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

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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

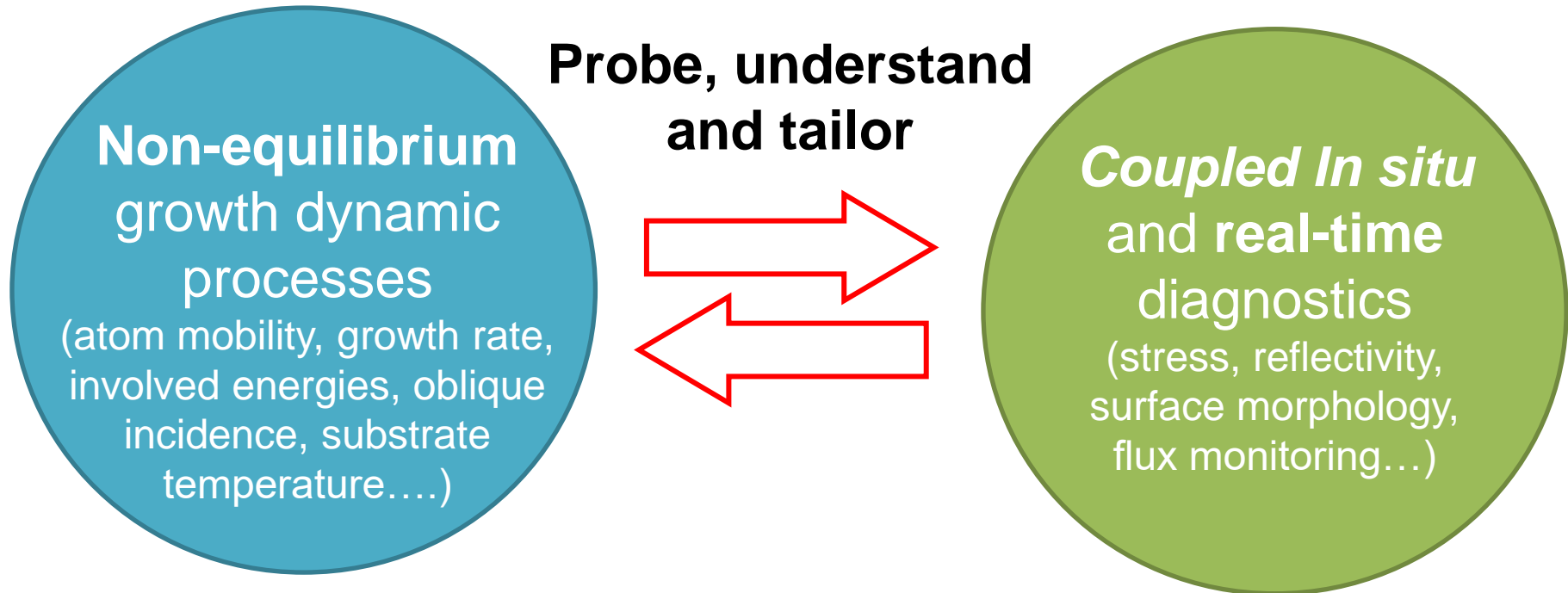
- > The case of GaAsBi growth

- > Conclusion

Non-equilibrium growth dynamic processes

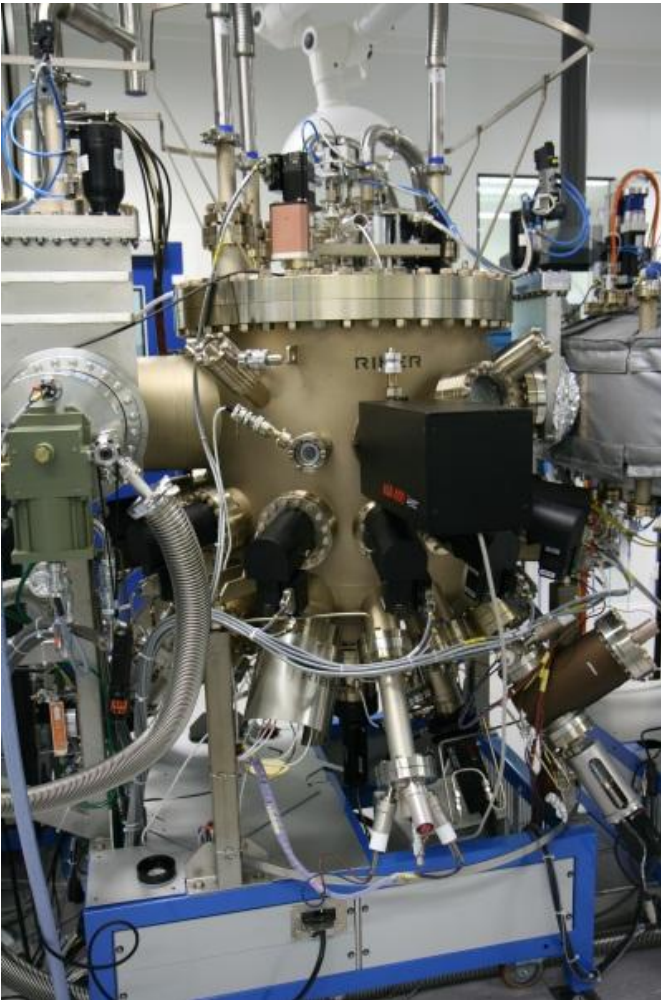
(atom mobility, growth rate,
involved energies, oblique
incidence, substrate
temperature....)

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)

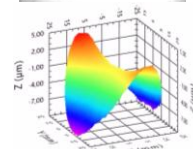
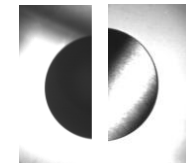
> **RHEED**: synchronised to rotation

- In-plane lattice parameter, streaks intensity

> **Roughness** (Diffuse Light Scattering)

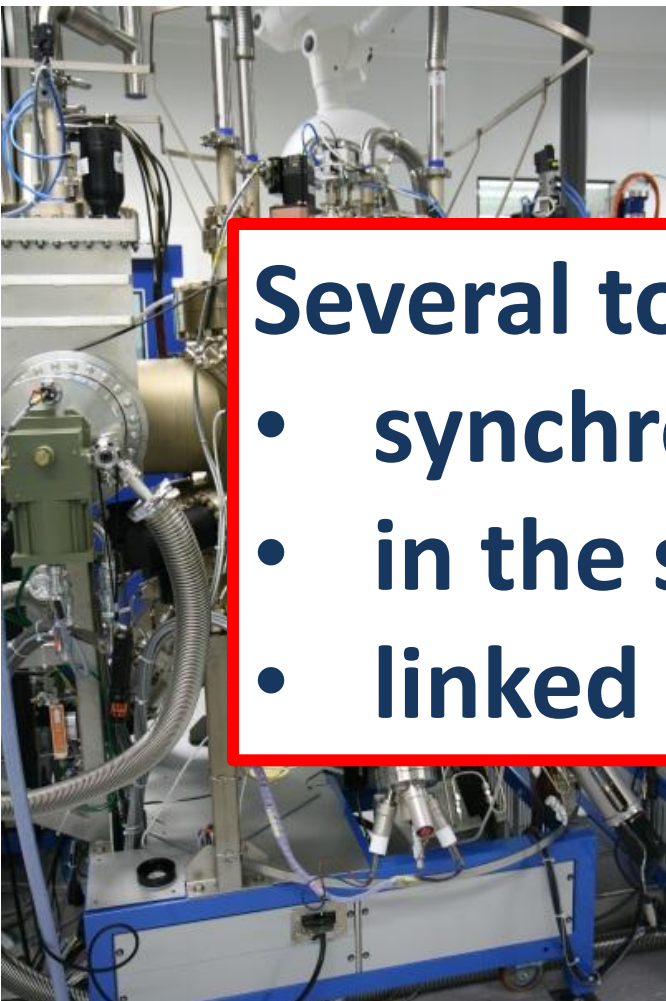
> **Curvature**

- 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**

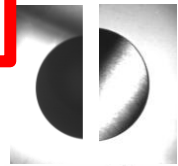
- White light source
- CCD sensors



Several tools

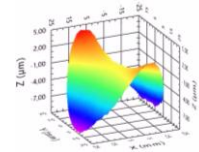
- synchronized to rotation
- in the same time base
- linked to MBE control software

> **Roughness (Diffuse Light Scattering)**

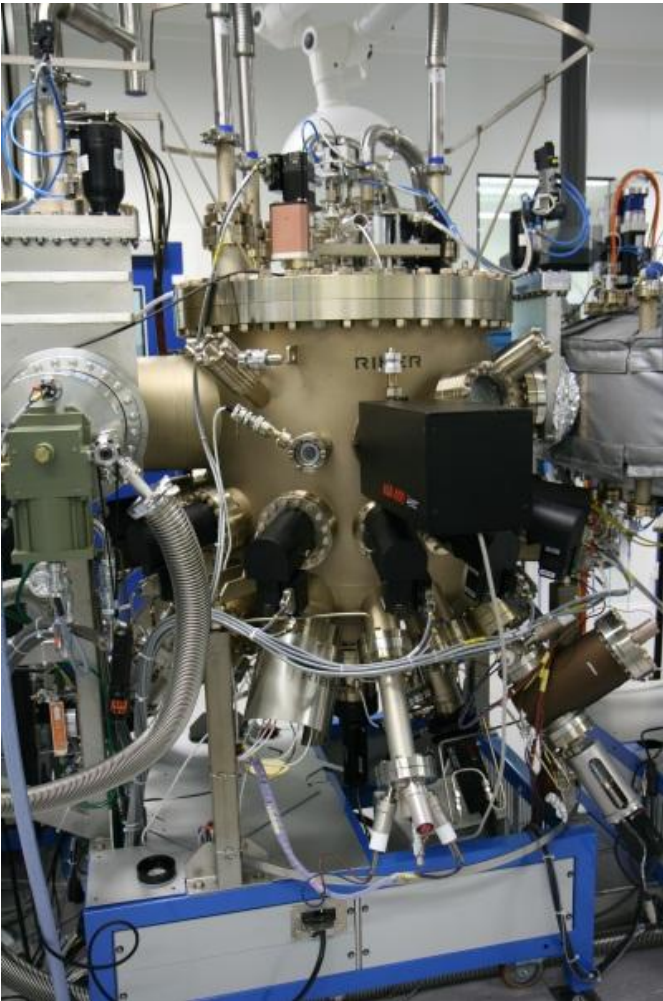


> **Curvature**

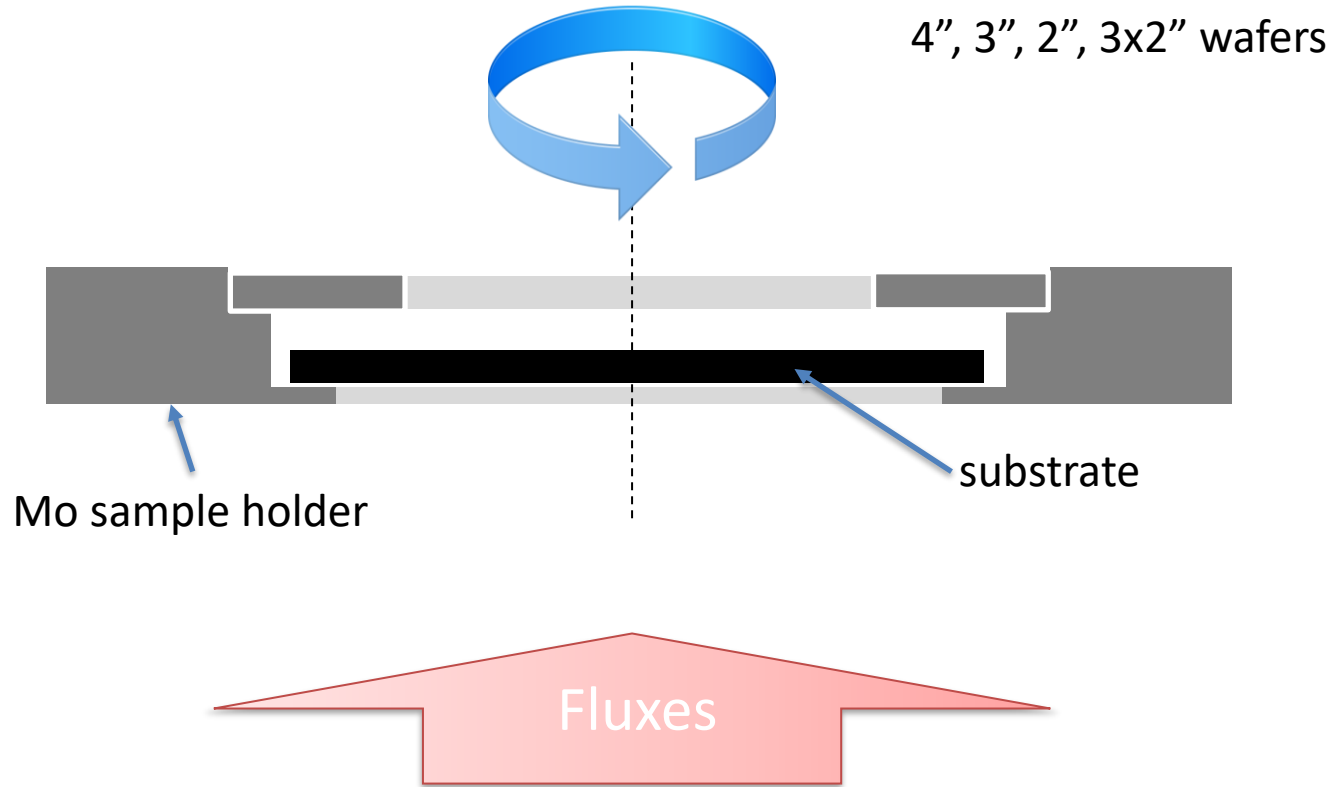
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MBE412 - 4" III-V chamber

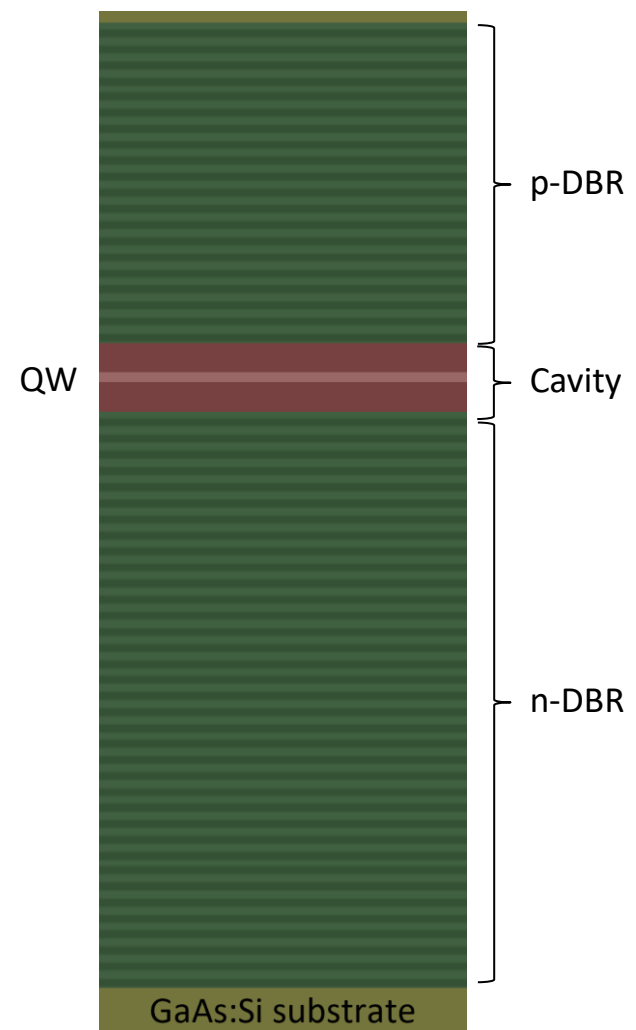


MBE412 - 4" III-V chamber

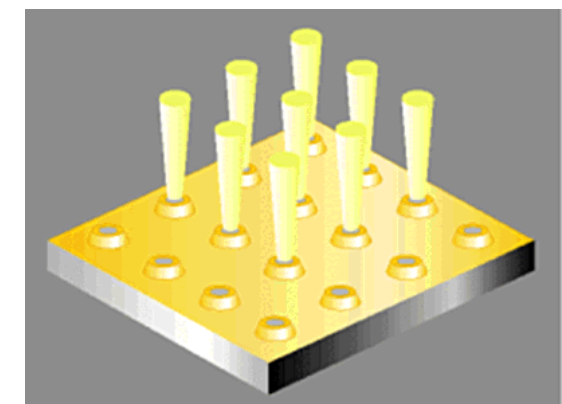
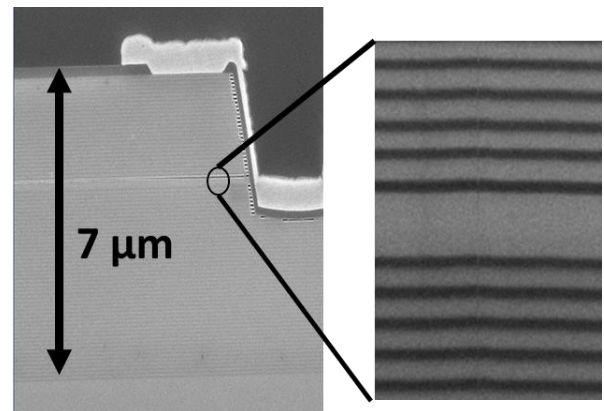


An example structure:
the growth of VCSELs

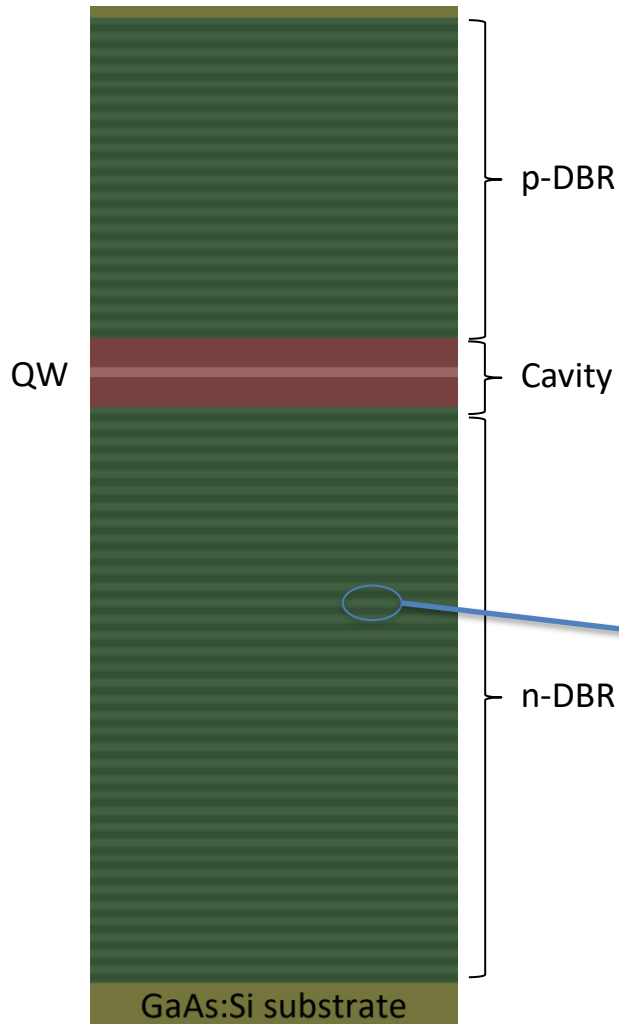
MBE growth of VCSELs



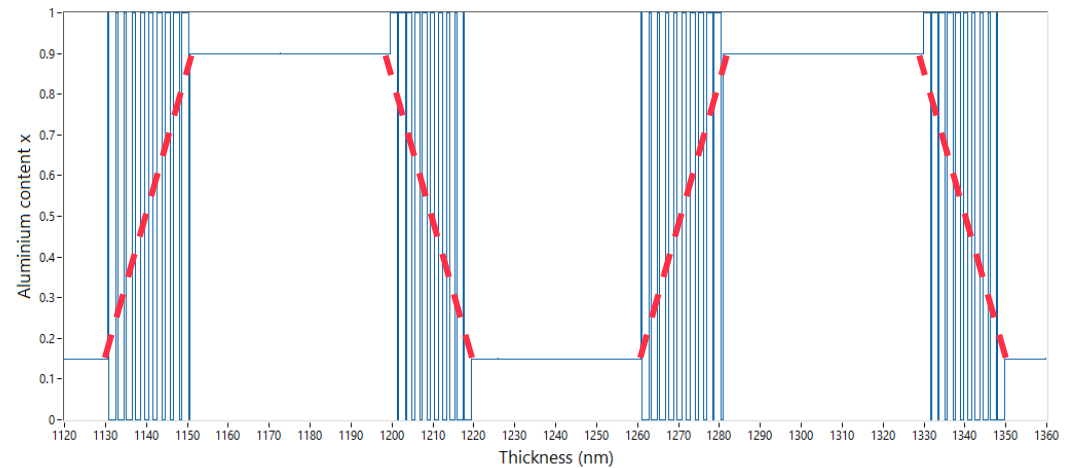
- Vertical Cavity Surface Emitting Lasers (VCSELs) are complex structures (>3000 layers, >17H growth)
- The vertical geometry permits the simultaneous processing of lasers, and the fabrication of laser matrices
- VCSELs are used in datacom, lidars, face recognition, etc...



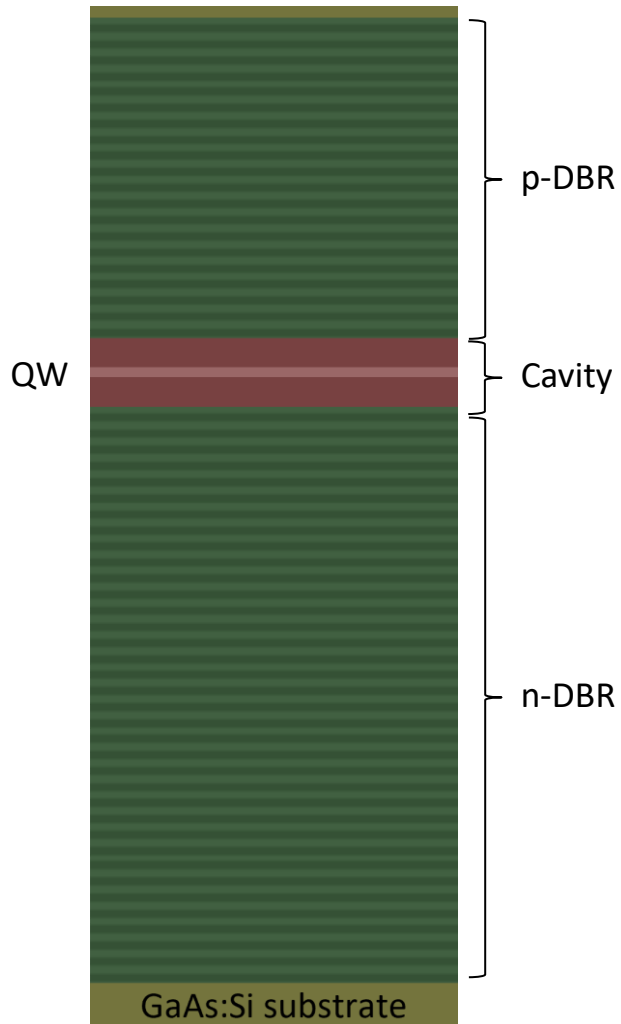
MBE growth of VCSELs



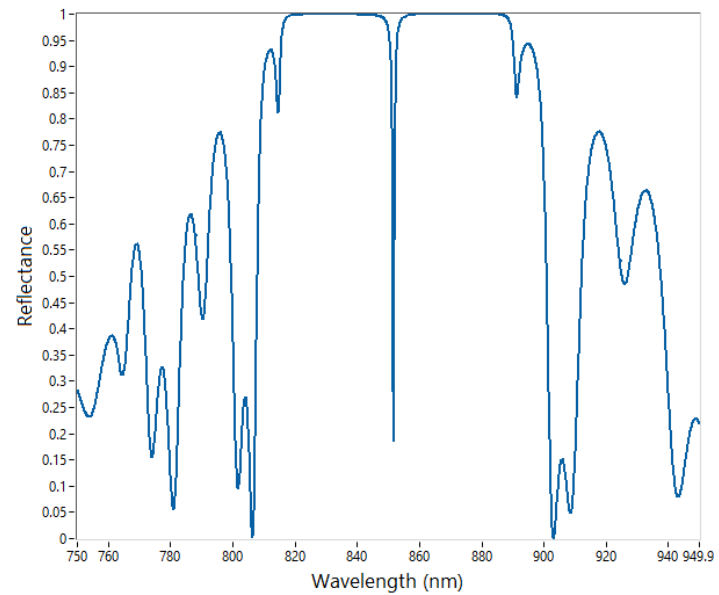
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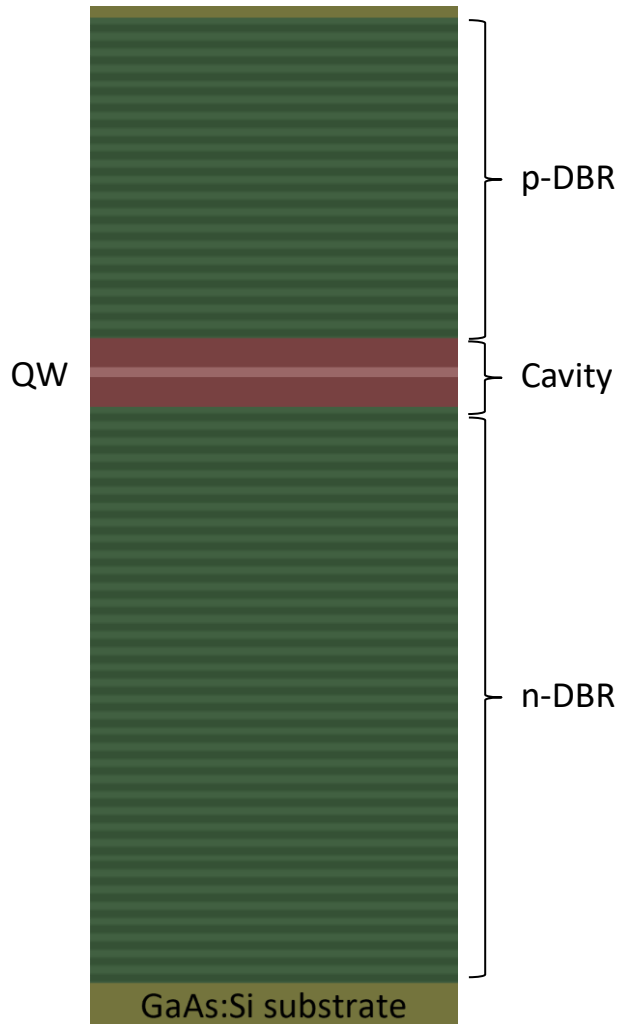
MBE growth of VCSELs



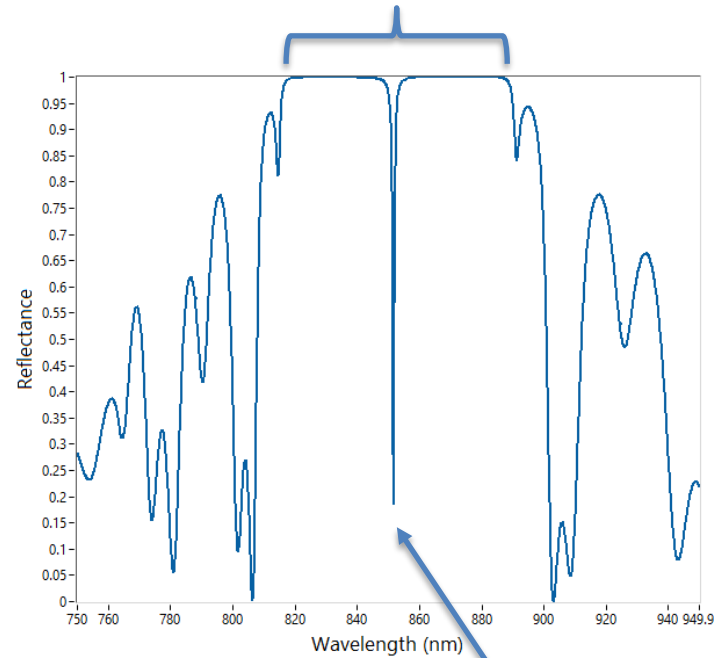
Reflectance spectrum of a VCSEL at RT



MBE growth of VCSELs

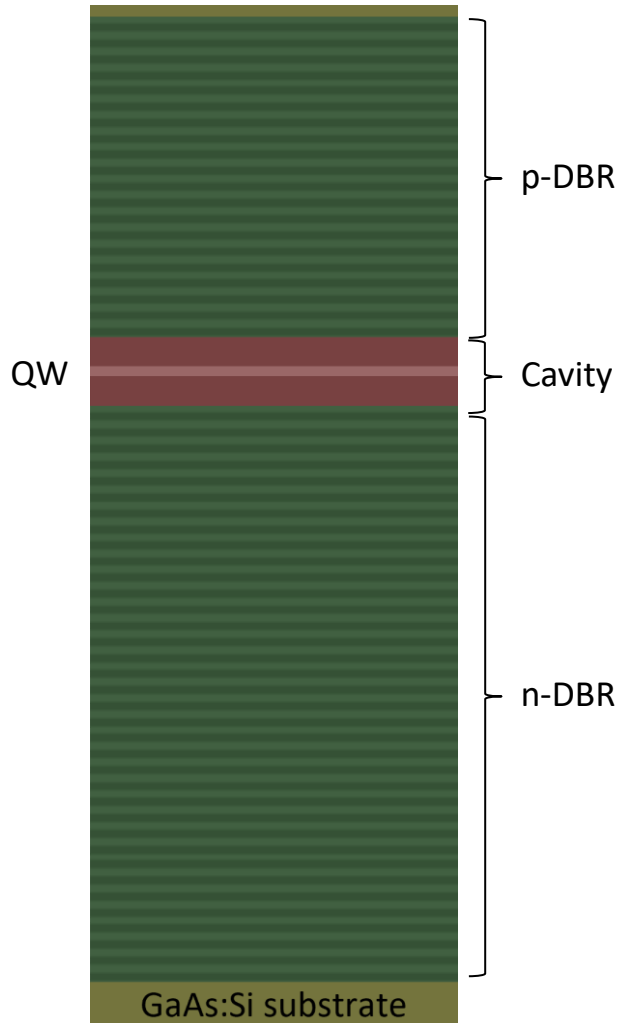


Reflectance spectrum of a VCSEL at RT
High reflectivity plateau

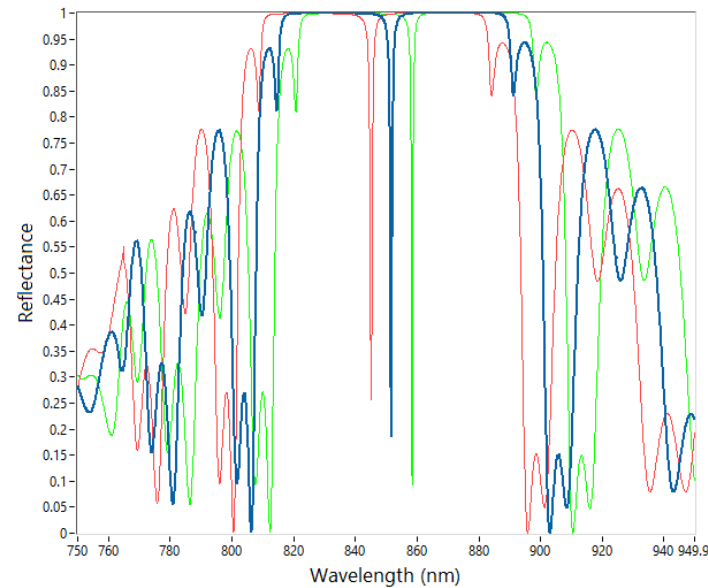


Fabry Perot dip

MBE growth of VCSELs



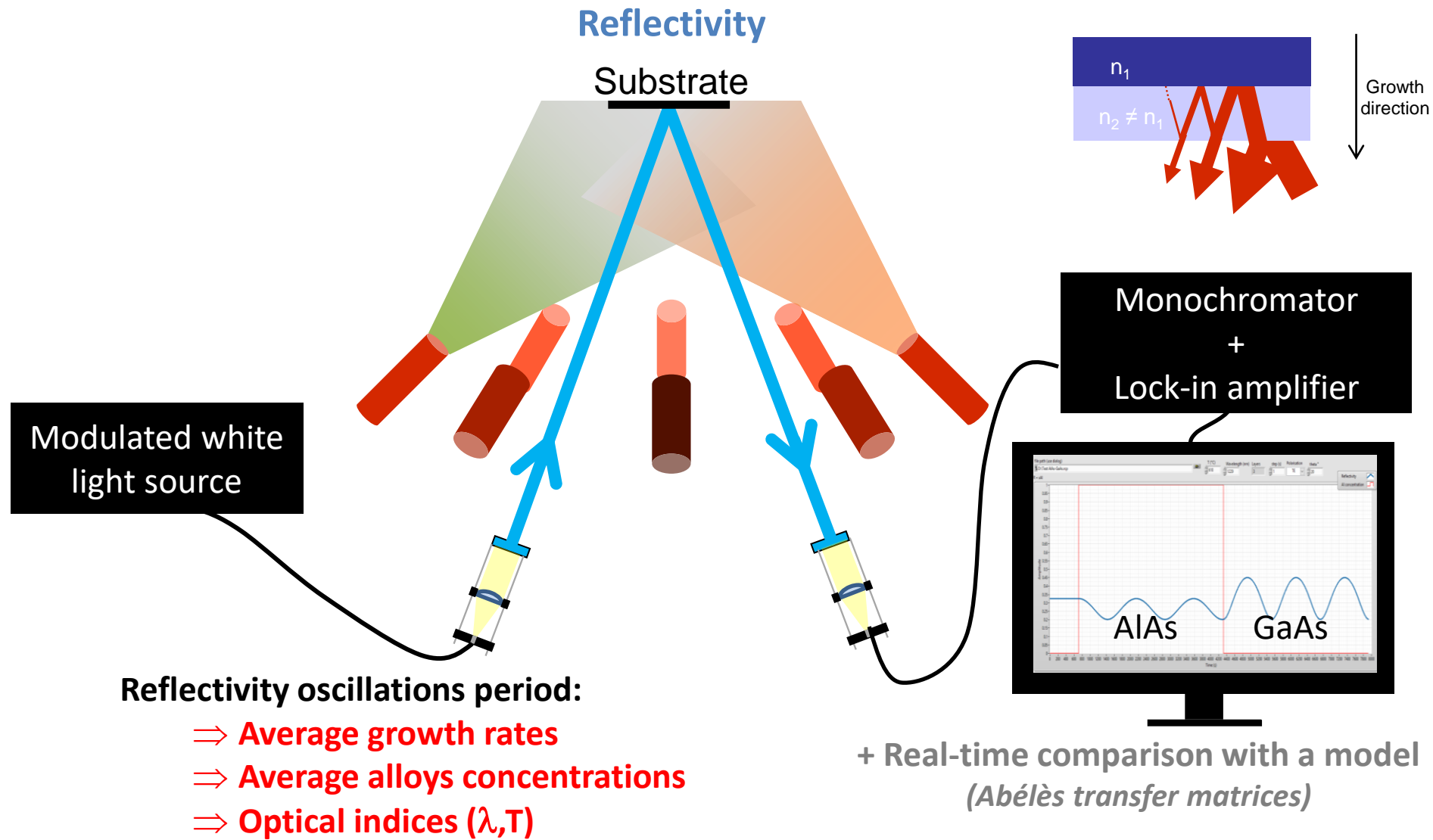
Reflectance spectrum of a VCSEL at RT



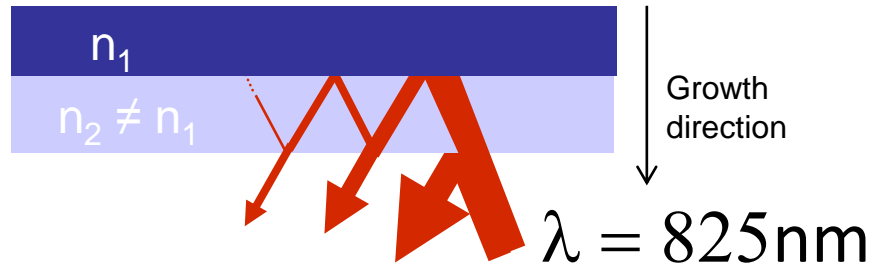
$\pm 1\%$ flux variation $\rightarrow \pm 6\text{nm}$ wavelength variation

In-situ characterization tools: *Spectral reflectivity*

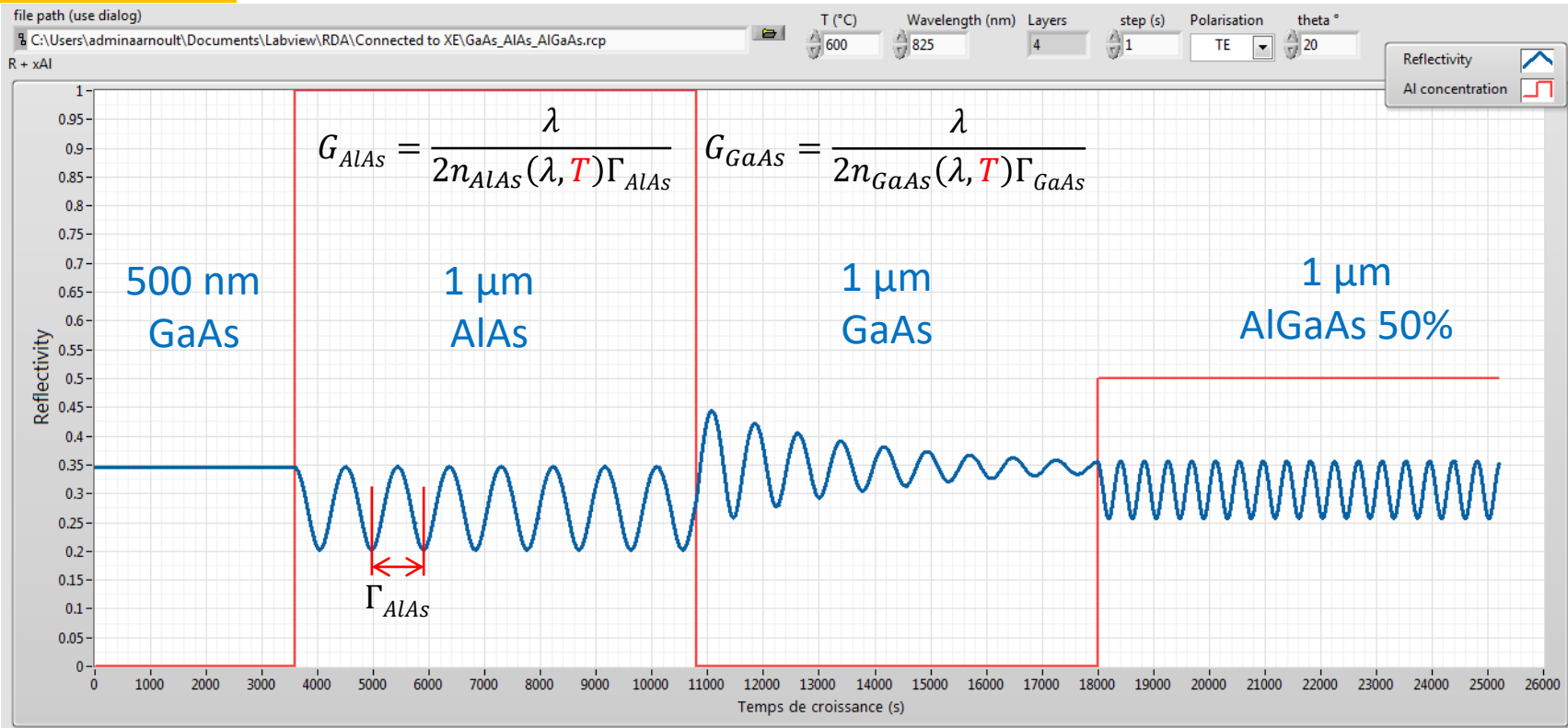
In situ characterization tools in MBE: Reflectivity



In situ characterization tools in MBE: Reflectivity

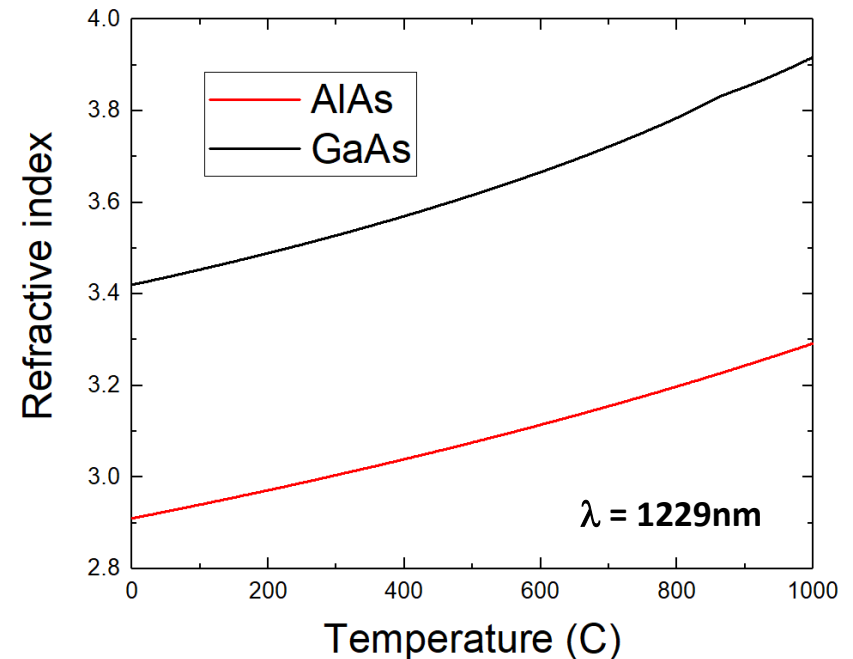
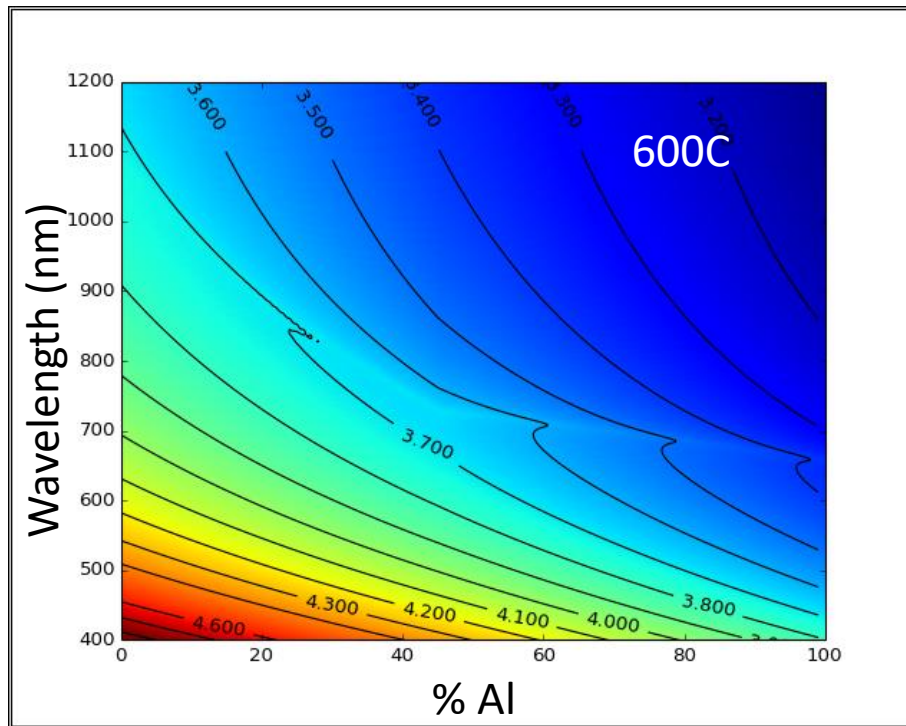


Reflectivity



In situ characterization tools in MBE: Reflectivity

- Optical index evolution with Al concentration and temperature



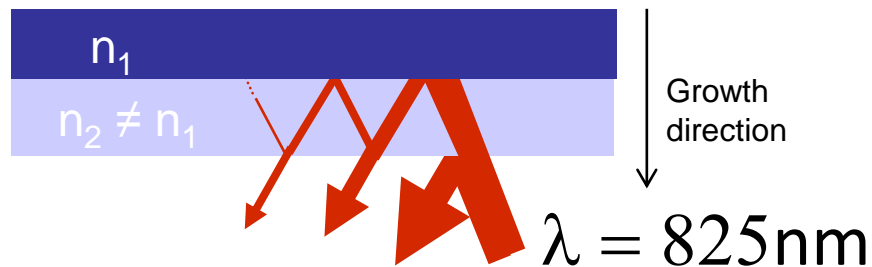
Données :

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

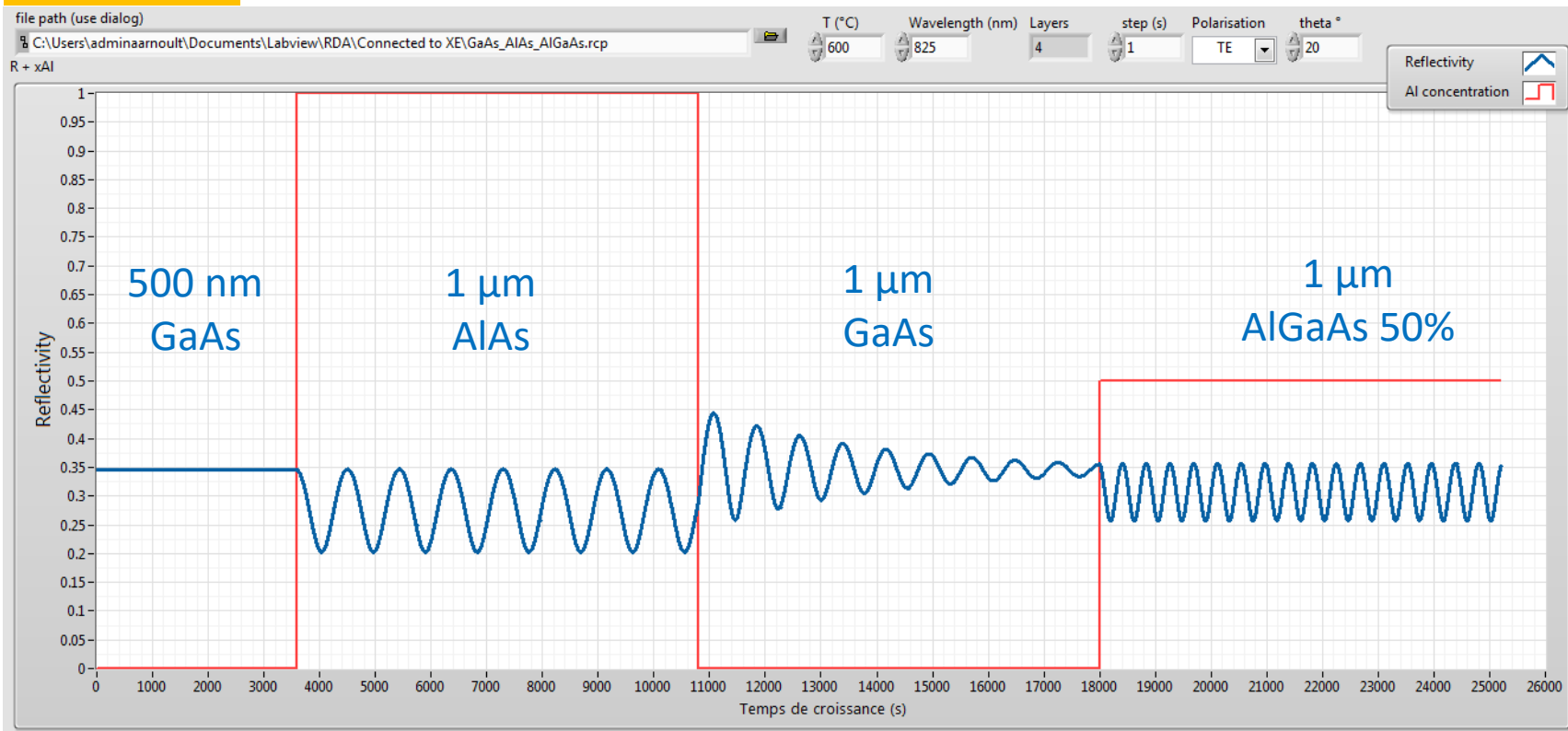
K.P. O'Donnell, *Appl. Phys. Lett.* **58**, 2924 (1991)

→ n evolves with T
Need to know precisely T

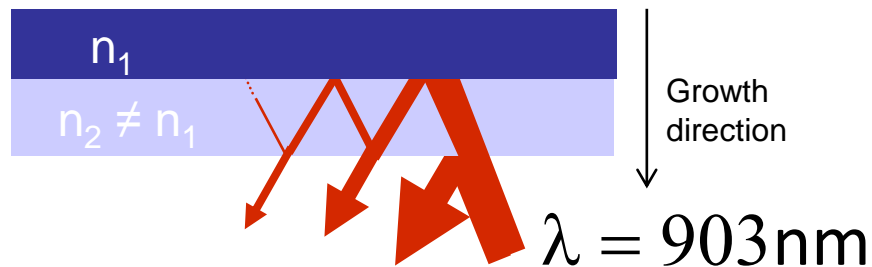
In situ characterization tools in MBE: Reflectivity



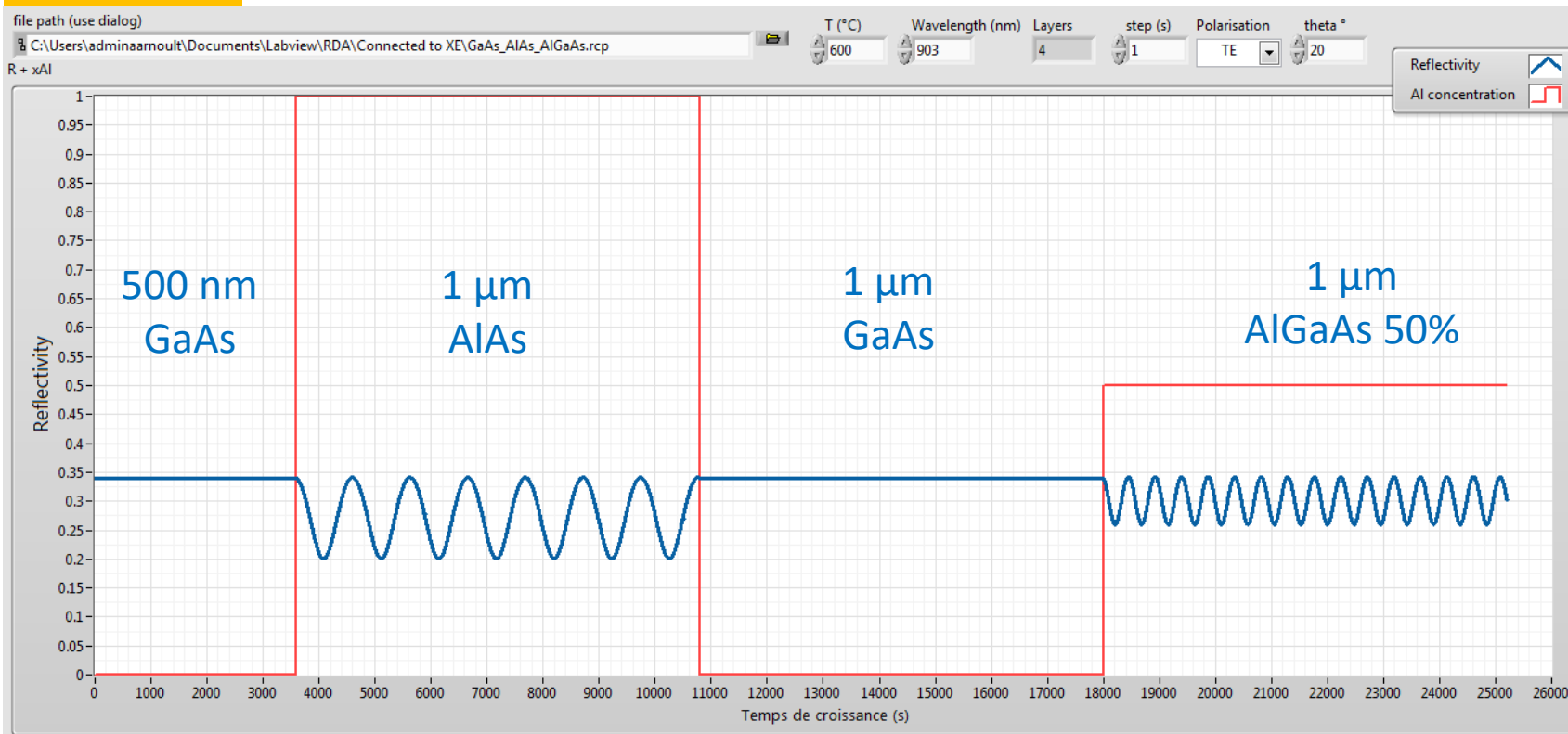
Reflectivity



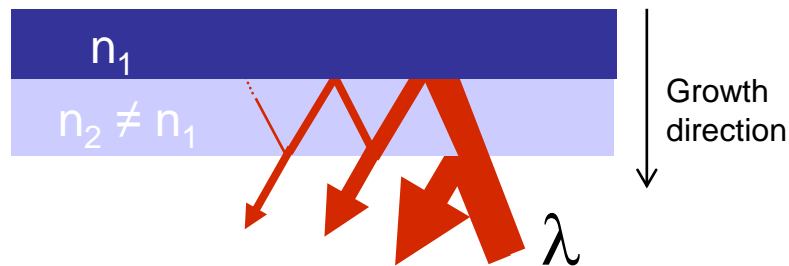
In situ characterization tools in MBE: Reflectivity



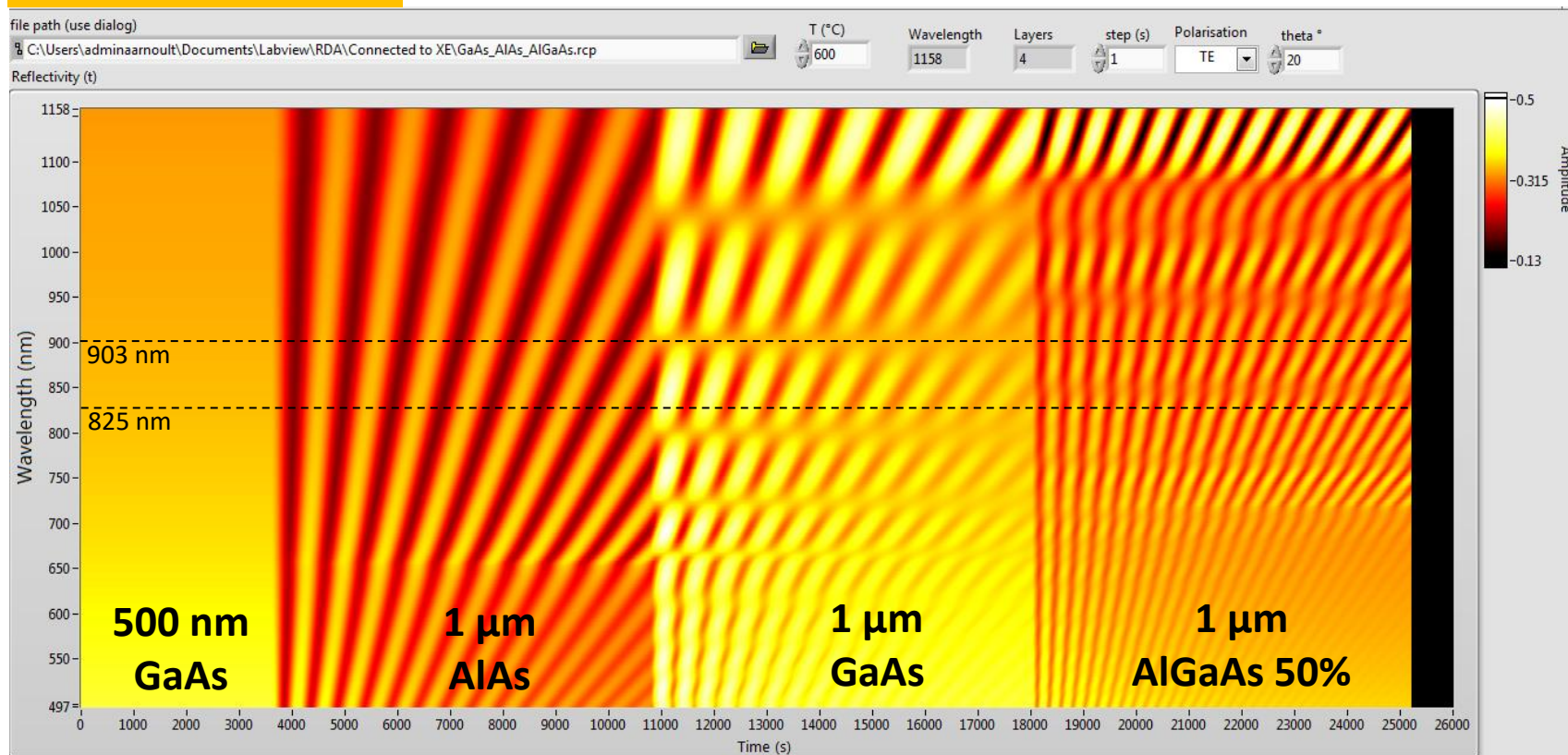
Reflectivity



In situ characterization tools in MBE: Reflectivity

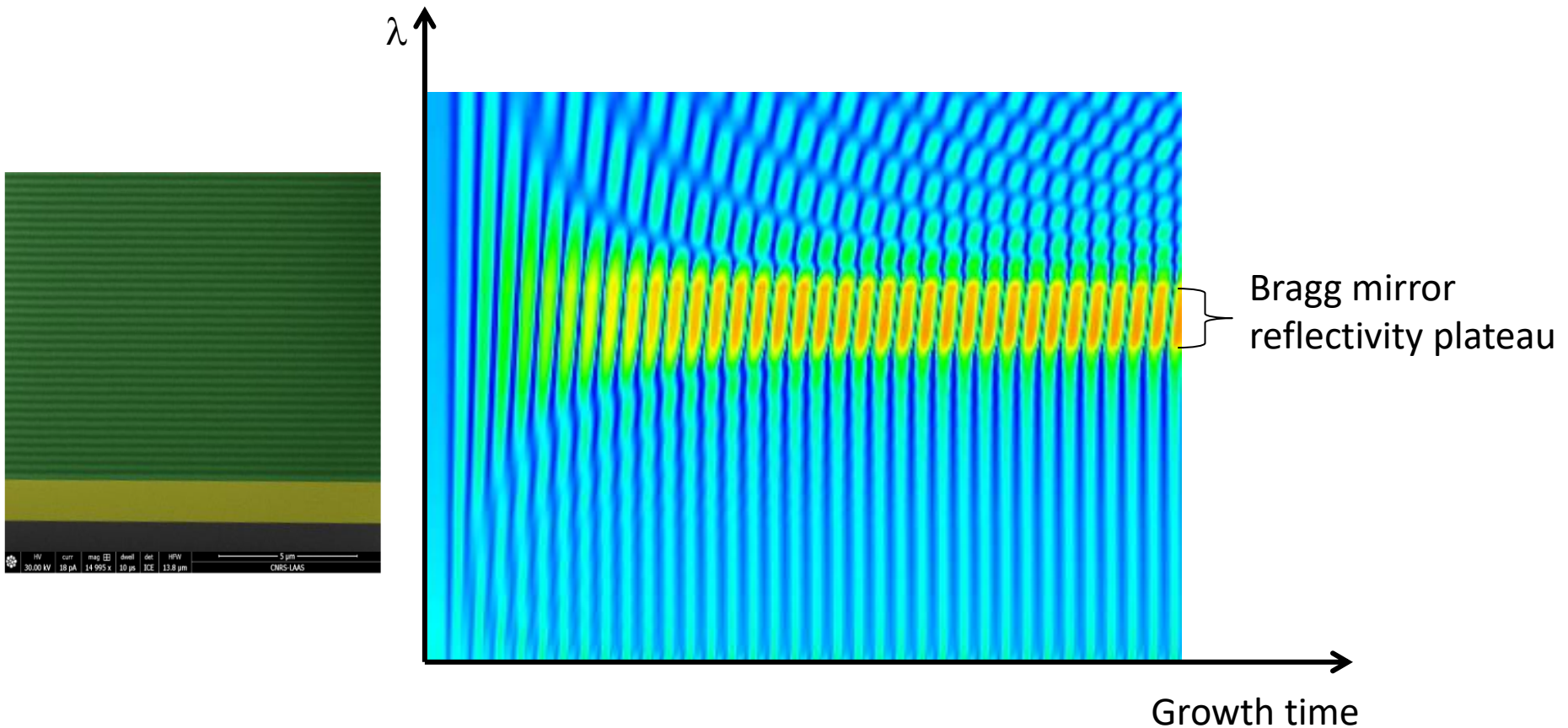


Spectral Reflectivity



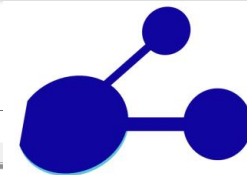
In situ characterization tools in MBE: Reflectivity

Spectral reflectivity during the growth of a Bragg mirror

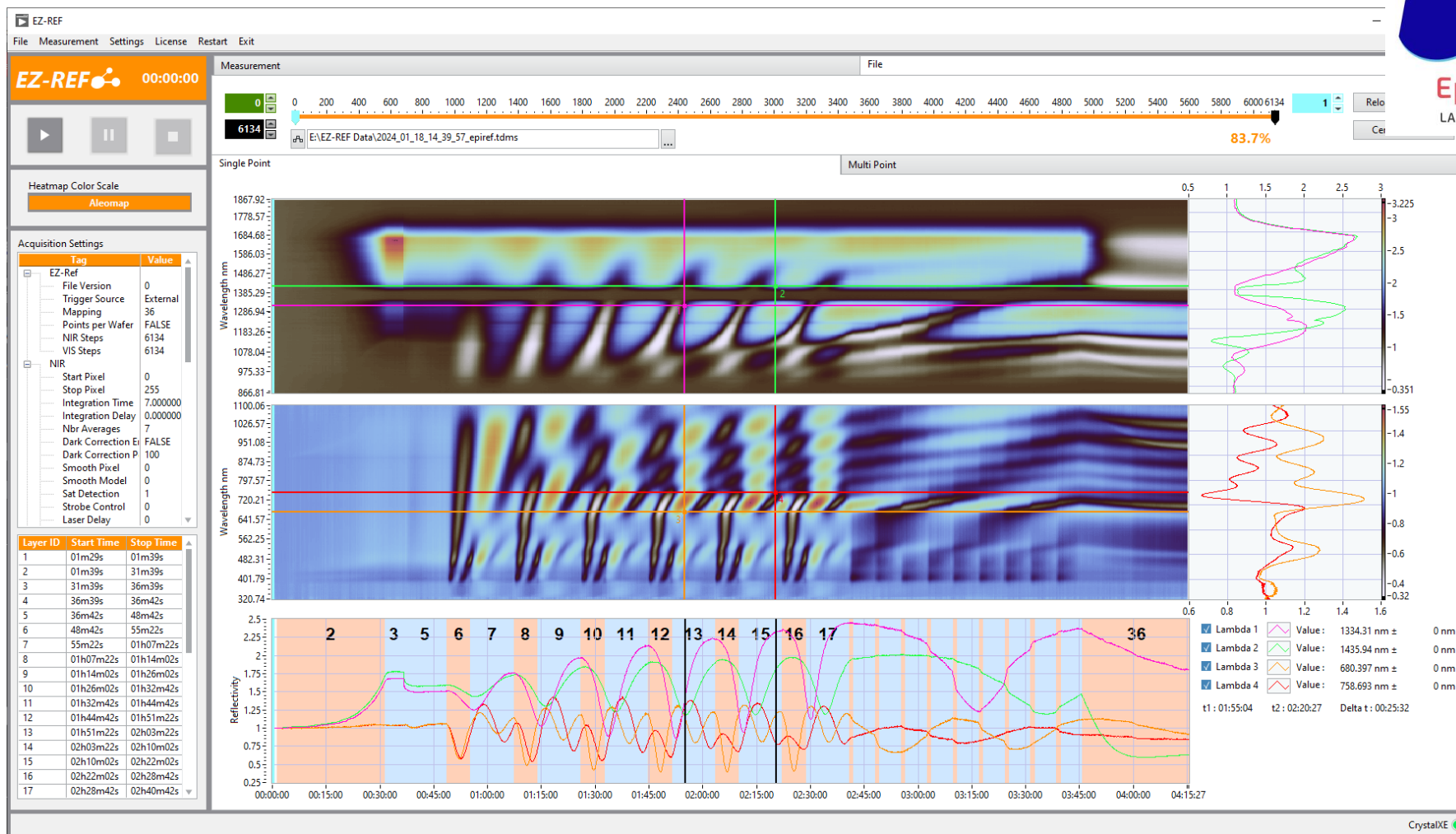


In situ characterization tools in MBE: Reflectivity

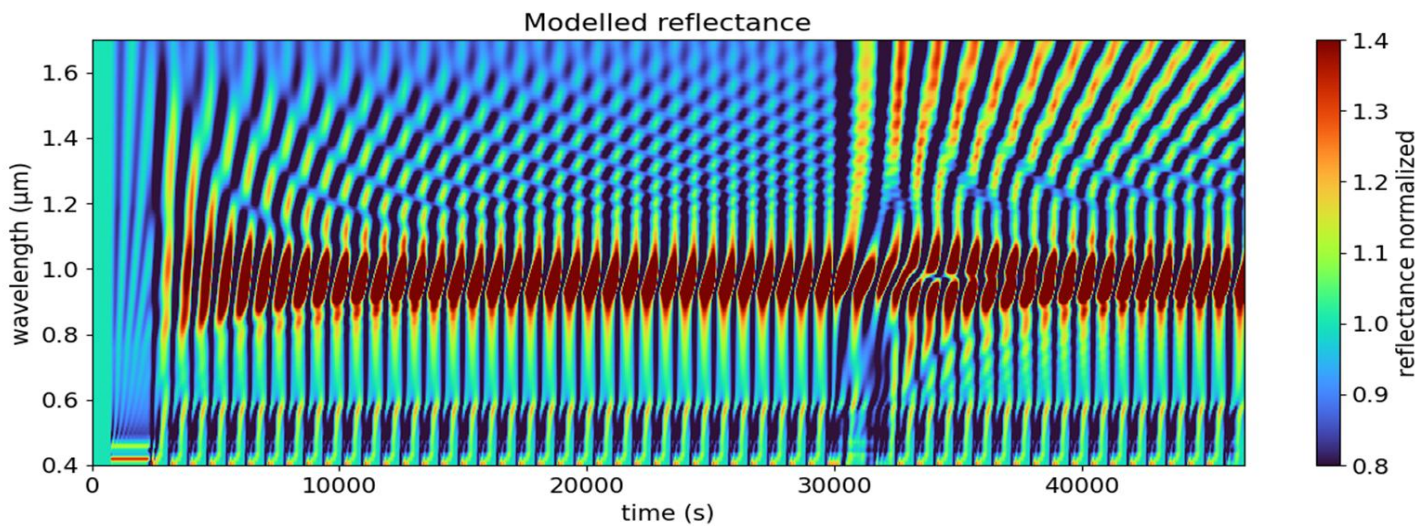
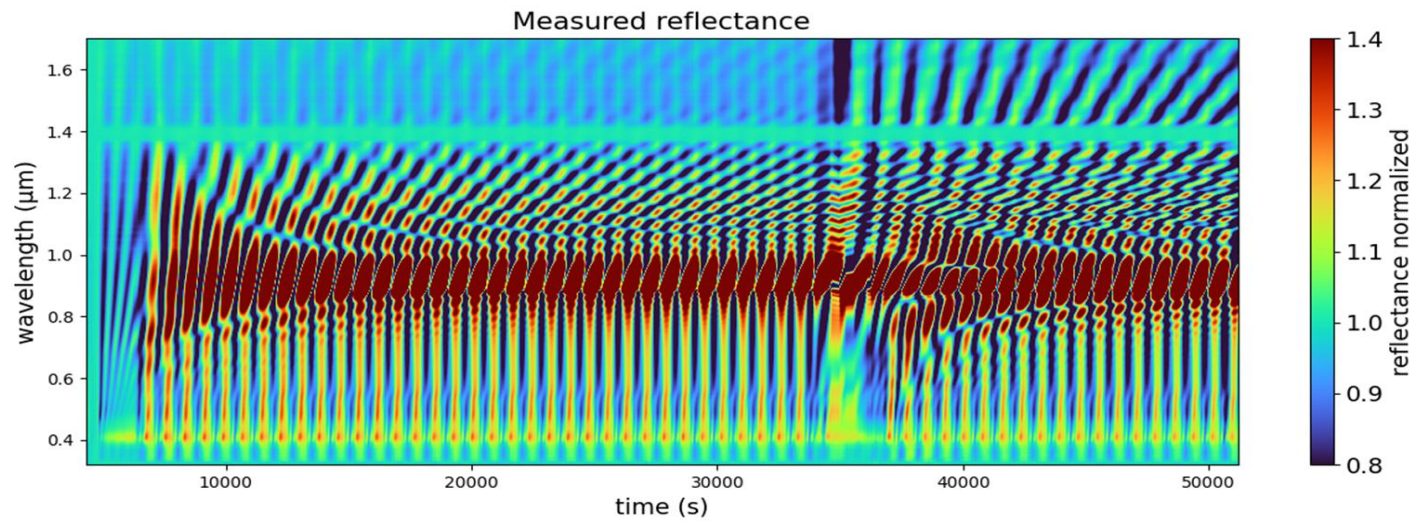
EZ-REF software developed within EpiCentre joint lab



EpiCentre
LAAS CNRS - RIBER



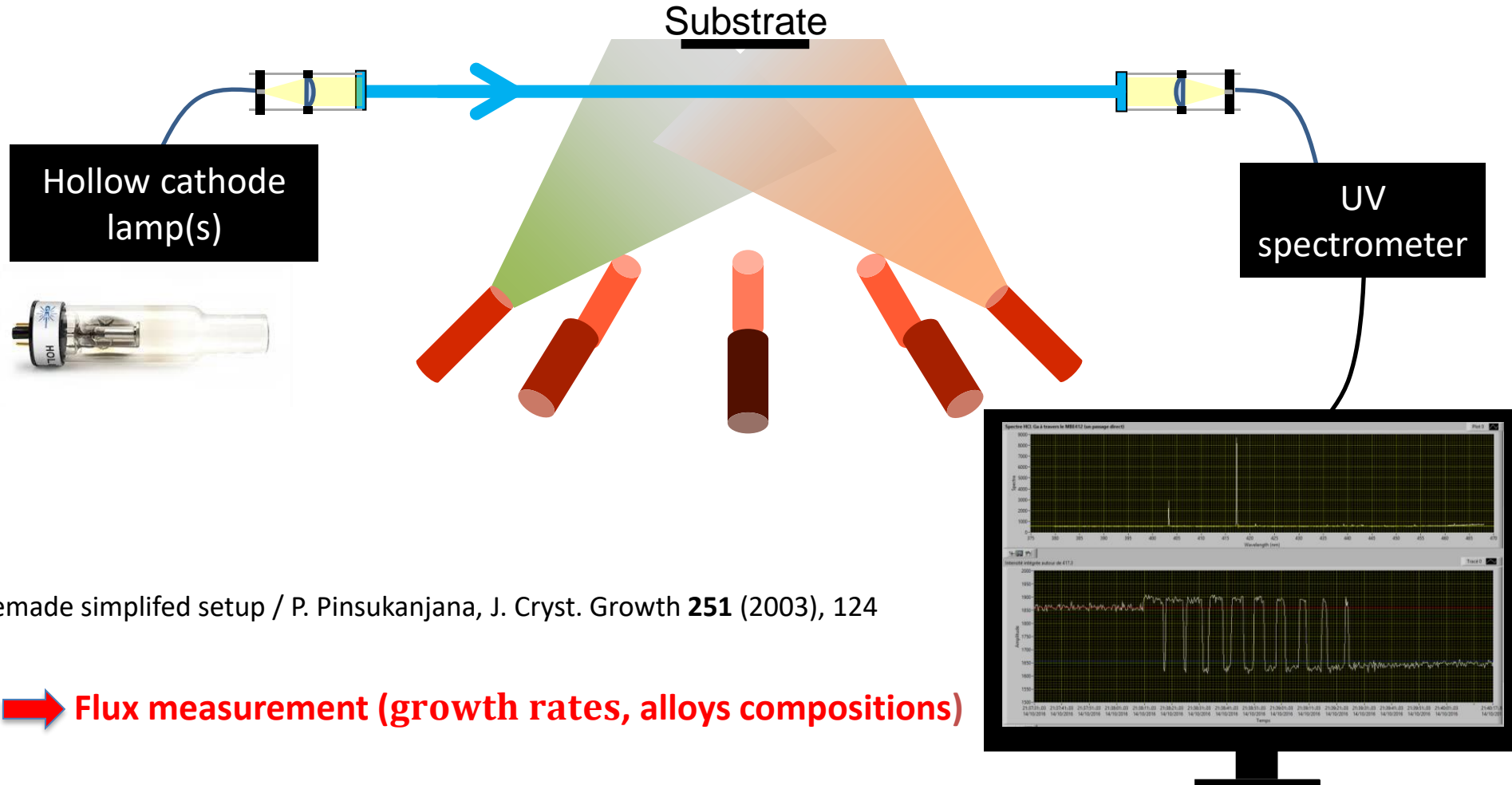
In situ characterization tools in MBE: Reflectivity



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

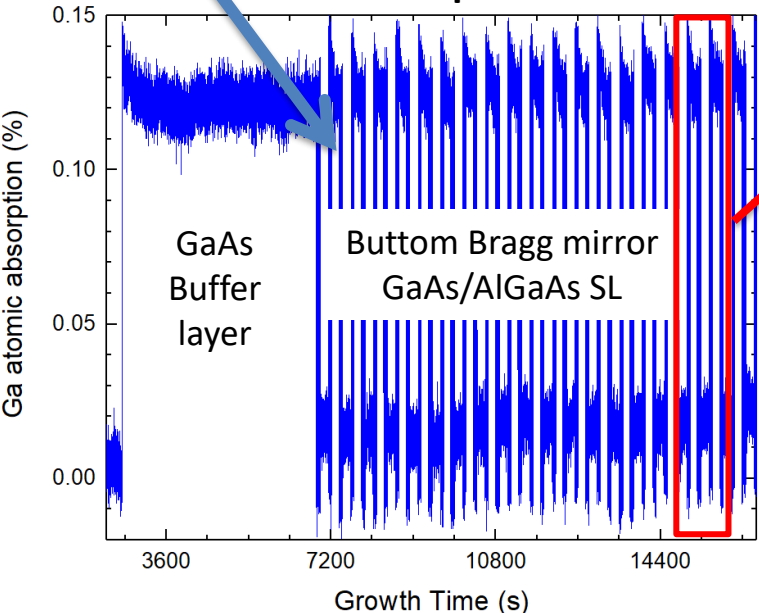
➔ Flux measurement (growth rates, alloys compositions)

In situ characterization tools in MBE: Atomic Absorption

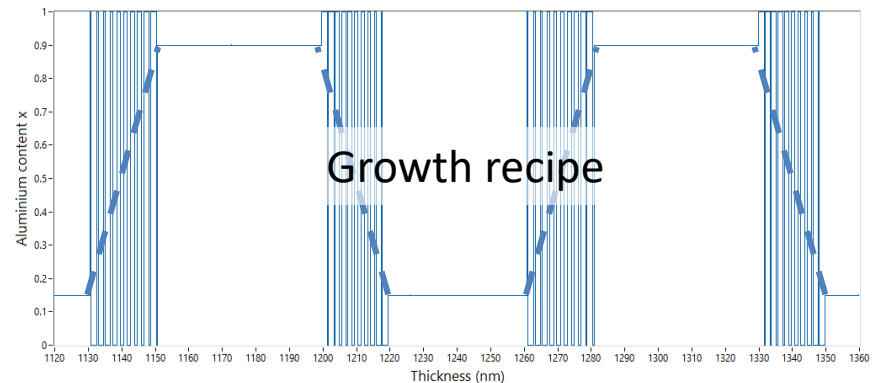
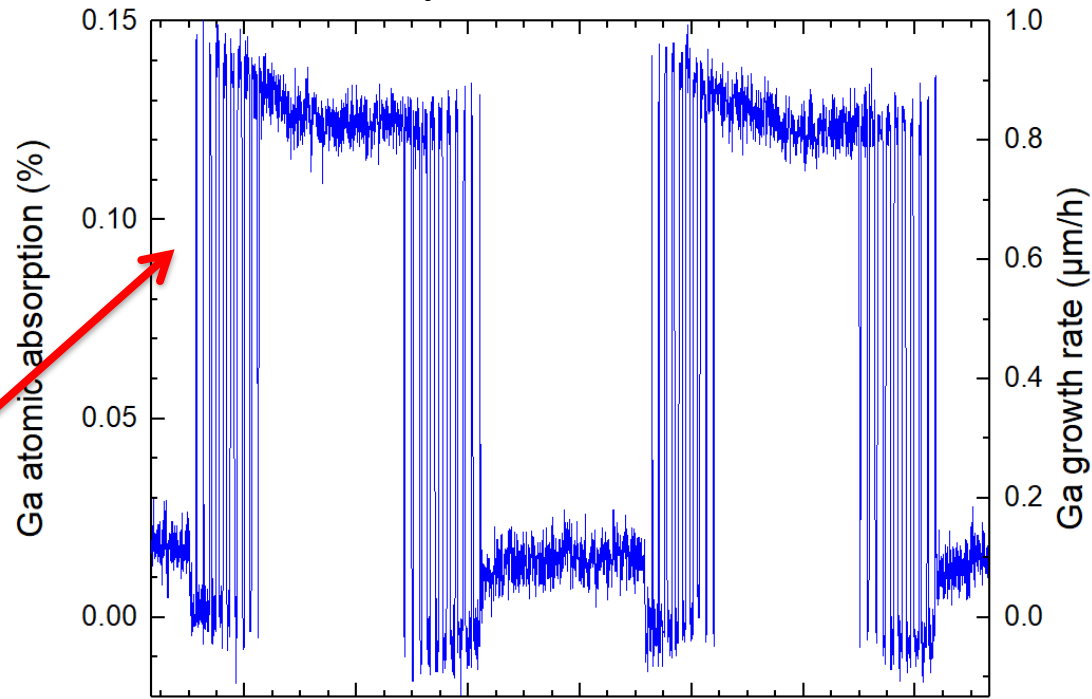
▪ SEM cross section



▪ In situ atomic absorption of Ga



▪ In situ atomic absorption of Ga

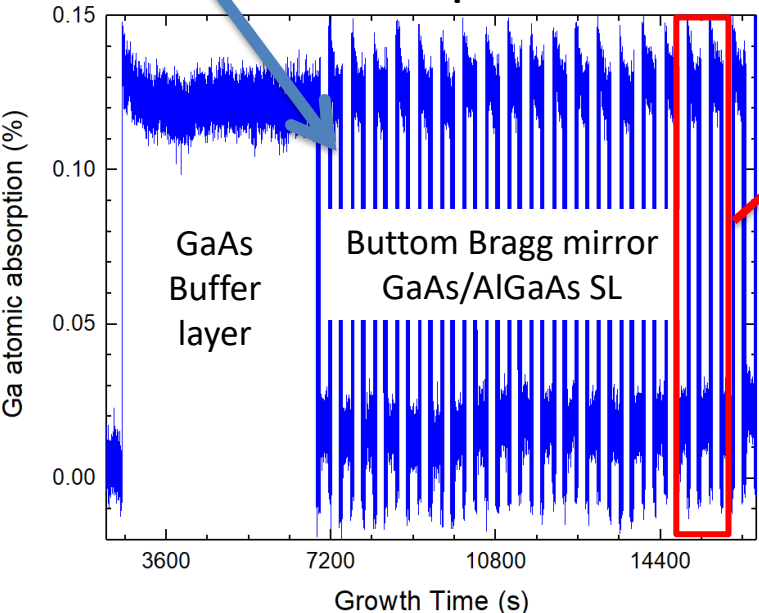


In situ characterization tools in MBE: Atomic Absorption

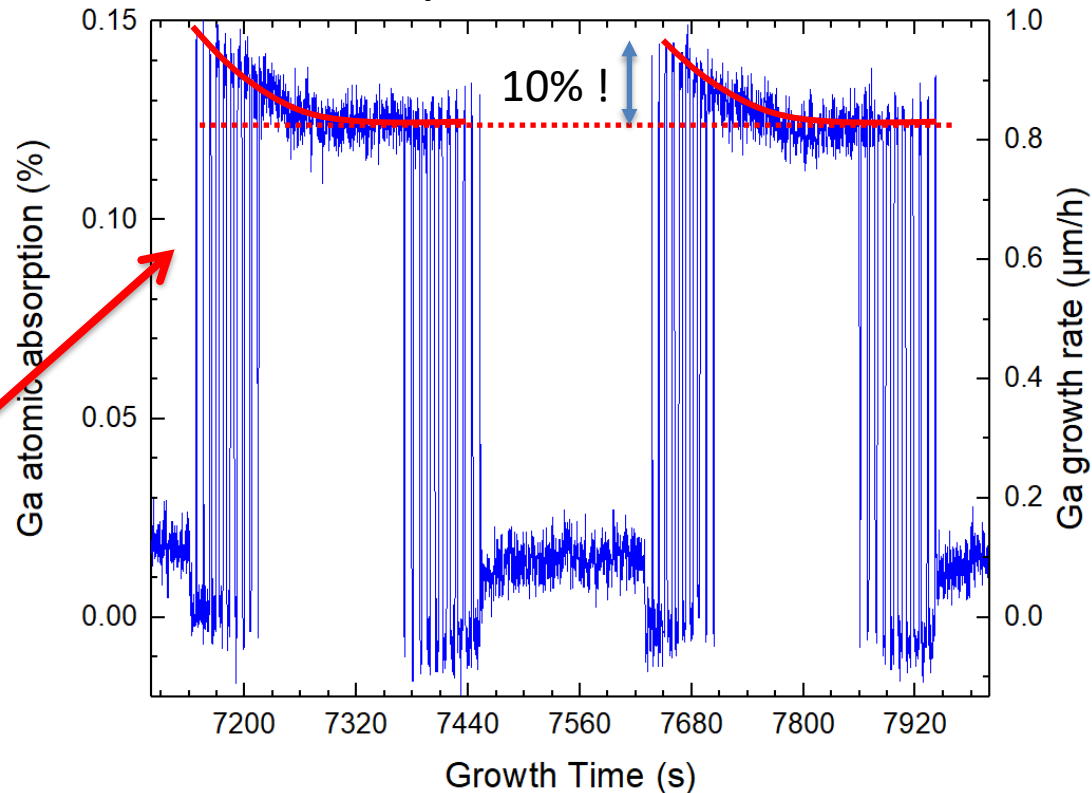
▪ SEM cross section



▪ In situ atomic absorption of Ga



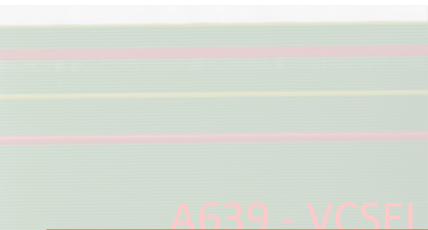
▪ In situ atomic absorption of Ga



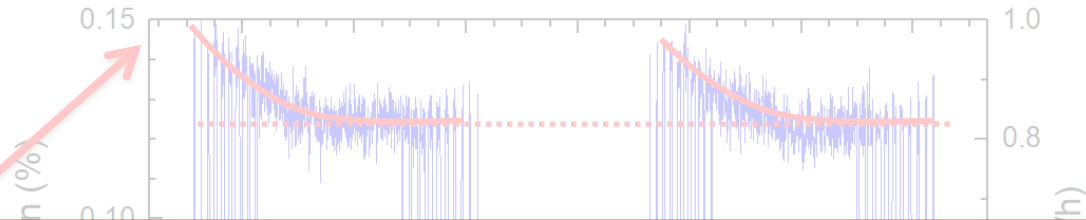
**Evidence of a systematic error:
flux transients of the Ga cell**

In situ characterization tools in MBE: Atomic Absorption

▪ SEM cross section



▪ In situ atomic absorption of Ga



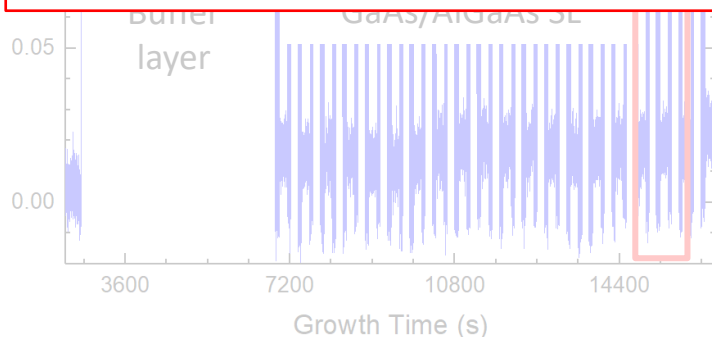
Result : 10% flux variations in some layers

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)

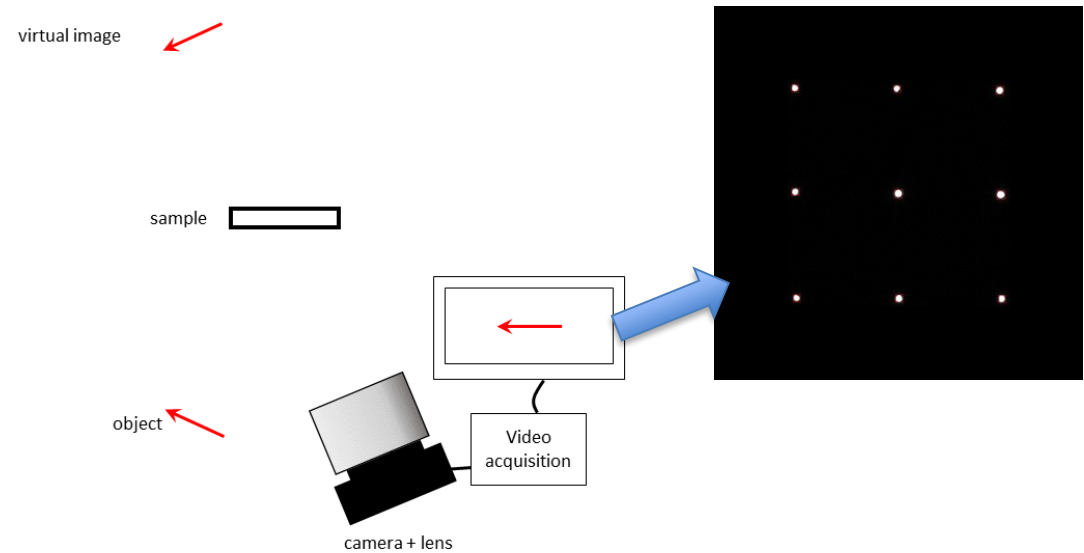


White light source

Camera

Highly stable and alignment-free measurements

High rate capability (100FPS)



$$\text{Curvature} = f(\text{magnification factor})$$

Curvature and stress are linked

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



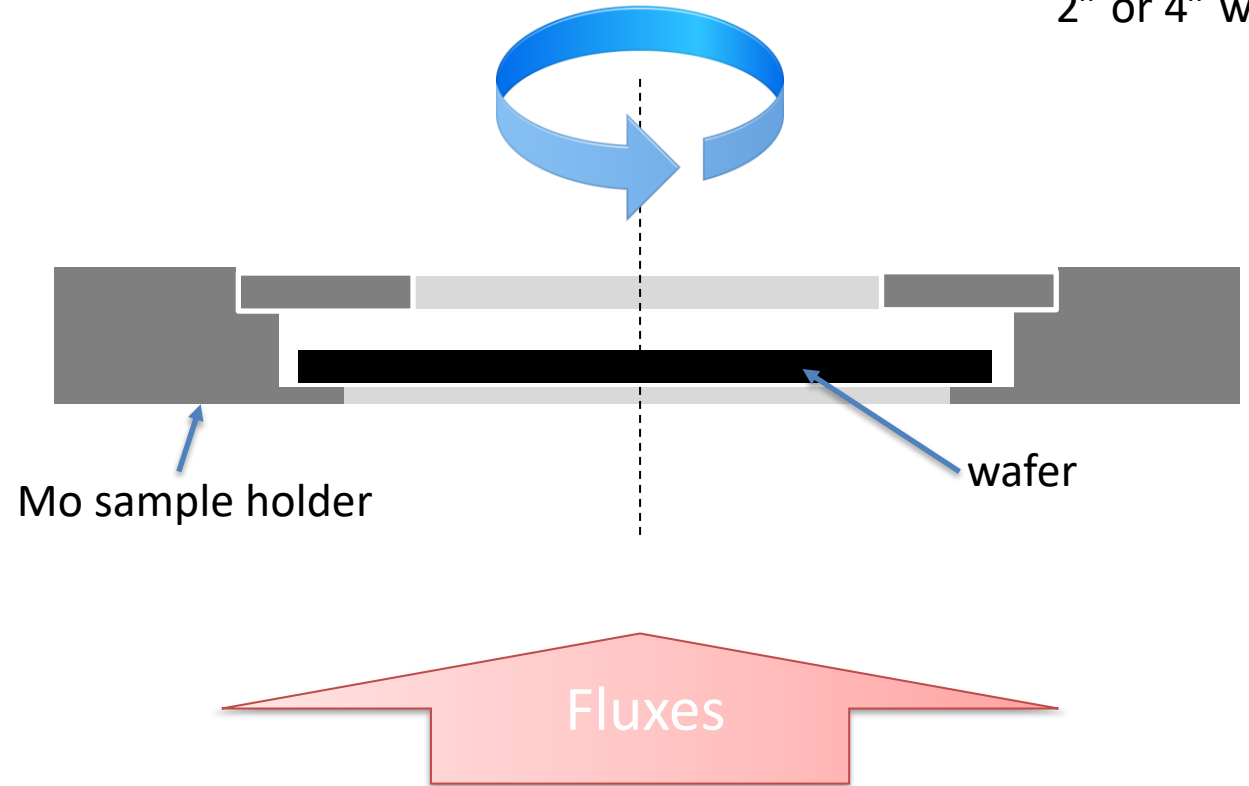
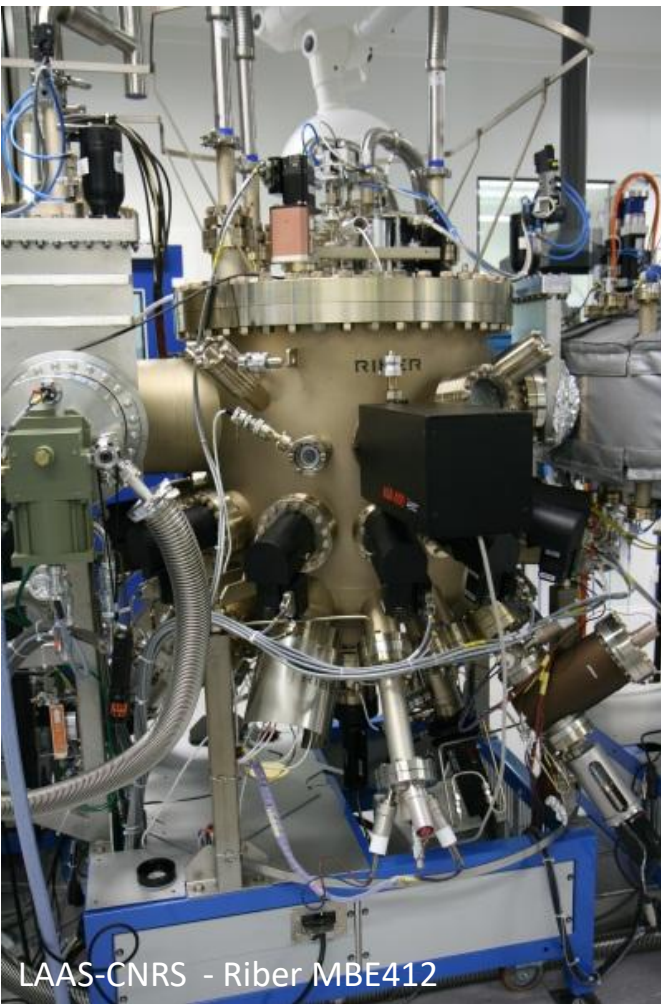
1. Extrinsic stress

- 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

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

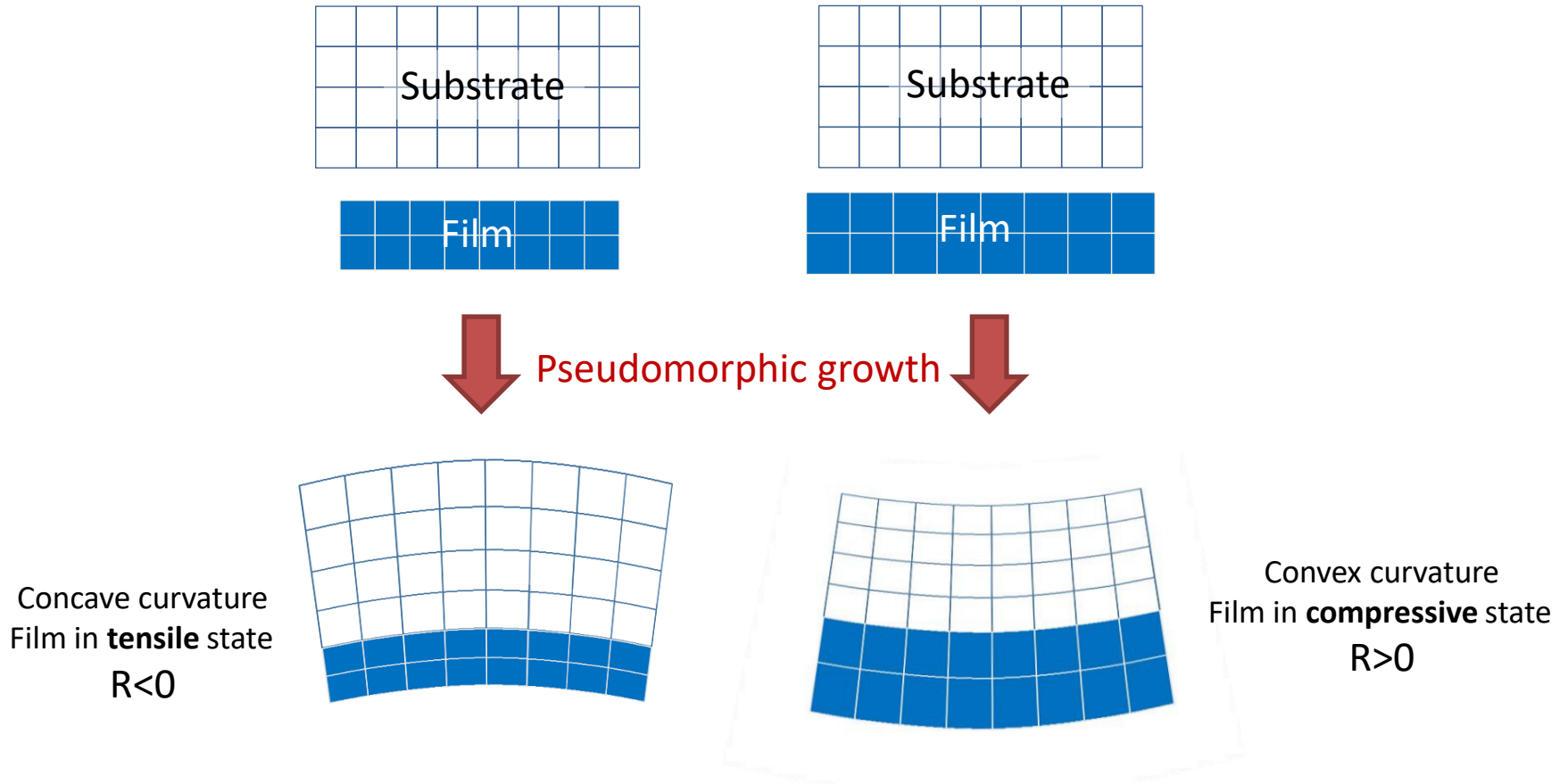
2. Intrinsic stress

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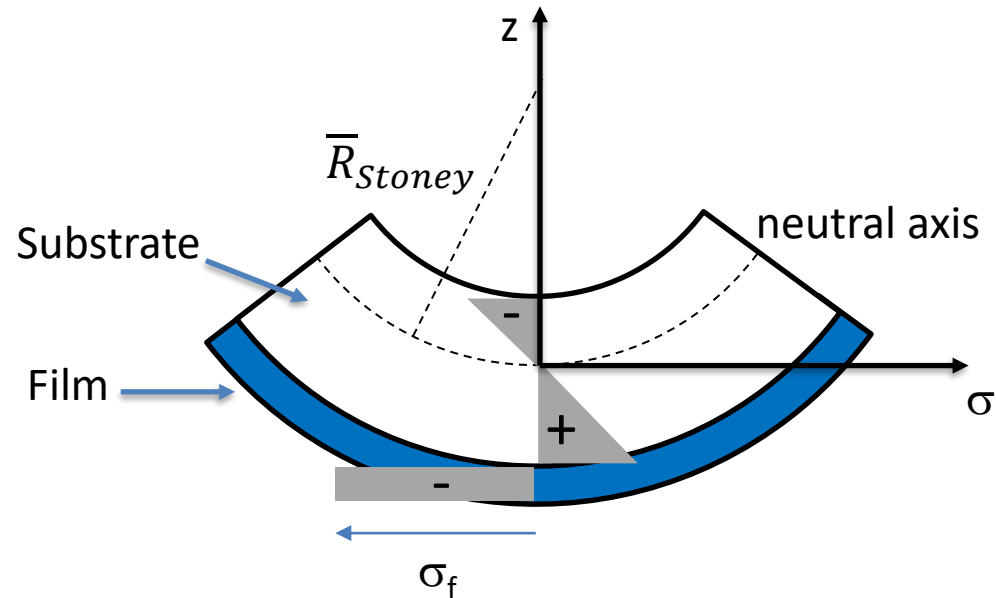
In situ characterization tools in MBE: Curvature

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

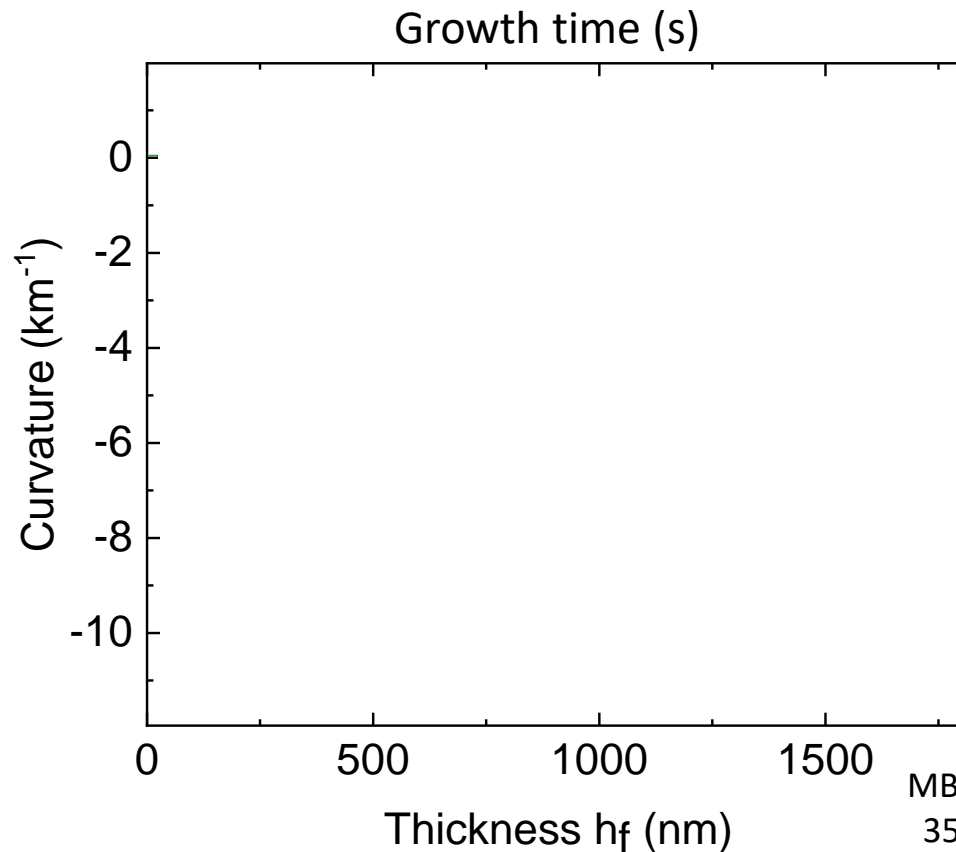
- > Satisfying equilibrium conditions ($\Sigma F = 0$ and $\Sigma M = 0$) leads to the **Stoney equation**

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

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

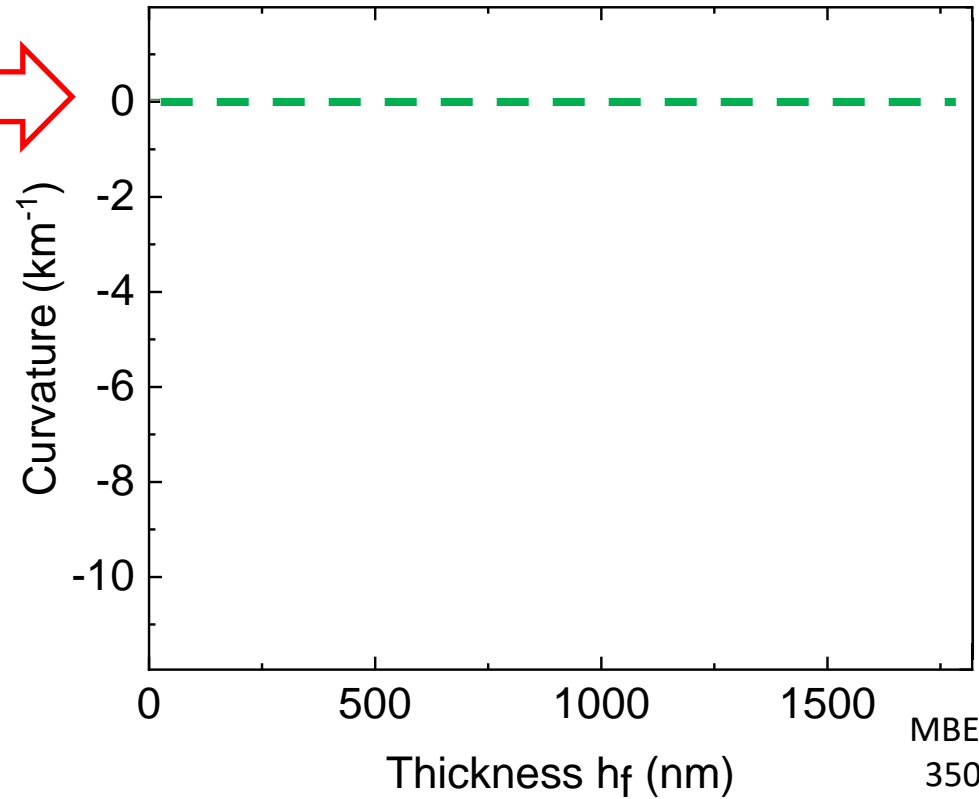


MBE growth of GaAs/AlGaAs on a rotating 350 μm -thick (001) GaAs wafer at 600°C

Curvature/Stress and MBE growth

Intrinsic stress

Zero curvature = initial state
(relative curvature changes)

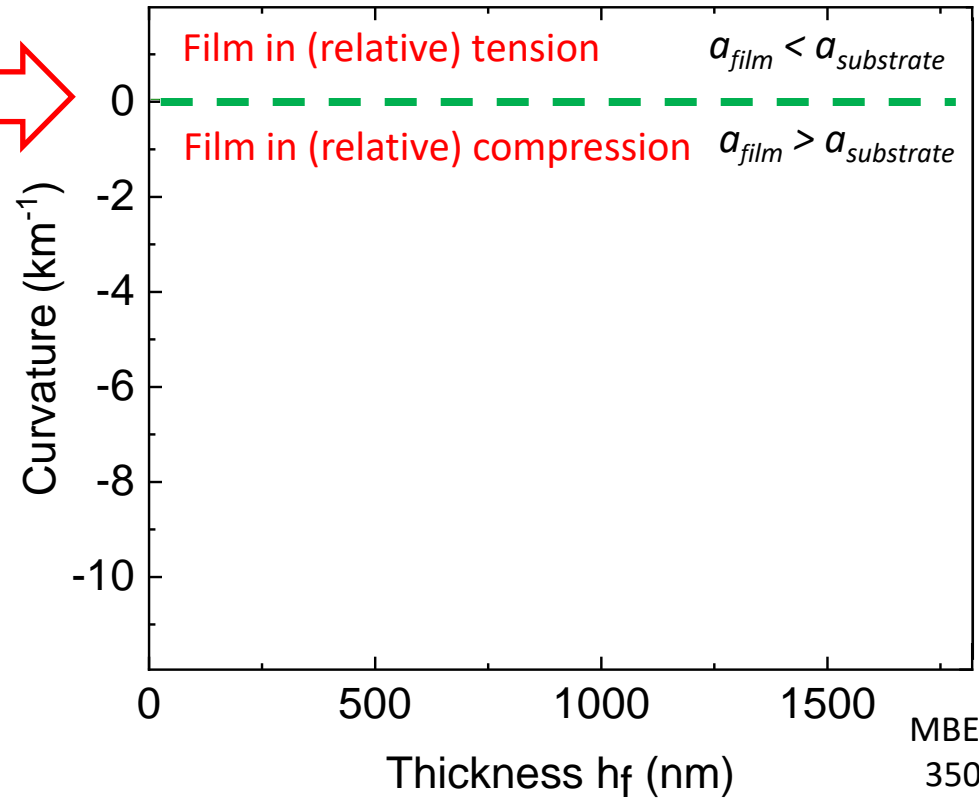


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Curvature/Stress and MBE growth

Intrinsic stress

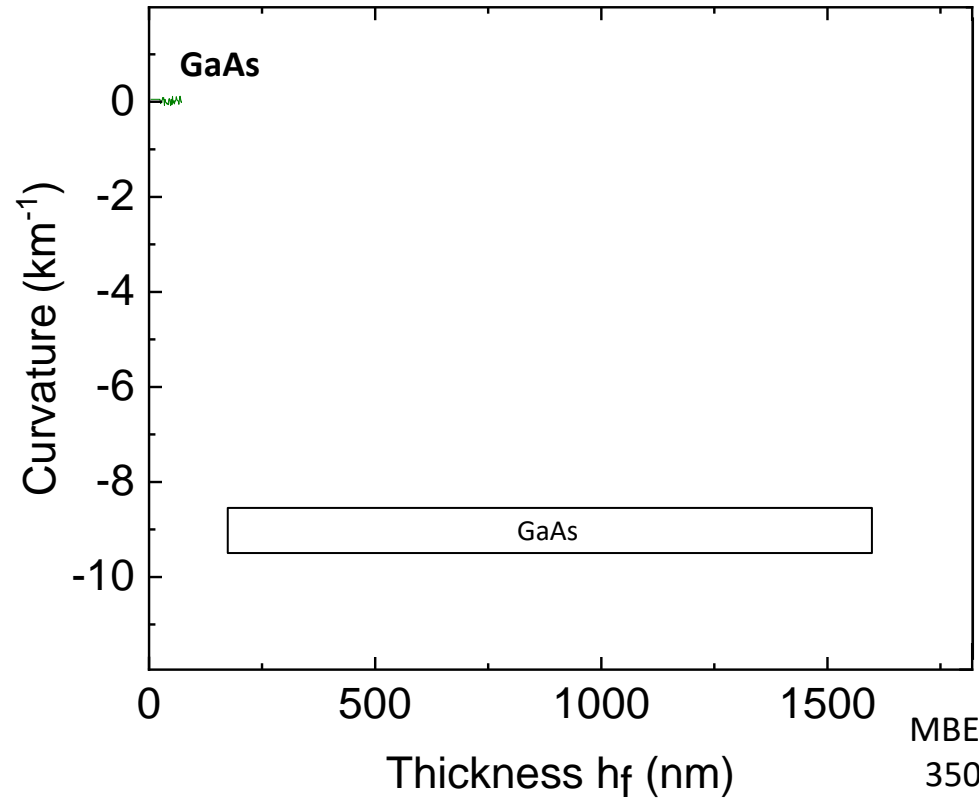
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Curvature/Stress and MBE growth

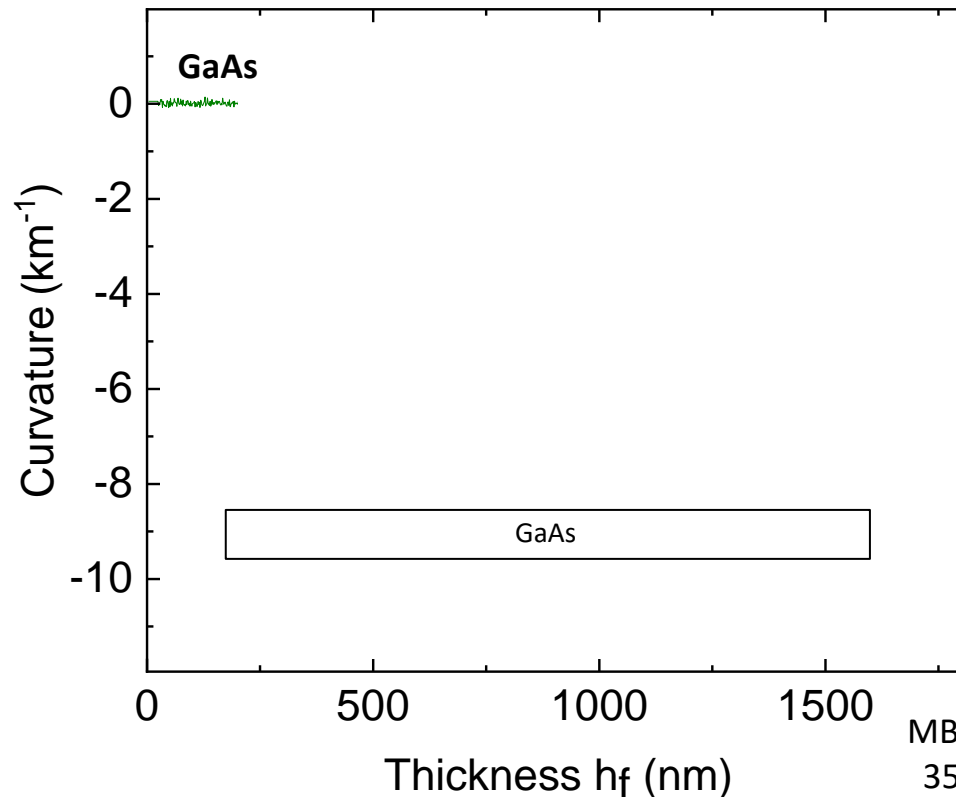
Intrinsic stress



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

Curvature/Stress and MBE growth

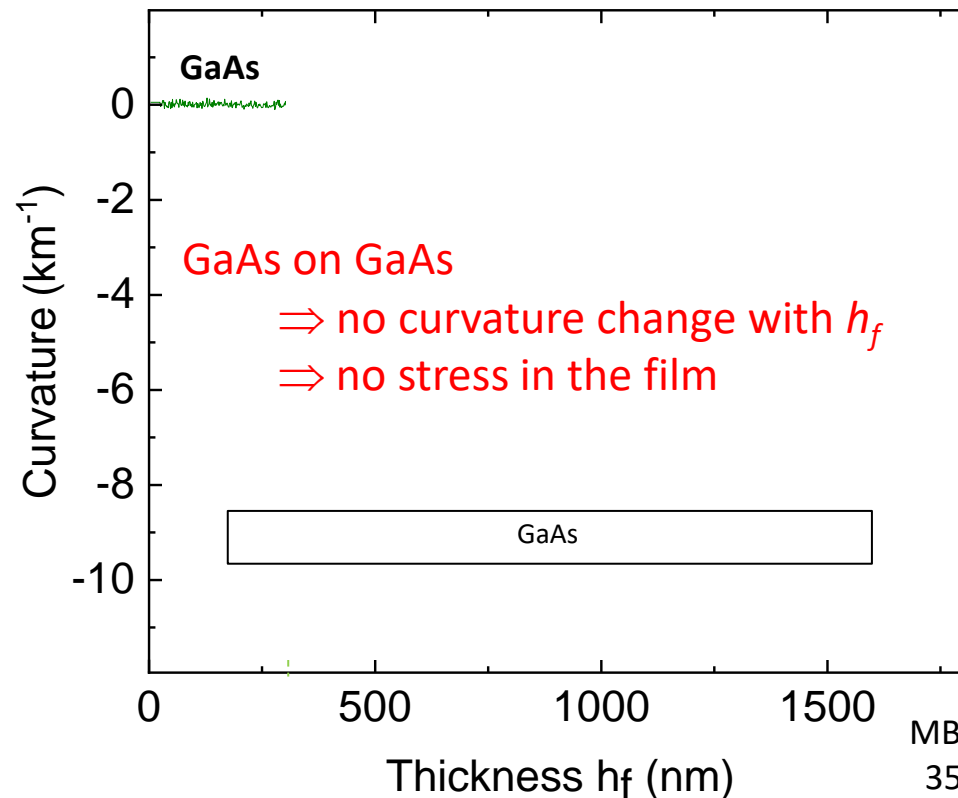
Intrinsic stress



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

Curvature/Stress and MBE growth

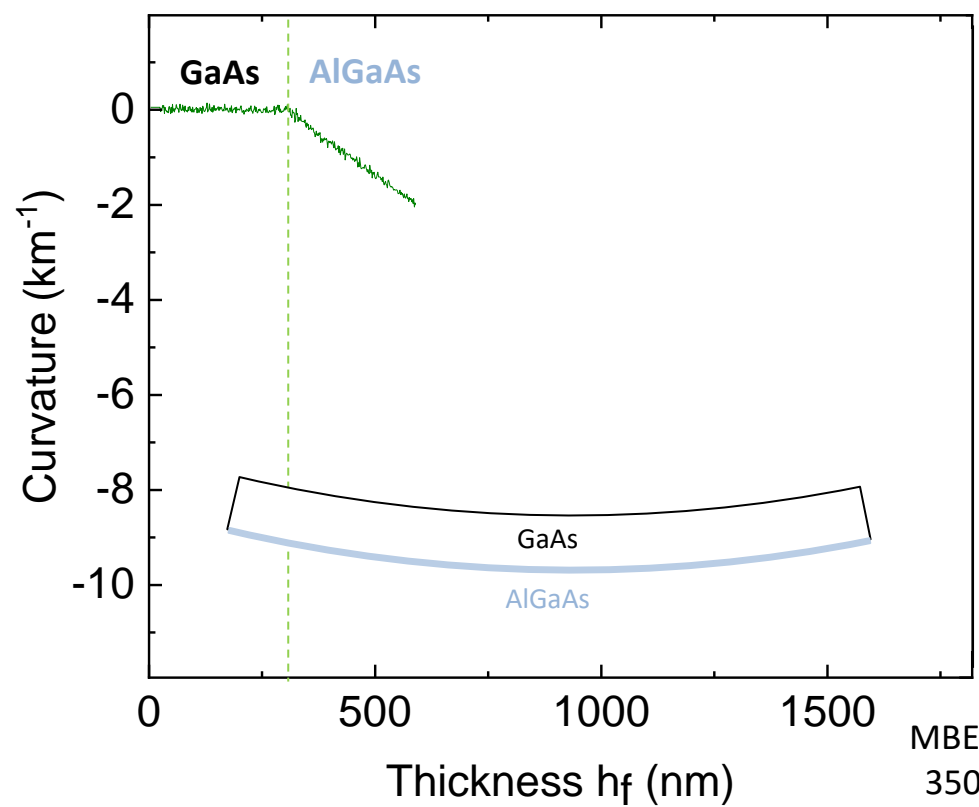
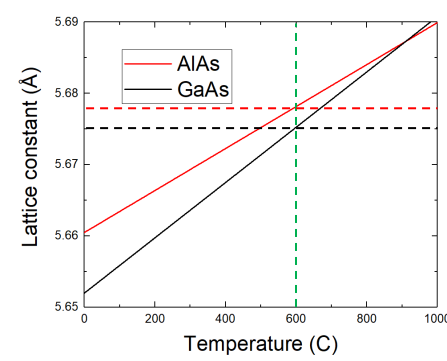
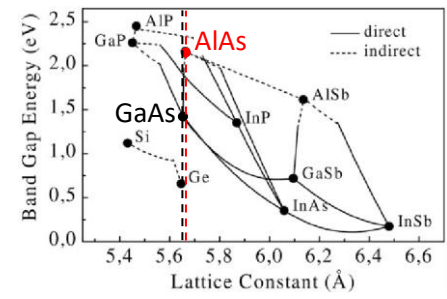
Intrinsic stress



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

Curvature/Stress and MBE growth

Intrinsic stress

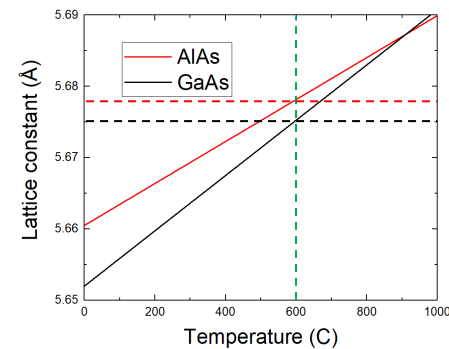
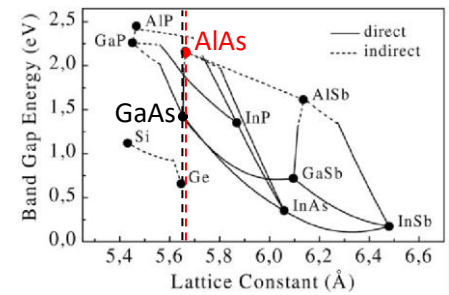


MBE growth of GaAs/AlGaAs on a rotating 350 μm -thick (001) GaAs wafer at 600°C

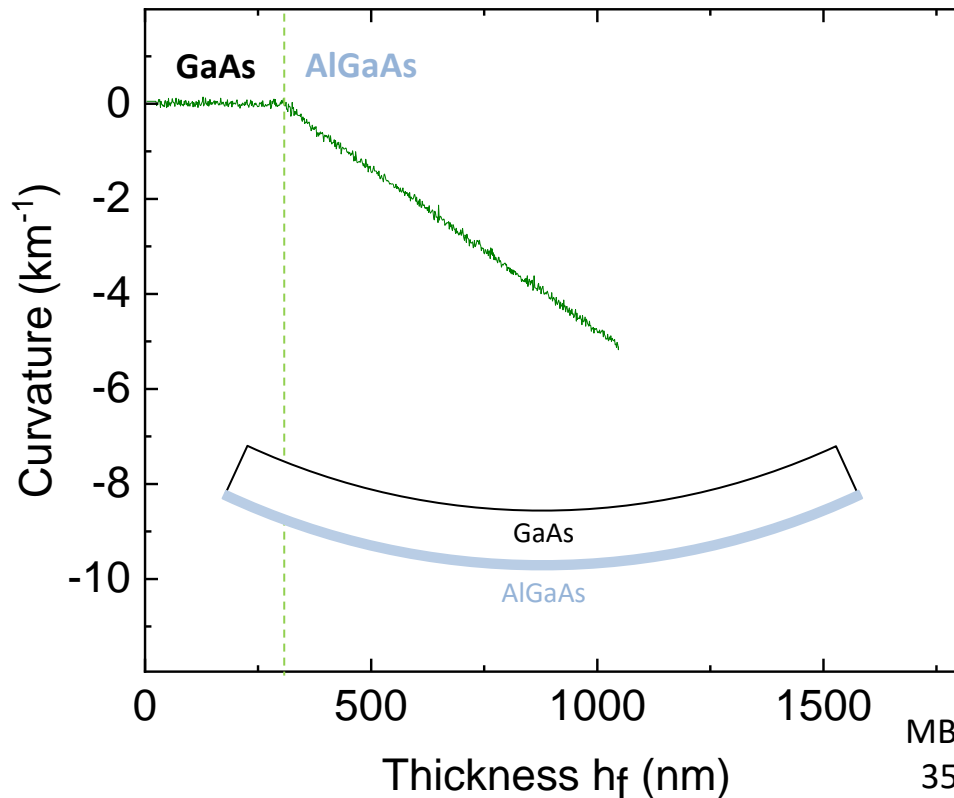
M. Ettenberg, R. J. Paff, J. Appl. Phys., 41, no.10, pp.3926-3927 (1970)

Curvature/Stress and MBE growth

Intrinsic stress



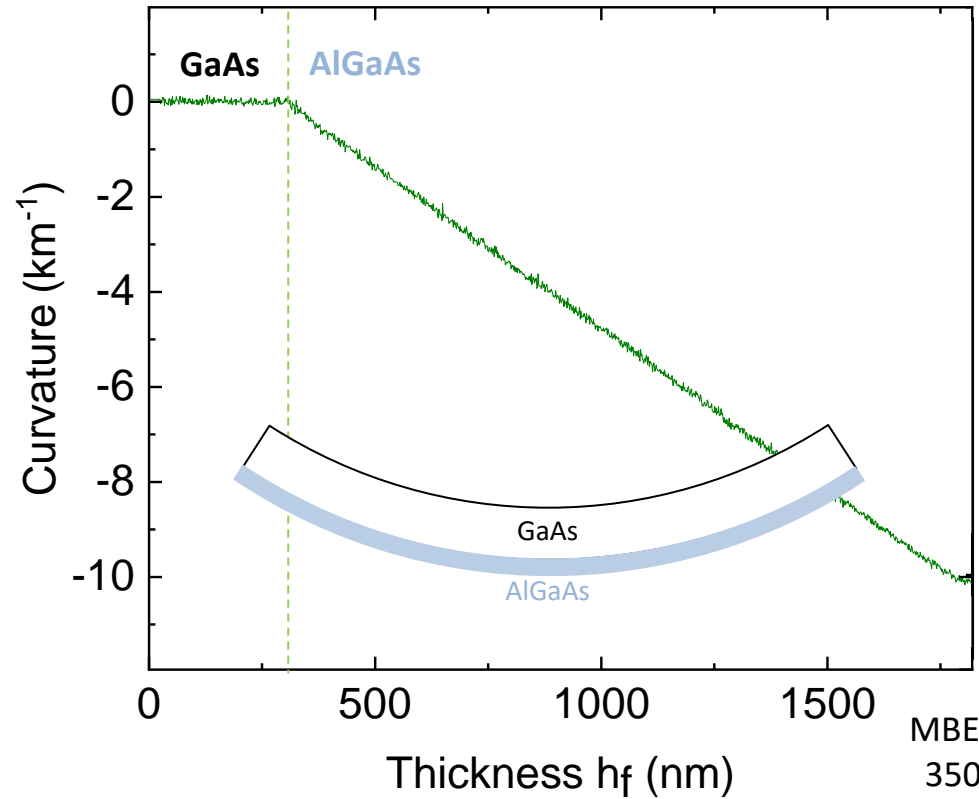
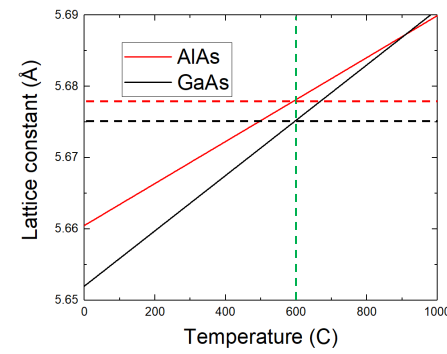
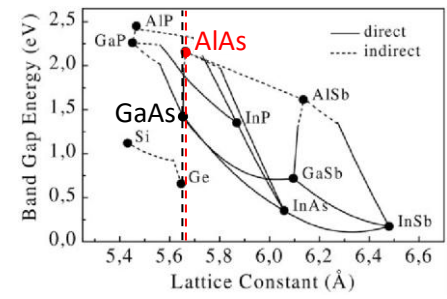
M. Ettenberg, R. J. Paff, J. Appl. Phys., 41, no.10, pp.3926-3927 (1970)



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

Curvature/Stress and MBE growth

Intrinsic stress

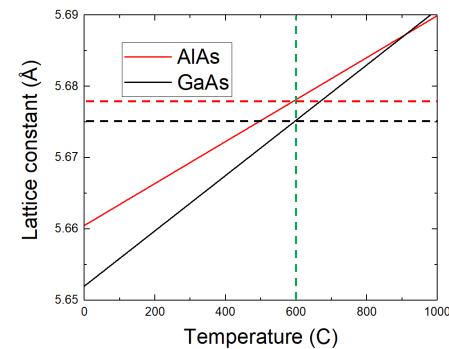
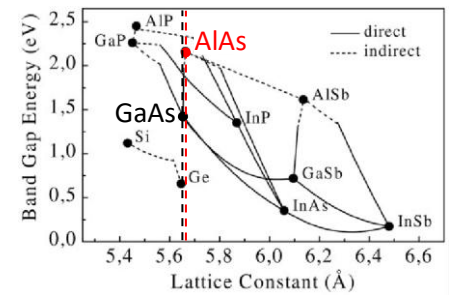


MBE growth of GaAs/AlGaAs on a rotating 350 μm -thick (001) GaAs wafer at 600°C

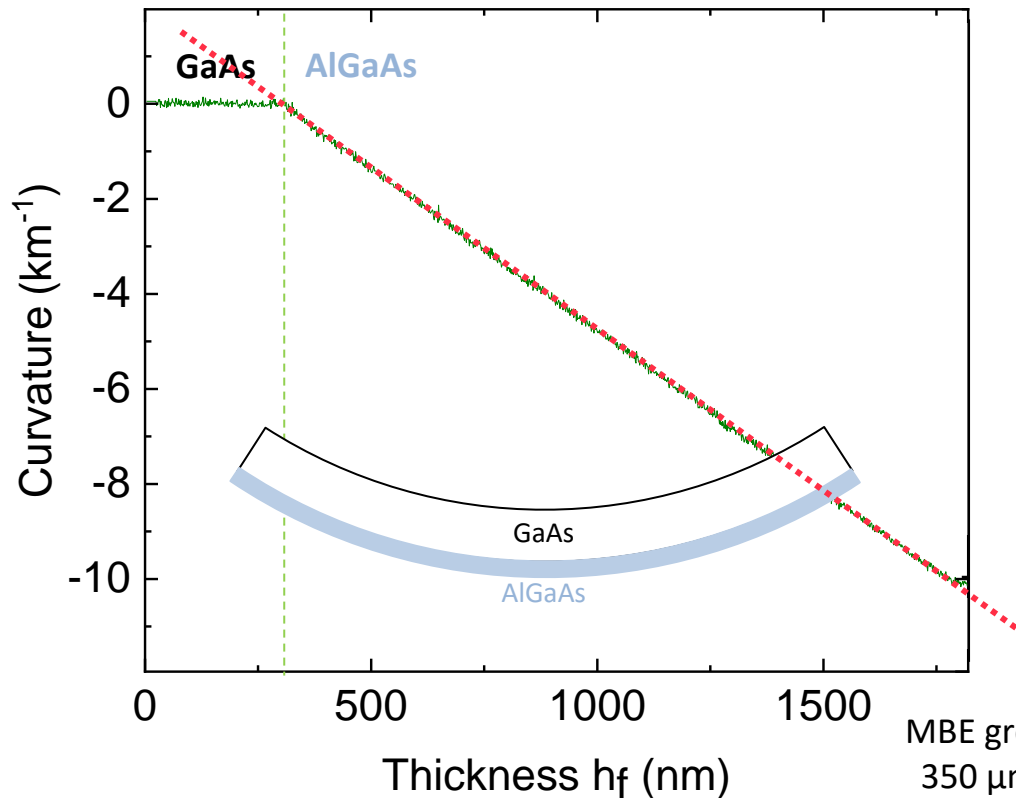
M. Ettenberg, R. J. Paff, J. Appl. Phys., 41, no.10, pp.3926-3927 (1970)

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



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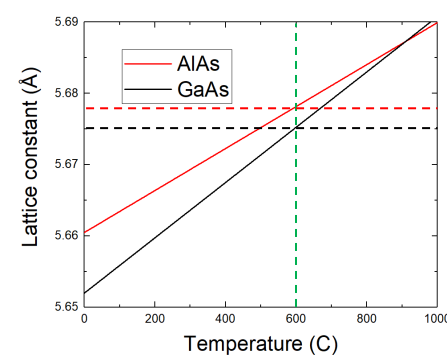
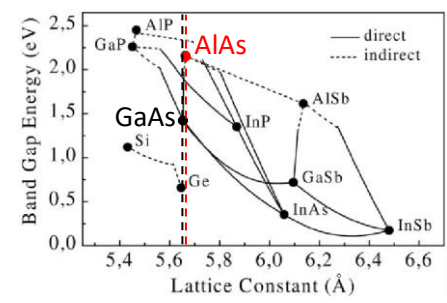
Intrinsic stress

Curvature
(m^{-1})

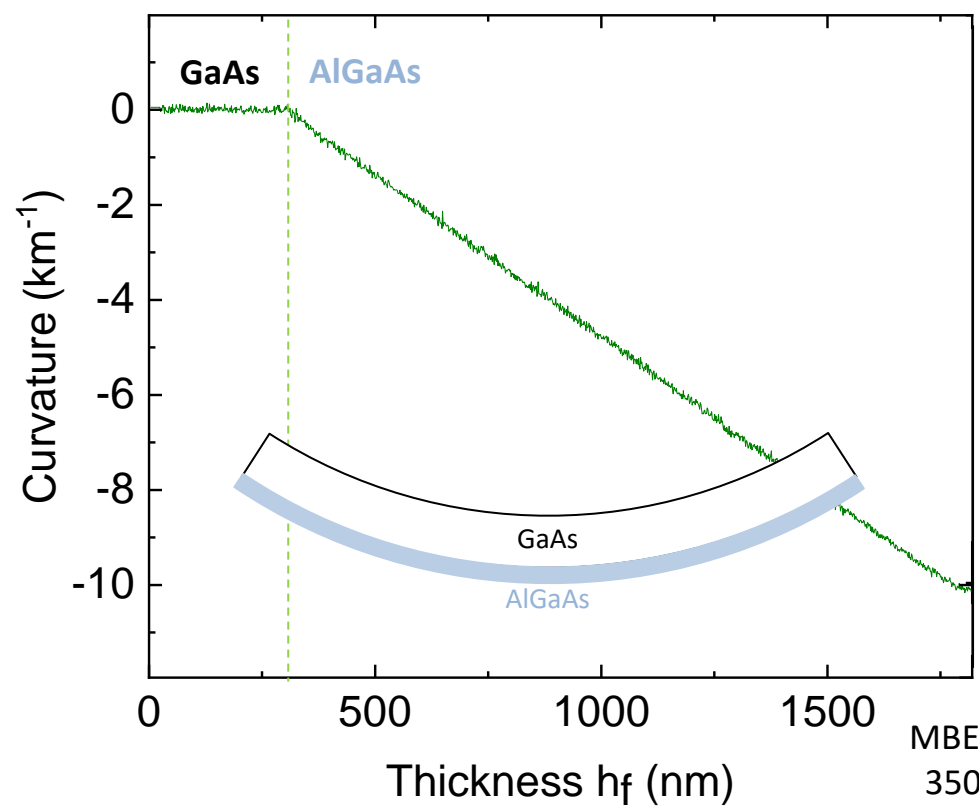
$$\kappa \cong \frac{6\overline{\sigma}_f}{M_s h_s^2} h_f$$

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

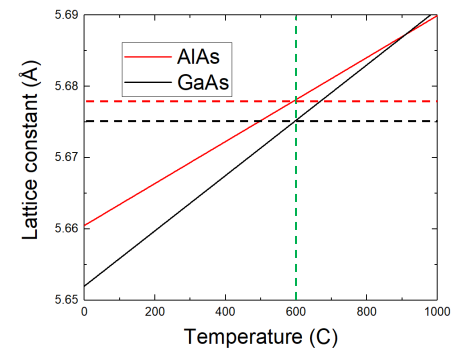
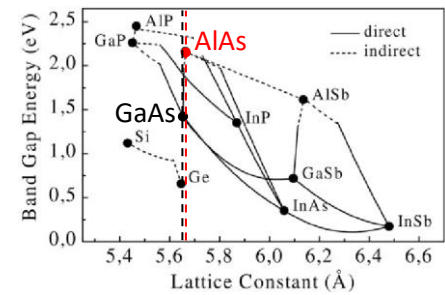
Curvature
(m⁻¹)

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

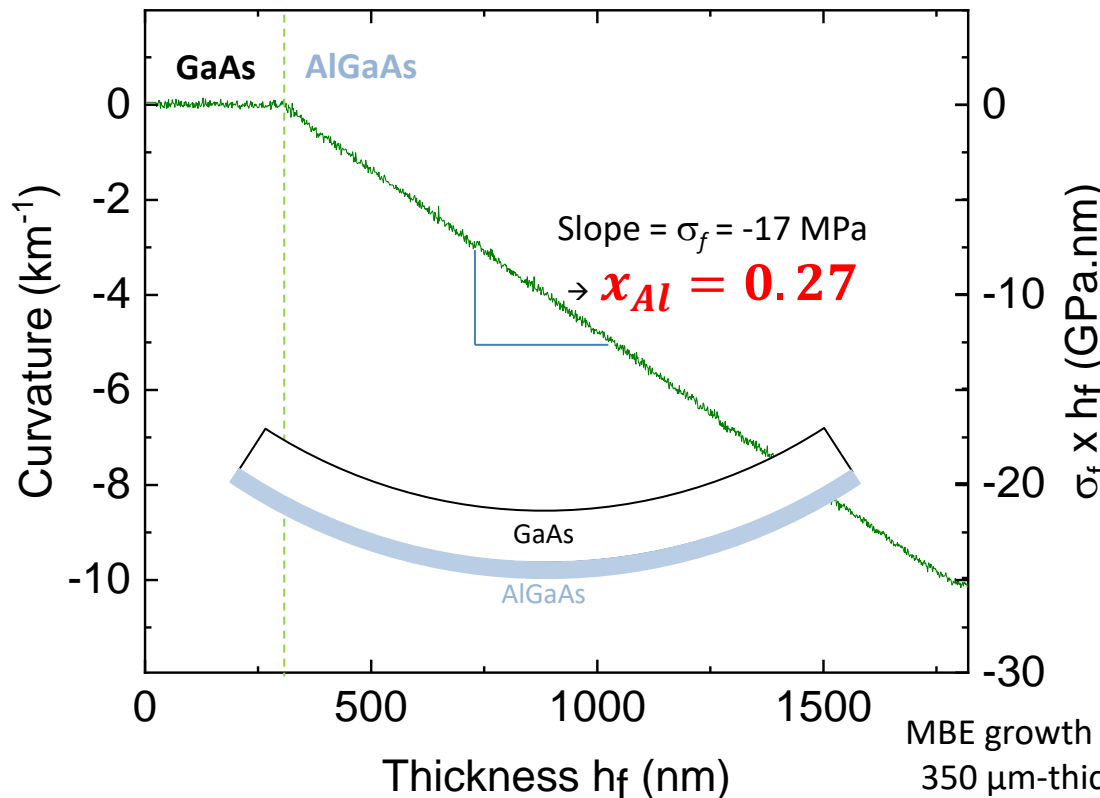
Constant for a given film on a given substrate

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

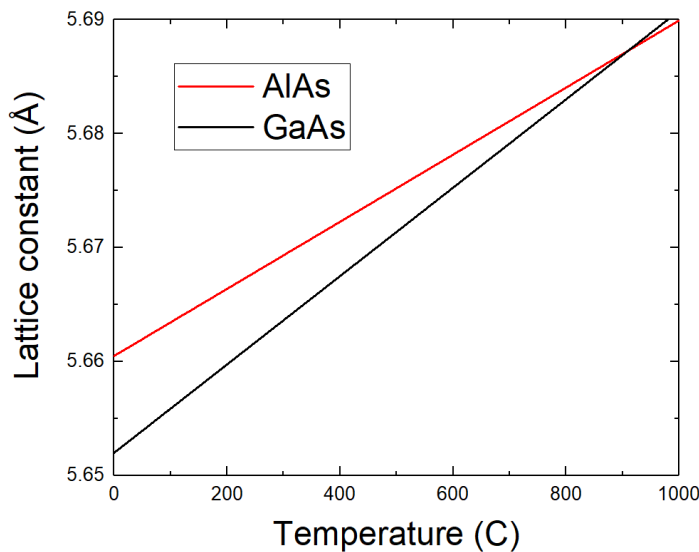
- Difference in **thermal expansion coefficients** between film and substrate



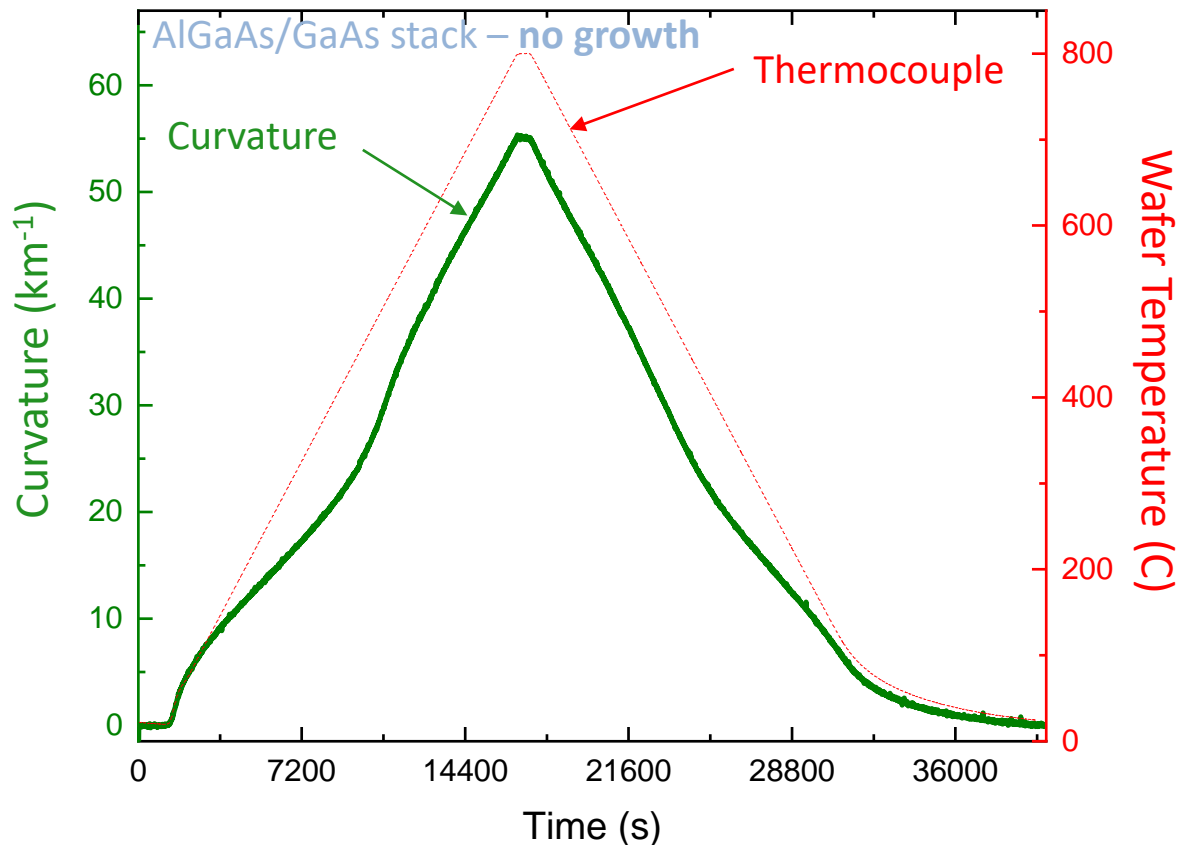
Stress/Curvature and crystal growth

Thermal stress

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



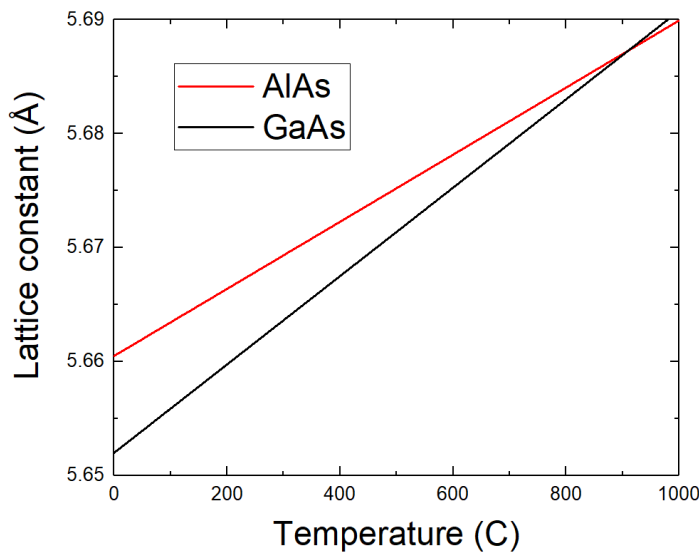
M. Ettenberg, R. J. Paff, *J. Appl. Phys.*, **41**, no.10, pp.3926-3927 (1970)



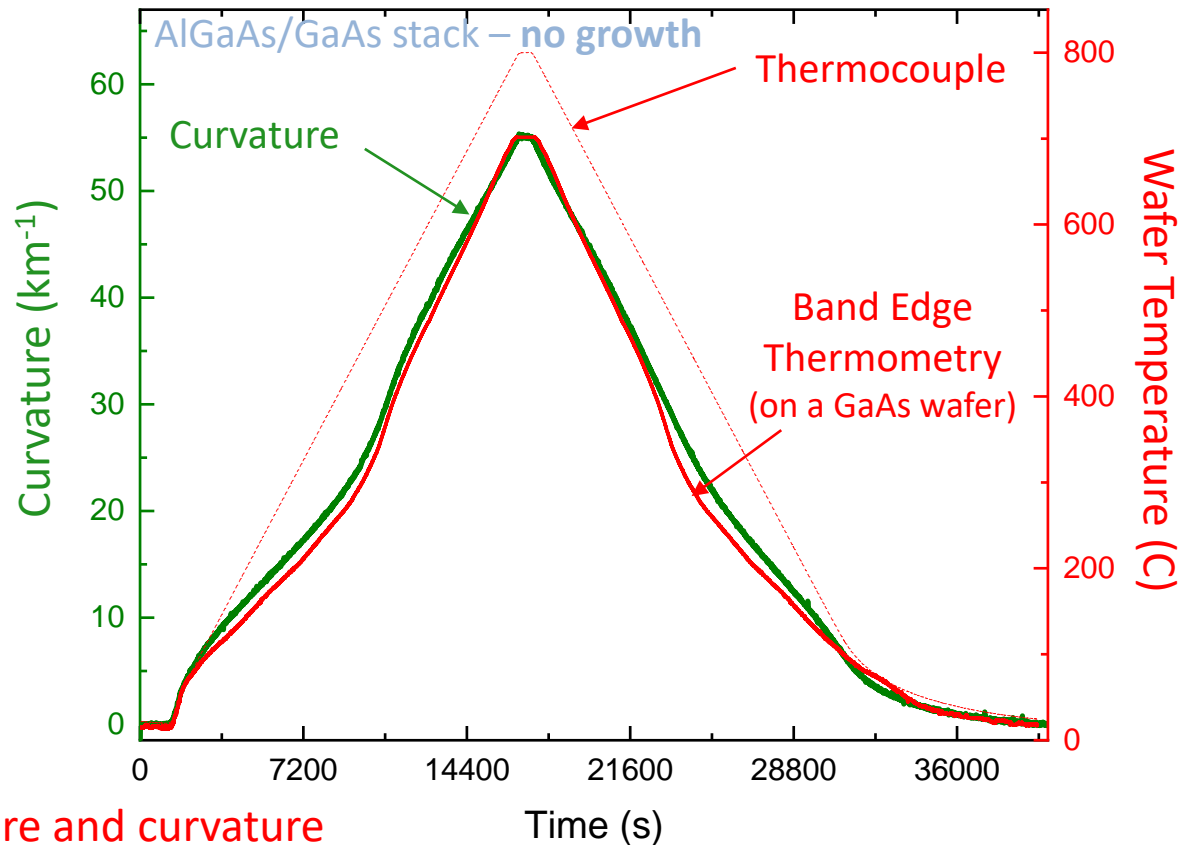
Stress/Curvature and crystal growth

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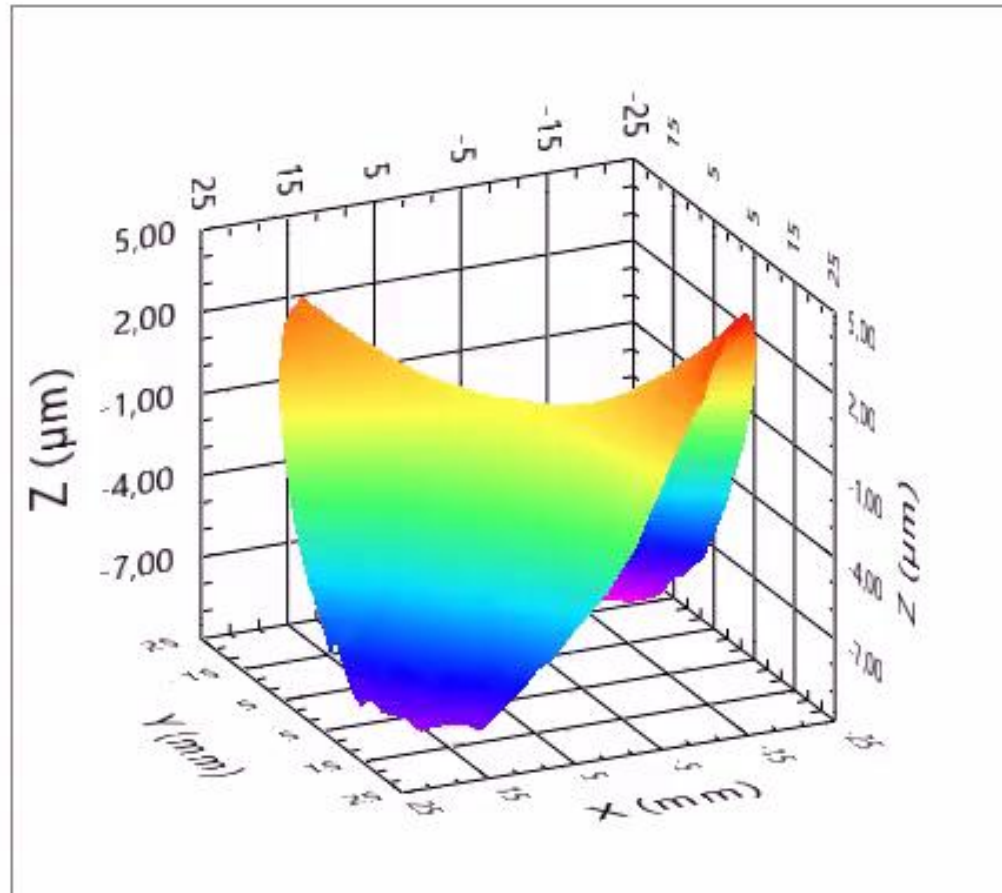


M. Ettenberg, R. J. Paff, *J. Appl. Phys.*, **41**, no.10, pp.3926-3927 (1970)



➡ 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

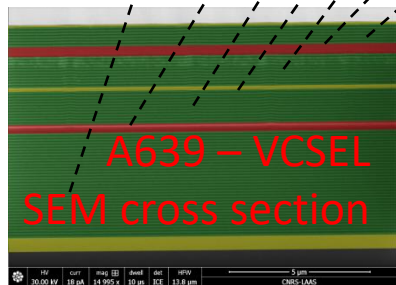
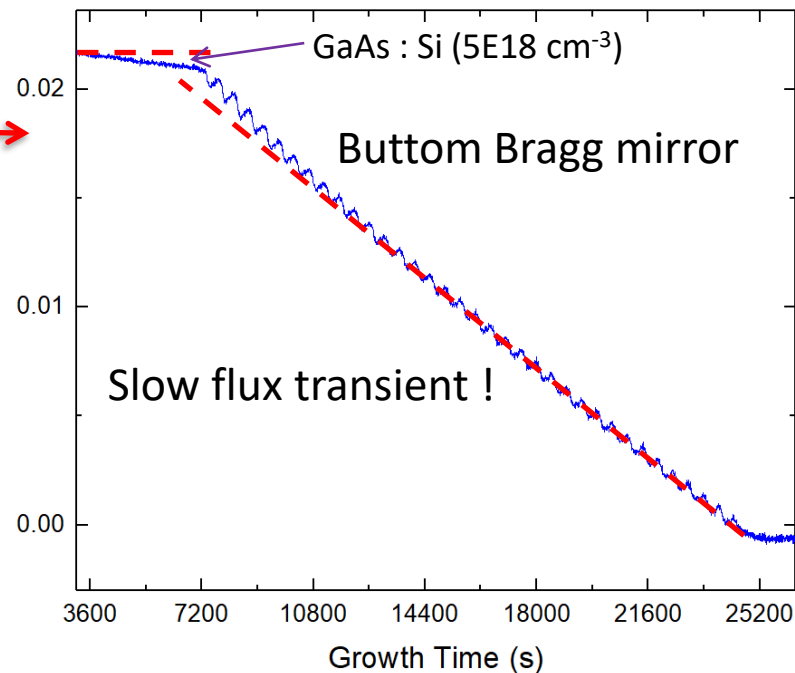
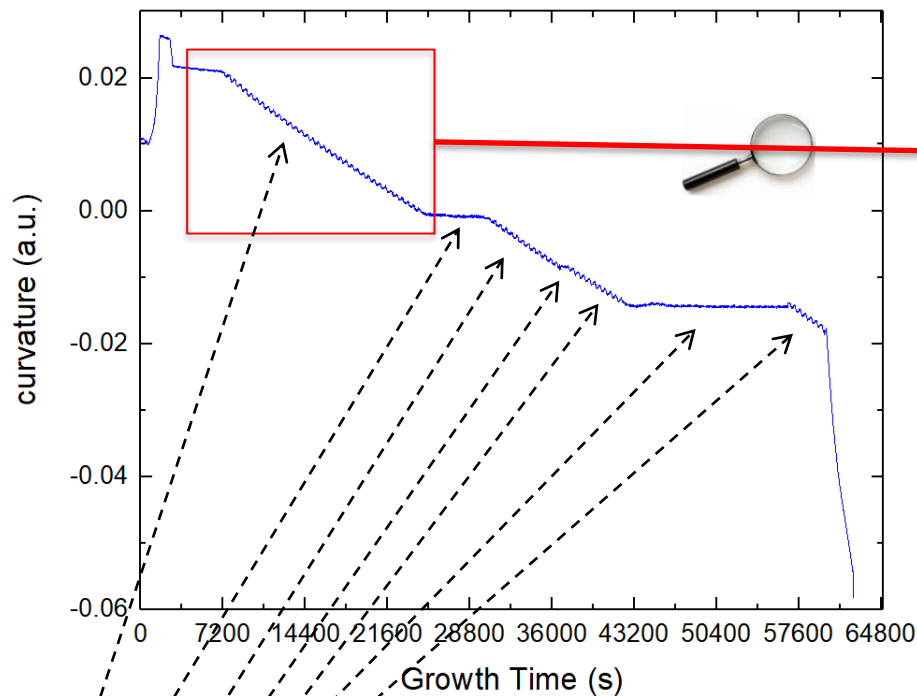
Because **substrate is rotating**, it is possible to measure the curvature in any direction, and to get a clear view of its shape **in live**

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



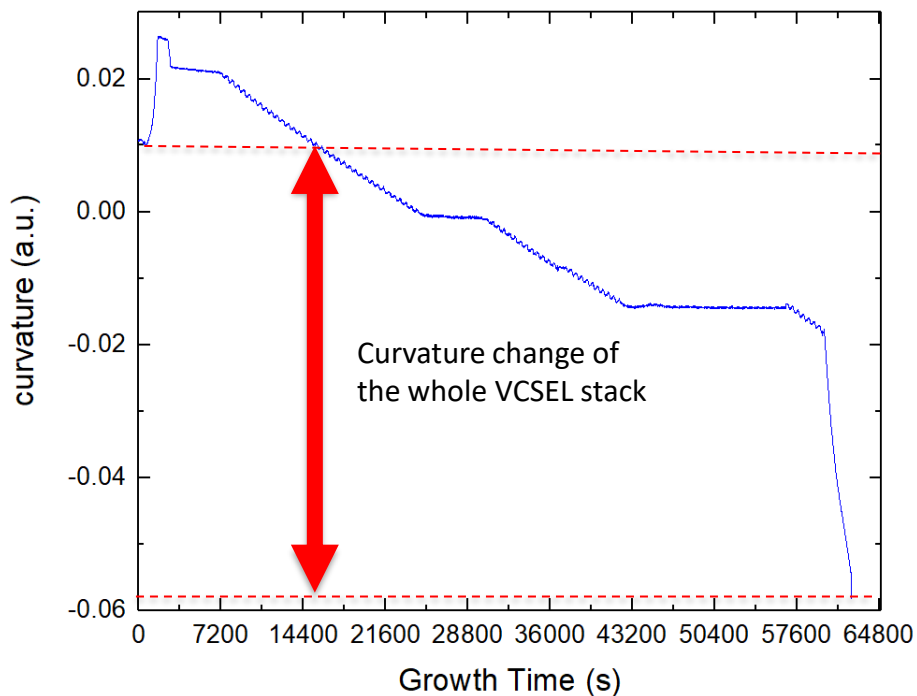
Low strain GaAs/AlGaAs system ($\Delta a/a = 0.046\%$ at 600°C)

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

Possibility to correct the deviations on parameters

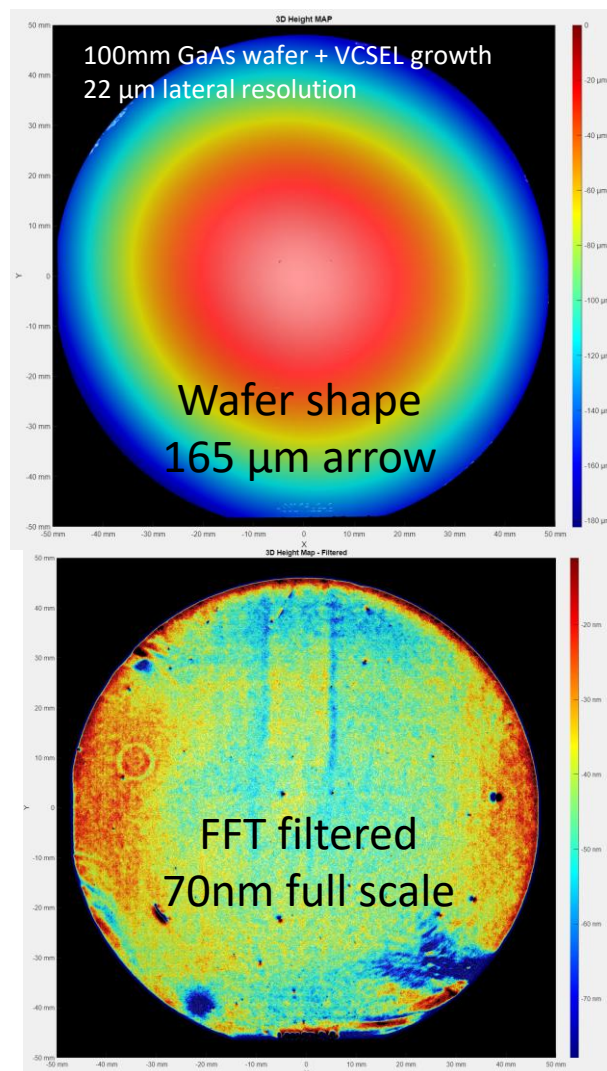
Ex-situ characterization of full wafer shape

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

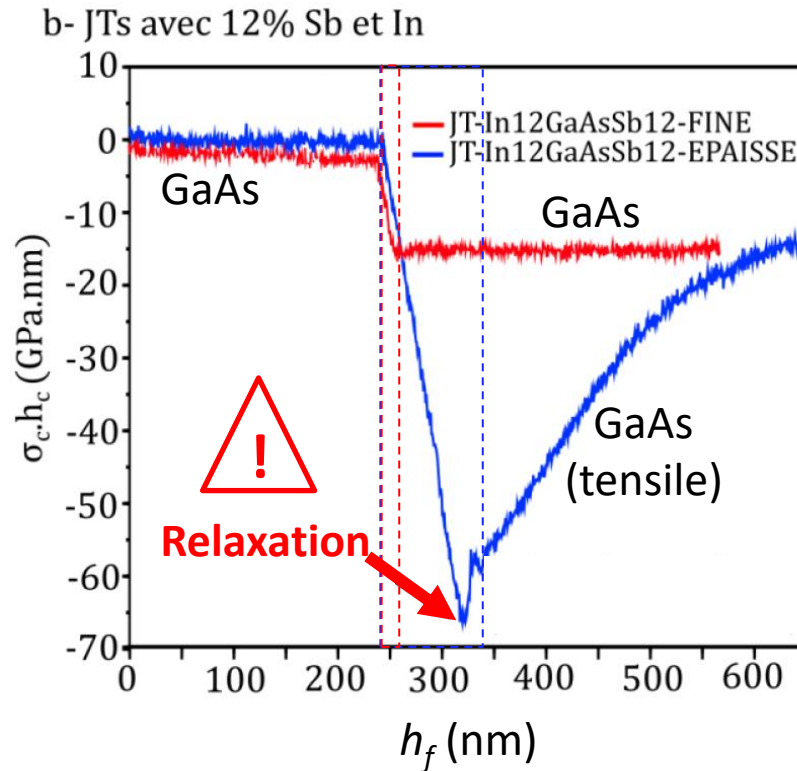
See www.dip-view.com

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

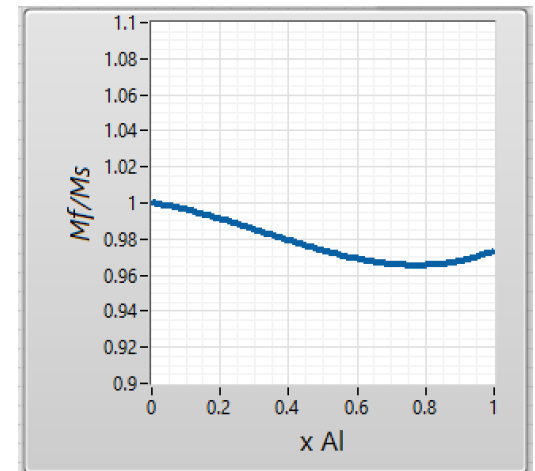
Avec $M = \frac{E}{1 - \nu}$

Poisson coefficient

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

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

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



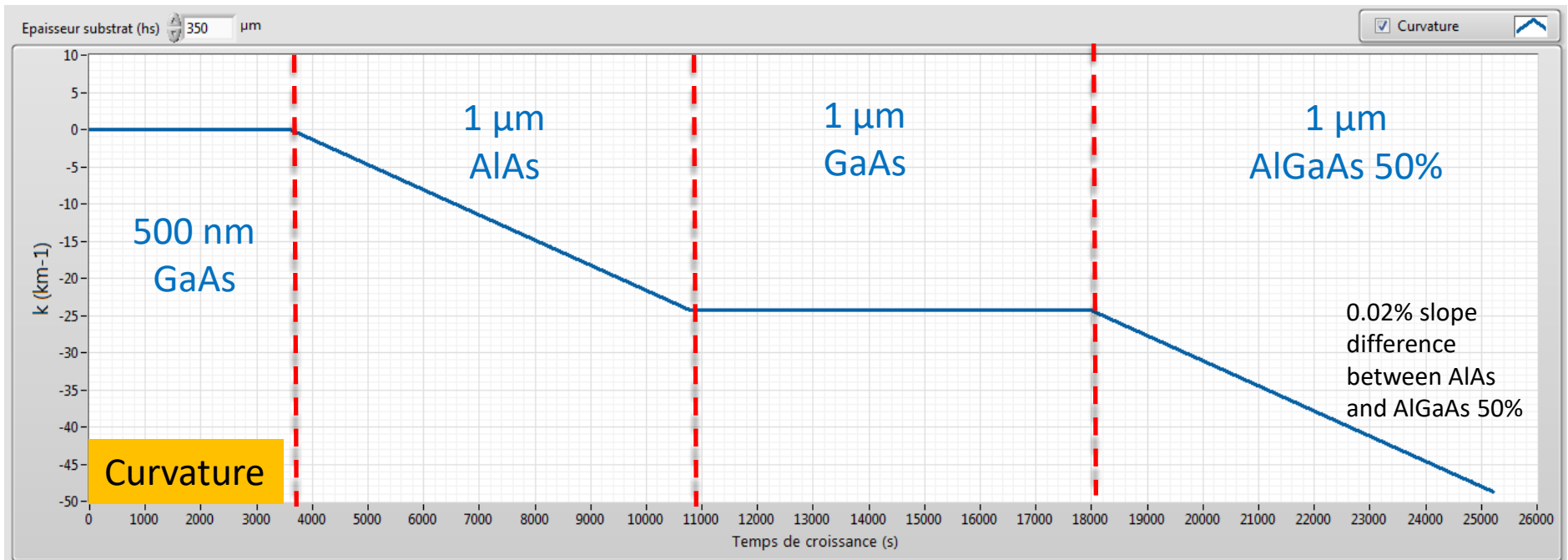
Compositional dependence of the elastic constants and the lattice parameter of AlGaAs
Gehristz et al.
PRB 60 (16), 1999

Growth rate: Curvature

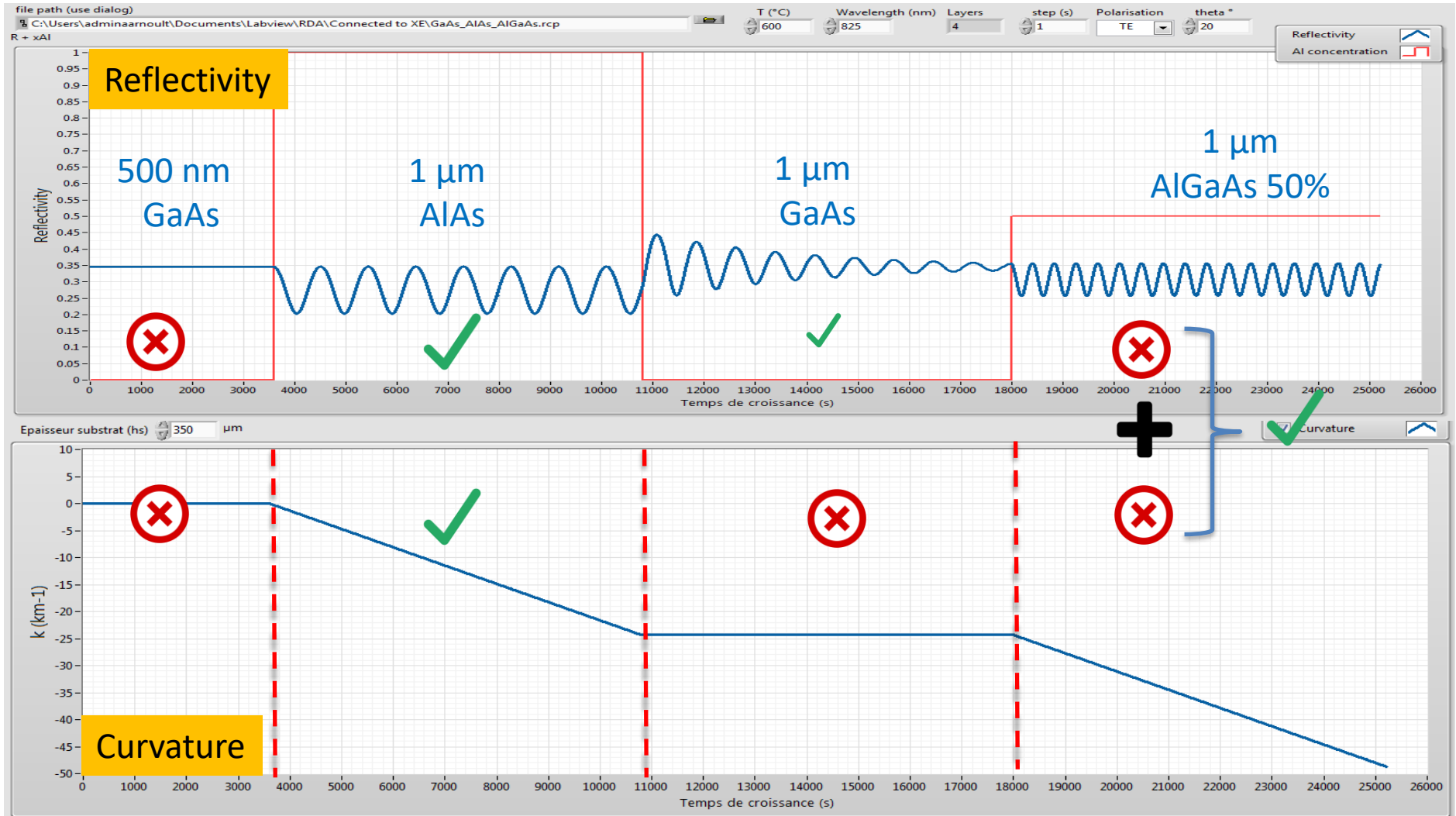
$$k \approx -\frac{6h_{AlGaAs}}{h_s^2} \times x \times \frac{a_{AlAs}(T) - a_{GaAs}(T)}{a_{GaAs}(T)}$$

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

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



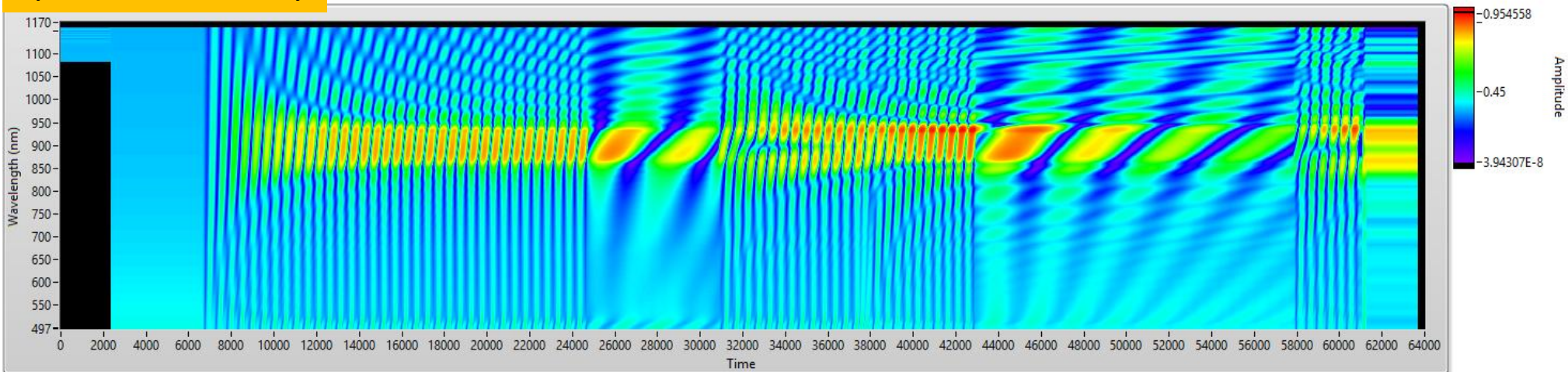
Reflectivity – Curvature complementarity



Complementarity and time scales

Complementarity and time scales

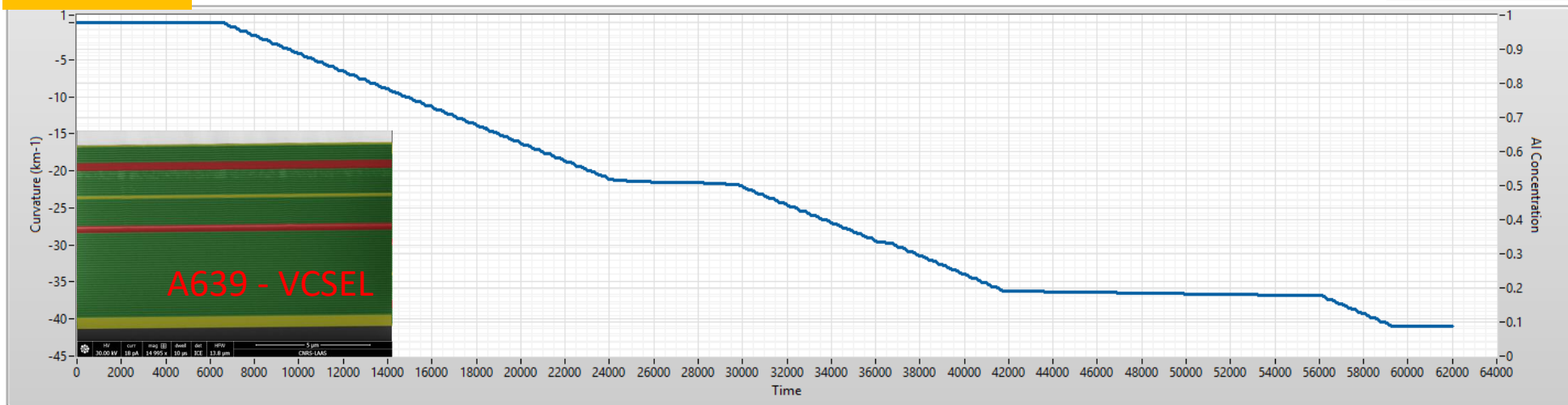
Spectral reflectivity



Curvature

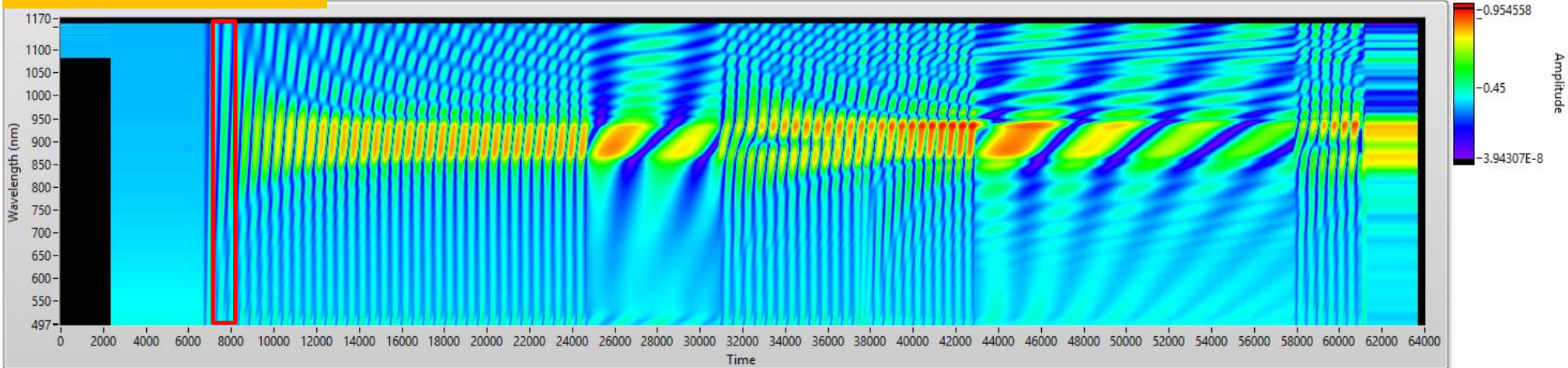
20H

Curvature
 AI Concentration



Complementarity and time scales

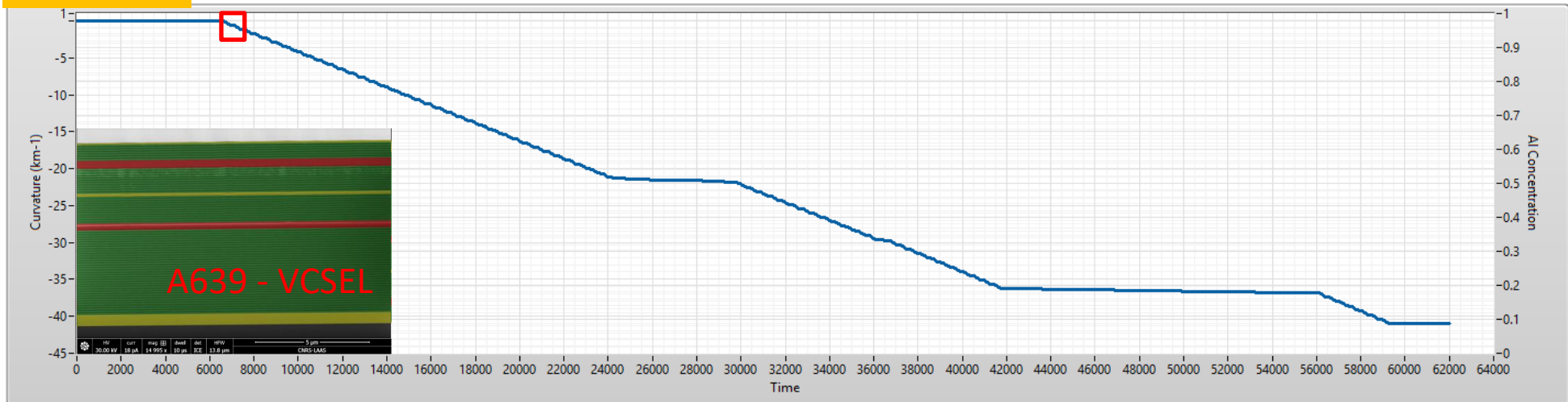
Spectral reflectivity



Curvature

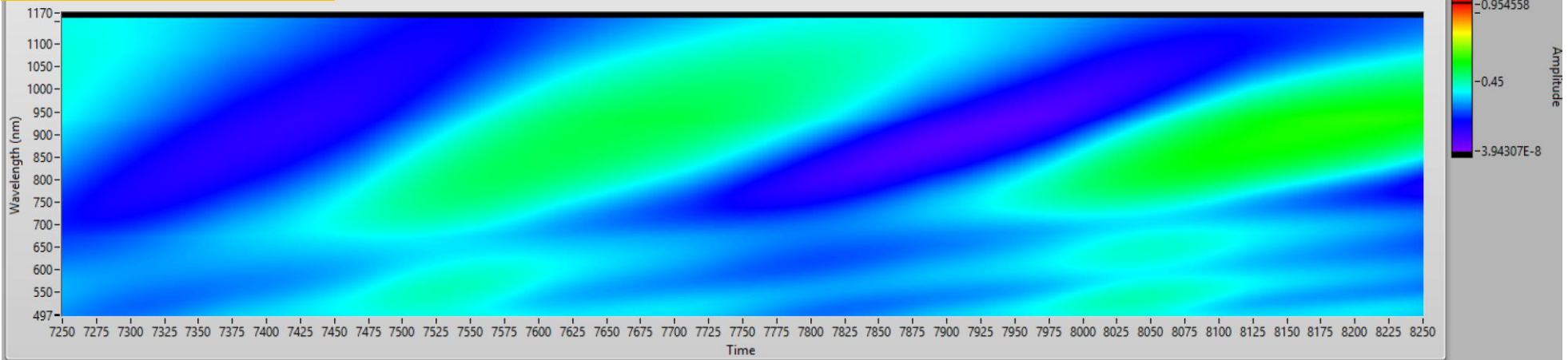
20H

- Curvature
- AI Concentration



Complementarity and time scales

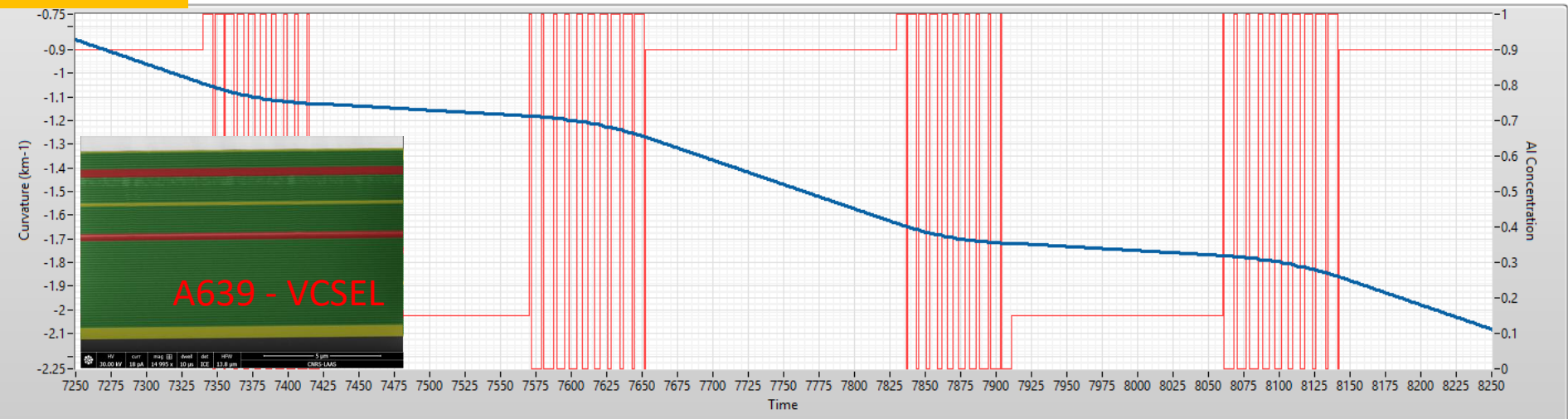
Spectral reflectivity



Curvature

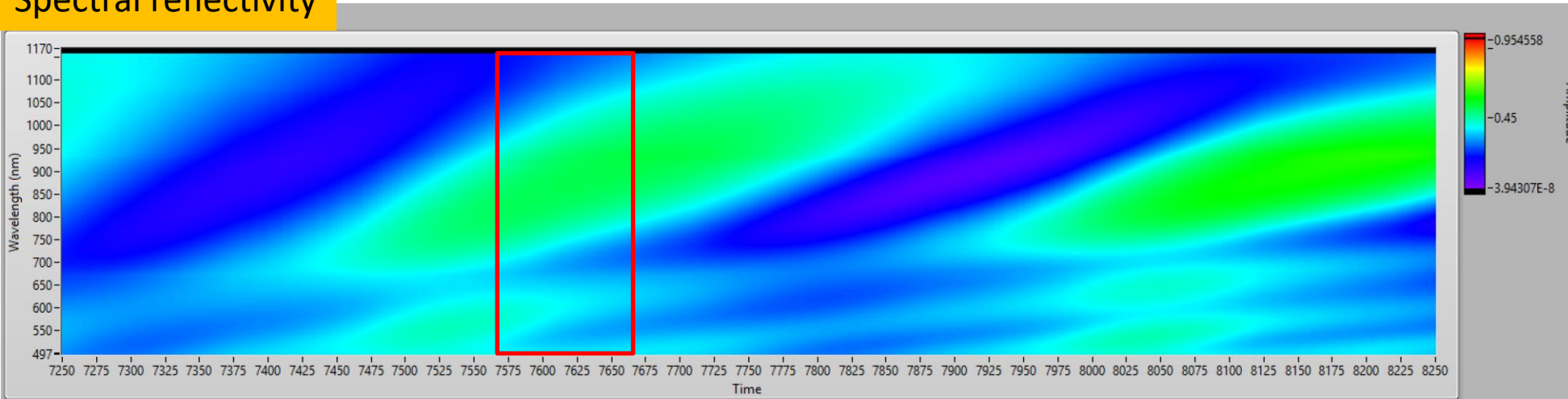
16:40

- Curvature
- AI Concentration



Complementarity and time scales

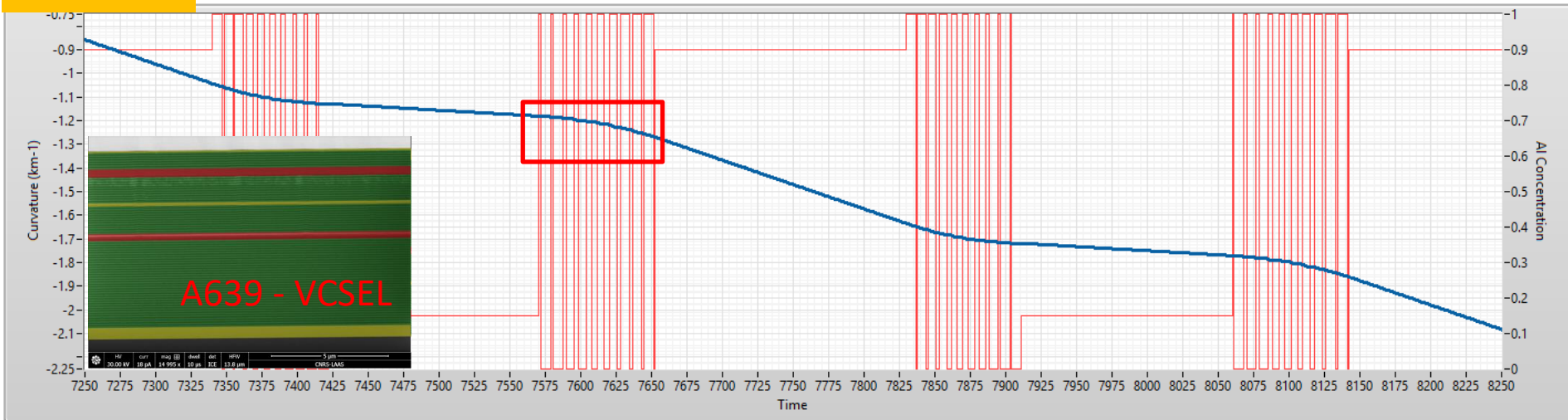
Spectral reflectivity



Curvature

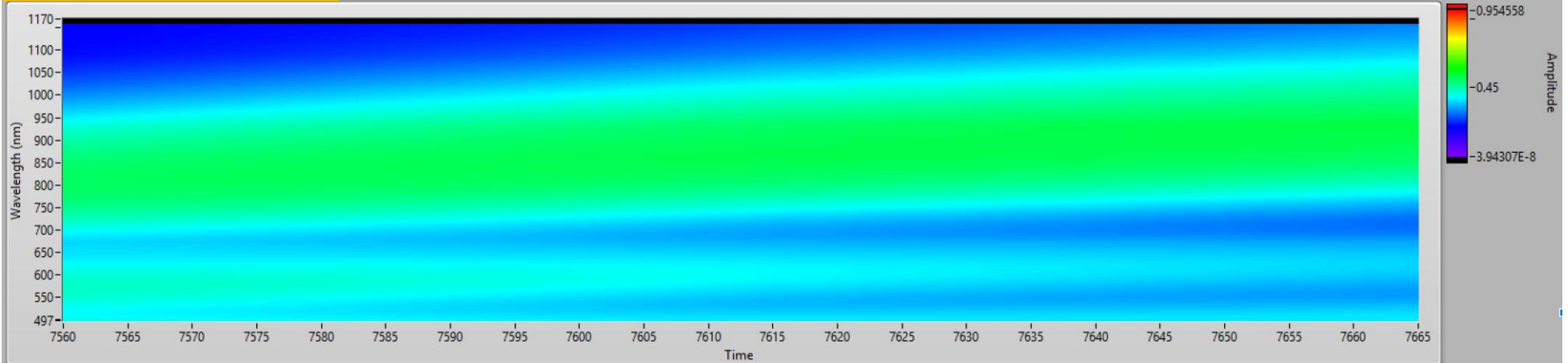
16:40

- Curvature
- AI Concentration



Complementarity and time scales

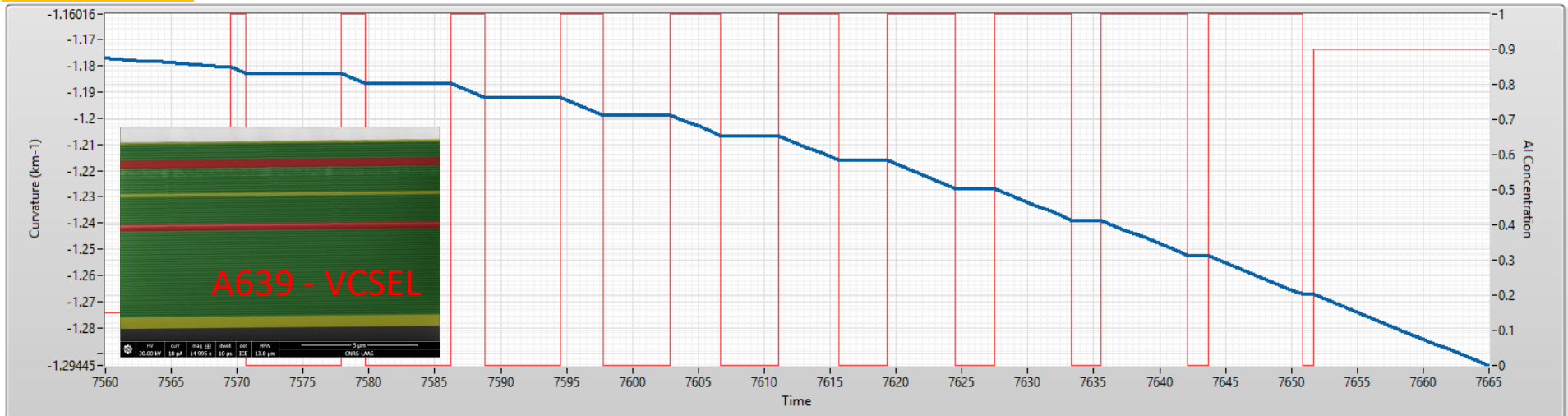
Spectral reflectivity



Curvature

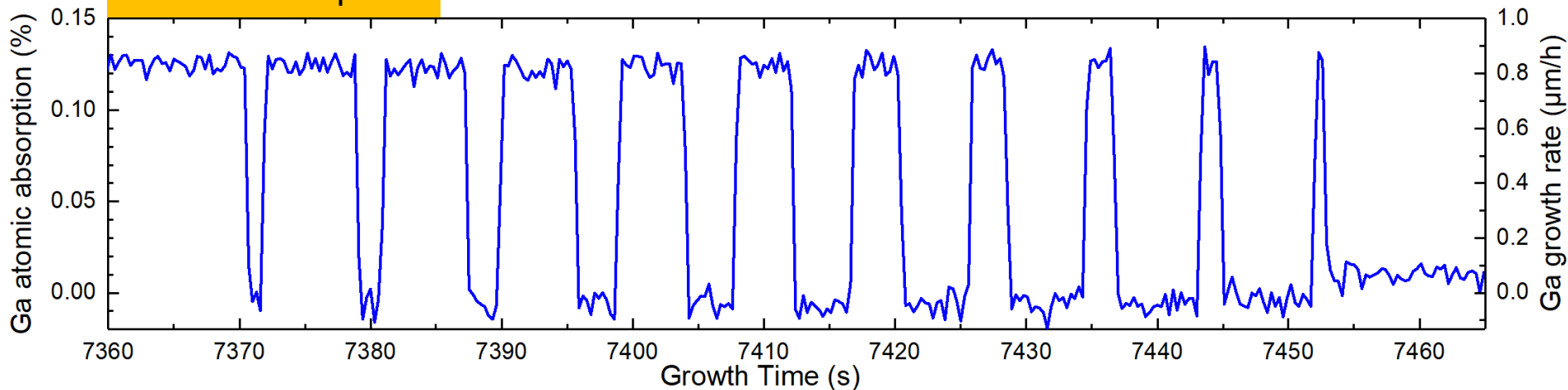
1:45

- Curvature
- AI Concentration



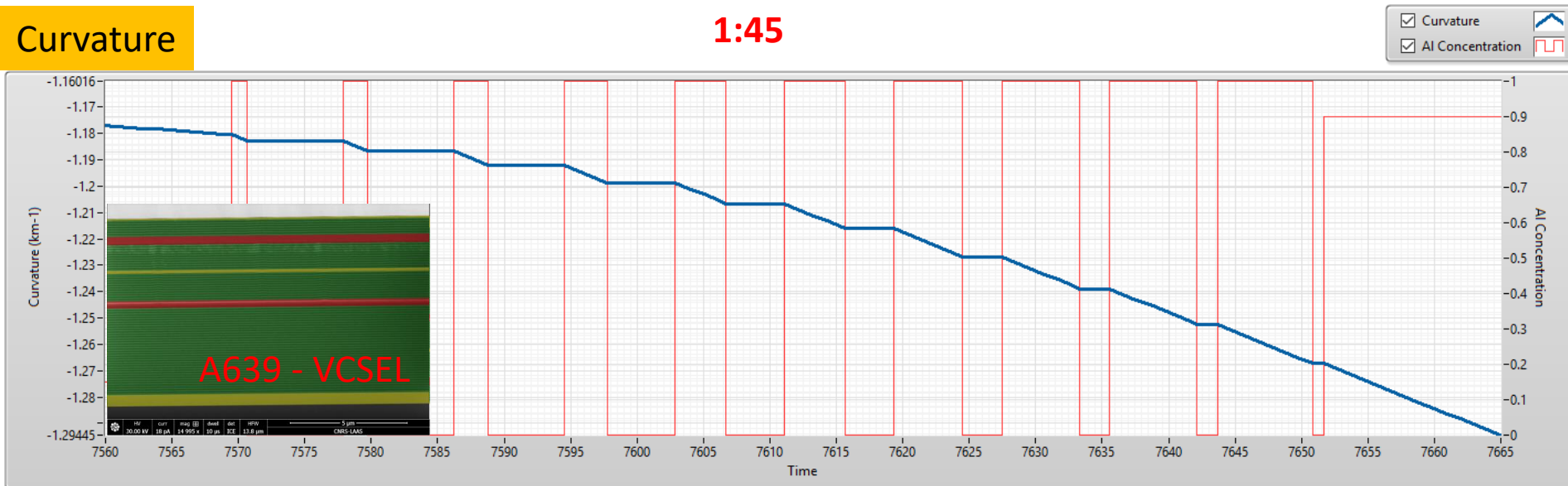
Complementarity and time scales

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	+	+++

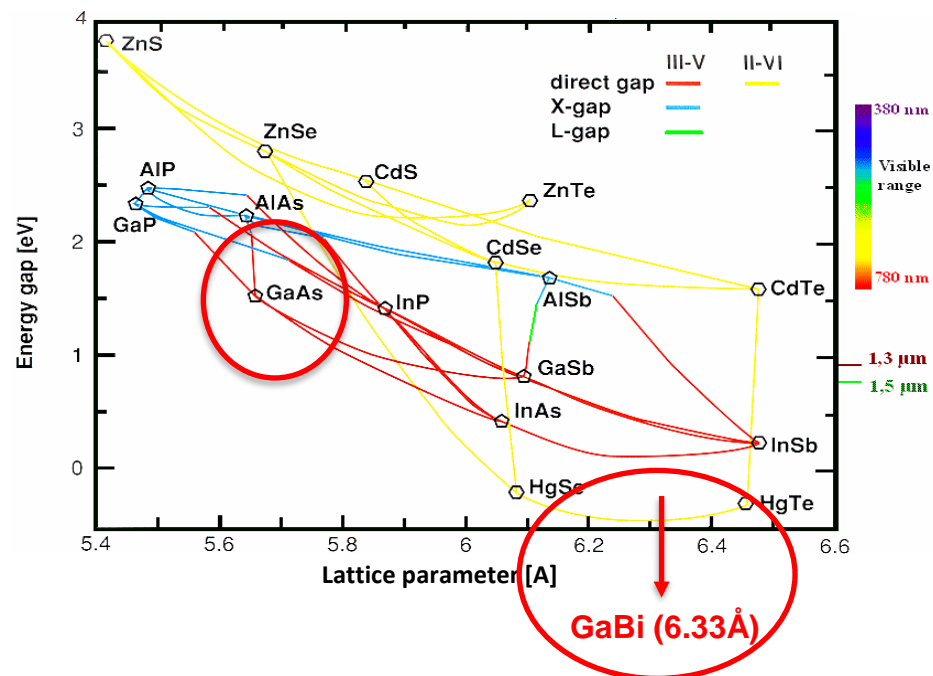
The case of GaAsBi growth

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: $\frac{\Delta a}{a} = 12\%$

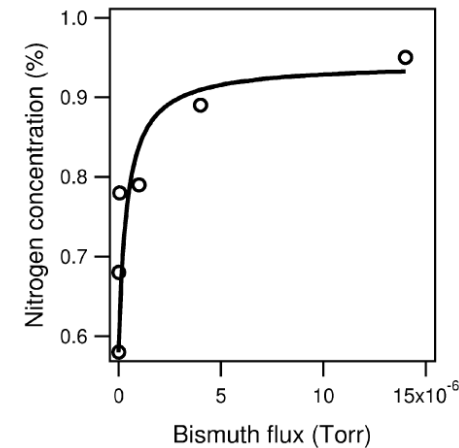
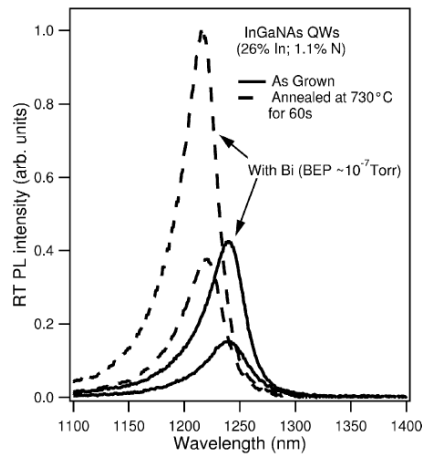
Bi incorporation in GaAs

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

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

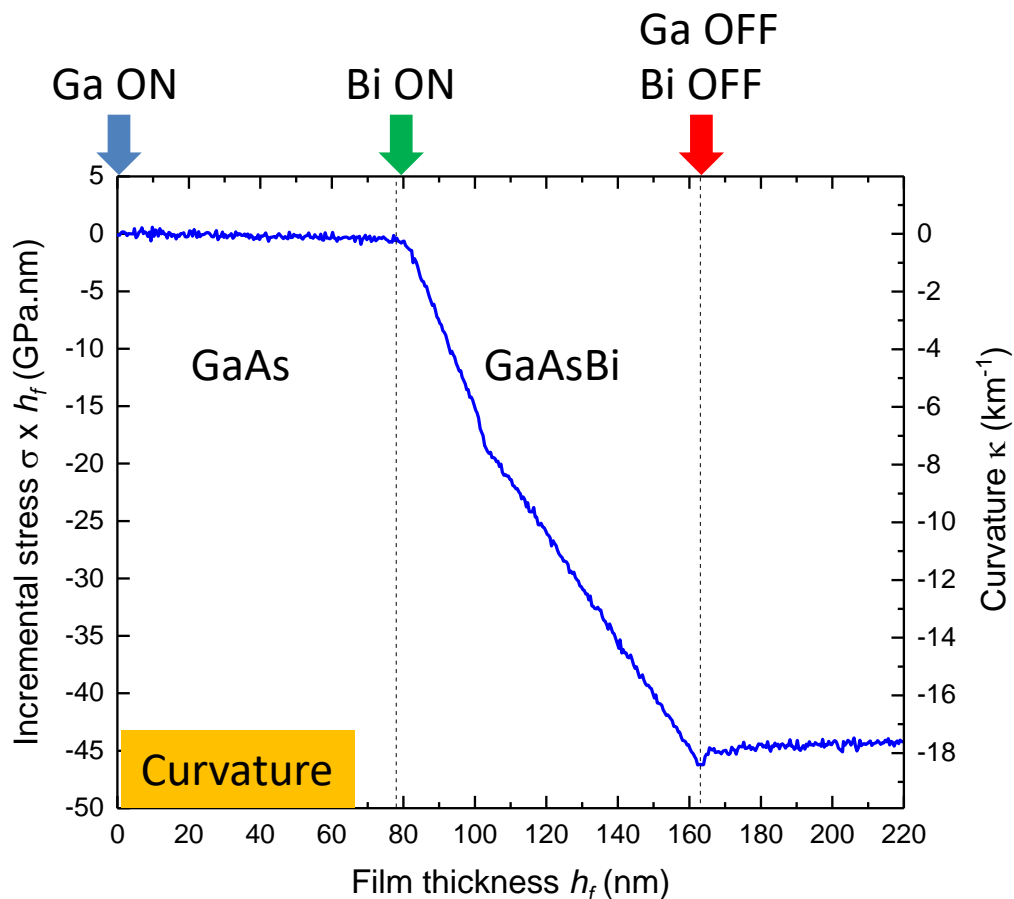
Any small changes in these conditions induce high difference in Bi composition, and different electrical, optical and mechanical properties of the alloy

→ Above 400°C : Bi acts as a surfactant



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

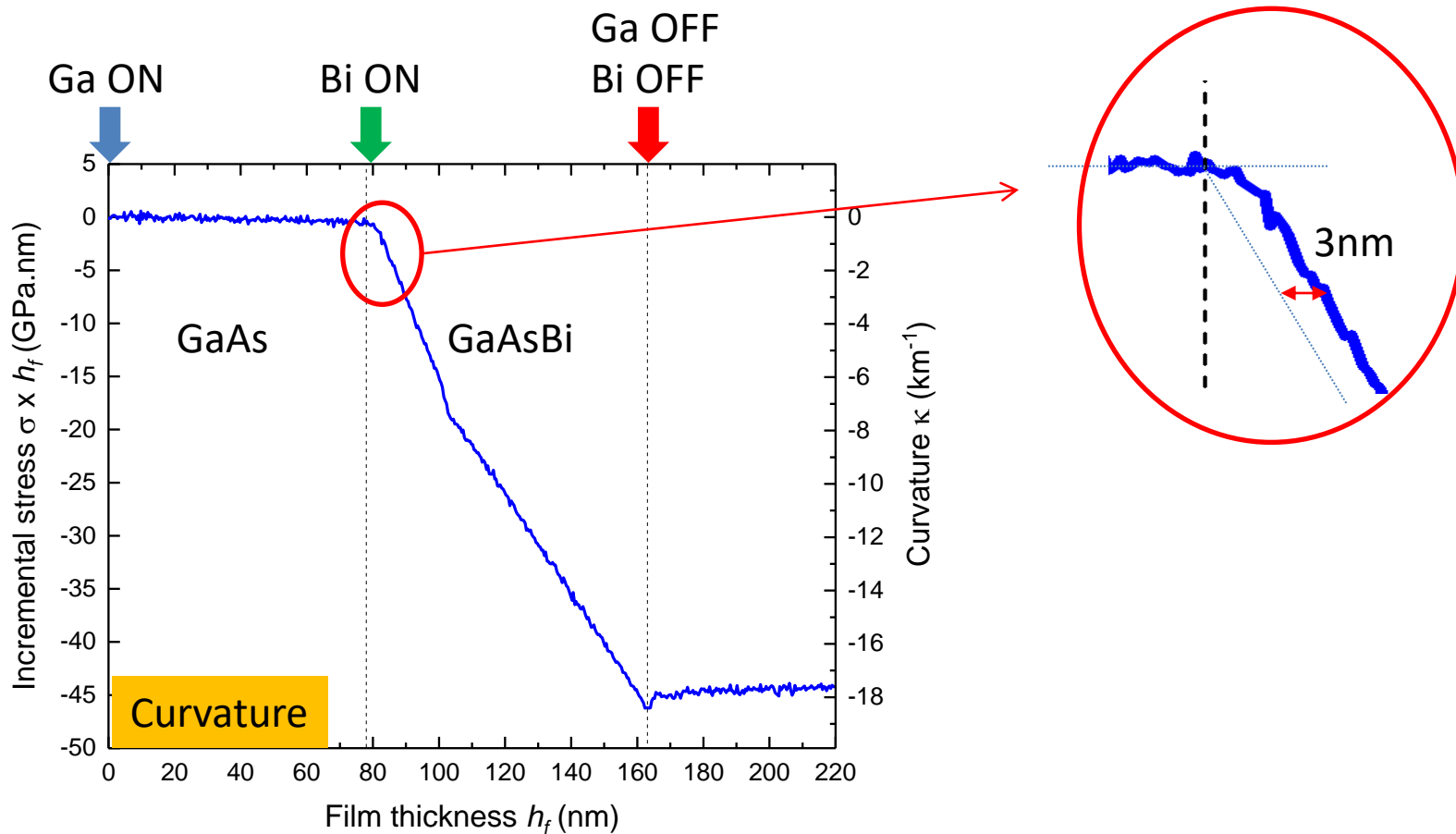
Curvature and GaAsBi Growth



- 350 μ m 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

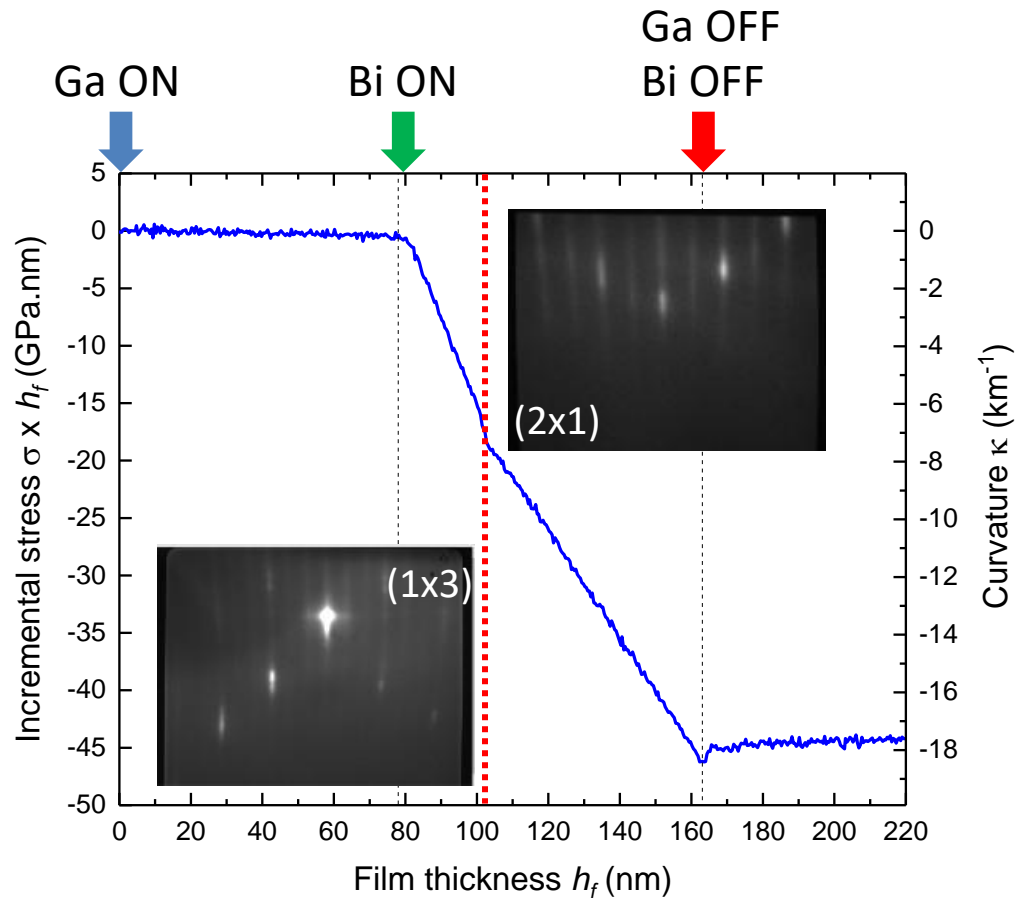
→ Some peculiar events during the growth

Curvature for GaAsBi Growth



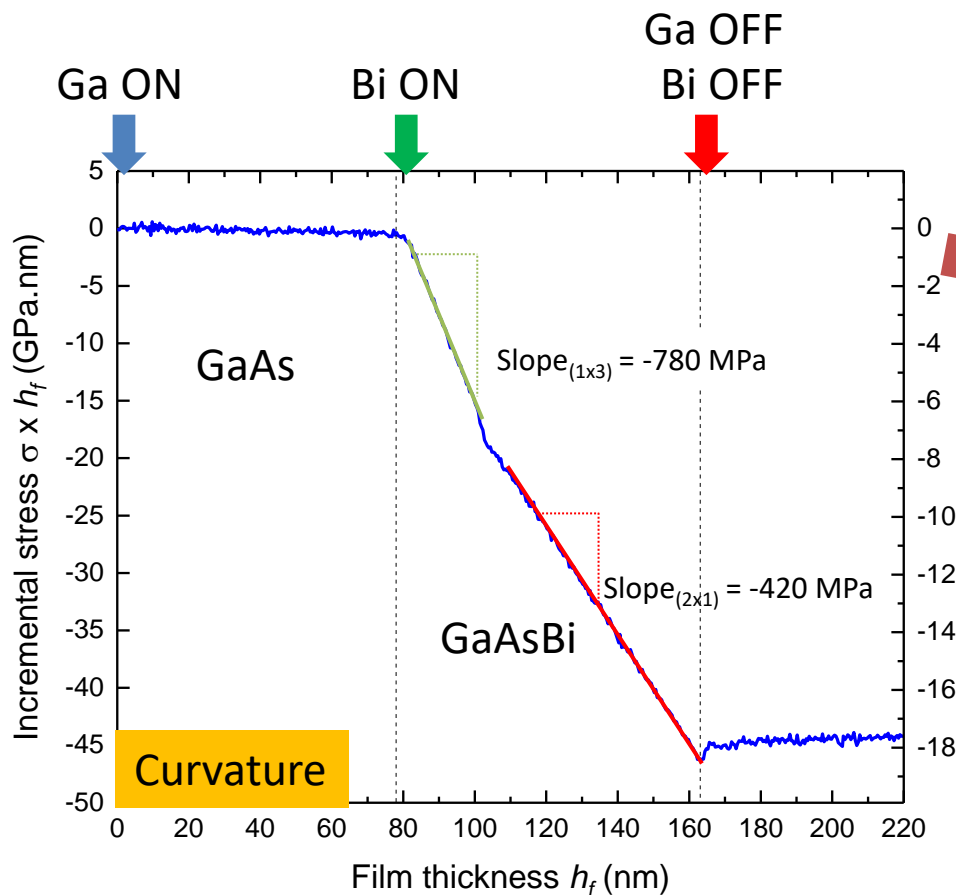
→ First nm: very low stress and incorporation (Bi segregation)

Curvature for GaAsBi Growth

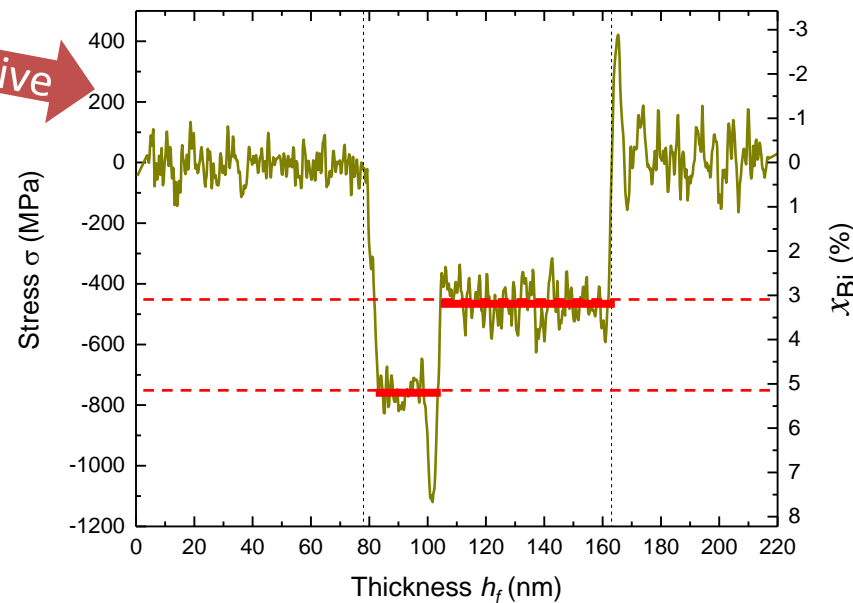


→ Change of surface reconstruction during GaAsBi layer

Curvature for GaAsBi Growth

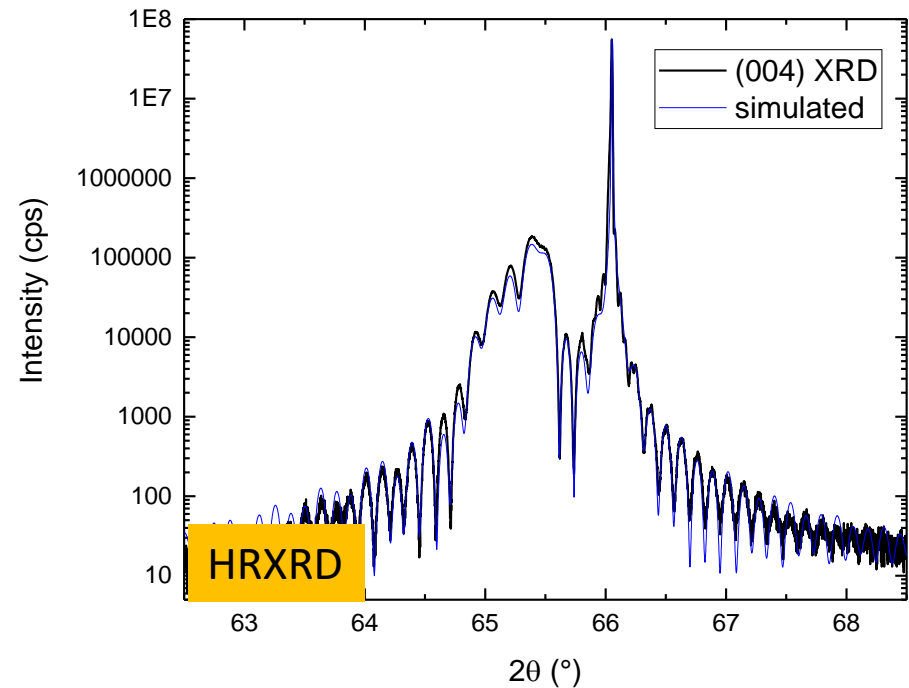
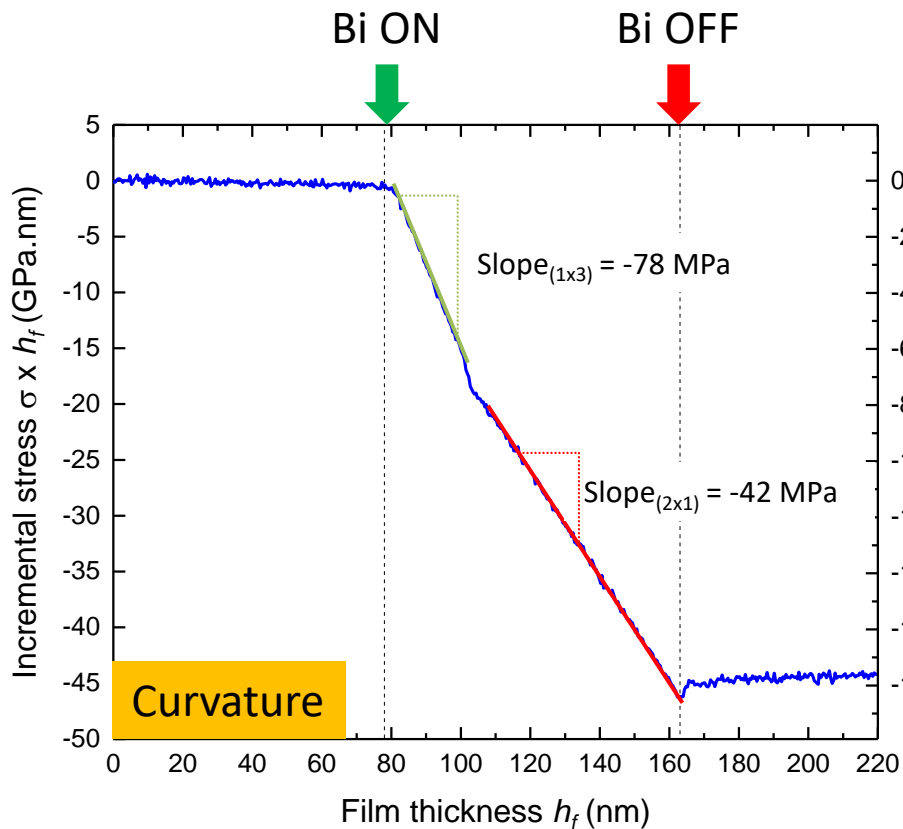


→ Observation of stress variation during growth



Constant growth parameters, two-step incorporation

Curvature for GaAsBi Growth

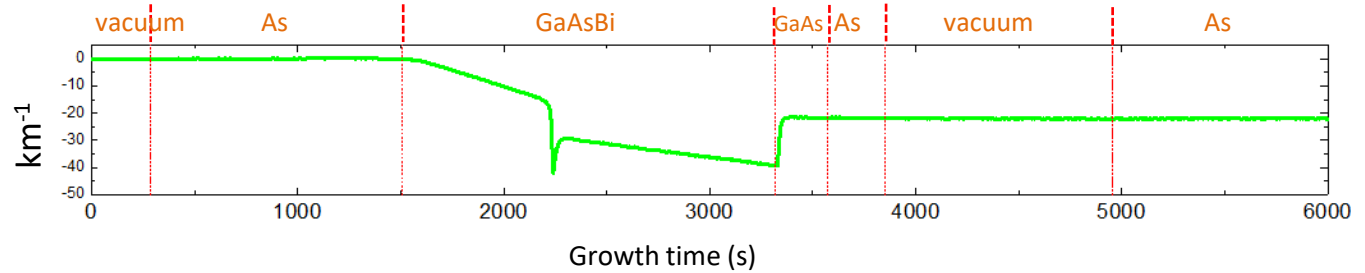


Material	Curvature		XRD	
	h_f (nm)	% Bi	h_f (nm)	% Bi
GaAsBi _(2x1)	60.5	2.9	57.3	3.6
GaAsBi _(1x3)	24.5	5.3	24.7	5.3
Substrate				

→ **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**



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

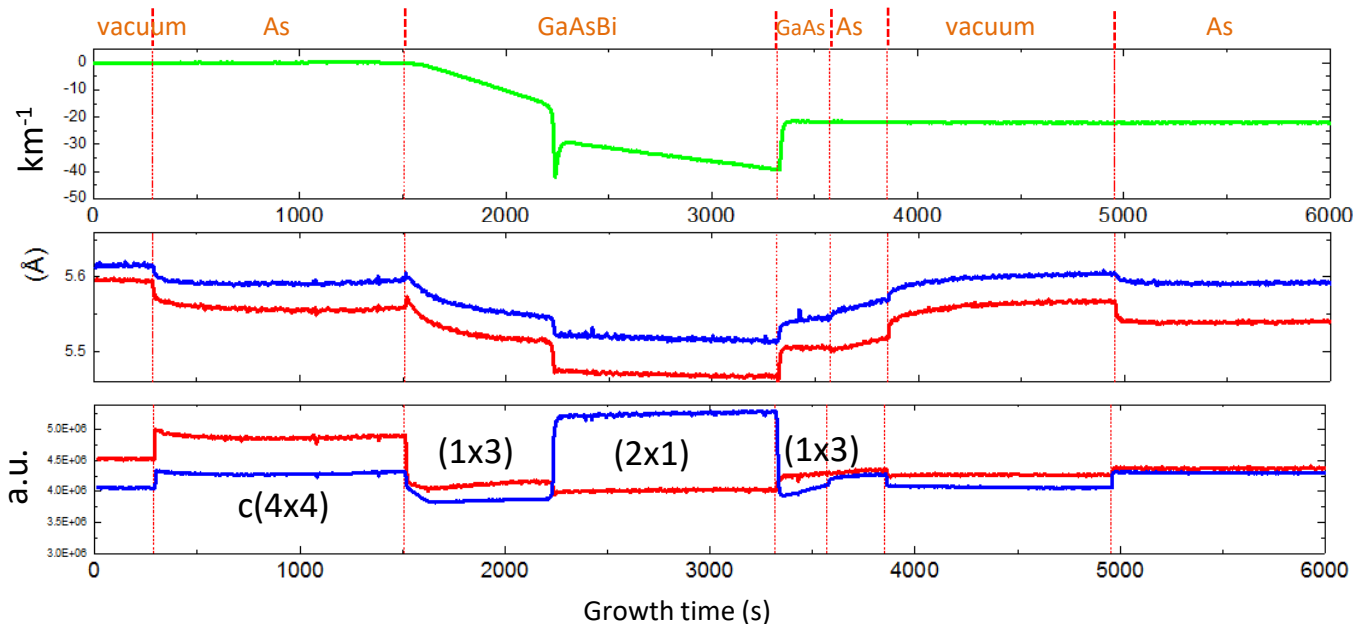
resolution x5.4!

Better understanding : coupling of in-situ techniques

Curvature

RHEED : $a_{//}$

RHEED : intensity



Better understanding : coupling of in-situ techniques

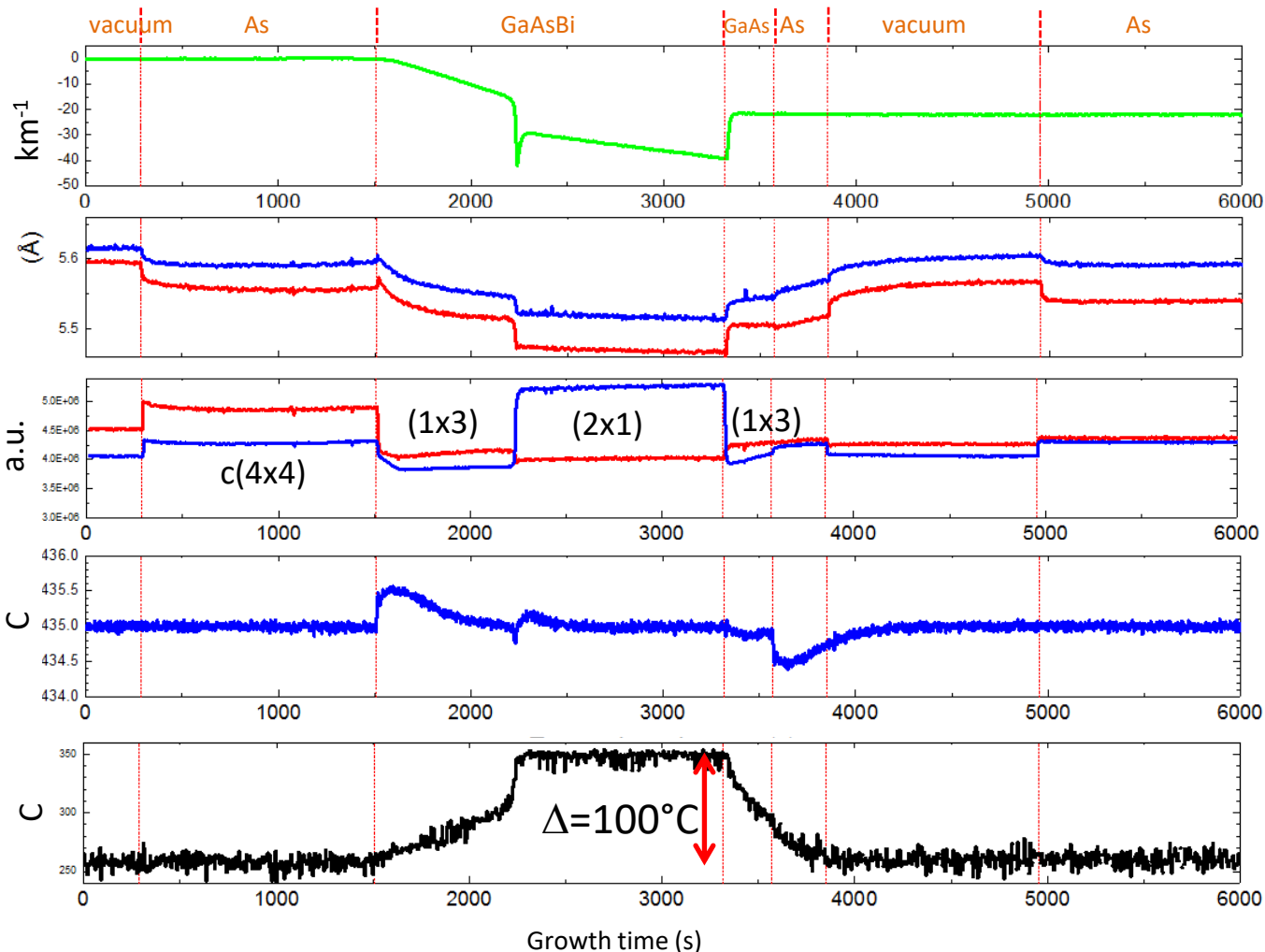
Curvature

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!

