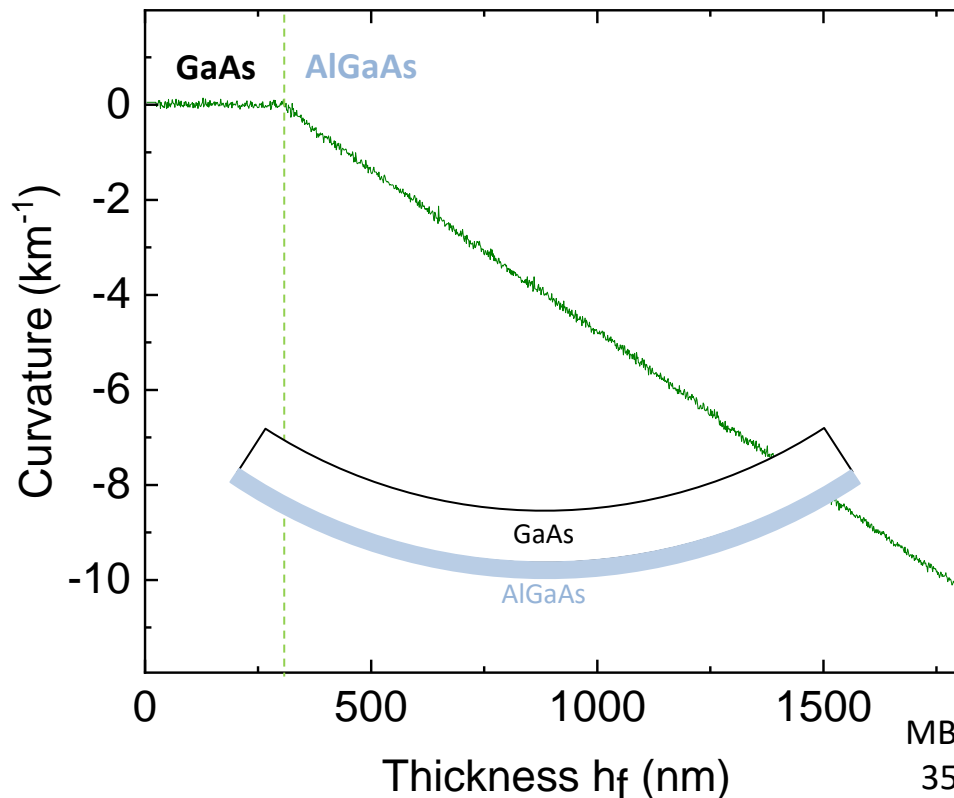
$$\kappa \cong \frac{6\overline{\sigma}_f}{M_s h_s^2} h_f$$

Constant for a given film on a given substrate

h_f = film thickness
 M_s = substrate biaxial modulus
 h_s = substrate thickness
 σ_f = stress in the film



M. Ettenberg, R. J. Paff, J. Appl. Phys., 41, no.10, pp.3926-3927 (1970)



MBE growth of GaAs/AlGaAs on a rotating 350 μm -thick (001) GaAs wafer at 600°C

Curvature/Stress and MBE growth

Intrinsic stress

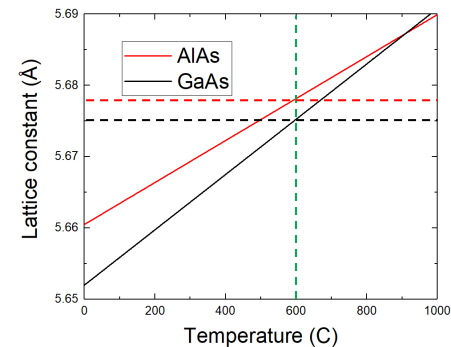
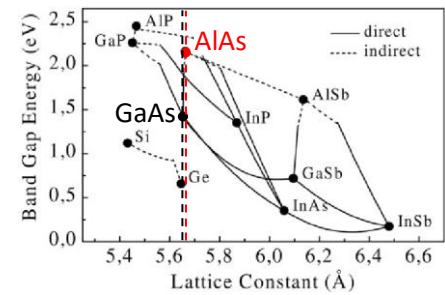
Curvature
(m⁻¹)

$$\kappa \cong \frac{6\overline{\sigma}_f}{M_s h_s^2} h_f$$

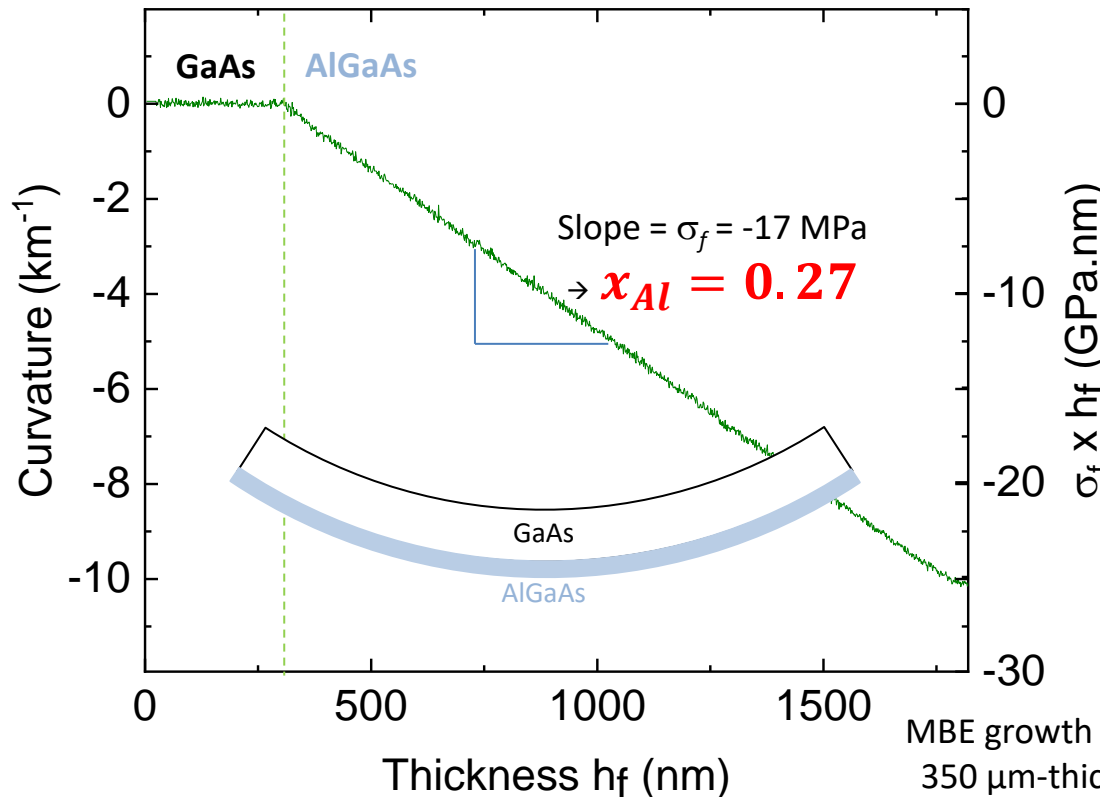
Constant for a given film on a given substrate

h_f = film thickness
 M_s = substrate biaxial modulus
 h_s = substrate thickness
 σ_f = stress in the film

$$\overline{\sigma}_f h_f \cong \frac{M_s h_s^2}{6} \kappa$$



M. Ettenberg, R. J. Paff, J. Appl. Phys., 41, no.10, pp.3926-3927 (1970)



MBE growth of GaAs/AlGaAs on a rotating 350 μ m-thick (001) GaAs wafer at 600°C

Curvature and stress are linked

> Usually, **three stress components** are distinguished:

1. Extrinsic stress

- Induced by external factors: mechanical loading, exposure to environment, ...

No extrinsic stress here

2. Intrinsic stress

- Stress source introduced during the MBE process : **lattice mismatch**, growth mode, relaxation, surface and/or interface stress, incorporation or desorption of impurities, phase transformations...

3. Thermal stress

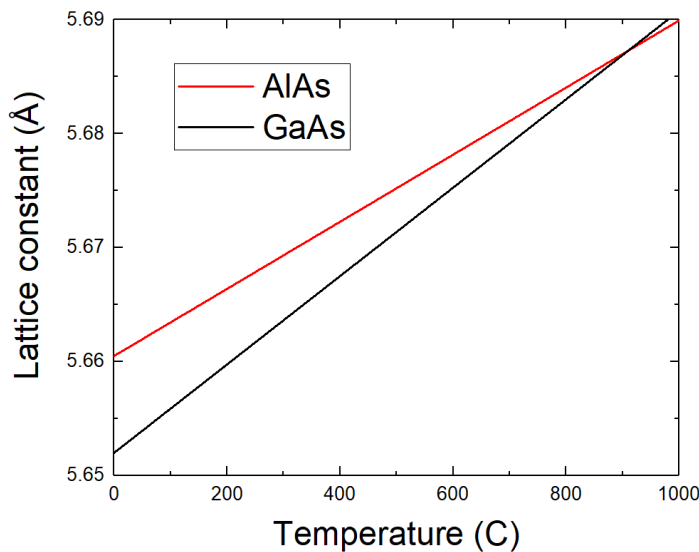
- Difference in **thermal expansion coefficients** between film and substrate



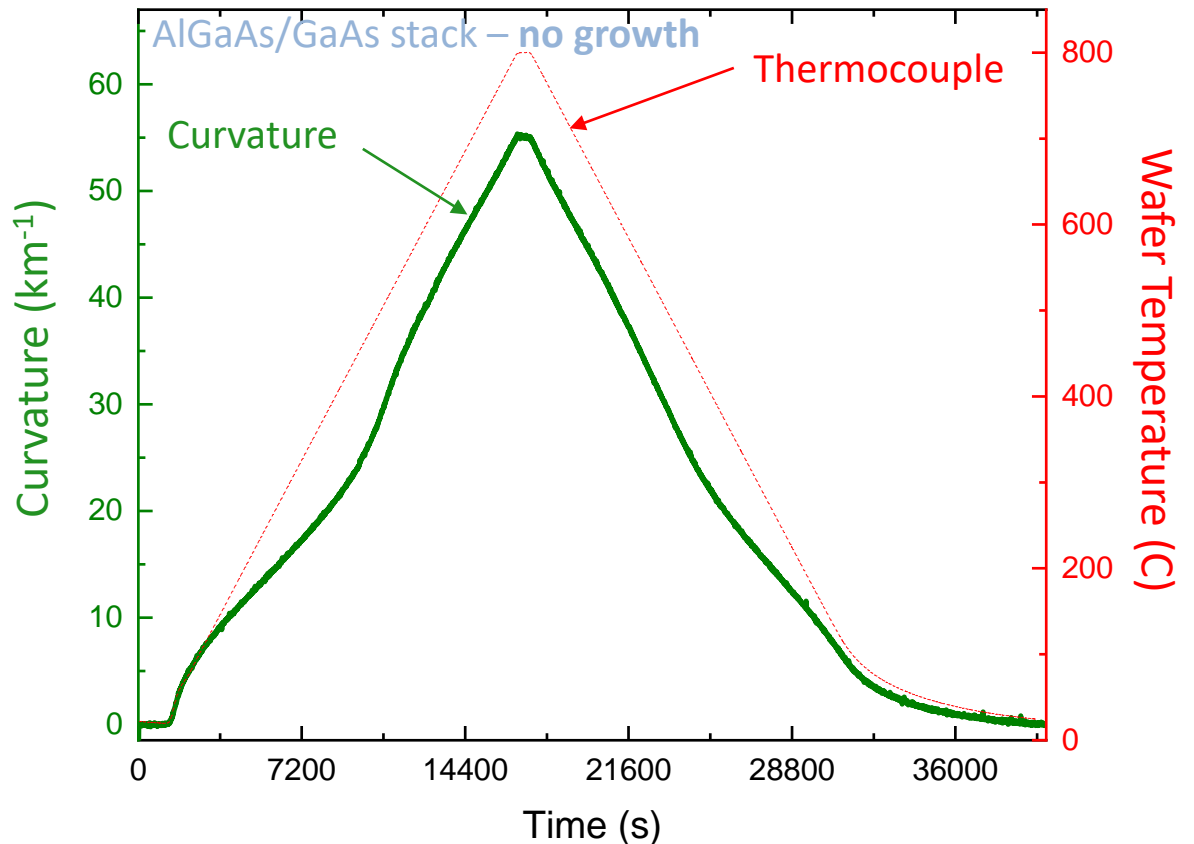
Stress/Curvature and crystal growth

Thermal stress

- > Because thermal expansion coefficient is material dependent, any change in temperature induces a change in stress/curvature of an heteroepitaxial stack.



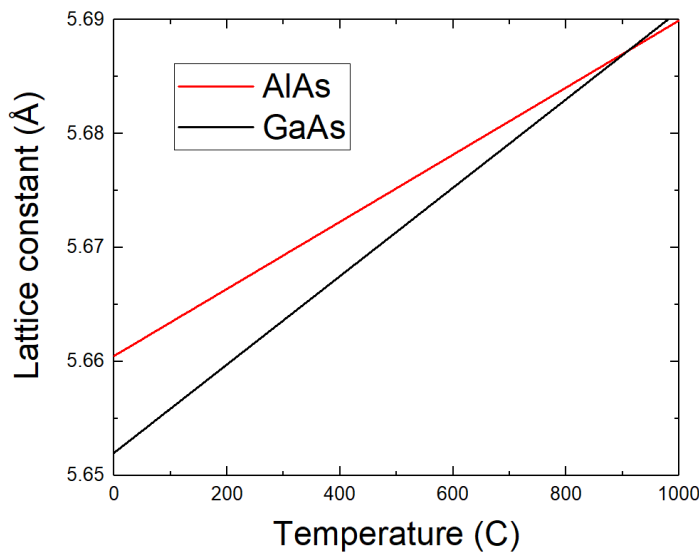
M. Ettenberg, R. J. Paff, *J. Appl. Phys.*, **41**, no.10, pp.3926-3927 (1970)



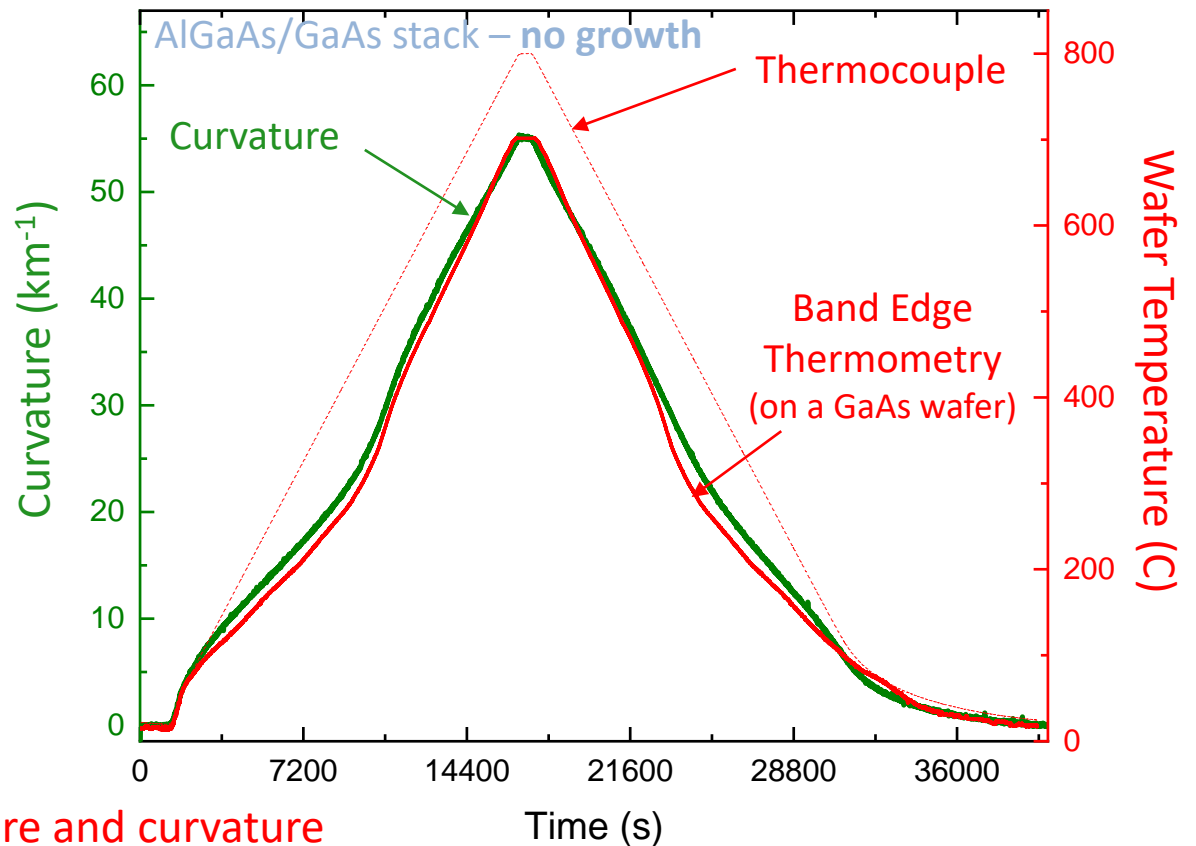
Stress/Curvature and crystal growth

Thermal stress

- > Because thermal expansion coefficient is material dependent, any change in temperature induces a change in stress/curvature of an heteroepitaxial stack.

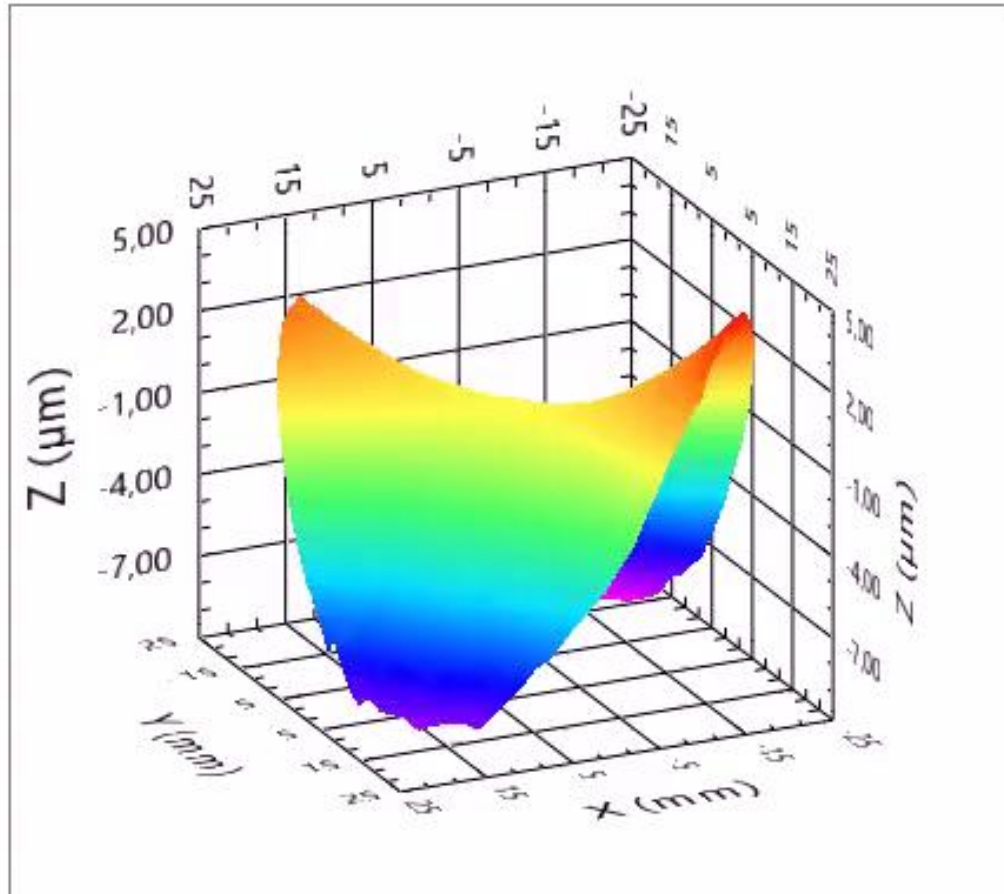


M. Ettenberg, R. J. Paff, *J. Appl. Phys.*, **41**, no.10, pp.3926-3927 (1970)



➡ Nice correlation between temperature and curvature

MIC Robustness to substrate rotation: anisotropy



Wafer :
 Single-side polished
 GaAs NID AXT (001)
 50mm diameter
 350 μ m thick
 Measured at 580C
 Rotation : 12RPM

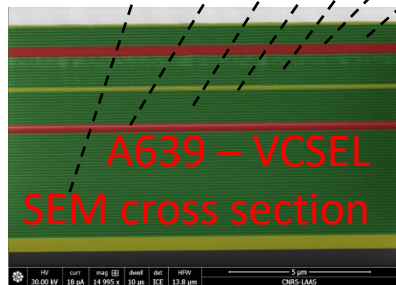
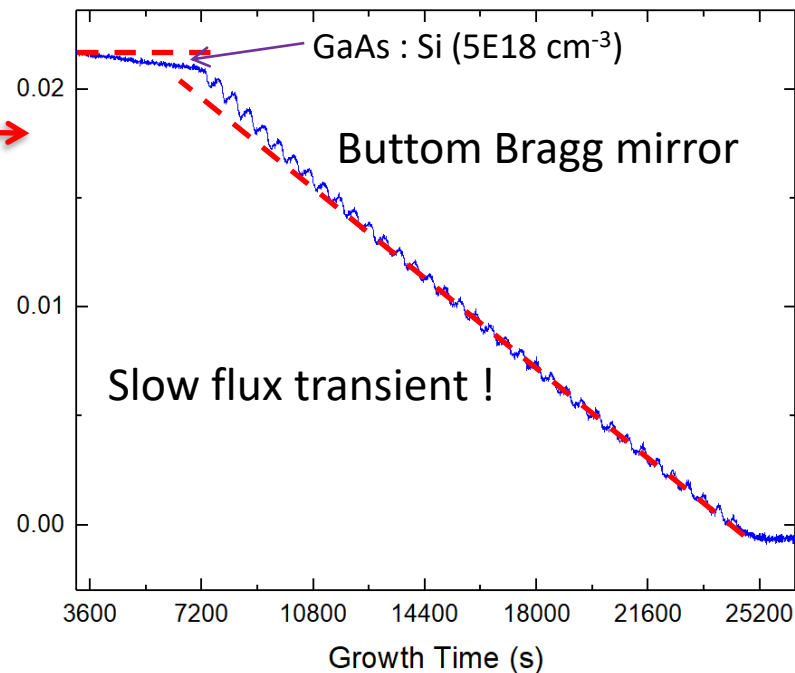
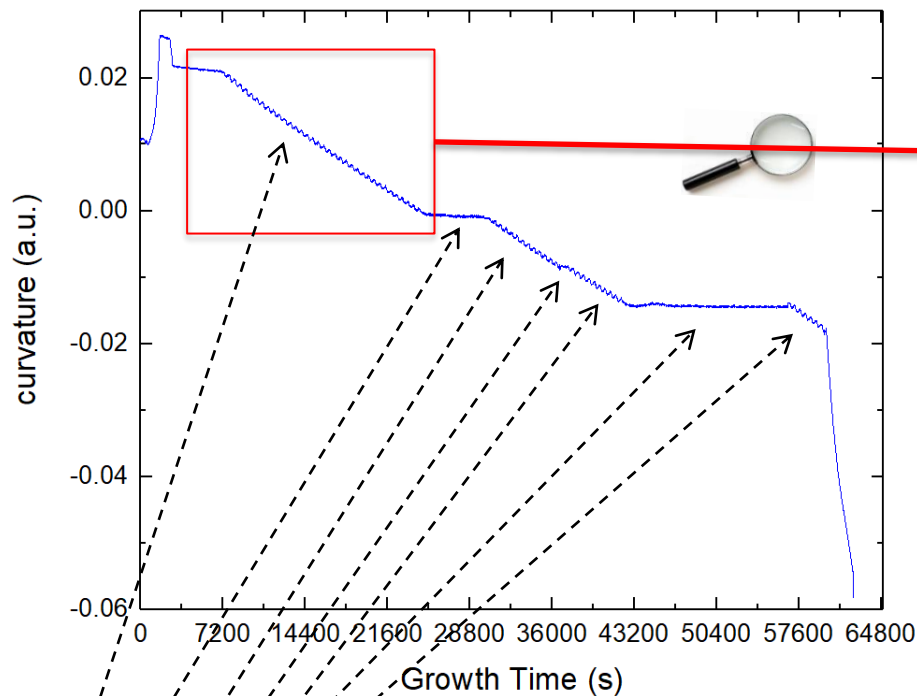
Because **substrate is rotating**, it is possible to measure the curvature in any direction, and to get a clear view of its shape **in live**

Note : It is also possible to measure this complete shape on non-rotating substrates at normal incidence

In situ characterization tools in MBE: Curvature

MIC : some experimental results

RIBER EZ-CURVE



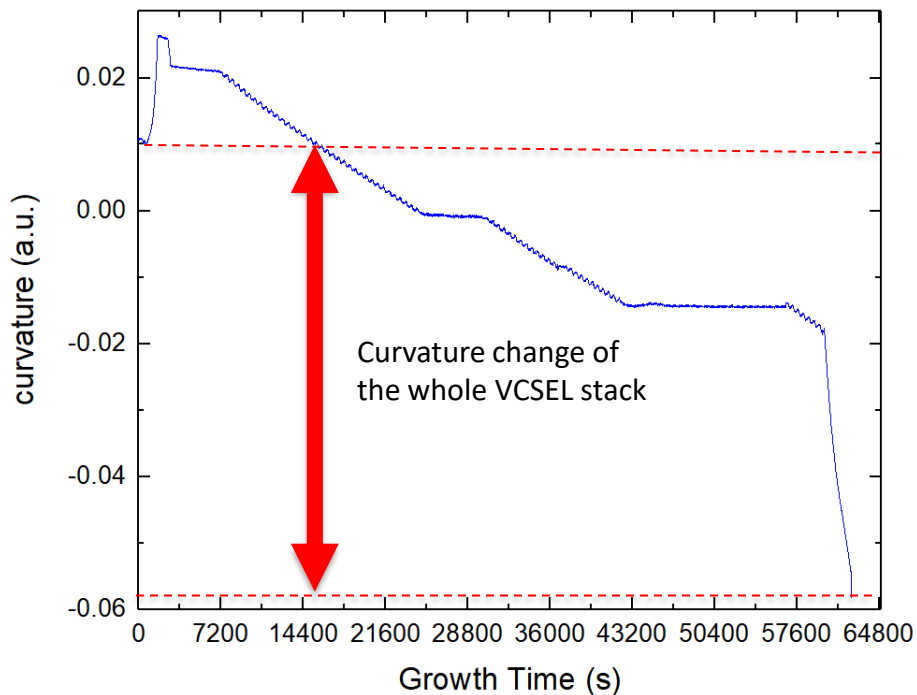
Low strain GaAs/AlGaAs system ($\Delta a/a = 0.046\%$ at 600°C)

Continuous observation of a complete VCSEL structure (+17H)

Possibility to correct the deviations on parameters

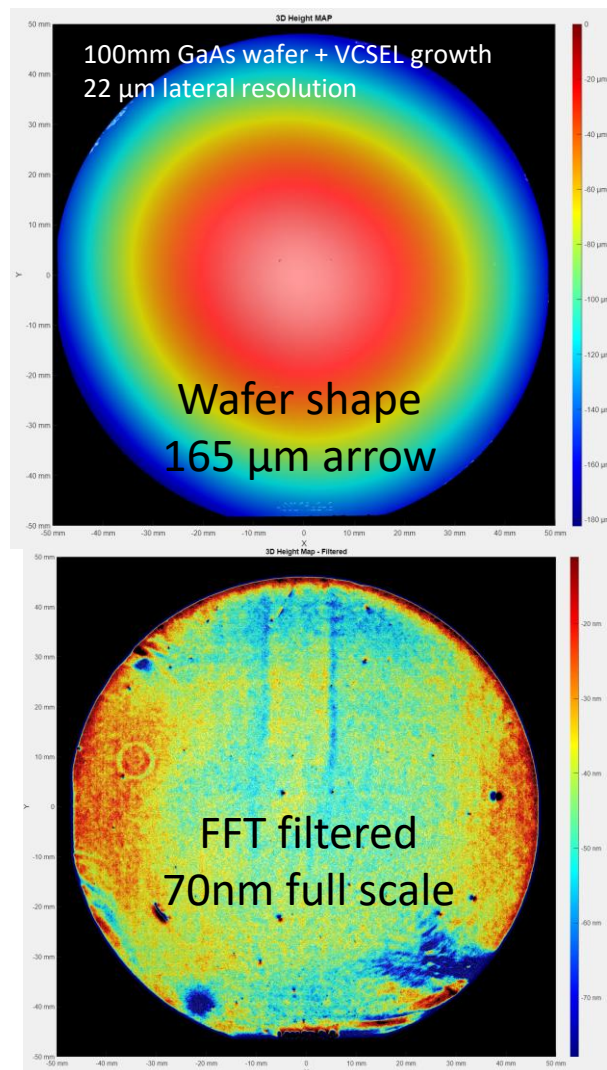
Ex-situ characterization of full wafer shape

In-situ curvature variation measurement



Patented technique based on white light phase shifting **deflectometry**

=



No alignment
1 s acquisition
1 min processing



measurement
that goes beyond limits

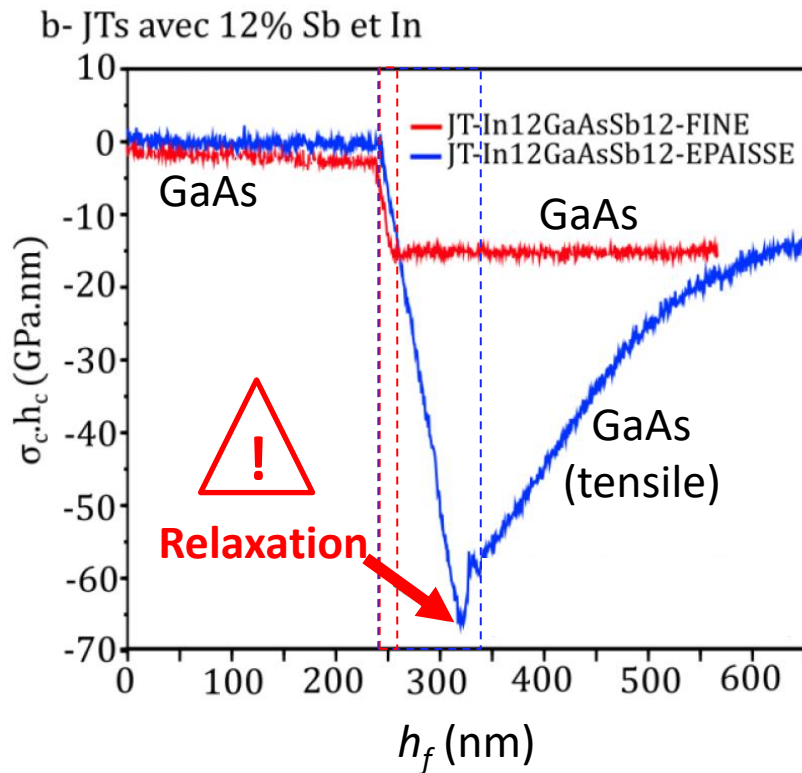
See www.dip-view.com

In situ characterization tools in MBE: Curvature

MIC : some experimental results

RIBER EZ-CURVE

Tunnel junctions for solar cells



➔ Real-time observation of relaxation

Complementarity for alloy concentration / growth rate measurement

Growth rate: Curvature

> Stoney equation:

$$\kappa \approx \frac{6\bar{\sigma}_f h_f}{M_s h_s^2} = 6 \frac{h_f M_f}{h_s^2 M_s} \varepsilon = -6 \frac{h_f M_f}{h_s^2 M_s} \frac{a_f - a_s}{a_s}$$

Young Modulus

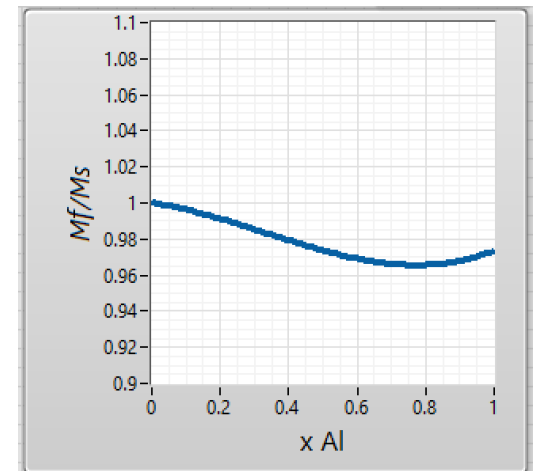
Avec $M = \frac{E}{1 - \nu}$

Poisson coefficient

For $\text{Al}_x\text{Ga}_{(1-x)}\text{As}$:

$$a_f = a_{\text{AlGaAs}} = x a_{\text{AlAs}} + (1 - x) a_{\text{GaAs}}$$

$$\kappa \approx - \frac{6 h_{\text{AlGaAs}}}{h_s^2} \times x \times \frac{a_{\text{AlAs}}(T) - a_{\text{GaAs}}(T)}{a_{\text{GaAs}}(T)}$$



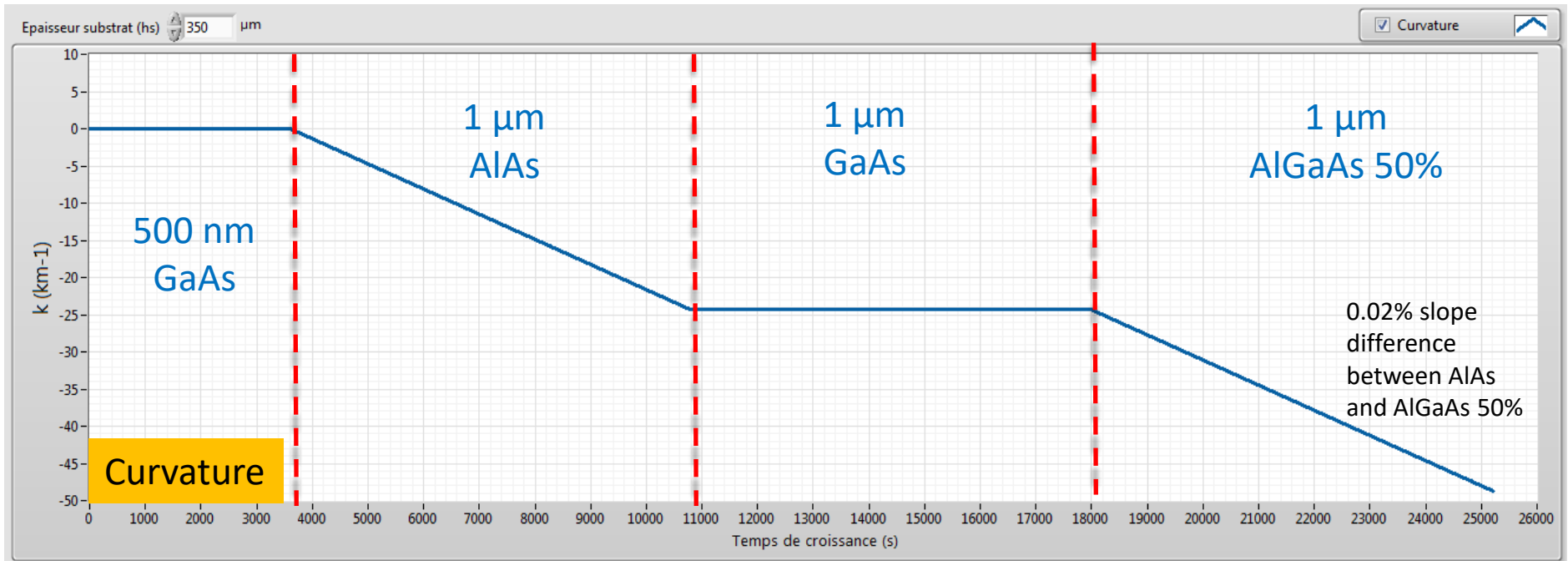
Compositional dependence of the elastic constants and the lattice parameter of AlGaAs
Gehristz et al.
PRB 60 (16), 1999

Growth rate: Curvature

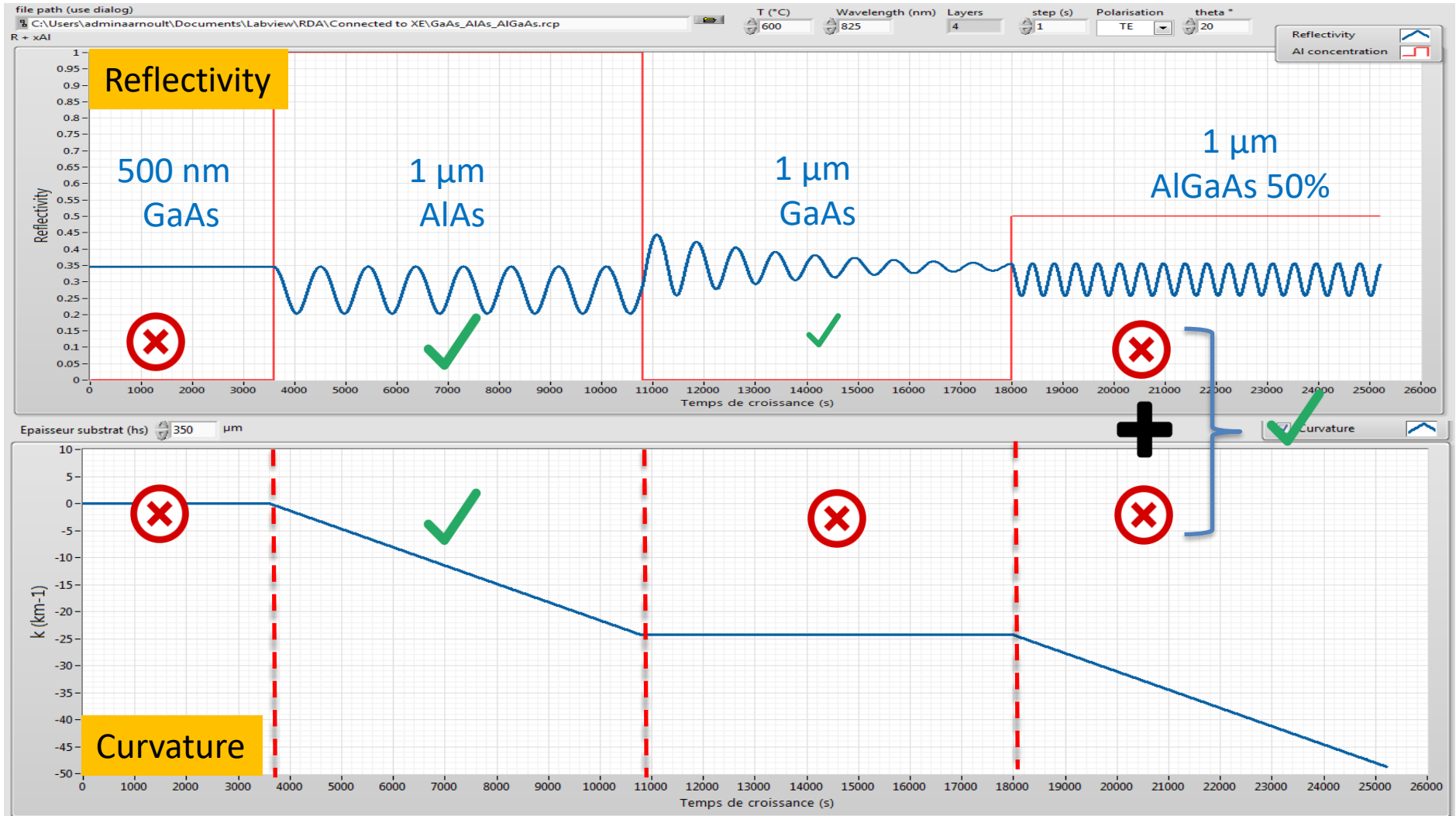
$$k \approx -\frac{6h_{AlGaAs}}{h_s^2} \times x \times \frac{a_{AlAs}(T) - a_{GaAs}(T)}{a_{GaAs}(T)}$$

$$\frac{\Delta k}{\Delta t} \approx -\frac{6 \times G_{AlAs}}{h_s^2} \times \frac{a_{AlAs}(T) - a_{GaAs}(T)}{a_{GaAs}(T)}$$

with $h_{AlGaAs} = G_{AlGaAs} \times t$
 $= (G_{GaAs} + G_{AlAs}) \times t$
 $x = \frac{G_{AlAs}}{G_{GaAs} + G_{AlAs}}$



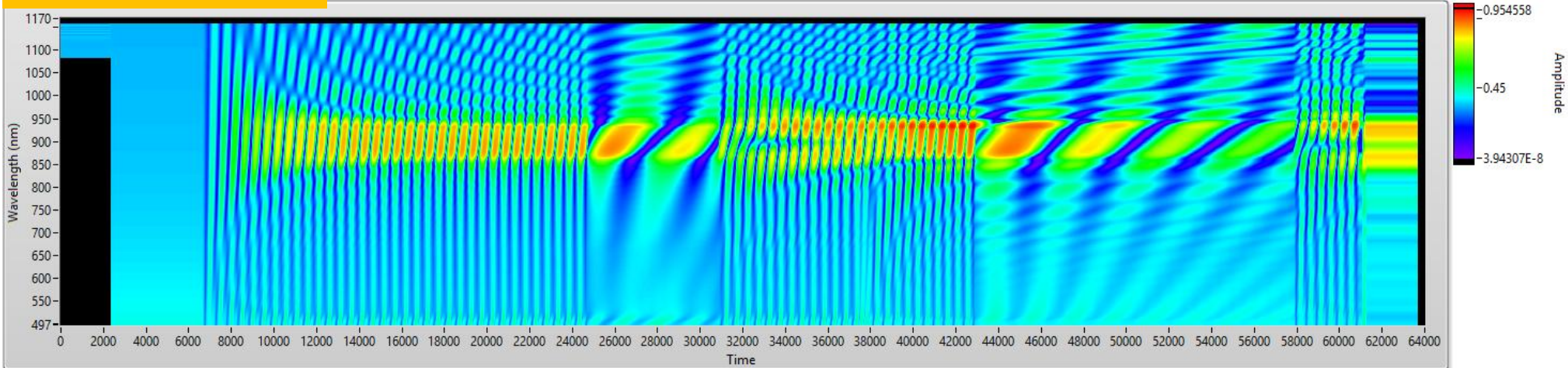
Reflectivity – Curvature complementarity



Complementarity and time scales

Complementarity and time scales

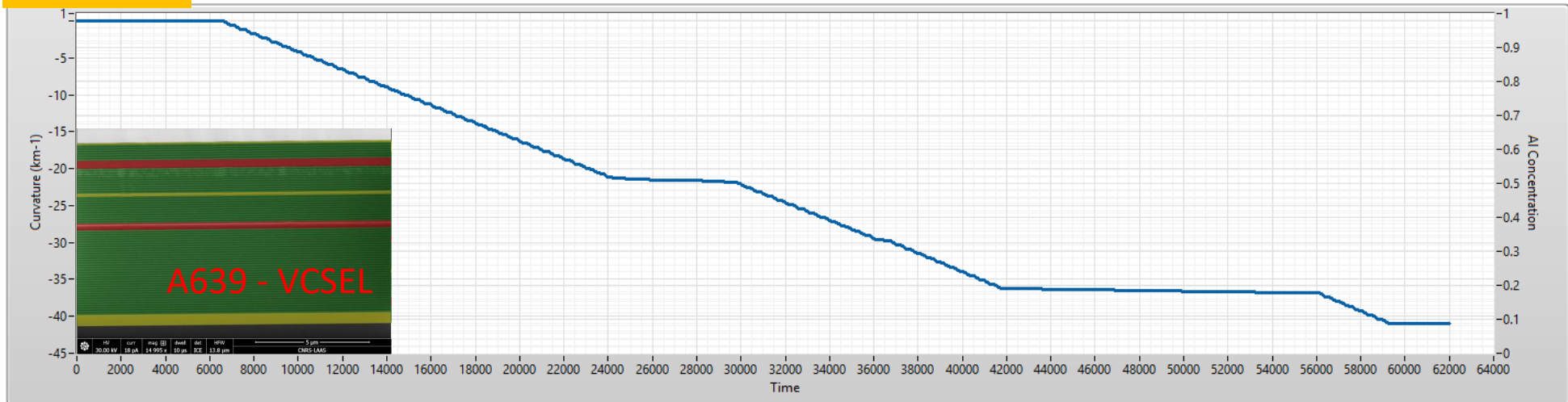
Spectral reflectivity



Curvature

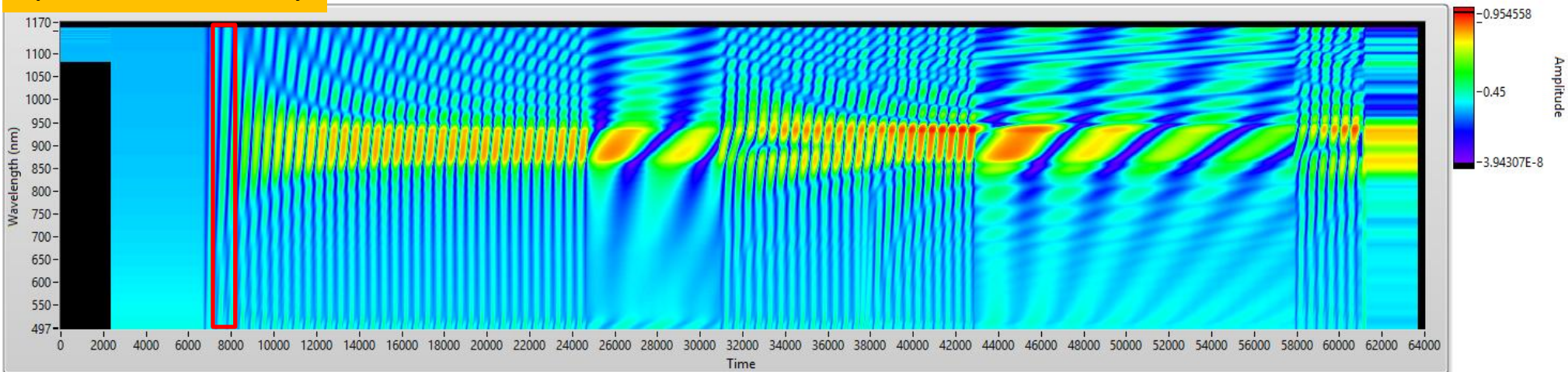
20H

- Curvature
- AI Concentration



Complementarity and time scales

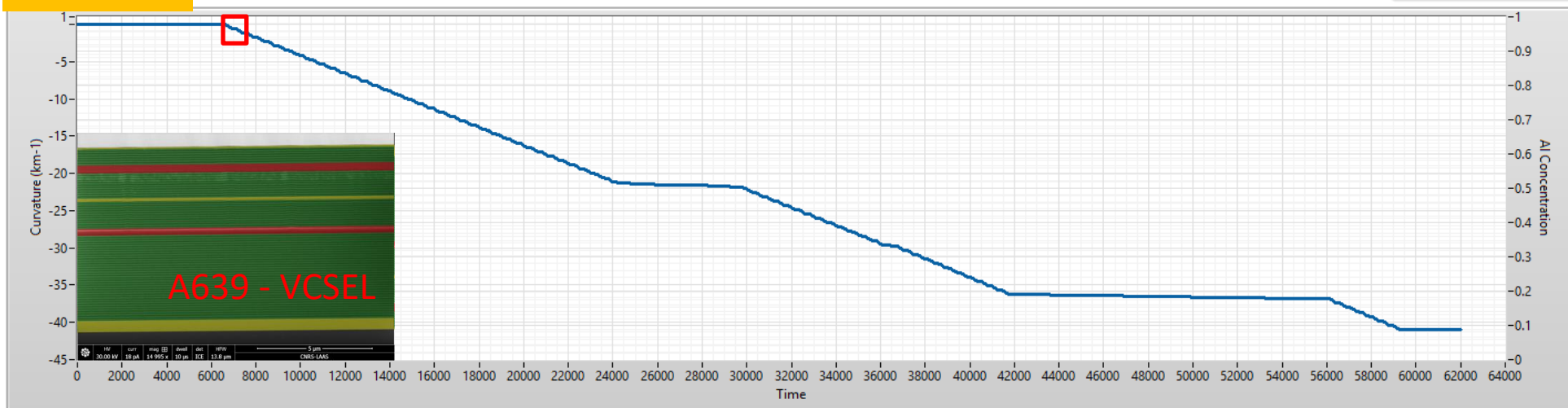
Spectral reflectivity



Curvature

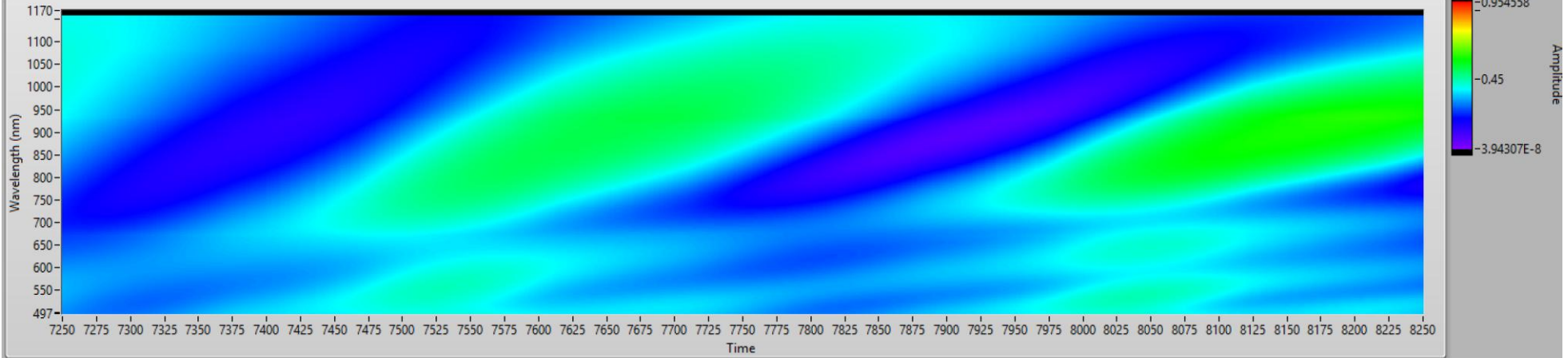
20H

- Curvature
- AI Concentration



Complementarity and time scales

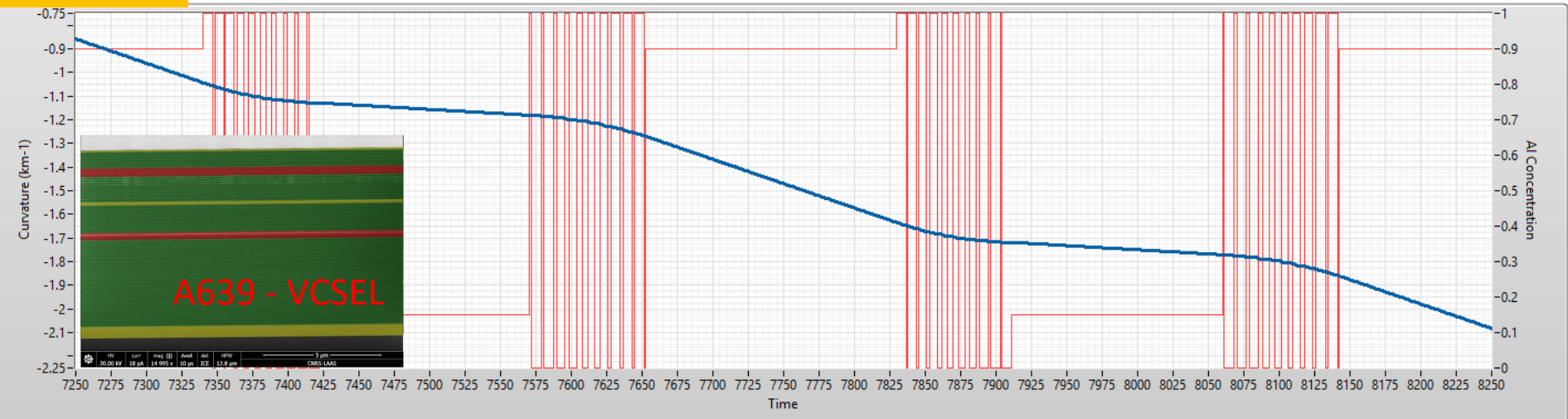
Spectral reflectivity



Curvature

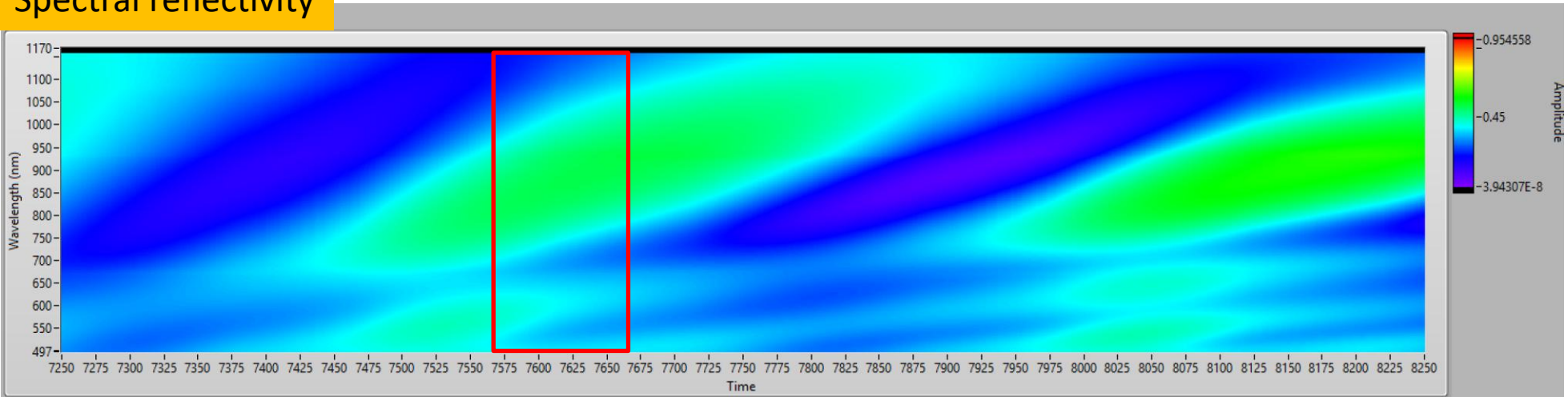
16:40

- Curvature
- AI Concentration



Complementarity and time scales

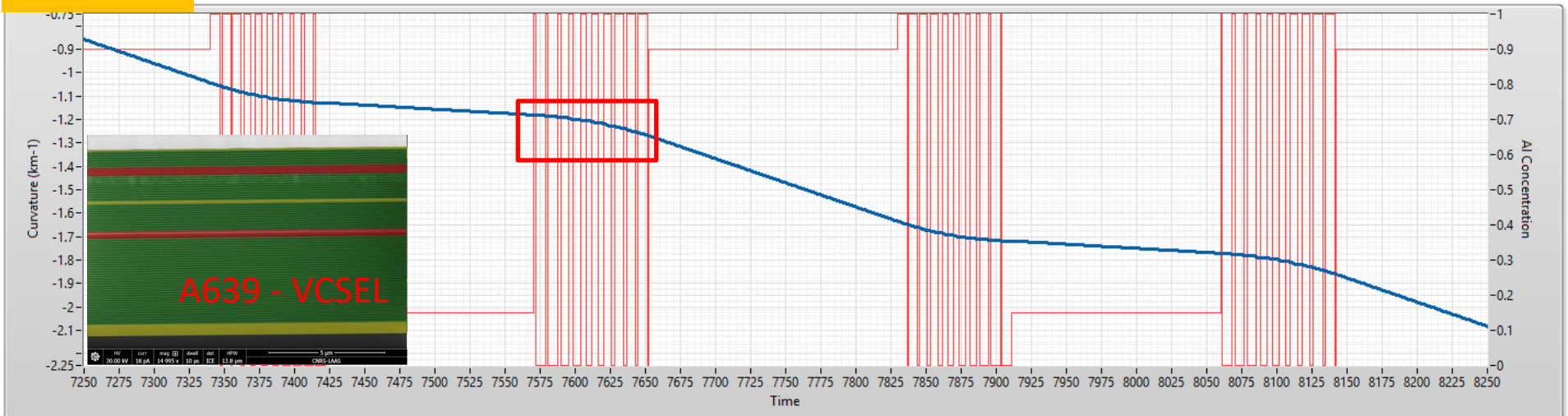
Spectral reflectivity



Curvature

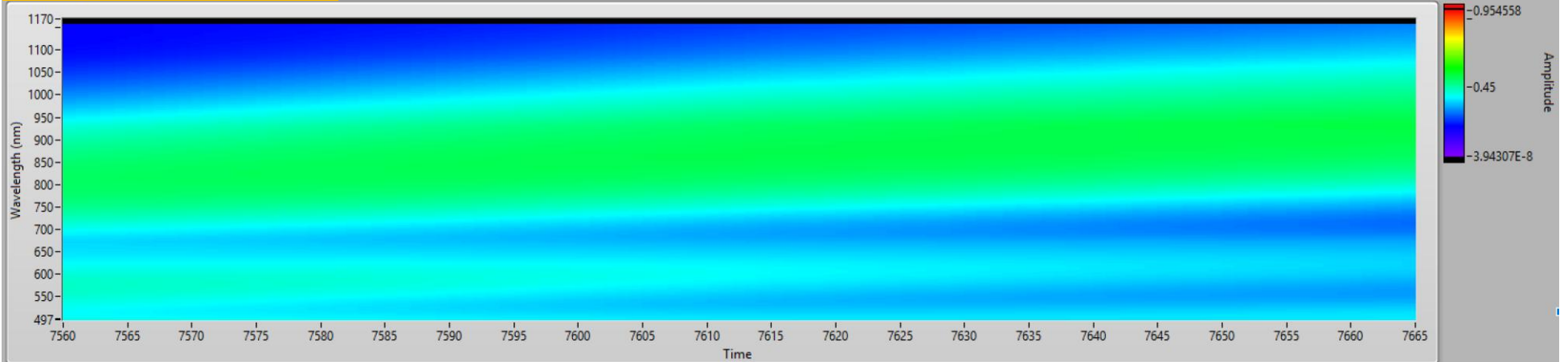
16:40

- Curvature
- AI Concentration



Complementarity and time scales

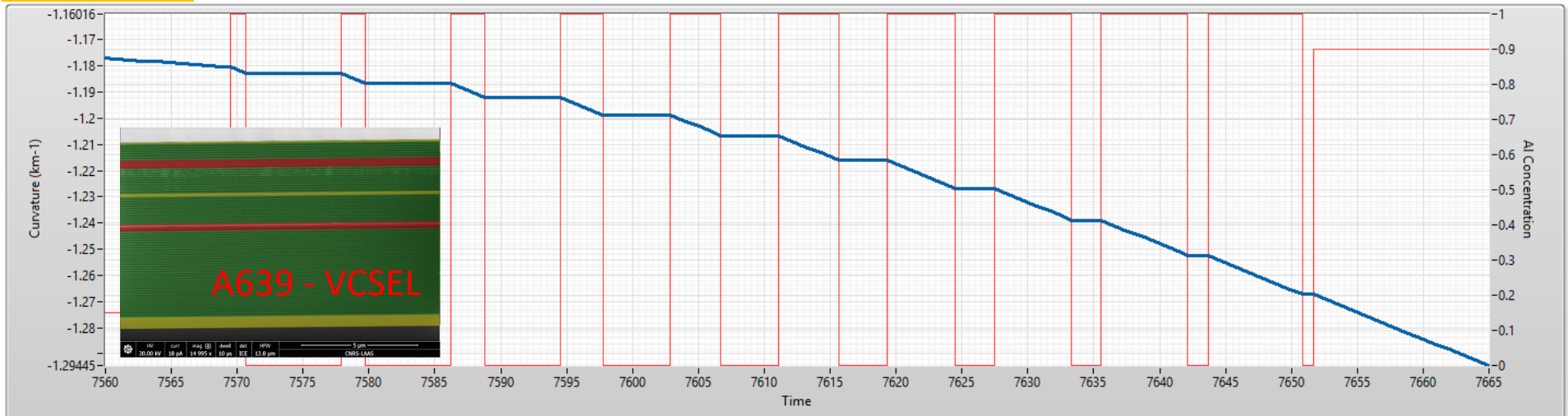
Spectral reflectivity



Curvature

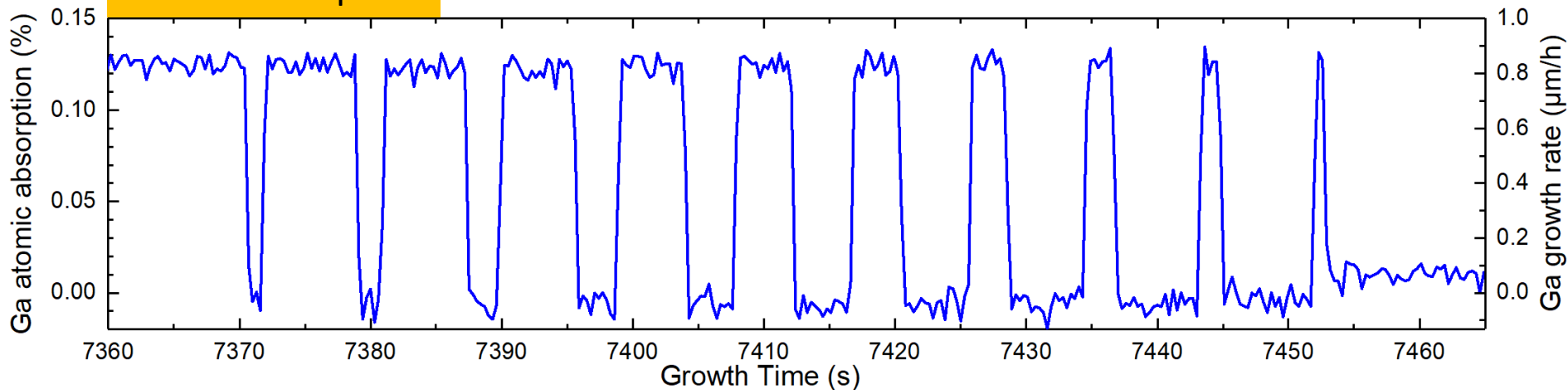
1:45

- Curvature
- AI Concentration



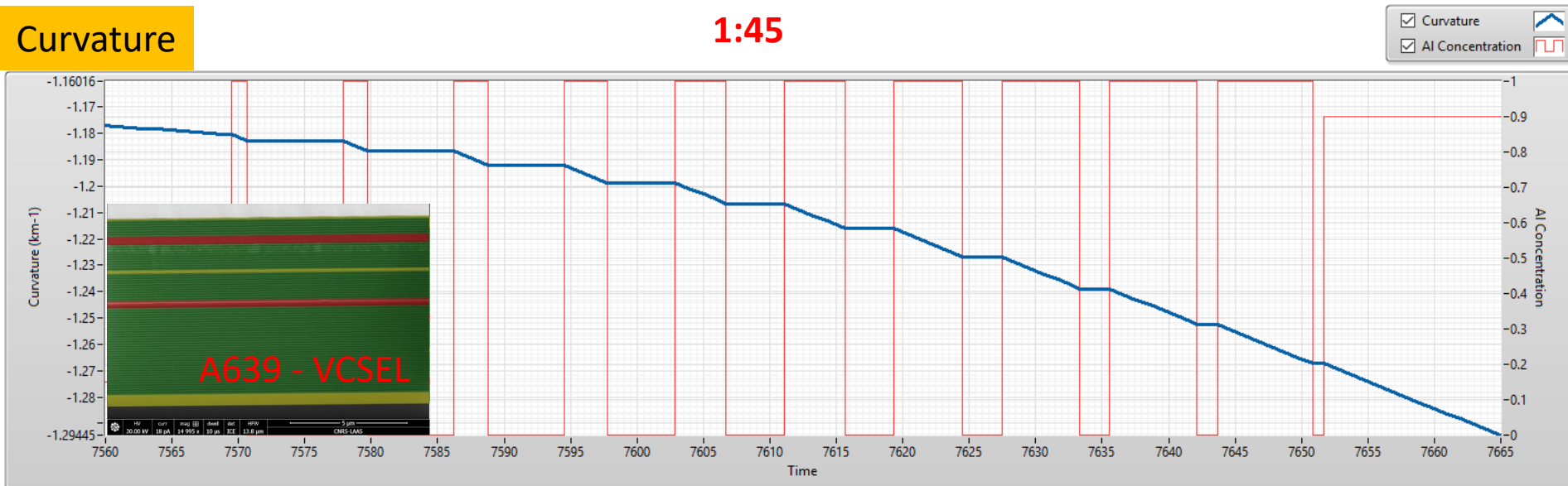
Complementarity and time scales

Atomic absorption



Curvature

1:45



Complementarity and time scales

- > Reflectivity, Atomic Absorption and Curvature address different time scales / thicknesses

	Reflectivity	Curvature	Atomic Abs.
10H / 10 μ m	+++	+++	+
1H / 1 μ m	++	+++	+
Minutes / 10 th nm	-	++	++
Seconds / ml	x	+	+++

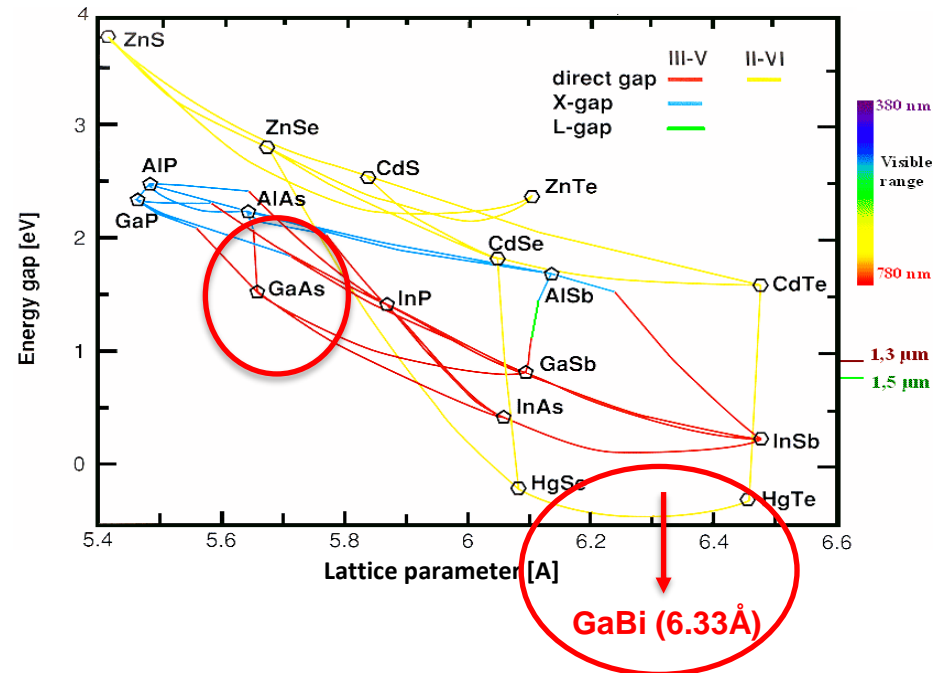
The case of GaAsBi growth

Case of $\text{GaAs}_{1-x}\text{Bi}_x$ MBE
growth studied with the
MIC curvature tool

GaAs_{1-x}Bi_x: a highly mismatched alloy

Wide range of applications for GaAs technology

- Solar cells
- Lasers
- Spintronics
- Photodiodes
- Thermoelectric materials
- Topological insulators



Alloy based on highly mismatched binary compounds: $\frac{\Delta a}{a} = 12\%$

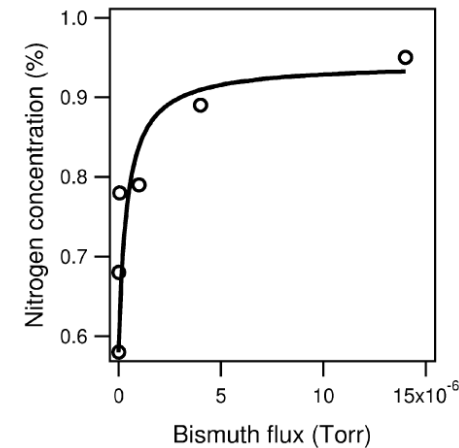
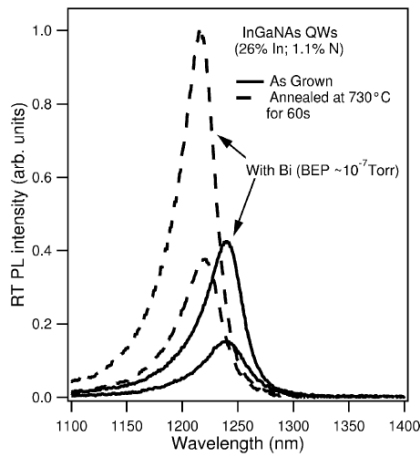
Bi incorporation in GaAs

→ Under 400°C : Bi incorporation with specific growth conditions

- V/III atomic ratio (~1!)
- Substrate temperature

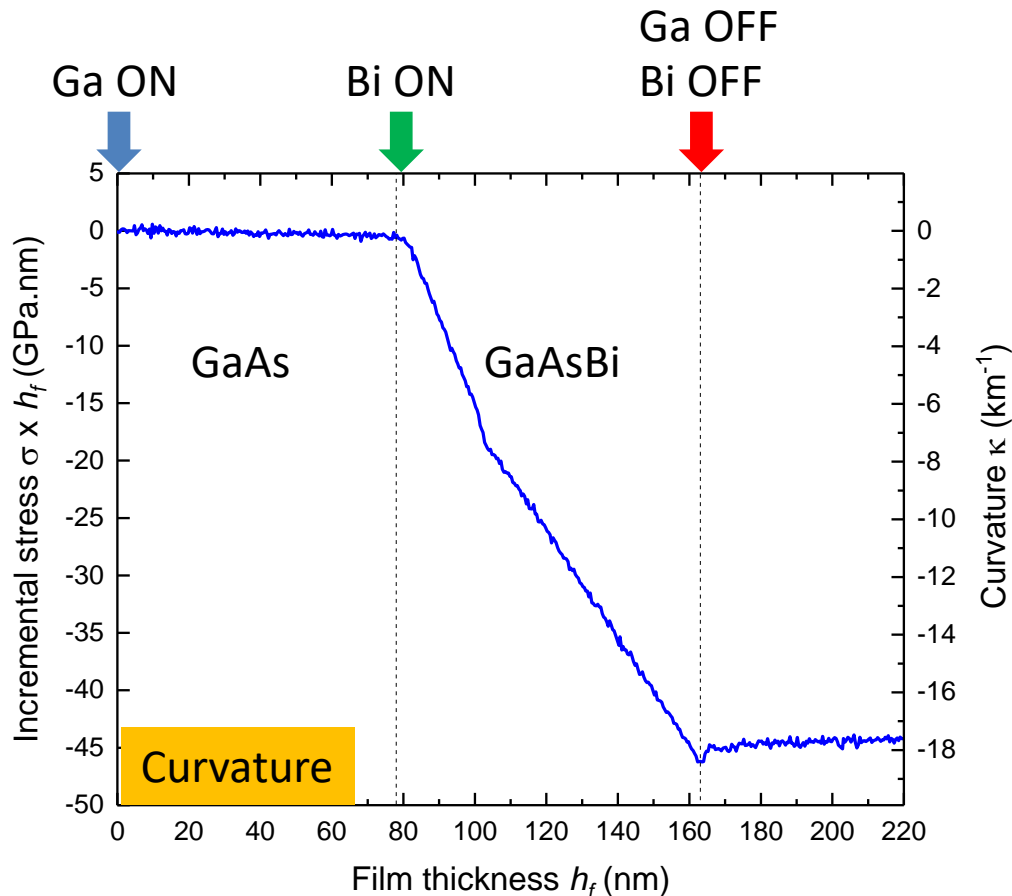
Any small changes in these conditions induce high difference in Bi composition, and different electrical, optical and mechanical properties of the alloy

→ Above 400°C : Bi acts as a surfactant



Surfactant enhanced growth of GaNAs and InGaNAs using bismuth, Tixier and al. , 2003

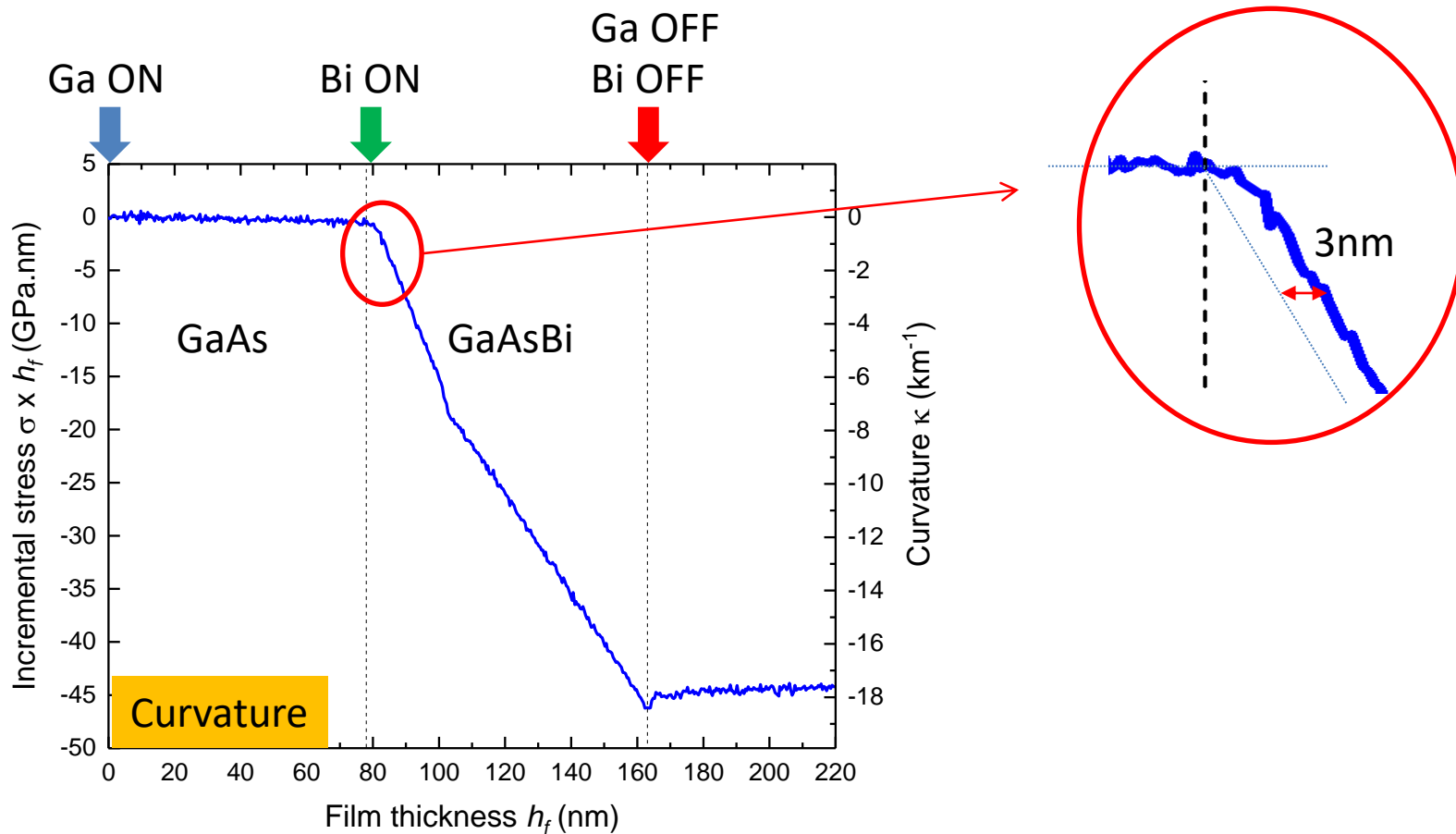
Curvature and GaAsBi Growth



- 350 μm thick, 50mm diameter substrate
- V/III atomic ratio near 1
- $G_{\text{GaAs}} = 0.3\mu\text{m/h}$
- $T_{\text{sub}} = 265^\circ\text{C}$ BandiT
- 12 RPM rotation

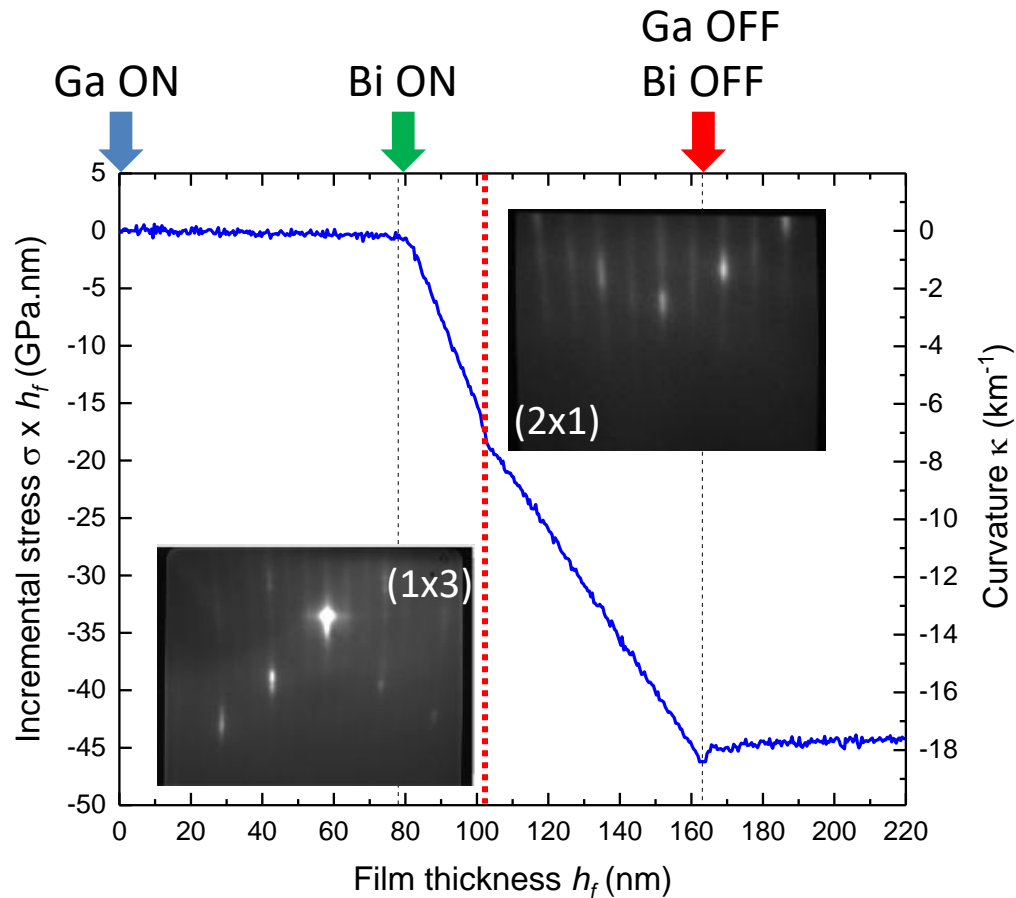
→ Some peculiar events during the growth

Curvature for GaAsBi Growth



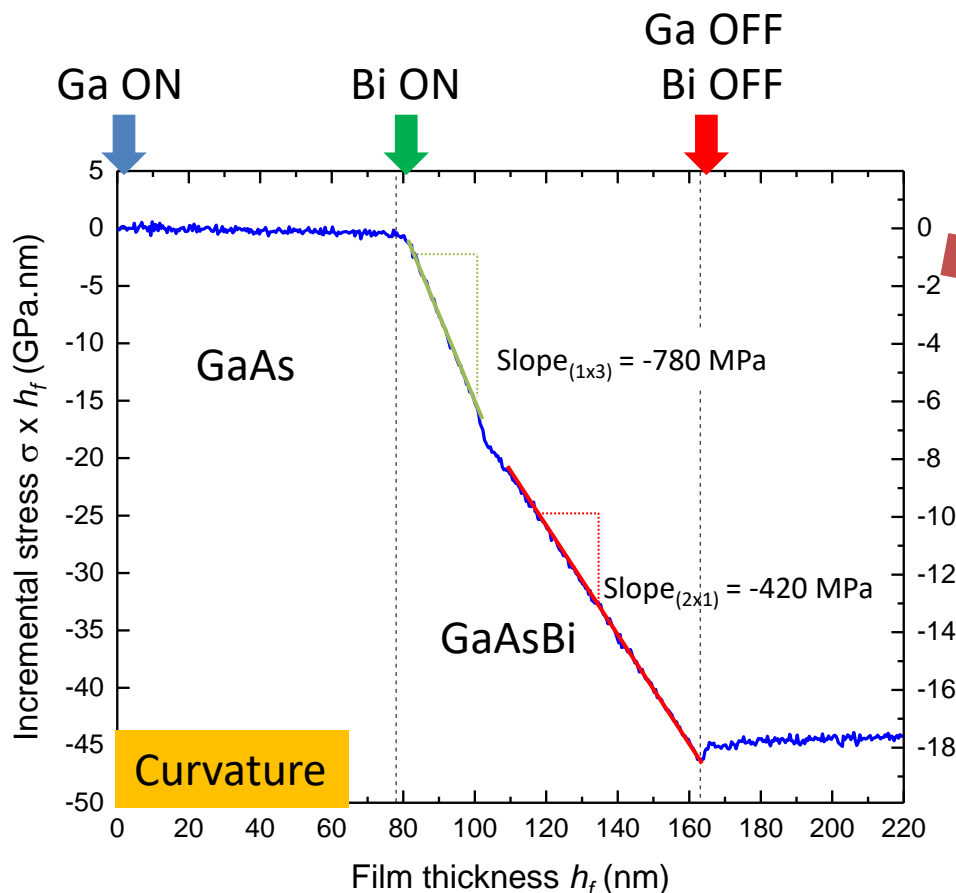
→ First nm: very low stress and incorporation (Bi segregation)

Curvature for GaAsBi Growth

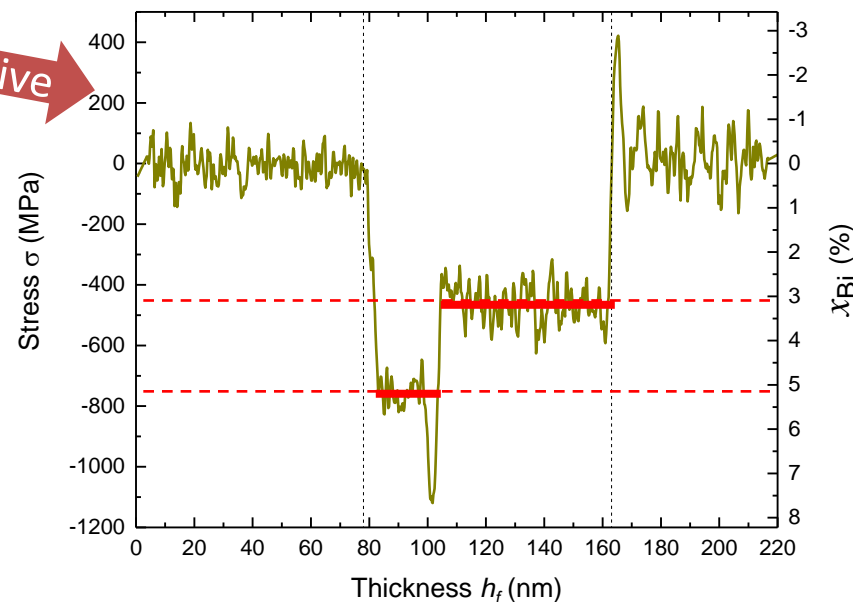


→ Change of surface reconstruction during GaAsBi layer

Curvature for GaAsBi Growth

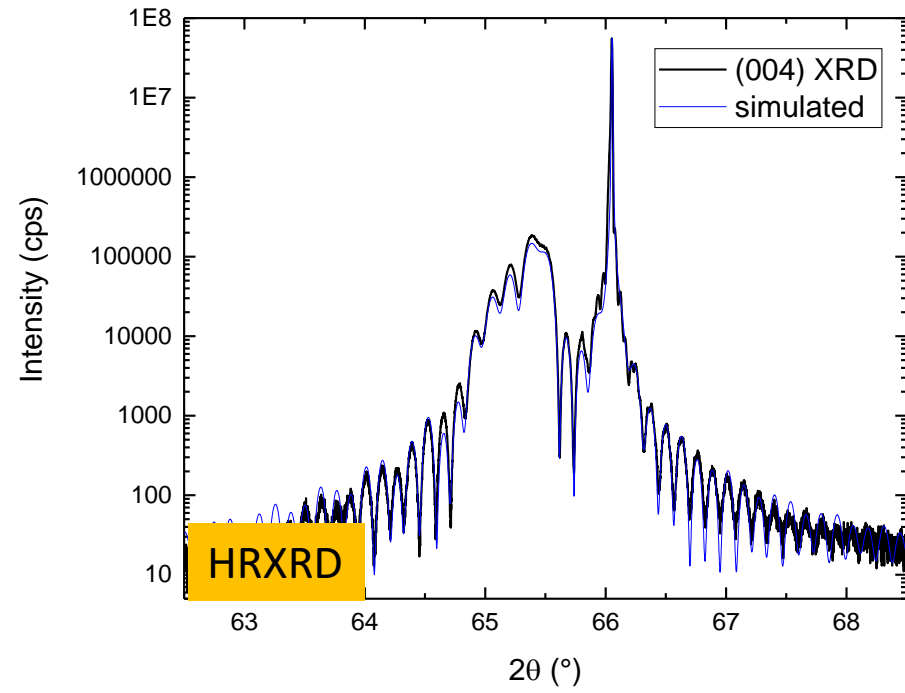
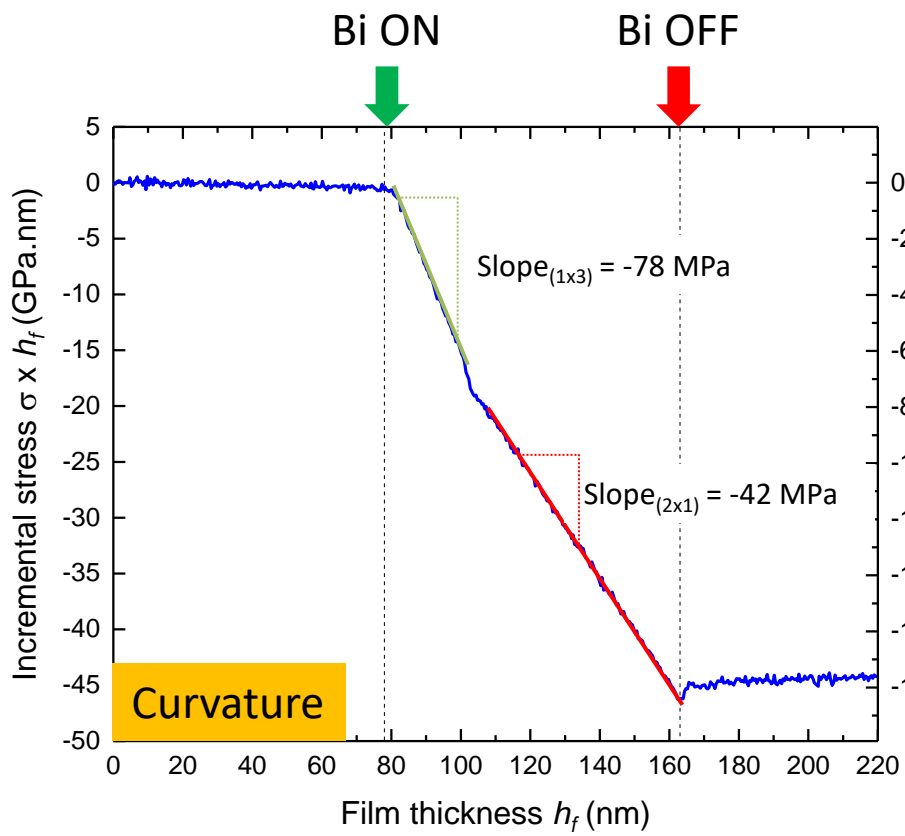


→ Observation of stress variation during growth



Constant growth parameters, two-step incorporation

Curvature for GaAsBi Growth

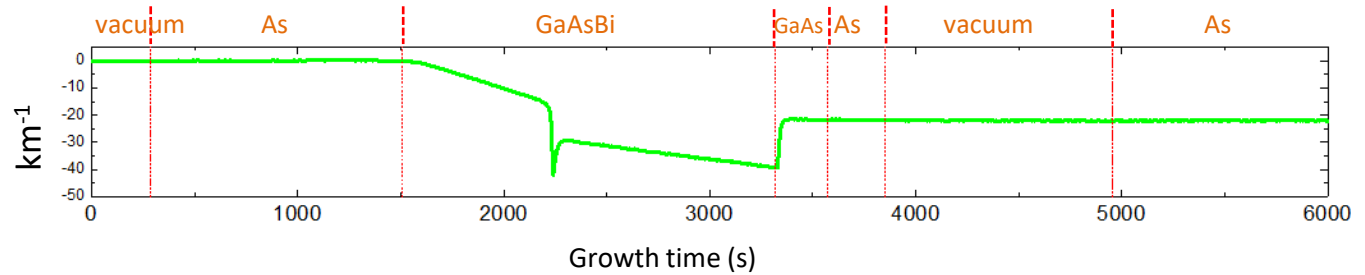


Material	Curvature		XRD	
	h_f (nm)	% Bi	h_f (nm)	% Bi
GaAsBi _(2x1)	60.5	2.9	57.3	3.6
GaAsBi _(1x3)	24.5	5.3	24.7	5.3
Substrate				

→ **Specific growth conditions**

- **different stress during (1x3) and (2x1) reconstructions**
- **different Bi incorporation in the two layers**

Curvature



Rotating substrate:

- (001) GaAs
- 50mm dia.
- **150 μm thick**



$$\kappa \approx 6 \frac{h_f}{h_s^2} \frac{\bar{\sigma}_f}{M_s}$$

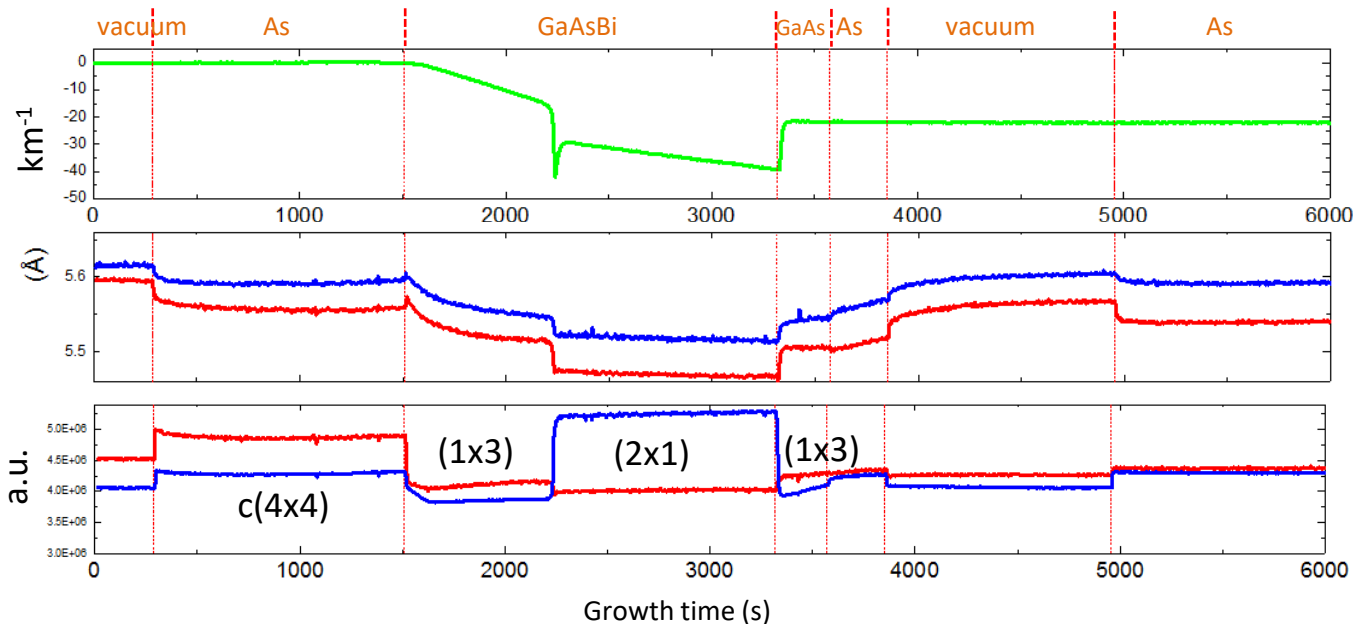
resolution x5.4!

Better understanding : coupling of in-situ techniques

Curvature

RHEED : $a_{//}$

RHEED : intensity



[110]
[1 $\bar{1}$ 0]

Better understanding : coupling of in-situ techniques

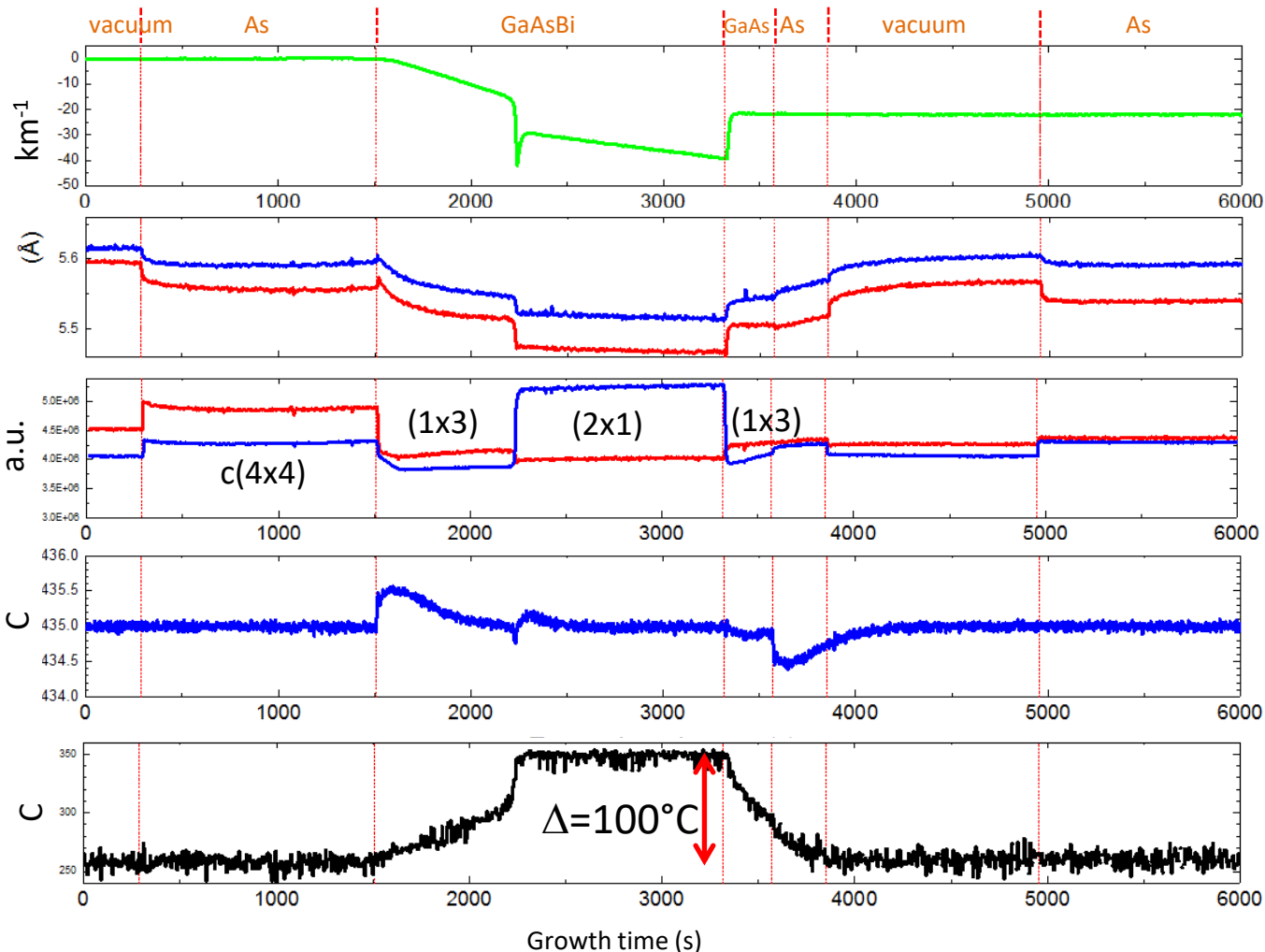
Curvature

RHEED : $a_{//}$

RHEED : intensity

Thermocouple temp.

BandiT temp.



[110]
[1 $\bar{1}$ 0]

➔ Coupling techniques is an efficient way to better understand the growth mechanisms

- ✓ When facing peculiar dynamic conditions, in-situ analysis tools are mandatory
- ✓ Curvature measurements provide extremely rich information – MIC makes it accessible to MBE
- ✓ Coupling in-situ tools
 - Further understanding of the growth mechanisms
 - Control of growth and properties of epitaxial materials and device structures

Thank you!

