

# Oxidation of III-V semiconductors and applications

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A. Monmayrant, H. Camon et G. Almuneau

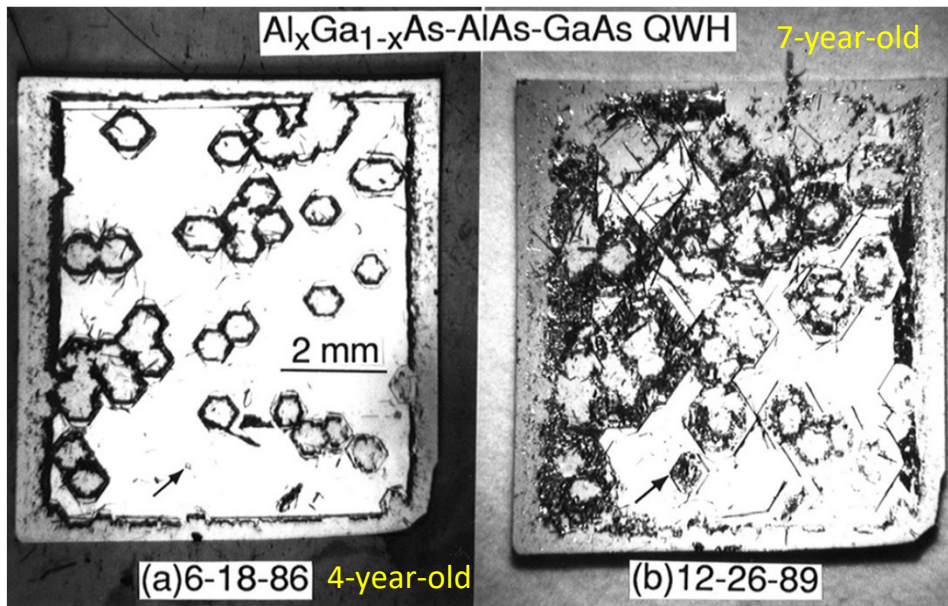
GDR Oxyfun – 14/03/2023

- Al-III-V-semiconductor oxidation
  - History
  - Applications
- Contributions from LAAS
  - In-situ monitoring
  - Oxidation Anisotropy
- Conclusions

# Al-III-V-semiconductor oxidation history

# Historical Perspective

> Oxidation of AlGaAs first observed in 1990

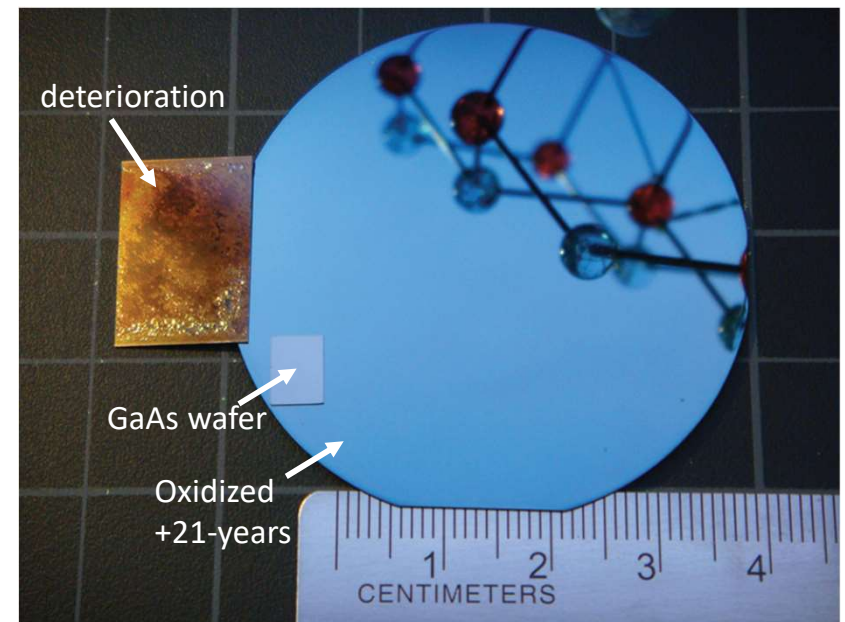


J.M. Dallesasse, N. Holonyak, *Appl. Phys. Lett.*, **56** (24), 2436 (1990)

High-Al layers degradation

> Oxidation process = accelerated aging i.e. water+high temperature

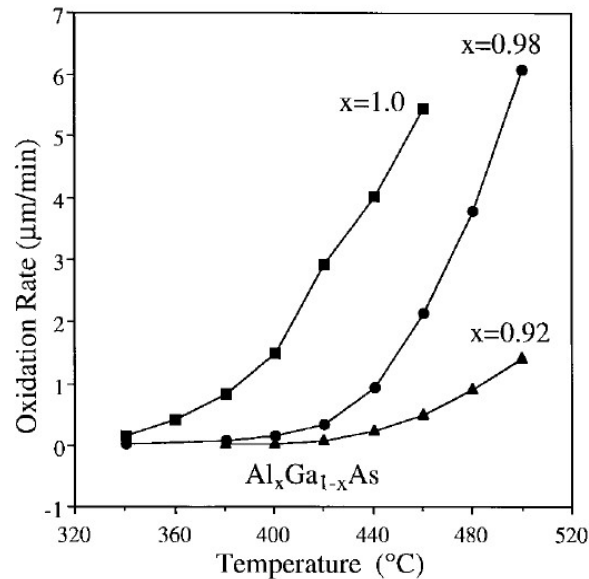
J.M. Dallesasse, N. Holonyak, *Appl. Phys. Lett.*, **57** (24), 2844 (1990)



J.M. Dallesasse, N. Holonyak, *J. Appl. Phys.*, **113**, 051101 (2013)

## > Compositional selectivity in AlGaAs

### ■ Experiments



Oxidation rate drops exponentially as the Al concentration diminishes

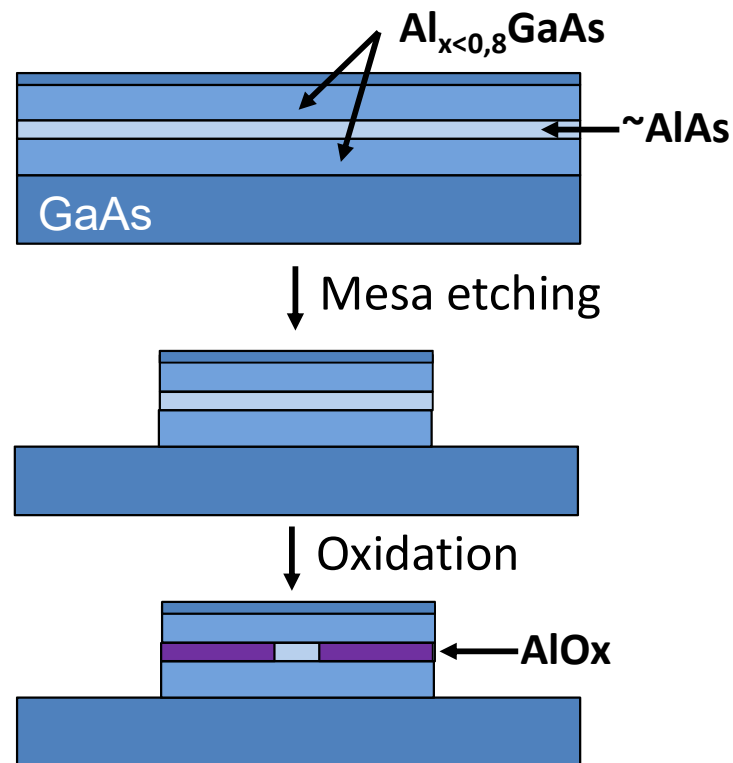
K.D. Choquette et al., *IEEE JSTQE*, **3**, 916 (1997)

### ■ Thermodynamics : C.I.H. Ashby et al, *J. Appl. Phys.*, **84**, 3134 (1997)

- $2\text{AlAs} + 6\text{H}_2\text{O} \rightarrow \text{Al}_2\text{O}_3 + \text{As}_2\text{O}_3 + 6\text{H}_2$        $\Delta G = -473 \text{ kJ/mol}$
- $\text{As}_2\text{O}_3(\text{l}) + 6\text{H} \rightarrow 2\text{As} + 3\text{H}_2\text{O}(\text{g})$        $\Delta G = -1226 \text{ kJ/mol}$
- $2\text{GaAs} + 6\text{H}_2\text{O} \rightarrow \text{Ga}_2\text{O}_3 + \text{As}_2\text{O}_3 + 6\text{H}_2$        $\Delta G = 10 \text{ kJ/mol}$       unfavorable

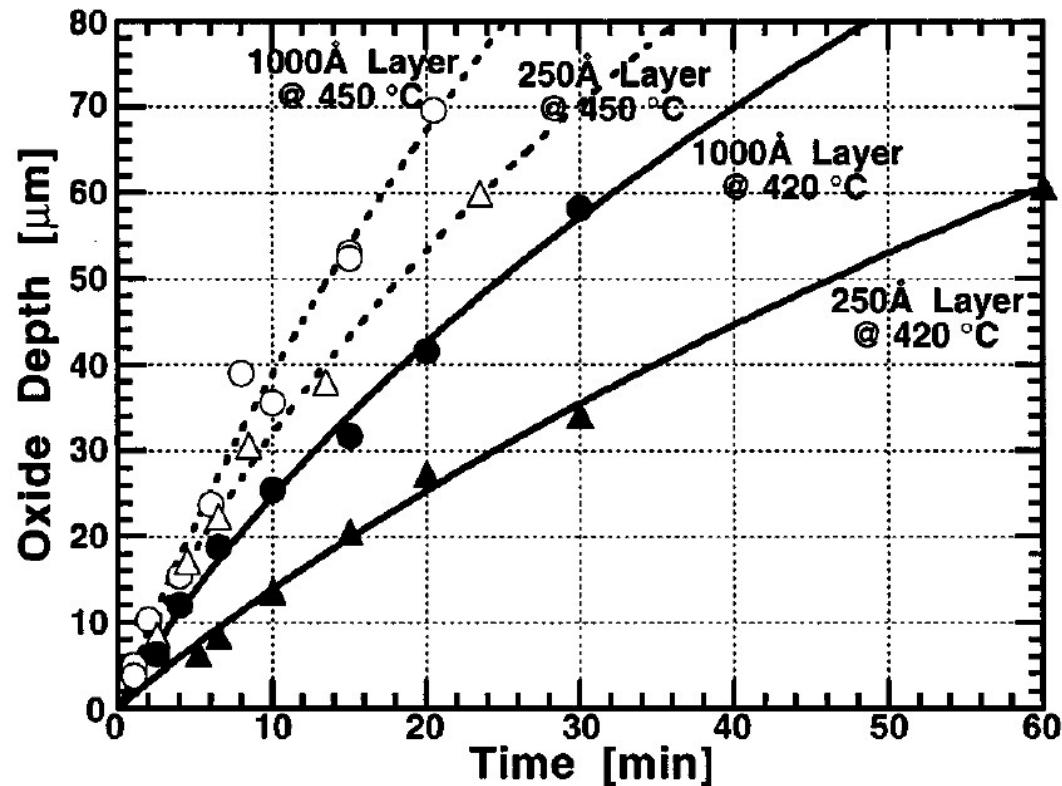
# III-V semiconductor oxidation

- > Selective (lateral) oxidation from an etched mesa



# III-V semiconductor oxidation

## > Length and thickness dependence



R.L. Naone et al., *J. Appl. Phys.*, **82**, 2277 (1997)

Extension of Si surface oxidation model  
(Deal & Grove, *JAP*, **36**, 3770 (1965))

$$x_{\text{ox}}^2 + Ax_{\text{ox}} = Bt$$

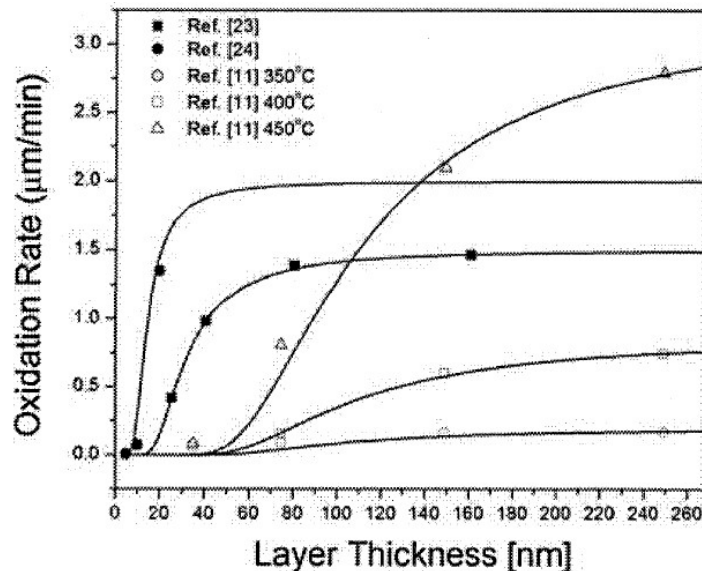
Through-oxide diffusion

chemical reaction

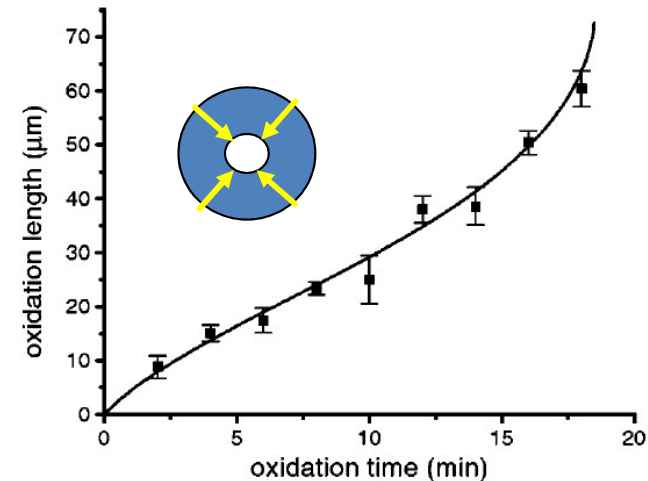
Through-oxide diffusion

> Extensions of Si-based (Deal & Grove, JAP, **36**, 3770 (1965)) oxidation model to include

- Lateral mesa geometry (=> acceleration as surface reduces)



P.-C. Ku et al, *JSTQE*, **39**, 577 (2003)



A.C. Alonzo et al, *JAP*, **84**, 6901 (1998)

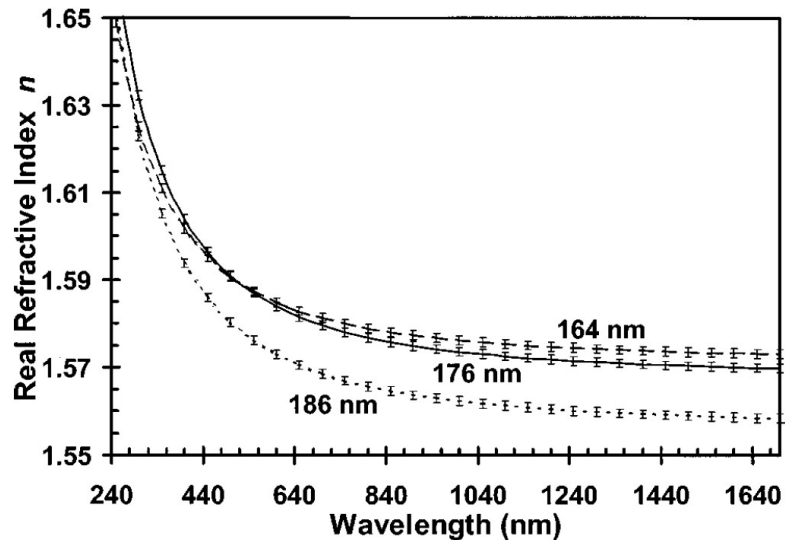
- Thickness-dependence (boundary interface/ grain size influence)

- But always assumed the oxidation to be isotropic

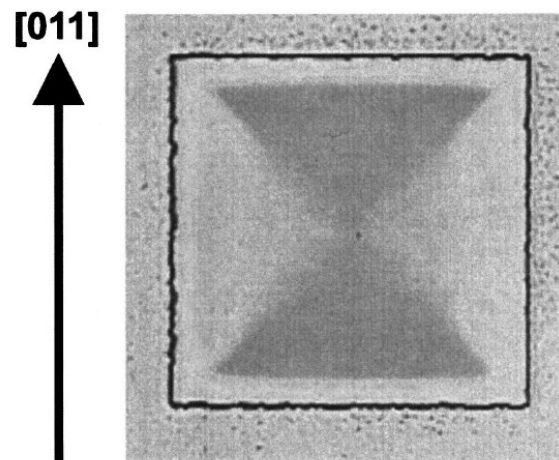


# AlOx material properties

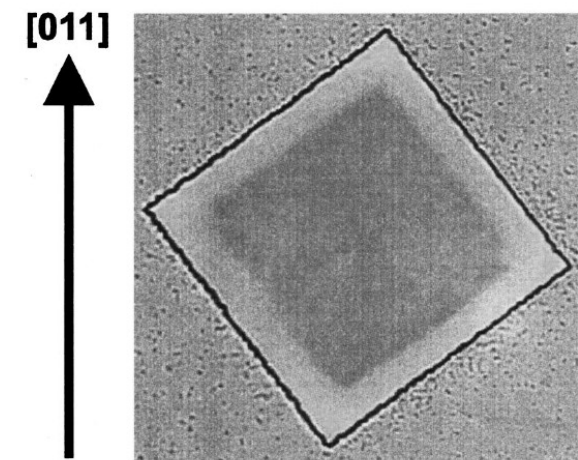
- > Al(Ga)Ox is an (electrically)-insulating material
- > Conversion of an optically high-index ( $n \sim 2.9$ ) into a low-index material ( $n \sim 1.6$ )
- > 5 to 12% volumic contraction



K.J. Knopp et al., *Appl. Phys. Lett.*, **73**, 3512 (1997)



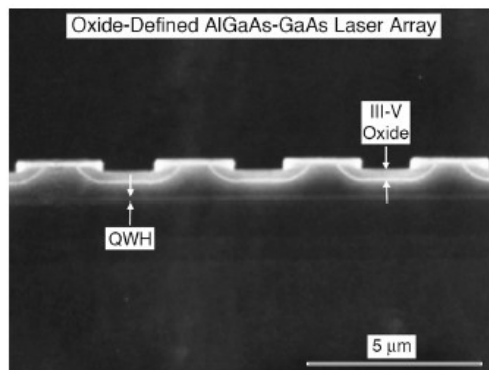
A.C. Alonzo et al., *J. Appl. Phys.*, **87**, 4594 (2000)



# Al-III-V-semiconductor oxidation applications

# Lasers using III-V oxidation

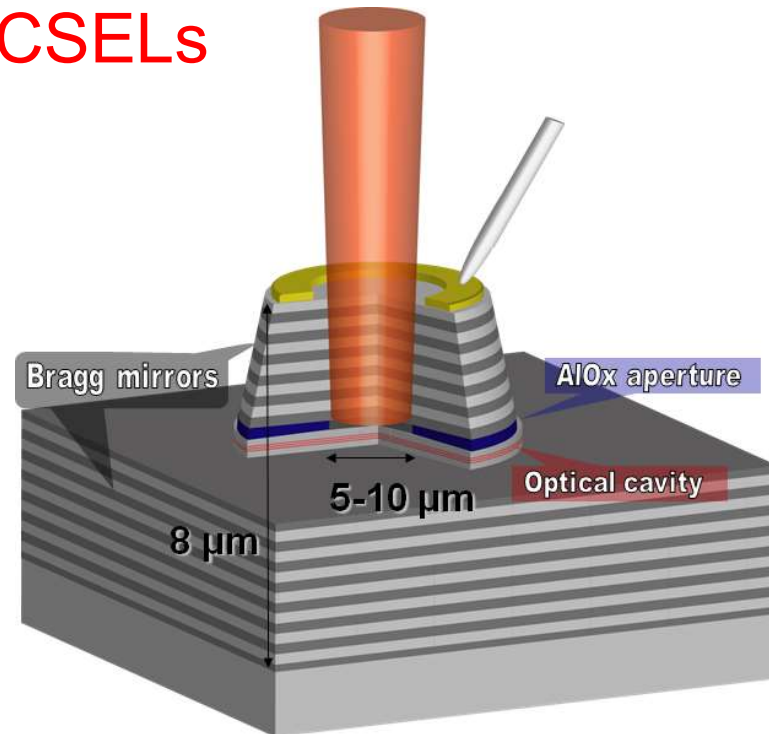
## Edge Emitting lasers



J.M. Dallesasse et al., *APL*, **58**, 834 (1991)

Electrical confinement

## VCSELs



D.L. Huffaker et al., *APL*, **65**, 97 (1994)

J.M. Dallesasse, *proc. IEEE*, **101**, 2234 (2013)

Electrical & Optical confinement

# VCSEL market and uses

## VCSEL benefits

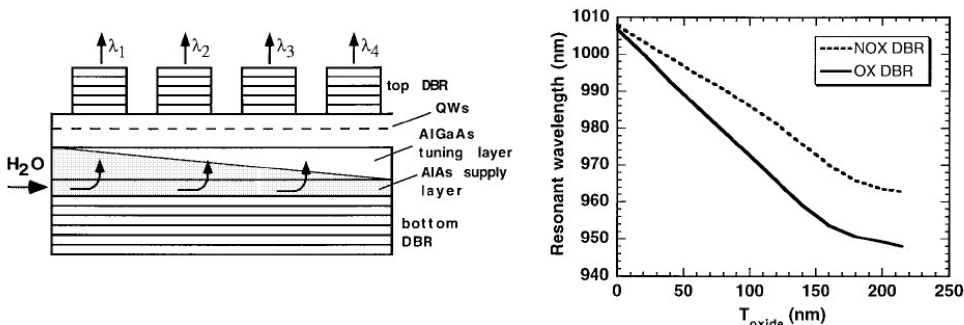
- ✓ Advantageous manufacturability
- ✓ Low energy consumption
- ✓ Good beam quality
- ✓ Matrix format



Trend | LEMON PHOTONICS VCSEL laser sensor chips have full production capability  
 Drivers that boost the growth of VCSEL market Source: 《VCSELs - Market and Technology Trends 2019》

## Graded-thickness AlOx layer

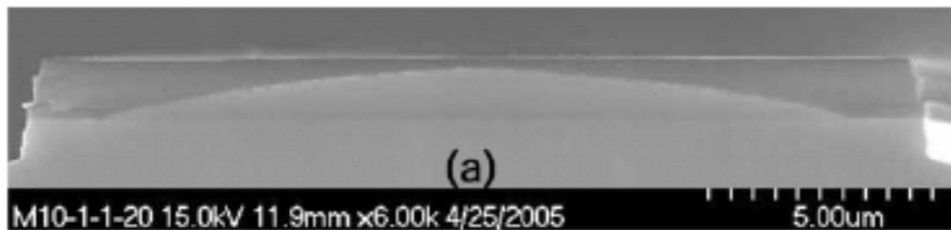
### Multiwavelength VCSEL matrix



A. Fiore et al., *JQE*, **35** (4), 616 (1999)

$$\lambda_k = \frac{2 \cdot (n_{unox}L + (n_{ox} - n_{unox}) \cdot L_{ox})}{k}$$

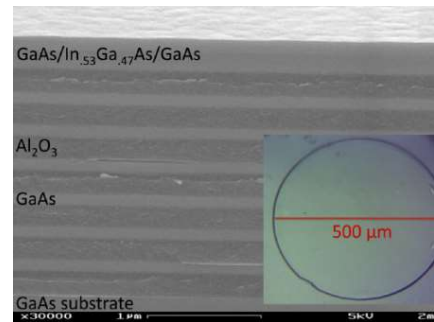
## Microlenses



K.S. Chang et al., *IEEE PTL*, **18** (1), 121 (2006)

## Wide-bandwidth mirrors

### SESAMs

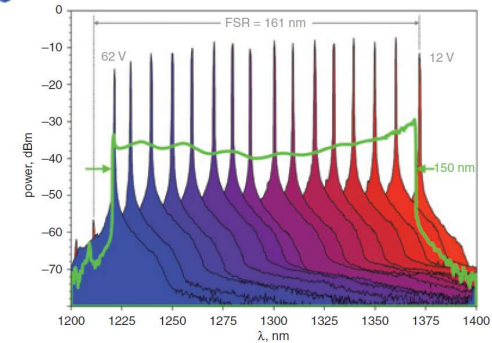
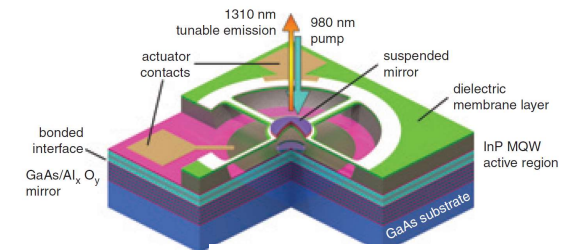


S.P. Nabanja et al., *JAP*, **113**, 161102 (2013)

$$\Delta\lambda = \frac{4}{\lambda\pi} \text{asin} \left( \frac{|n_H - n_L|}{n_H + n_L} \right)$$

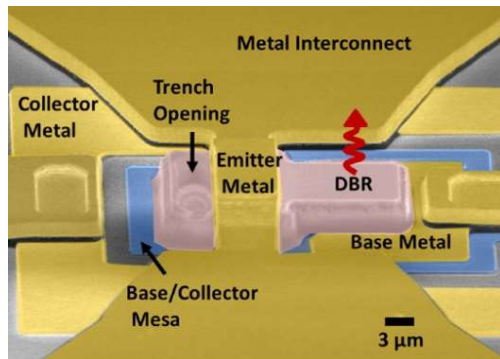
$n_H = 3.45$  (GaAs)  
 $n_L = 2.9$  (AlAs) 1.6 (AlOx)

### Widely-tunable VCSELs



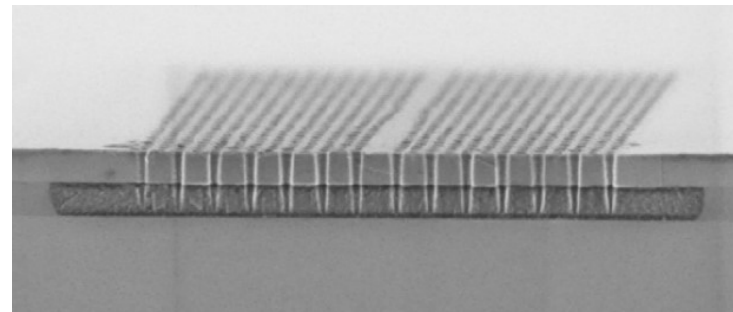
V. Jayaraman et al., *Electron. Lett*, **48** (14), 867 (2012)

## Transistor lasers



M. Liu et al., *APL*, **114**, 163104 (2013)

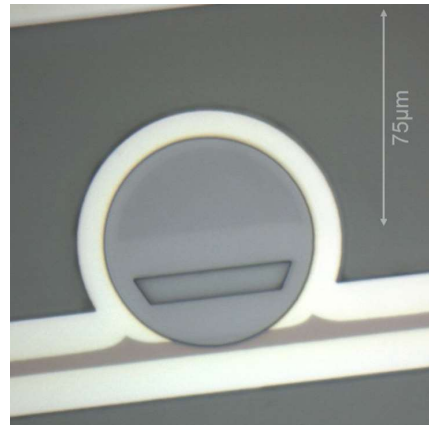
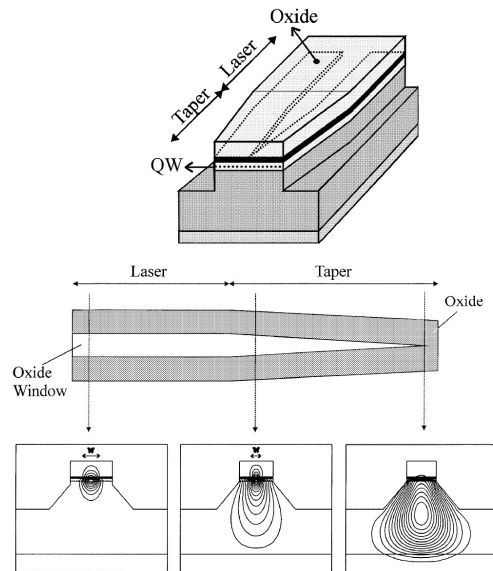
## Photonic crystal waveguides



K. Welna et al., *Photon & Nanostruct.*, **11**, 139 (2013)

# Photonic devices using III-V oxidation

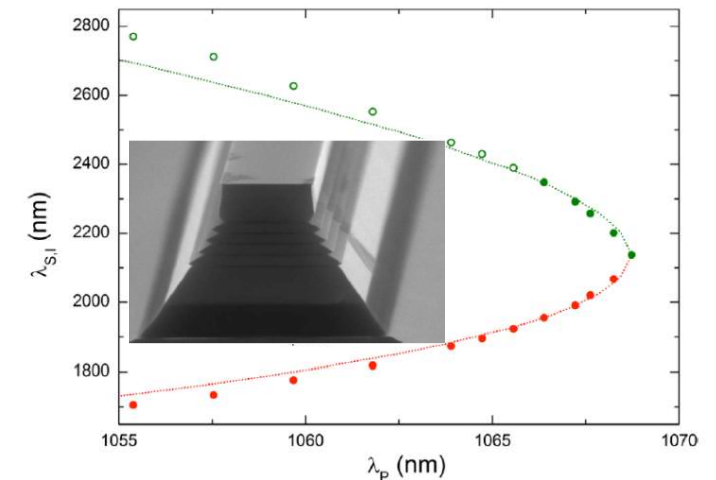
## Photonic Integrated Circuits



S. Calvez et al., *PTL*, **27**, 982 (2015)

K. De Mesel et al., *JSTQE*, **8** (6), 1372 (2002)

## NLO waveguides



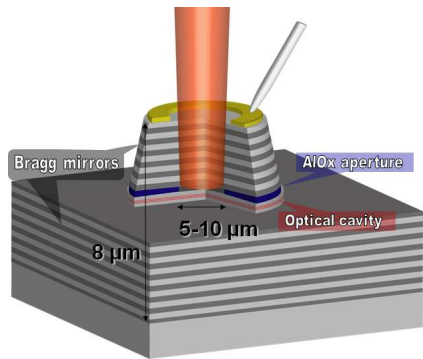
A. Fiore et al., *Nature*, **391**, 463 (1998)

M. Savanier et al., *APL*, **103**, 261105 (2013)

# Contributions from LAAS

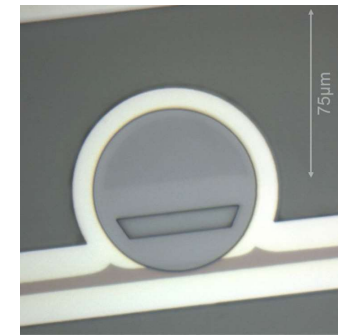


# Need for controlled oxide apertures



D.L. Huffaker et al., *APL*, **65**, 97 (1994)

J.M. Dallesasse, *proc. IEEE*, **101**, 2234 (2013)



S. Calvez et al., *PTL*, **27**, 982 (2015)

> Aperture size controls MM/SM

> Singlemode devices

- SM size limit is shape independent
- Shape influence
  - Emission surface
  - Thermal/electrical resistance
  - Fibre-coupling efficiency

■ **Controlling the aperture shape and dimensions is important!**

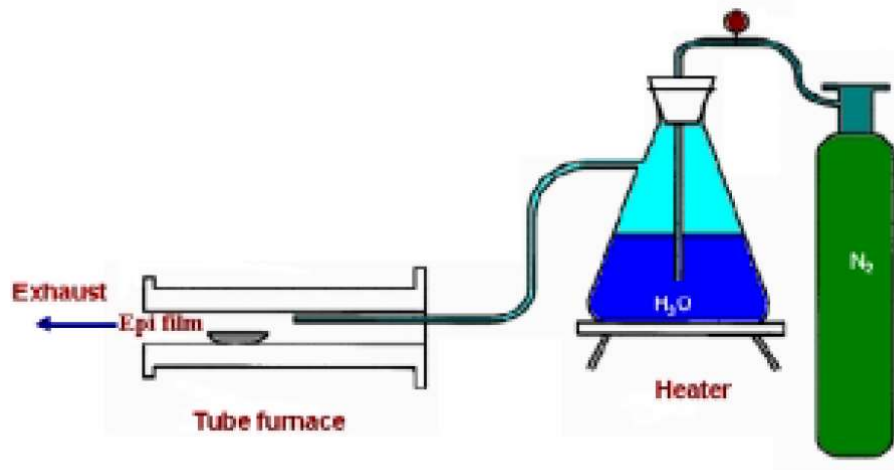
> Aperture shape defines propagation direction and modal content

> Basic shapes

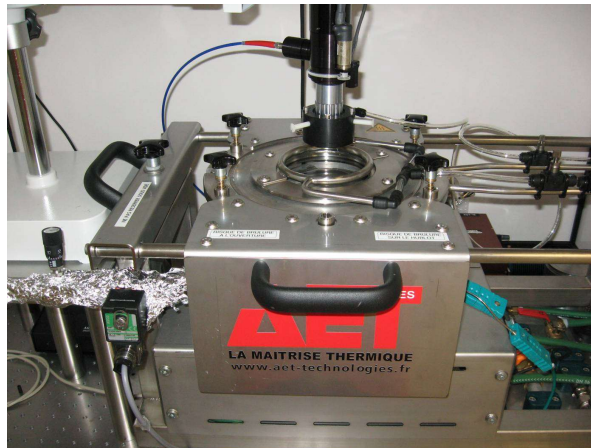
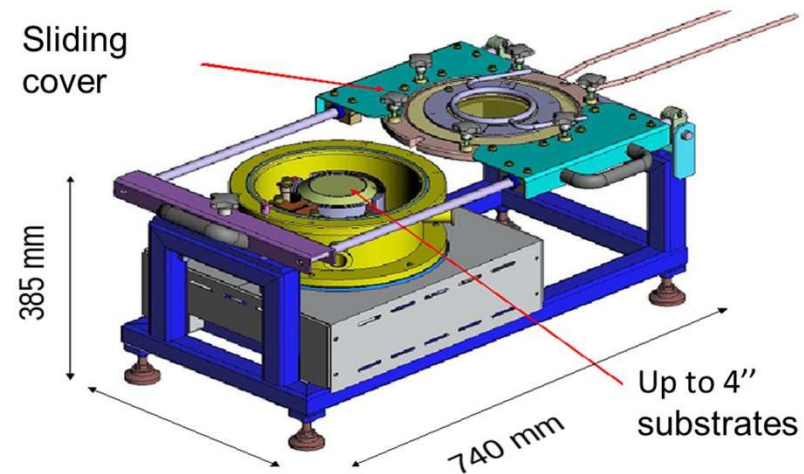
- Straight waveguides
- Curved waveguides

# III-V oxidation furnace with monitoring

# AIOx Furnace



- Dedicated oxidation furnace
  - Co-designed with AET Technologies / AIOxTec
  - Reduced pressure oxidation
  - Gaz injectors instead of bubblers
- Up to 4'' wafers
- Improved uniformity & reproducibility
- **Optical view port for in-situ monitoring**

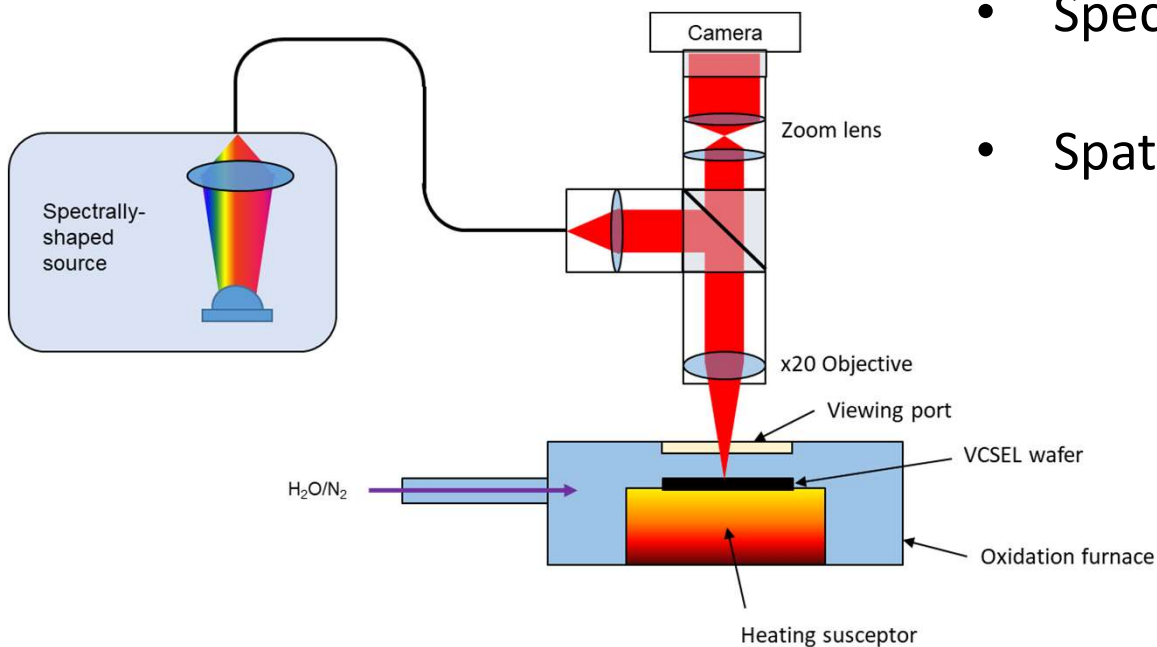


# In-situ real-time monitoring

- **Micro-reflectometry system**

- Change of refractive index upon oxidation  
=> local change of reflectivity
- NIR illumination (700-950nm)
  - Spectrally-resolved illumination

G. Almuneau et al, *Semicon. Sc. Technol*, **23**, 105021 (2008)

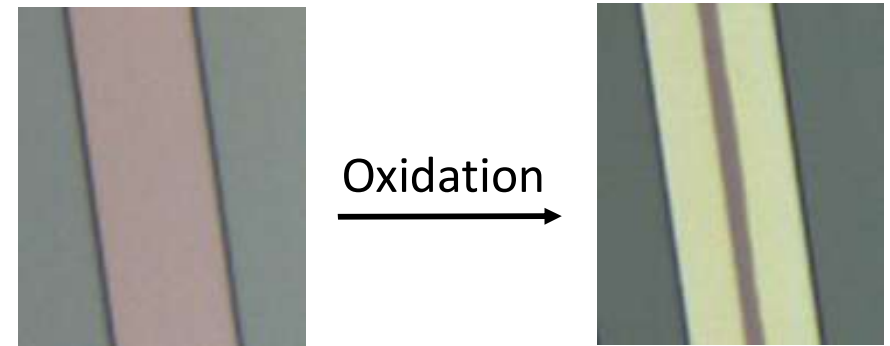


G. Almuneau et al, *Semicon. Sc. Technol*, **23**, 105021 (2008)

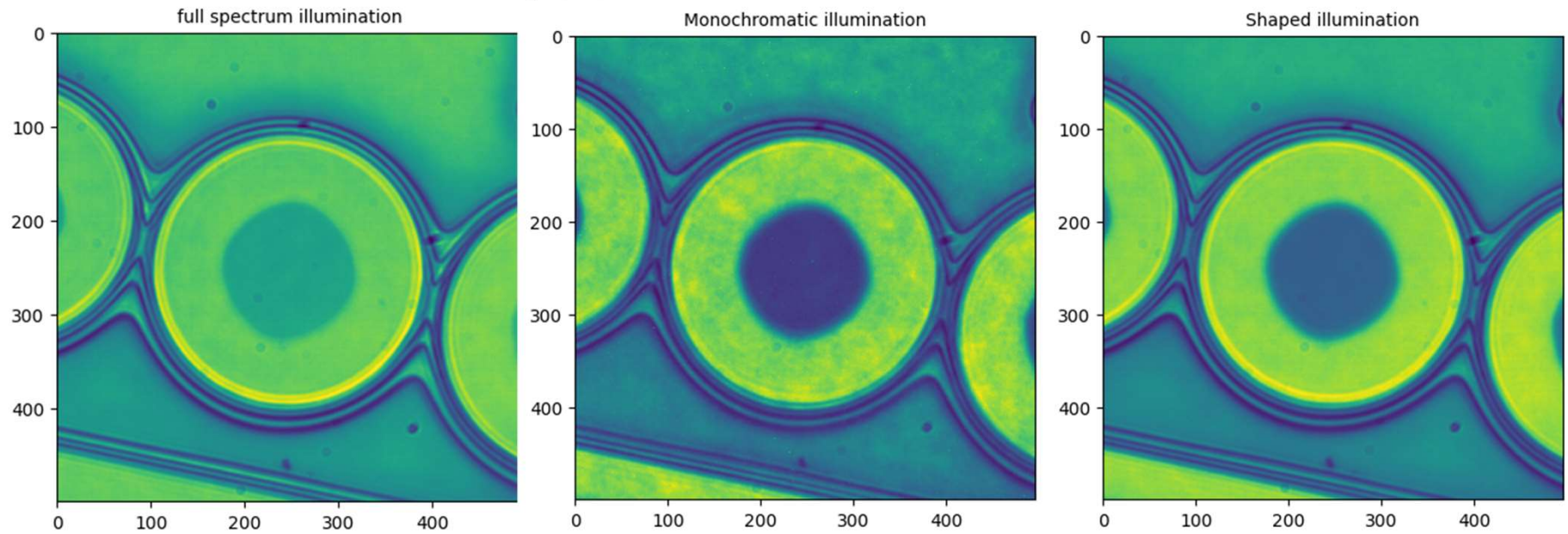
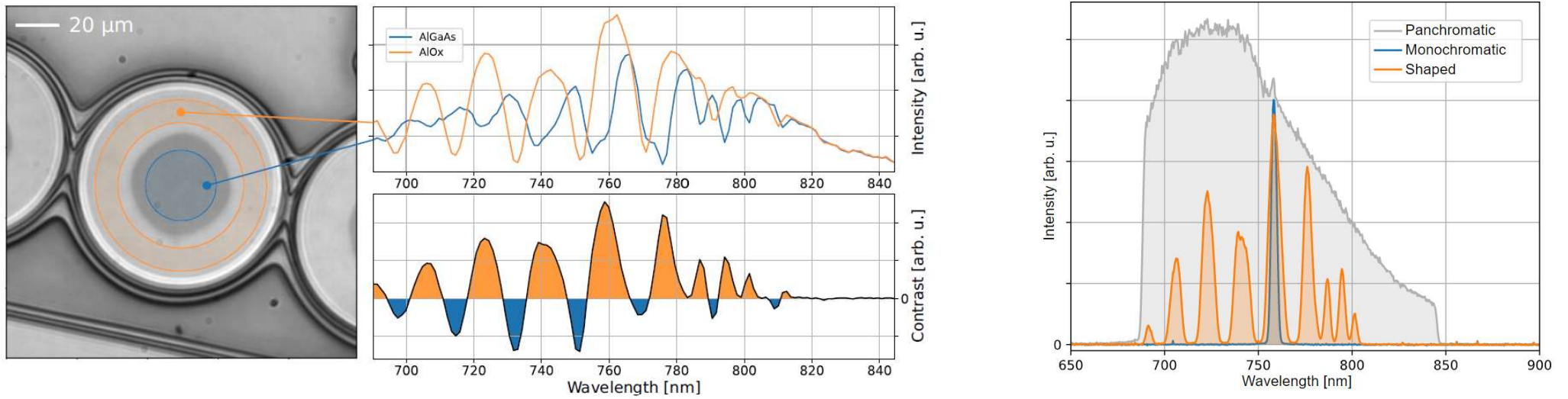
- Spectrally-shaped illumination

N. Monvoisin et al, *Opt. Express*, **31**, (2023)

- Spatial resolution  $\sim 1\mu\text{m}$

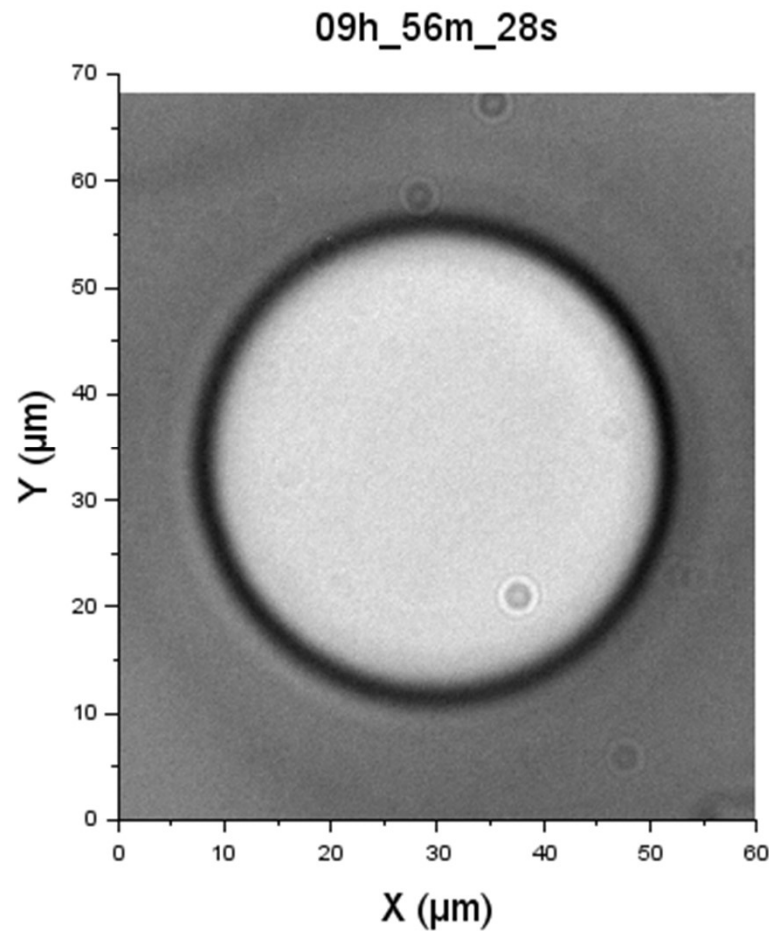


# Oxidation monitoring



N. Monvoisin et al, *Opt. Express*, **31**, (2023)

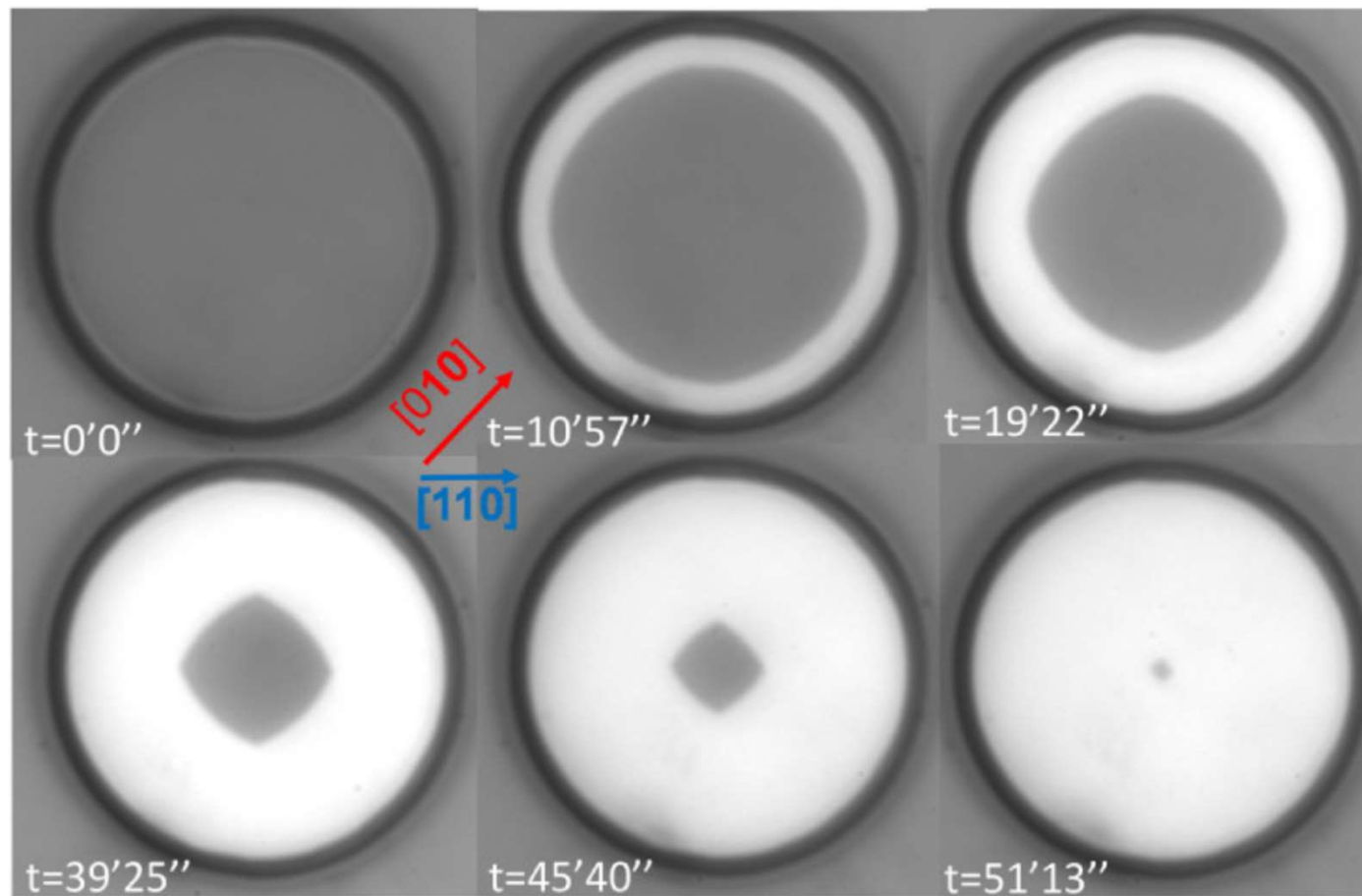
# Oxidation monitoring



## Benefits

- ✓ Improved industrial manufacturability
- ✓ Datasets for science

# Oxidation anisotropy



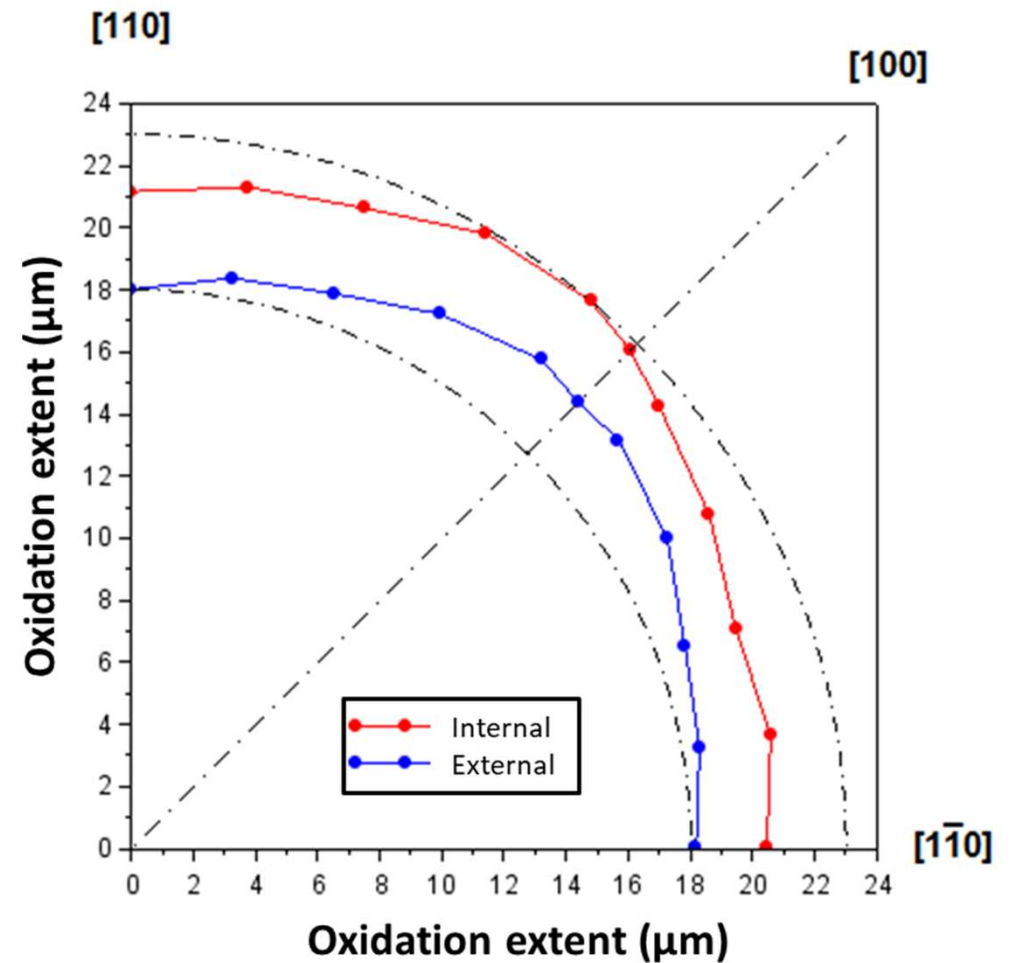
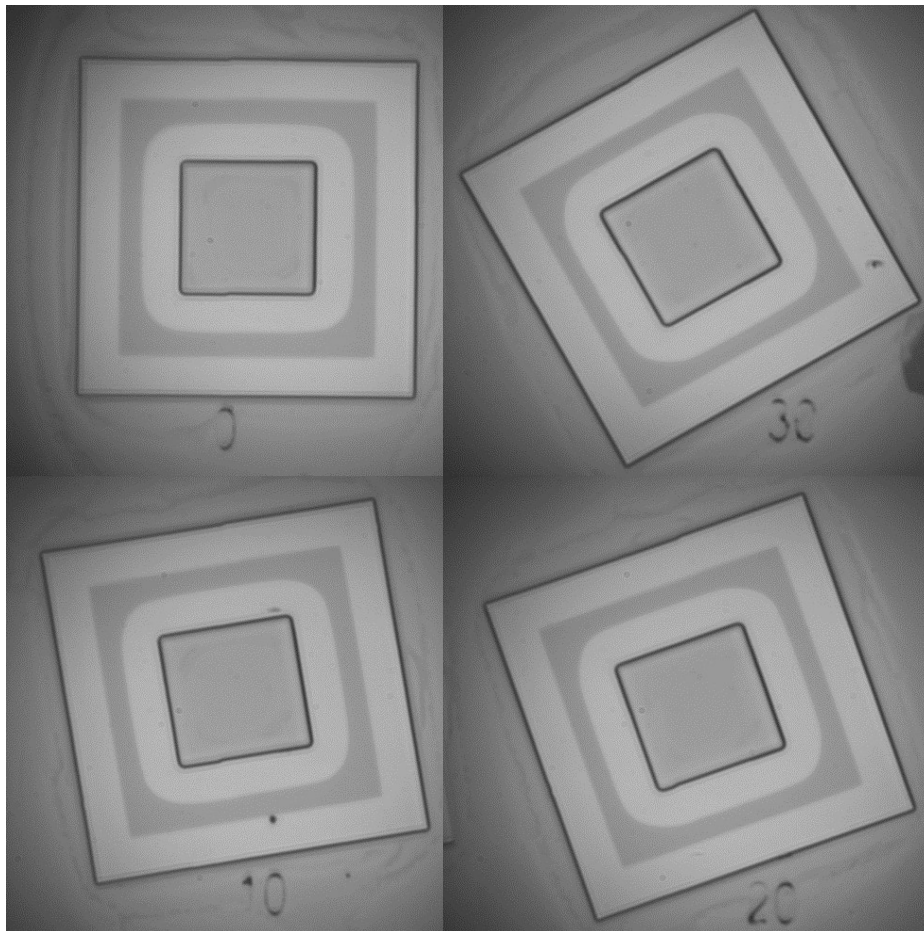
Aperture shape  $\neq$  Mesa shape

# III-V oxidation anisotropy



# Measuring in-plane anisotropy

## > Direction-dependent measurement

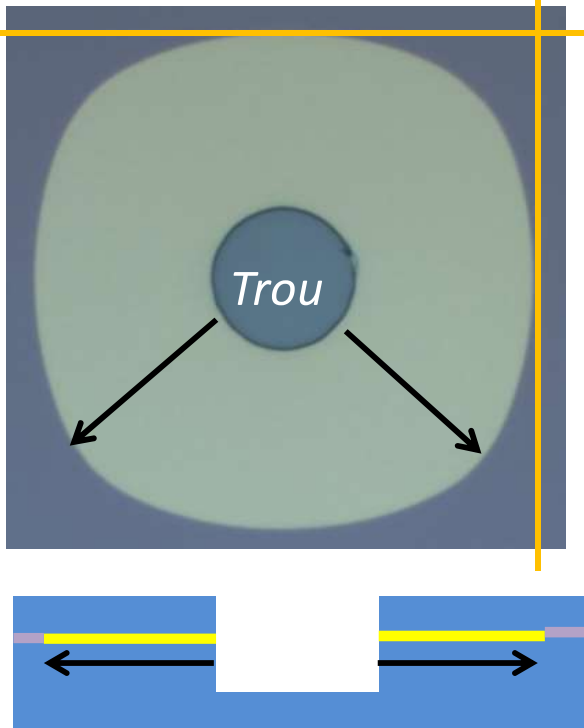


# Long-range anisotropic oxidation patterns

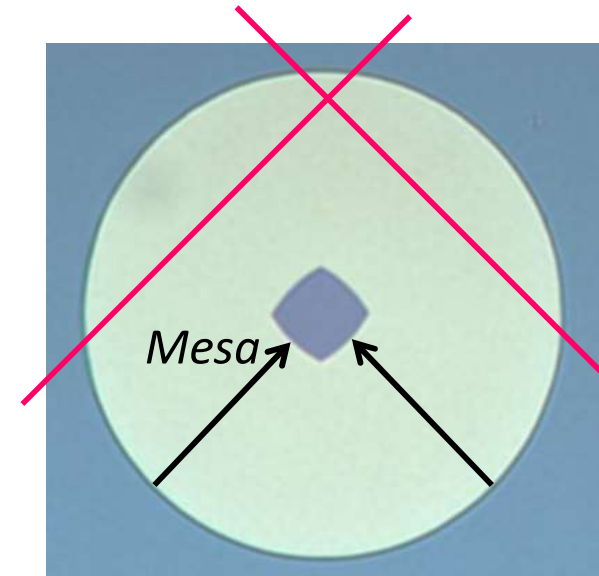
Concave Mesa

Convex mesa

Slow-oxidation planes



[100]  
[110]



Fast-oxidation planes

III-V semiconductor oxidation follows Jaccodine's rules\* (wet etching)

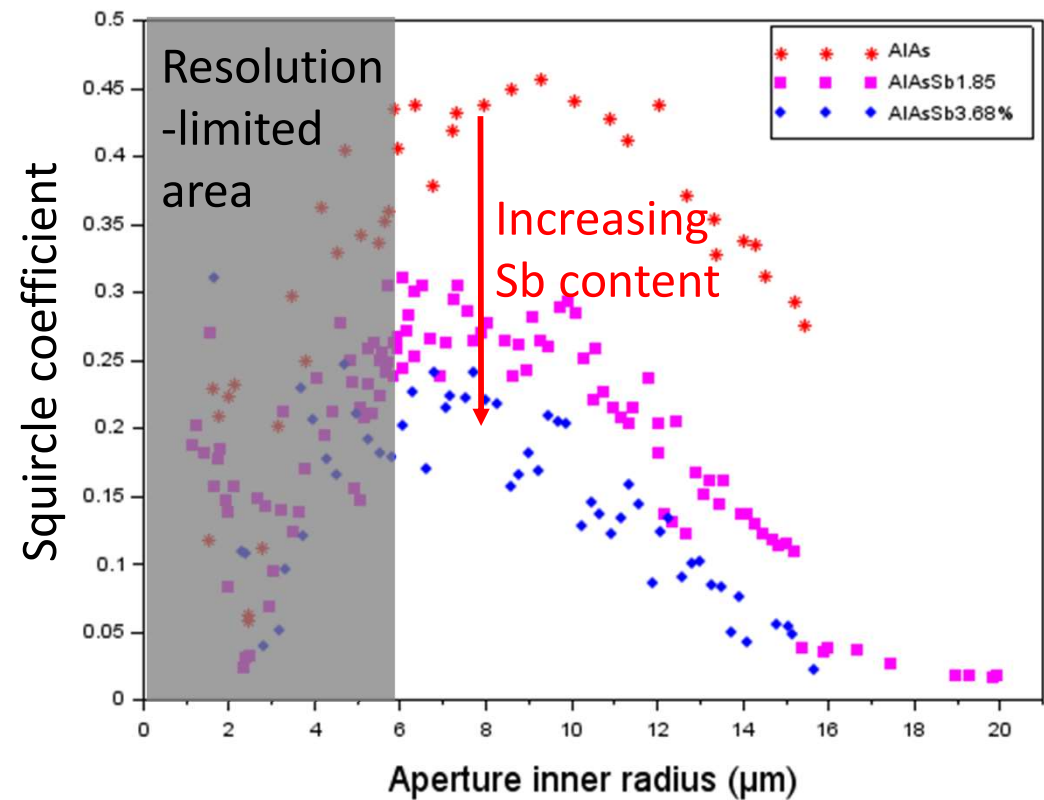
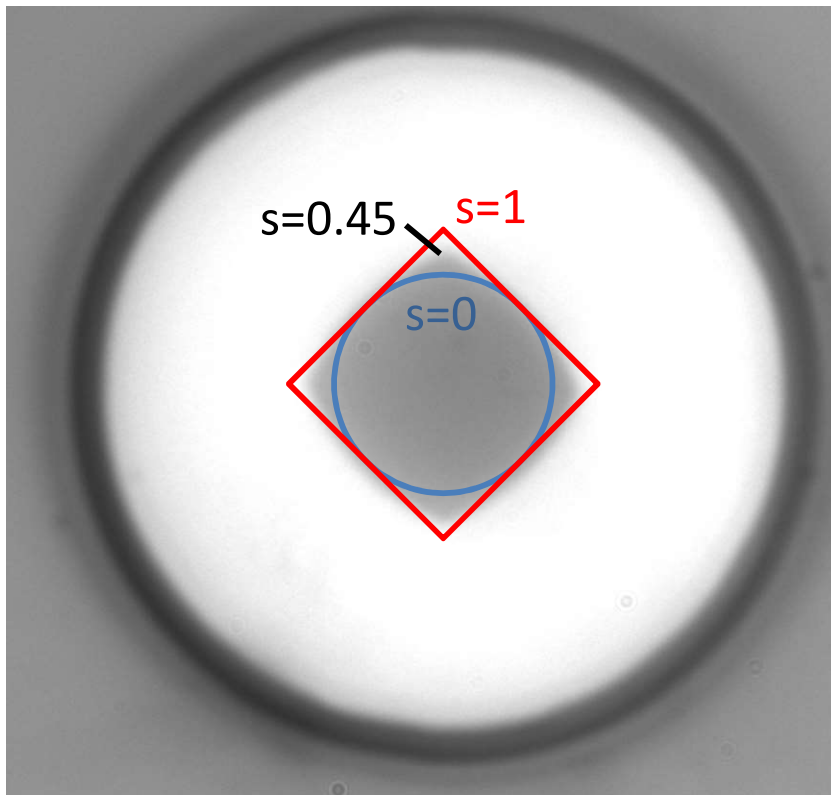
Concave mesa: **slow-rate planes** control the oxidation contour

Convex mesa: **fast-rate planes** control the oxidation contour

\* R.J. Jaccodine, *J. Appl. Phys*, **33** (8), 2643 (1962) ---- G. Lafleur, PhD, Université Paul Sabatier (2016)

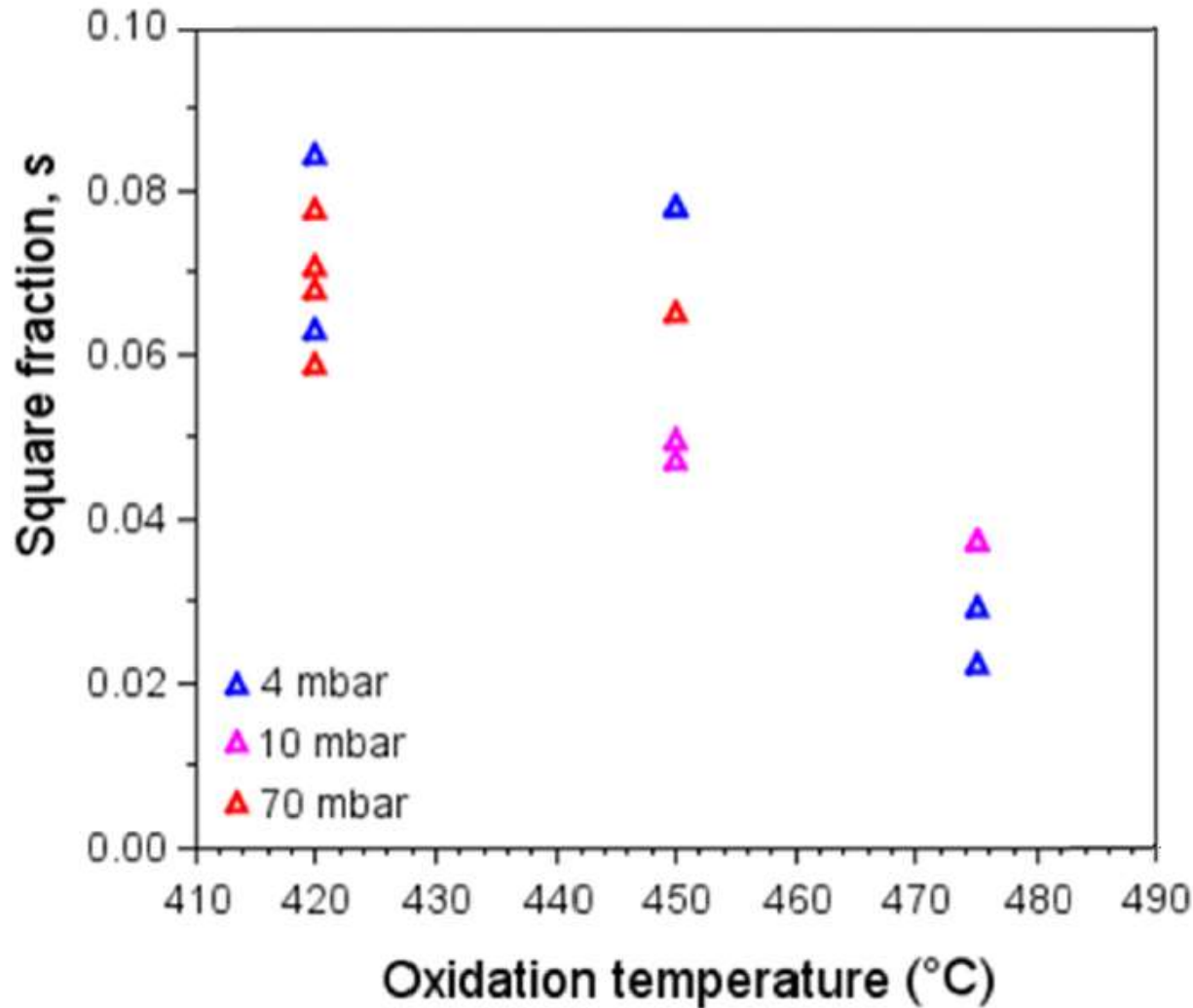
# Measuring in-plane anisotropy

- > Oxidation from circular mesas
- > Ad-hoc shape fitting using squircles (rectellipses)



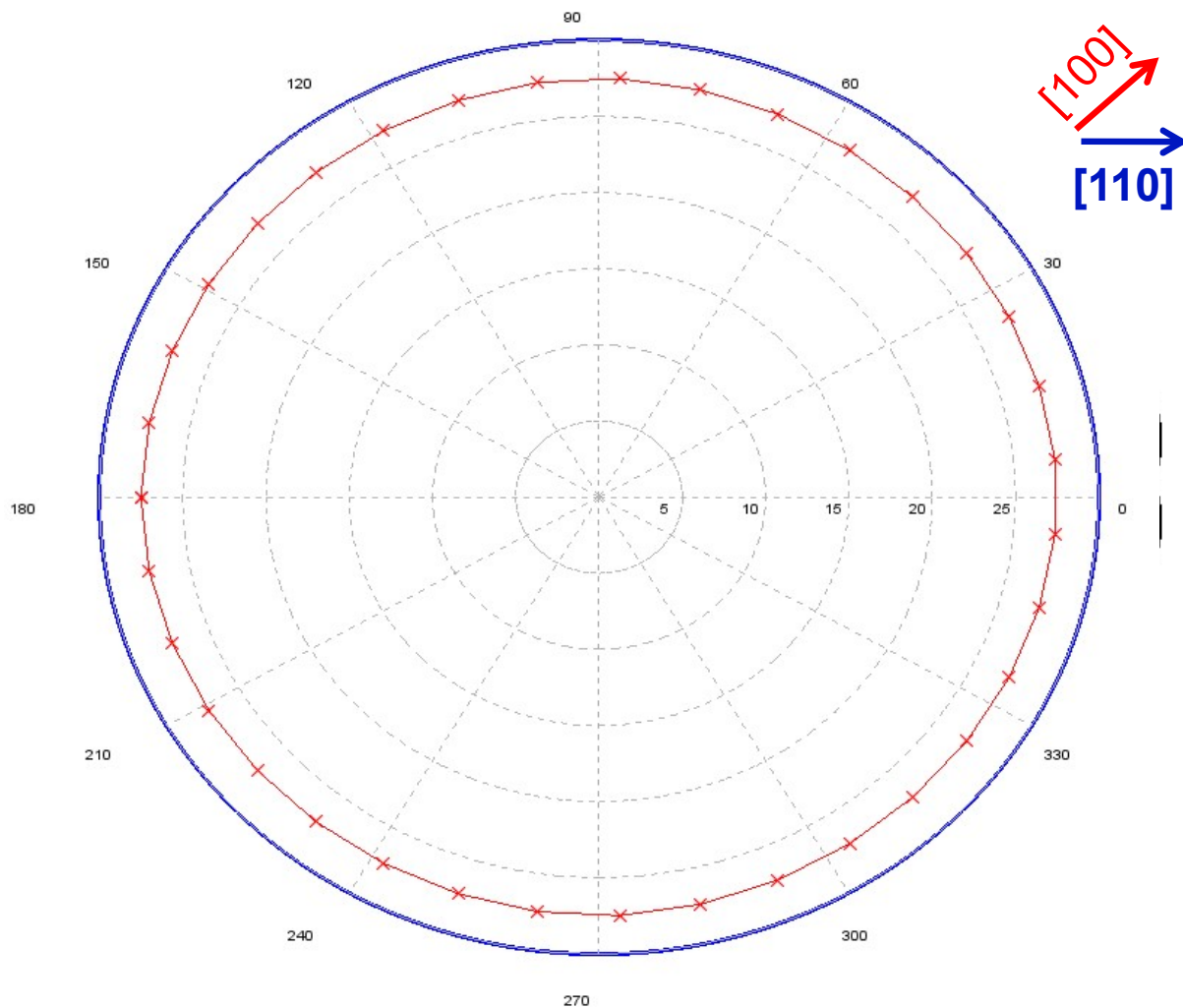
S. Calvez et al, *AIP Advances*, **11**, 125010 (2021);

# Controlling AlOx anisotropy: Process



- > Process parameters
  - Pressure
  - Wafer temperature
  - H<sub>2</sub>O flow
- > **Reduced anisotropy at high temperatures (diffusion-limited)**
- > **Not fully isotropic process**

G. Lafleur et al, *Opt. Materials Express*, **8** (7), 1788 (2018)



## ➤ Model Principles

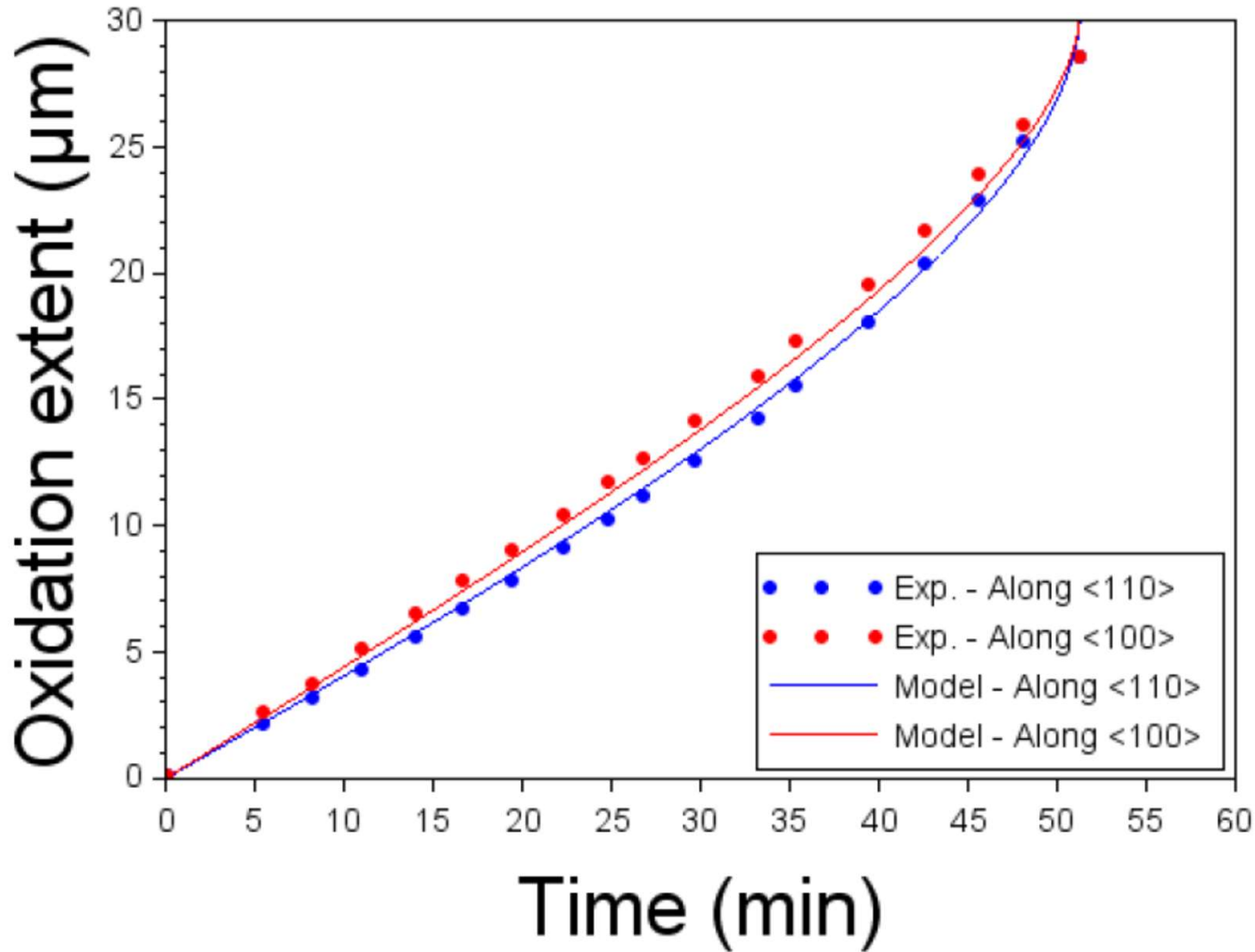
- Iterative model
- Isotropic diffusion
- Uniform concentration at the oxide aperture
- Point-like anisotropic oxidation reactions

$$k(\theta) = k_{moy} \left( 1 - \frac{b}{2} + b \sin^2(2\theta) \right)$$

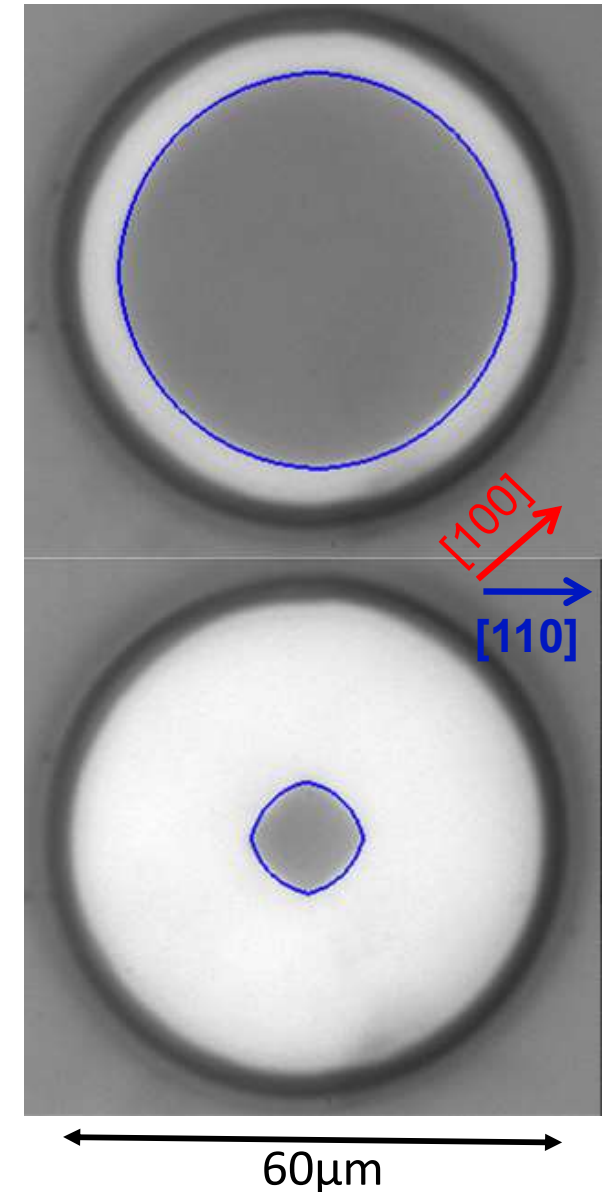
$0 < b < 2$

S. Calvez et al, *Opt. Materials Express*, **8** (7), 1762 (2018)

# Controlling AlOx anisotropy: Model Results



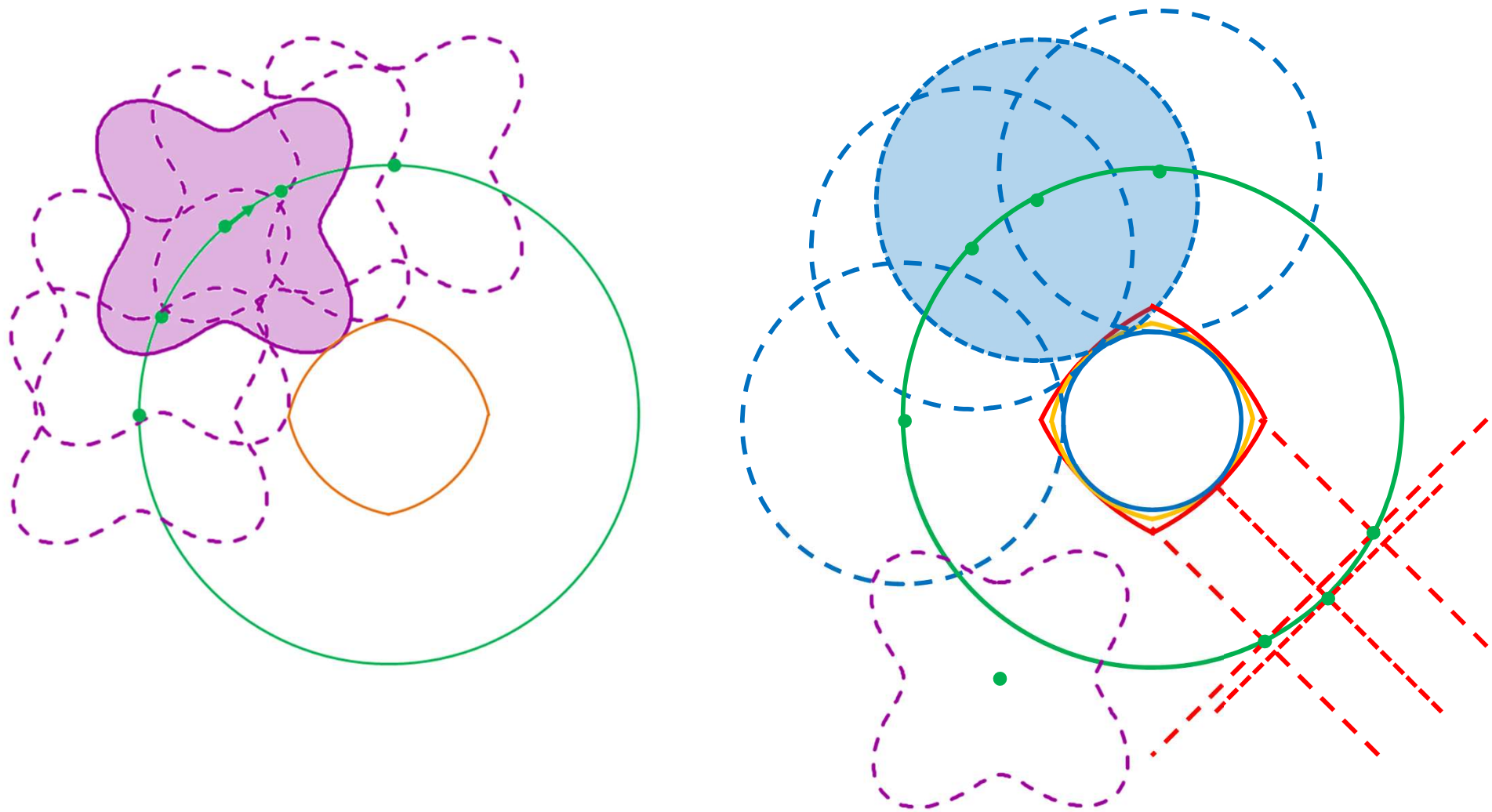
S. Calvez et al, *Opt. Materials Express*, 8 (7), 1762 (2018)



# AlOx anisotropy: Mesa shape prediction

- > Able to reproduce an anisotropic oxidation
- > What about tackling the inverse problem ?
  - Define target aperture shape
  - Find the mesa shape for a set oxidation time

# Controlling AlOx anisotropy: Forward Model



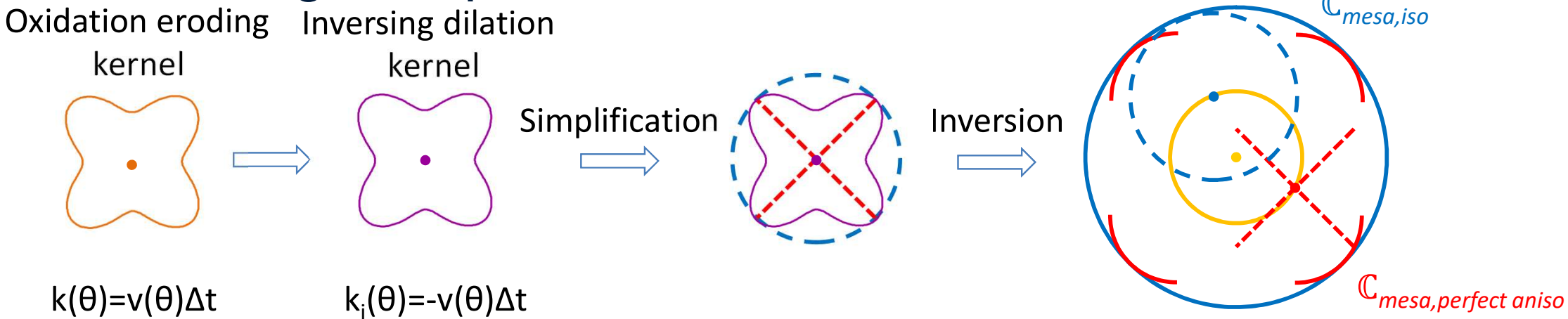
Oxide aperture is bounded by isotropic and perfectly-anisotropic shapes

S. Calvez et al, *Semicon. Sc. Technol*, **34**, 015014 (2019)



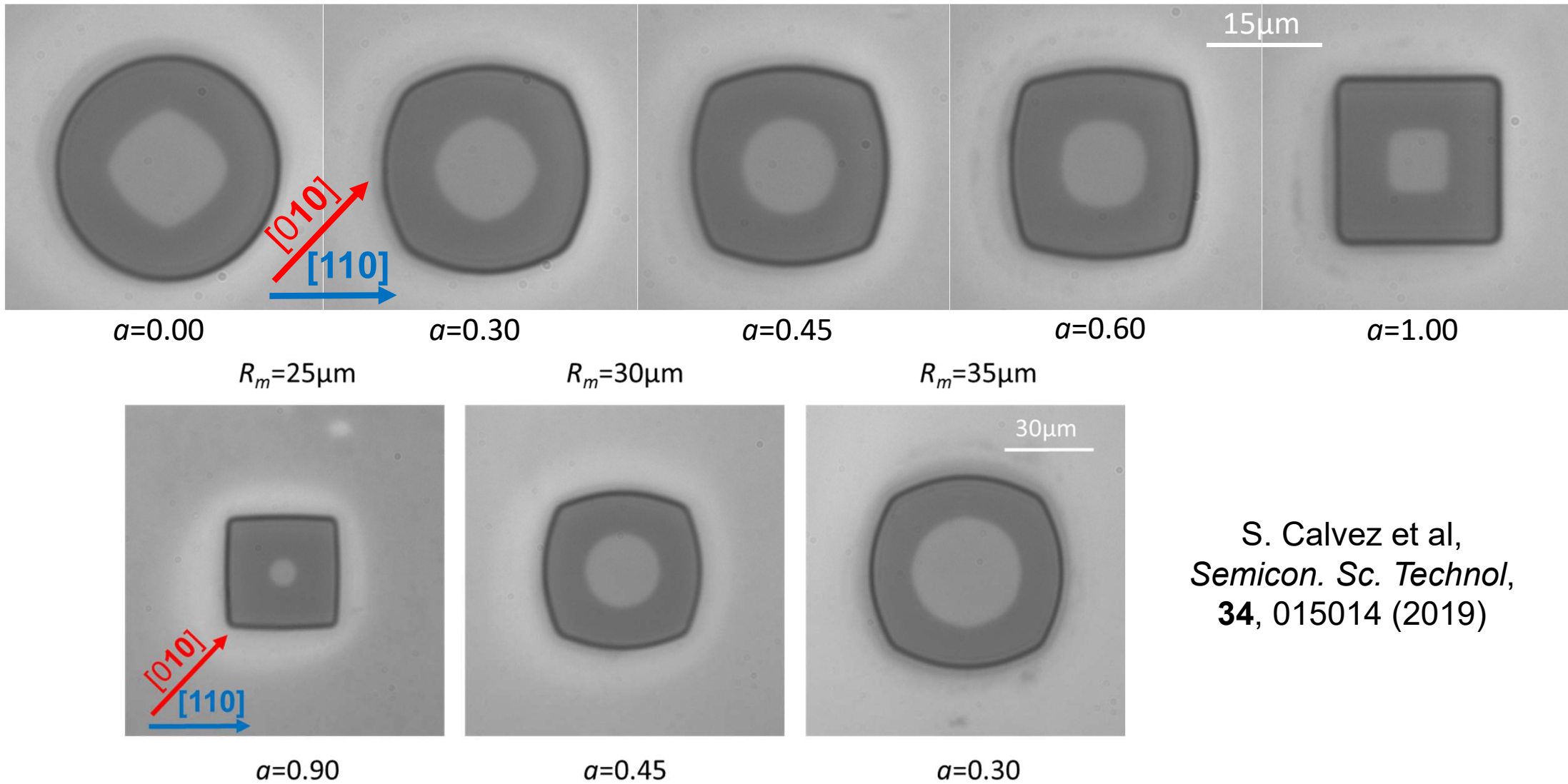
## > Inversion: mesa to obtain a given aperture

### ■ Single-step erosion



- Simplification to avoid detailed kernel assessment
- Appropriate shape is bounded by isotropic and perfectly-anisotropic cases

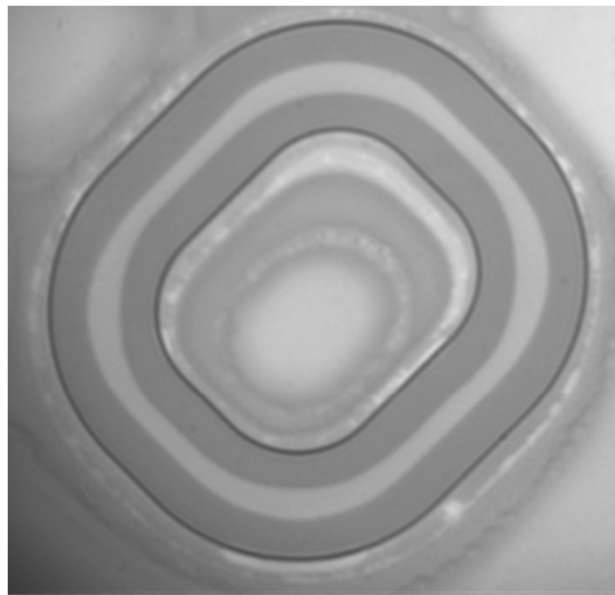
# Controlled anisotropy: Inverse Model Results



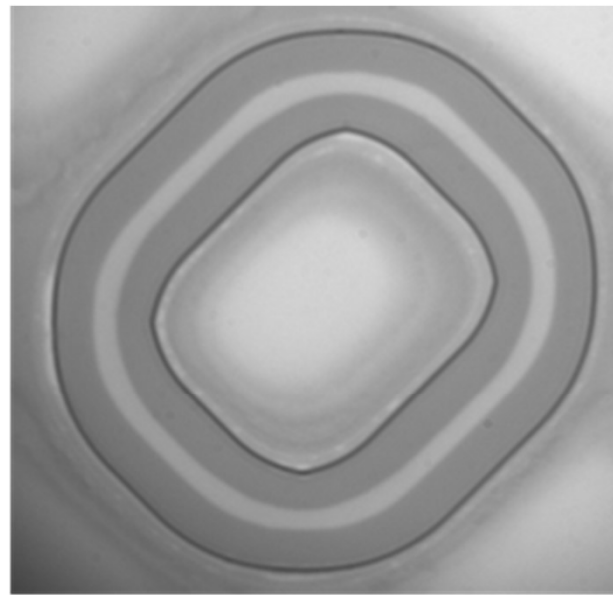
S. Calvez et al,  
*Semicon. Sc. Technol*,  
**34**, 015014 (2019)

Successful for inward-progressing oxidation

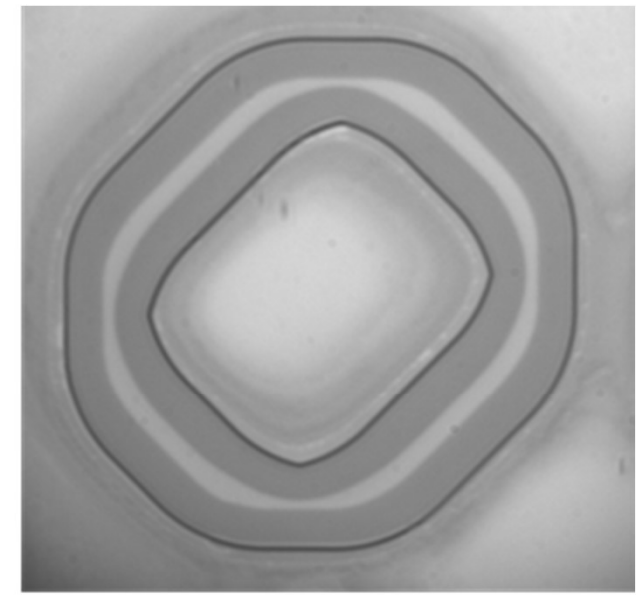
- > Extension for use in photonics integrated circuits
  - Address inwards & outwards oxidation



$$a_{\text{in}} = a_{\text{ext}} = 0.00$$



$$a_{\text{in}} = a_{\text{ext}} = 0.35$$



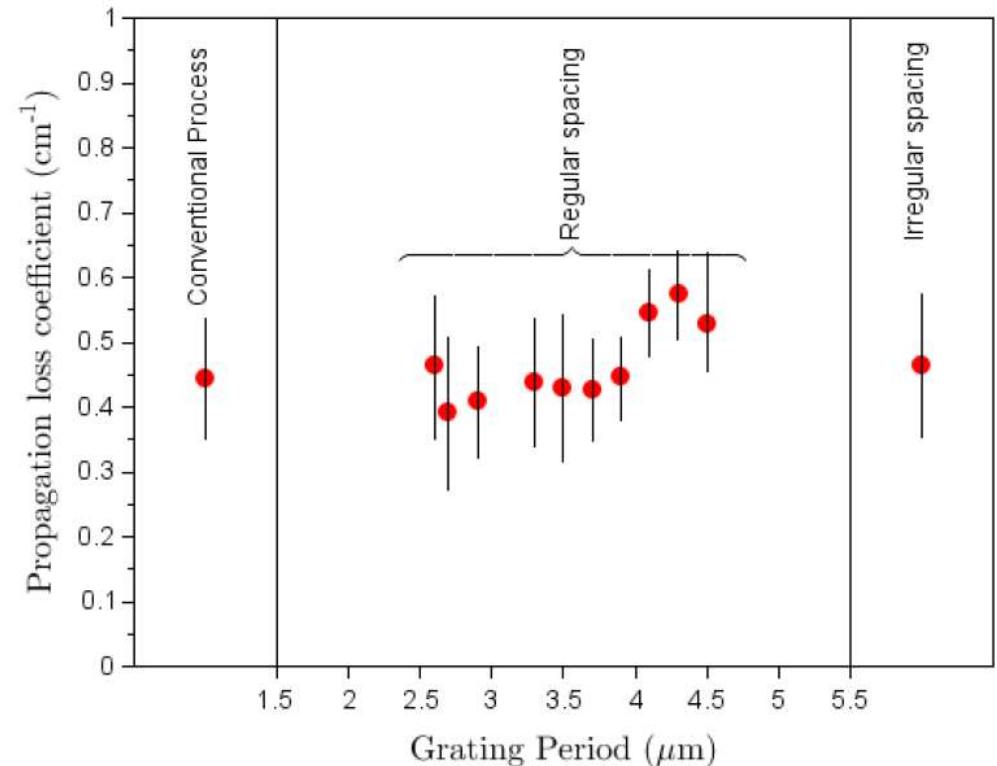
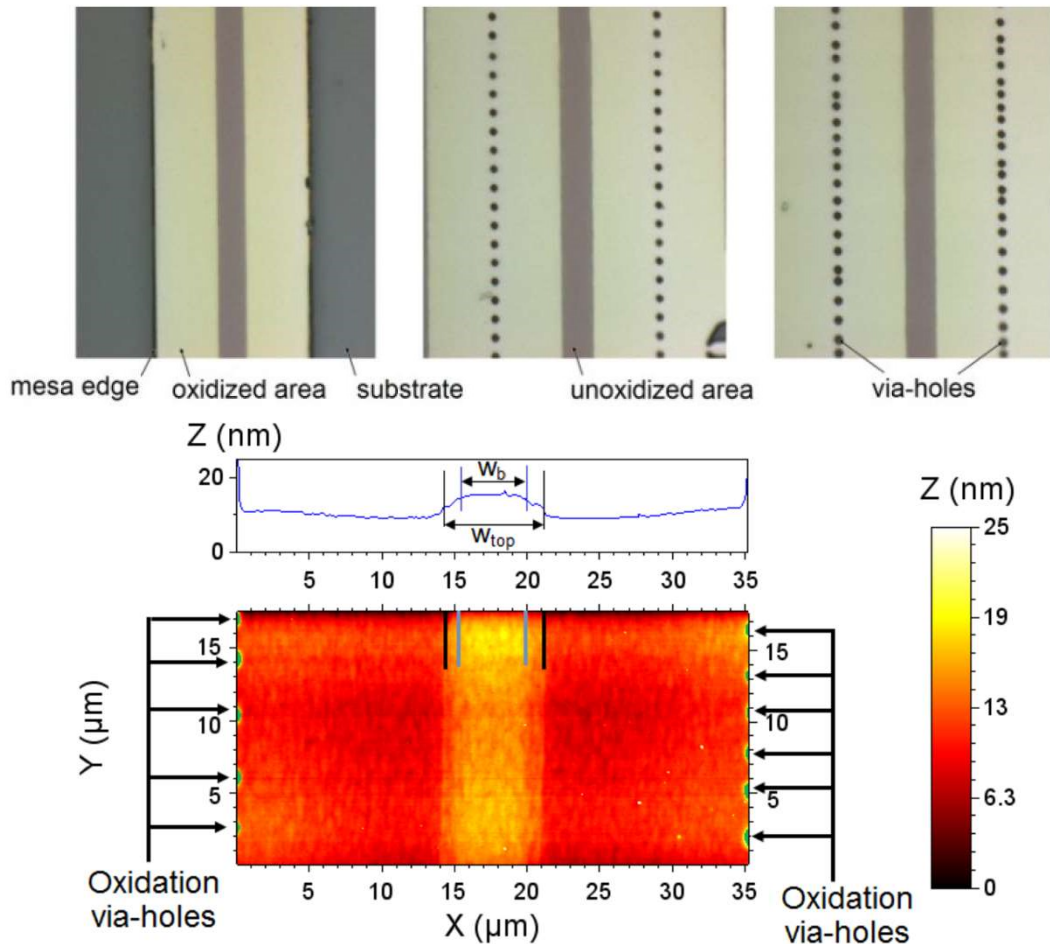
$$a_{\text{in}} = a_{\text{ext}} = 1.00$$

S. Calvez et al, *International Conference on Transparent Optical Networks*, Invited Talk Th.C5.1, (2019).

# Inherent oxidation anisotropy: conclusions

- > Defined oxidation anisotropy quantification methods
- > Oxidation process conditions (temperature) and layer composition can influence the anisotropy
- > Oxidation of circular mesas can be reproduced using erosion-based model
- > Inverse-problem (mesa design) can be tackled to create circular apertures and curved waveguides
  
- > Inherent anisotropy properties
  - Subject to crystalline orientation
  - Relatively weak anisotropy ( $v_{\text{fast}}/v_{\text{slow}} \sim 1.1$ )
  - Oxide aperture with smooth contours

# Oxidation smoothing effect



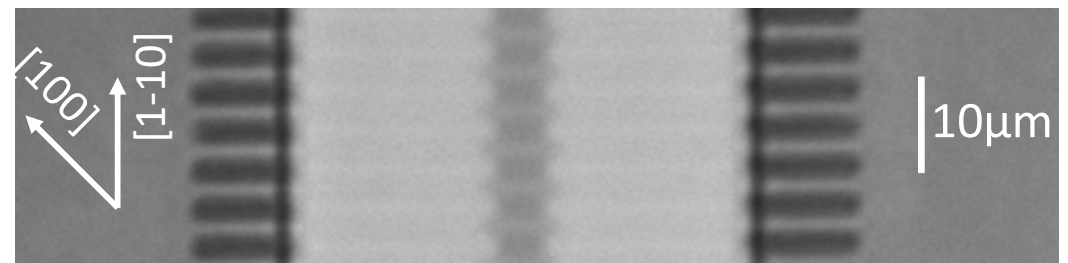
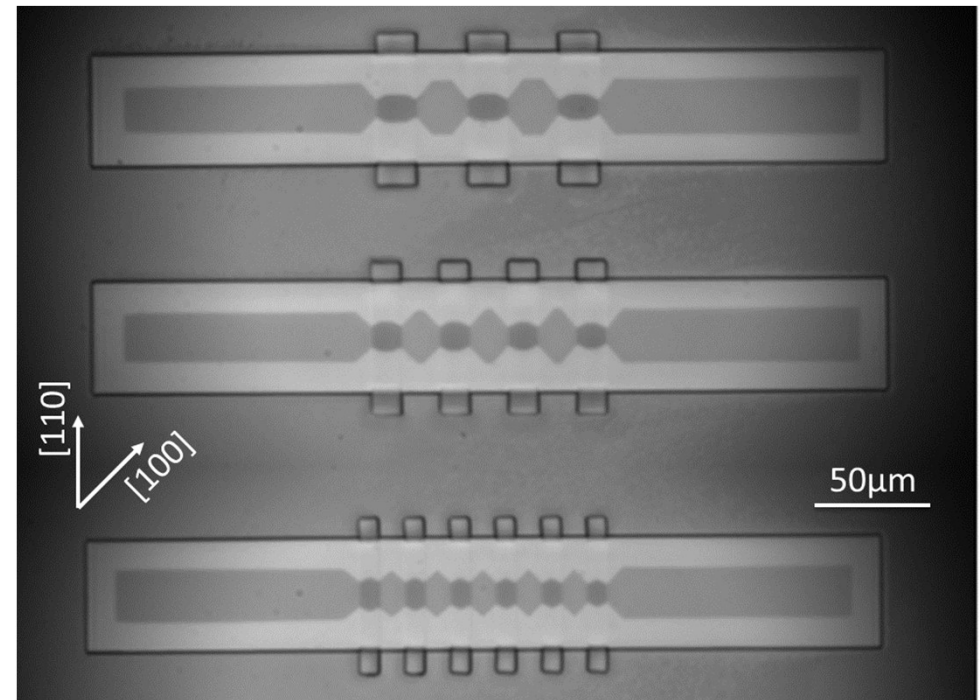
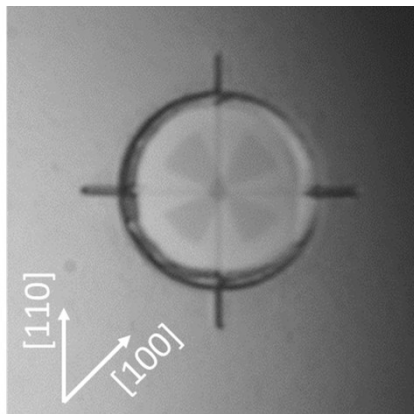
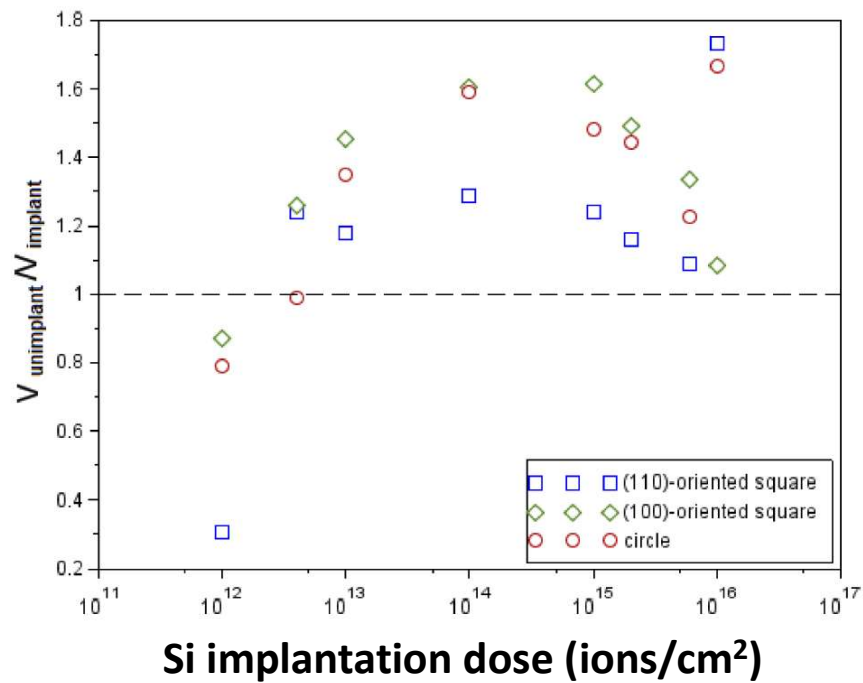
Oxidation diffusive nature prevents (sharply)-corrugated edges

S. Calvez et al, *Opt. Express*, **25** (16), 19275 (2017)

# Artificial oxidation anisotropy

- > Interest for artificial anisotropy
  - Oxide aperture with sharp contours
    - Waveguides with side (DFB) gratings
    - Closely-packed matrix of VCSELs
  
- > How to implement local oxidation anisotropy ?
  - Local modification of composition : implantation of Ga, As (L.-H. Laih et al, *IEEE PTL*, **16** (6), 1423 (2016))
  - Local electrical conductivity change: doping (Si, C) (F. A. Kish, et al, *Appl. Phys. Lett.* **60**(25), 3165–3167 (1992).)
  - Generation of defects ((impurity-free) vacancy-disordering) (T. Gi et al, *Jpn. J. Appl. Phys.* **55** (11), 110303 (2016))

# Artificial oxidation anisotropy



S. Calvez et al, *Opt. Mater. Express* **11**, 3600 (2021).

- > III-V-semiconductor oxidation : a ~30-year history
- > LAAS Contributions
  - Furnace with in-situ monitoring
  - Anisotropic oxidation
    - Methods were defined to quantify the anisotropy
    - Oxidation process conditions (temperature) and layer composition can influence the anisotropy
    - Oxidation of circular mesas can be reproduced using erosion-based model
    - Inverse-problem (mesa design) can be tackled to create circular apertures and curved waveguides
    - Artificial anisotropy allows the creation of « unusual » oxidation patterns



# Acknowledgements and discussion

> Thank you for your attention !

> Financial support



> Any questions ???