

GaAs nanowires: crystal phase engineering and application for water photoelectrolysis

Ph.D. thesis of **Dr. Thomas Dursap**

Director: A. Danescu

Co-supervisors: J. Penuelas, M. Bugnet



ÉCOLE
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N A M E

GDR NANOmaterials for Energy applications



Journées Plénières GDR NAME, 8-10 Nov. 2023



Dr. Thomas DURSAP

- **PhD**, ECLyon - 12/05/2022
- **Postdoc (C2N)**, Saclay, group of Dr. L. Vincent) 06/2022-07/2023
- **Researcher at IMEC** (Leuven, Belgium) 11/2023

Collaborators (apologies if anyone is missing...)

- *M. Fadel, C. Tapia Garcia, M. Koepf, V. Artero [LCBM, CEA Grenoble]*
- *I. Dudko, M. Vettori, C. Botella, P. Regreny, M. Gendry, C. Chevalier, H. S. Nguyen, E. Drouard, S. Brottet [INL, Lyon]*
- *N. Blanchard [iLM Lyon]*
- *M. Dupraz, M-I. Richard [ESRF, Grenoble]*
- *T. Zhou, M. V. Holt [APS, ANL, USA]*
- *S. Labat, O. Thomas [IM2NP, Marseille]*
- *A. Barbier, H. Magnan [CEA Saclay]*

Funding



BEEP project (ANR-18-CE05-0017)
LCBM (CEA Grenoble), **SPEC** (CEA Saclay),
MATEIS, ICJ, INL.

1 – Context

2 – The growth of GaAs nanowires

3 – Crystal phase engineering

4 – III-V nanowire for water splitting

1 – Context

2 – The growth of GaAs nanowires

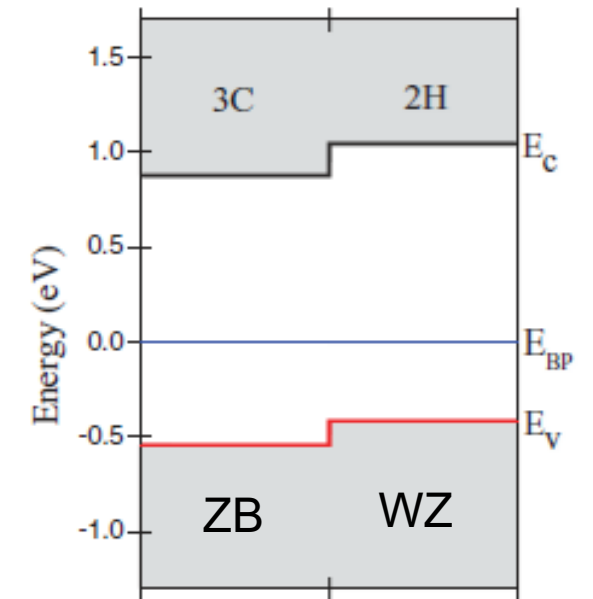
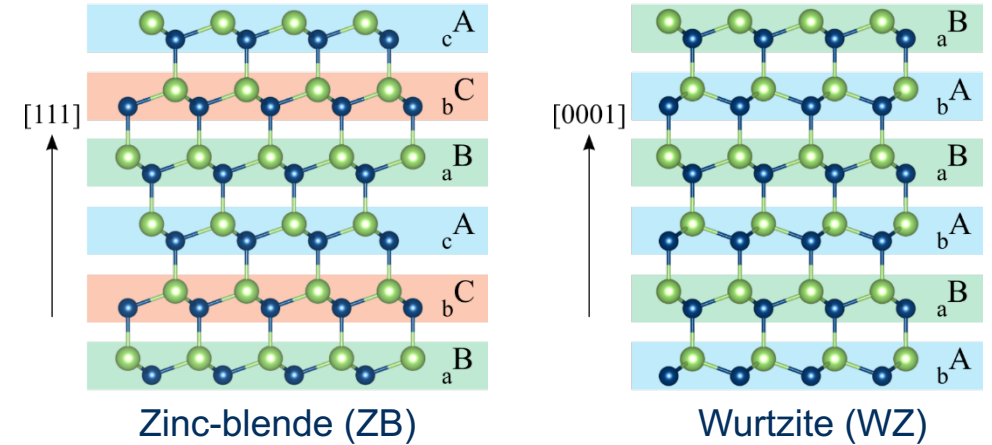
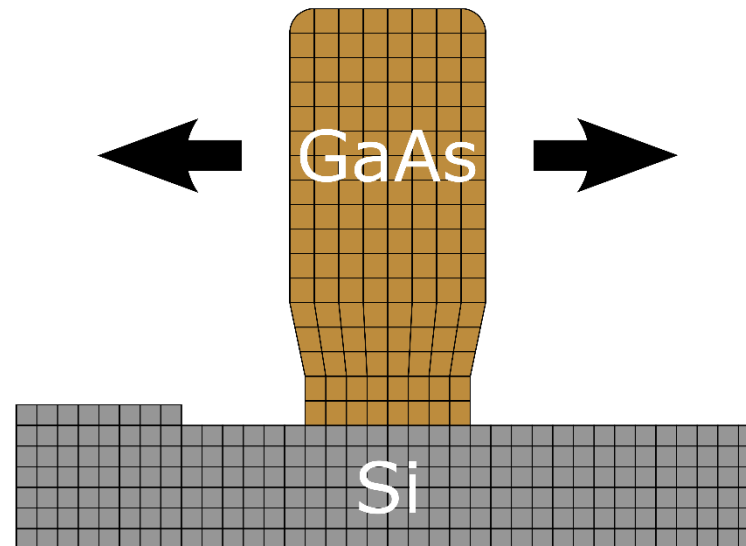
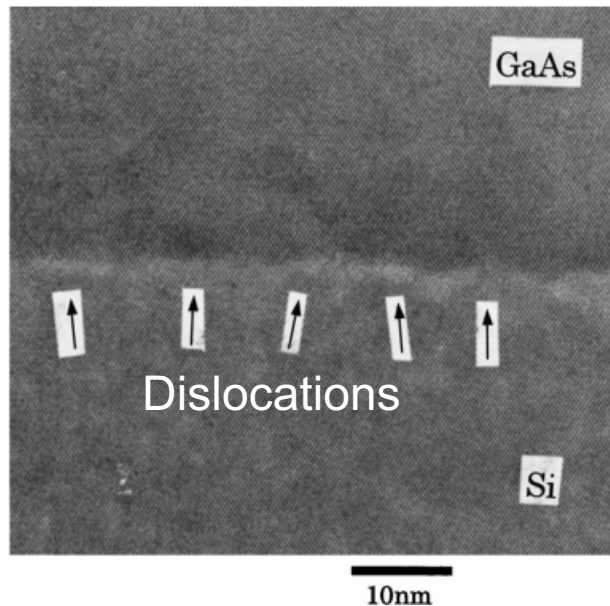
3 – Crystal phase engineering

4 – III-V nanowire for water splitting

1 – Photonic integration on silicon

- **Light emission** integrated in the **silicon** industry
 - **GaAs** appears as an **adequate** candidate
 - **Direct bandgap**
 - Lattice mismatch: **4.1%**
 - **Nanowire** geometry allows lateral relaxation

N. Chandrasekaran *et al.*
APL, 82, 22 (2003)

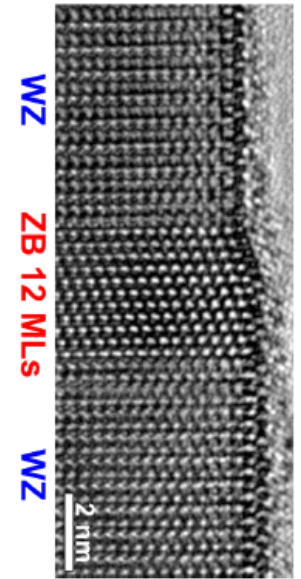
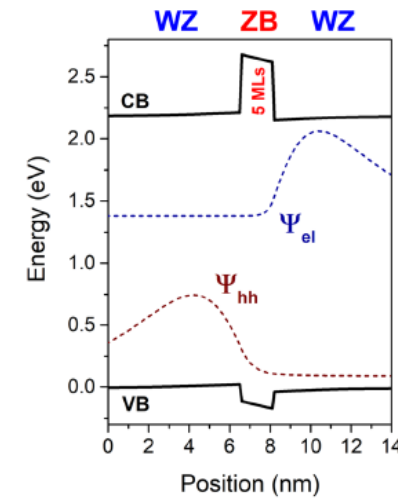


A. Belabbes *et al.*
PRB, 86 (2012)

- **Crystal phase quantum well emission** using GaP nanowires. A. Assali *et al.*, *Nano Lett.* 17 (2017)

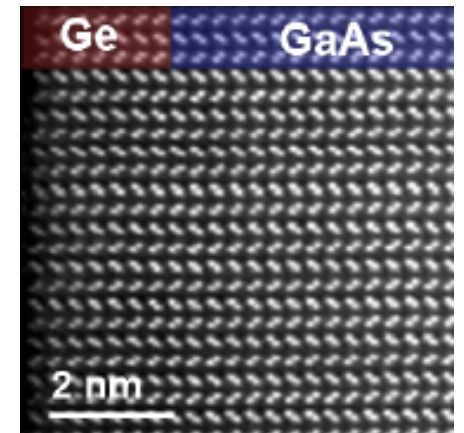
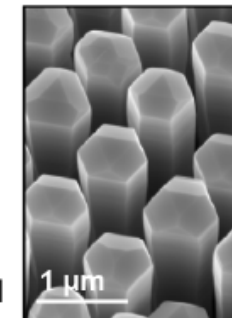
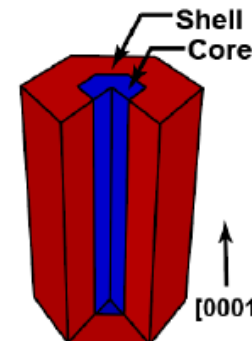
- **ZB** and **WZ** alternations to create quantum wells

Crystal engineering
for segmented phases



- Integration of **group-IV** elements in **silicon** technology
 - Hexagonal **SiGe** alloy recently demonstrated as **direct band-gap light emitter**. E. M. T. Fadaly *et al.*, *Nature*, 580, 7802 (2020)
 - Possible to synthesize through **III-V nanowire phase transfer**

Crystal engineering
for extended pure-phases

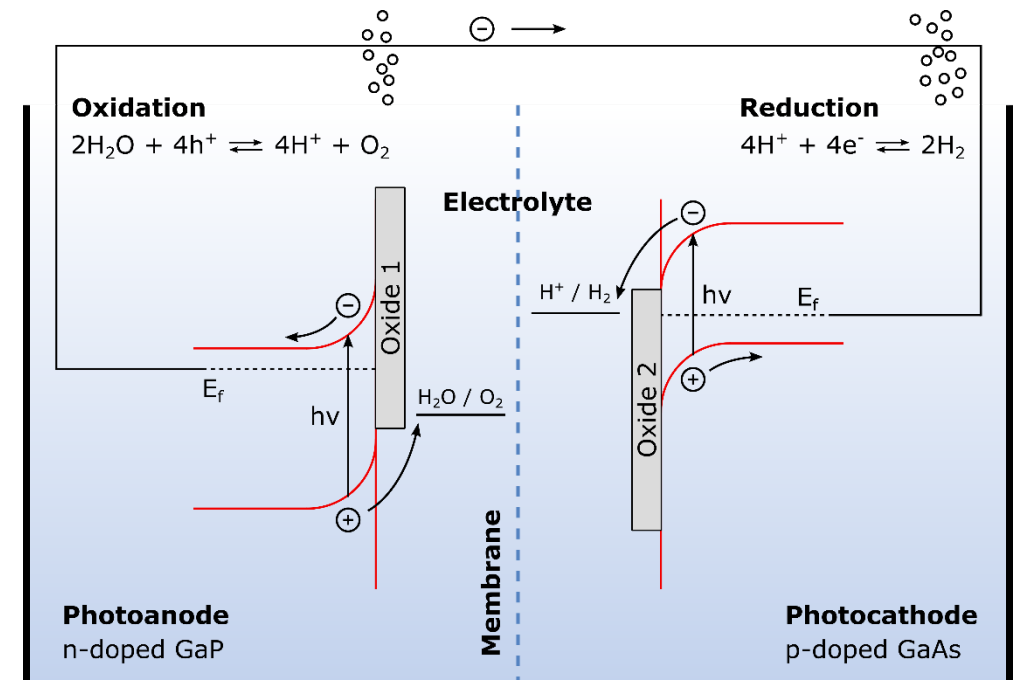


1 – Water splitting

- **Solar energy** conversion, an **alternative** to fossil fuel.
 - **Hydrogen** generation
 - Efficient storage
 - 142 MJ/kg (Fuel: 47 MJ/kg; Li-ion battery: 0,46-0,70 MJ/kg)
- **Photoelectrochemical** water splitting reaction occurs at the liquid/electrode interface.
 - Oxygen evolution reaction (OER)

$$2H_2O + 4h^+ \rightleftharpoons 4H^+ + O_2$$
 - Hydrogen evolution reaction (HER)

$$4H^+ + 4e^- \rightleftharpoons 2H_2$$

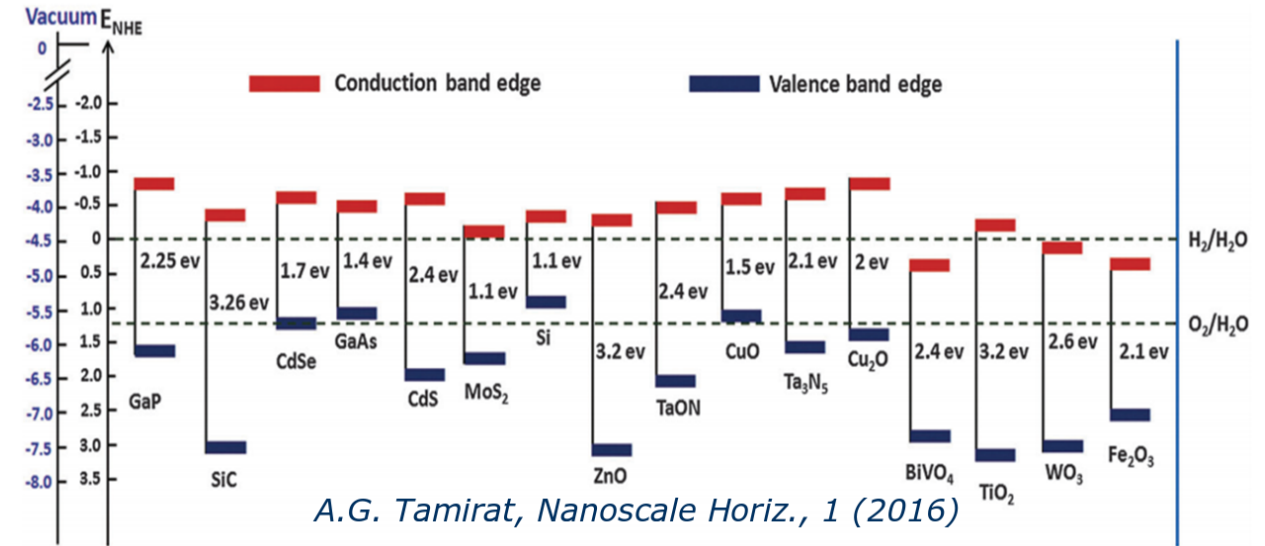


1 – Water splitting

- **III-V semiconductors**

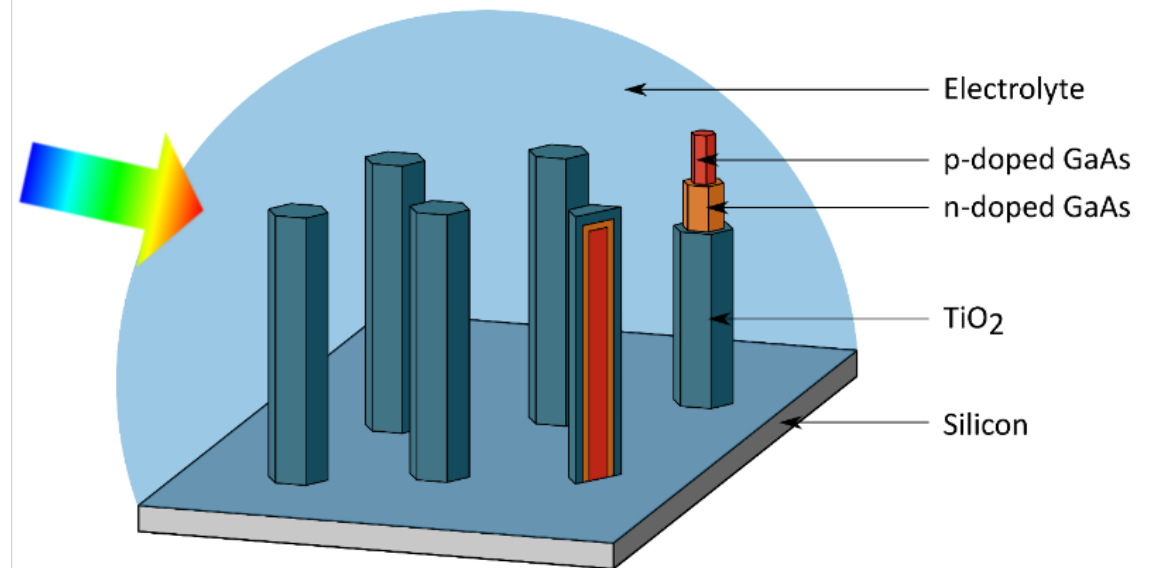
- **Bandgap adapted to solar spectrum**

- GaAs: 1.4 eV
 - GaP: 2.25 eV



- **Enhanced efficiency using nanowires**

- Wide interaction surface
 - Charge separation
 - Enhanced light absorption



1 – Context

2 – The growth of GaAs nanowires

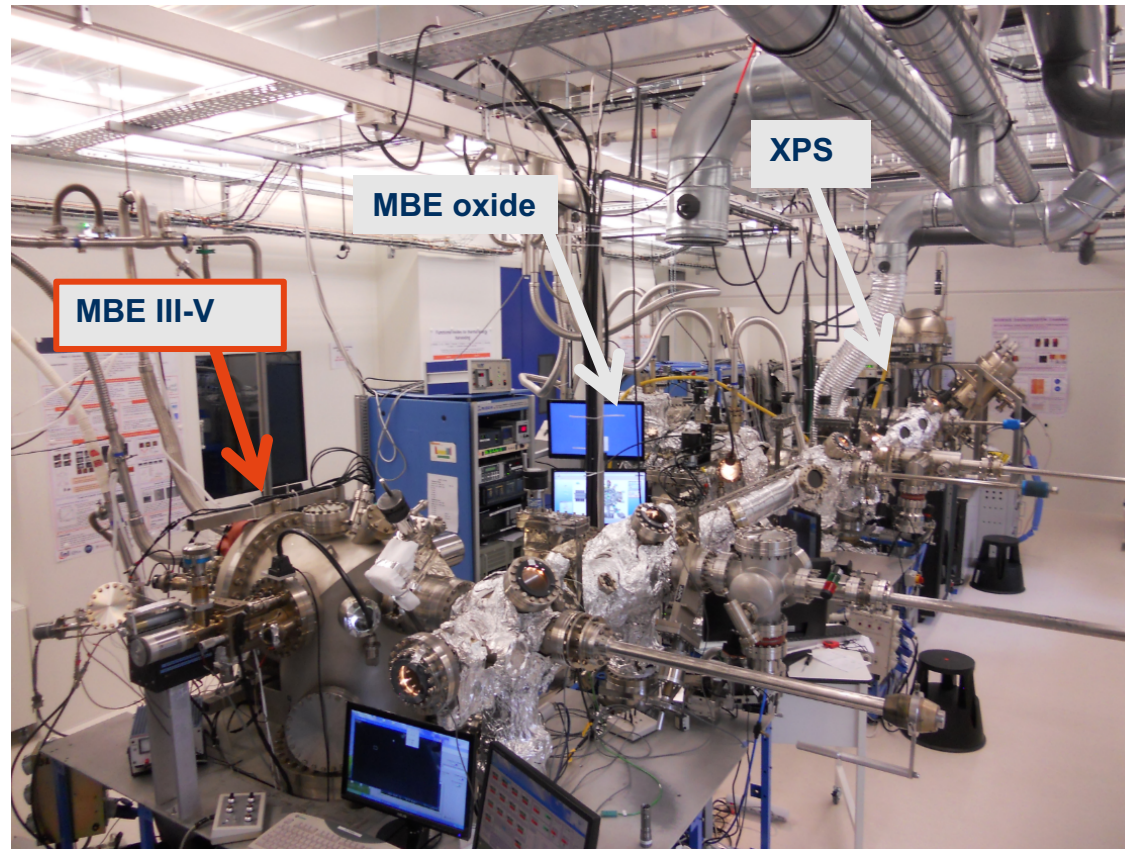
3 – Crystal phase engineering

4 – III-V nanowire for water splitting

2 – The growth of GaAs nanowires

- **Molecular beam epitaxy (MBE) – vapor-liquid-solid (VLS) mechanism**

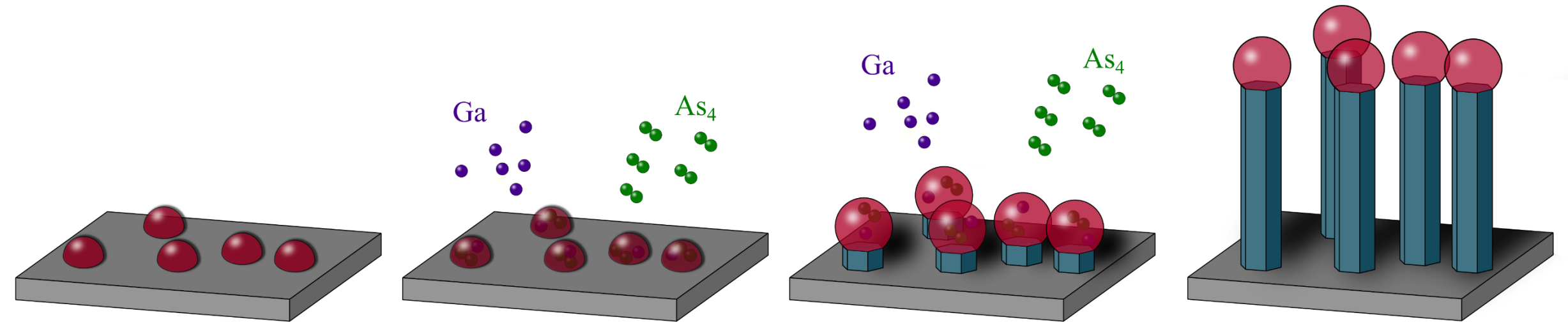
R. S. Wagner and W. C. Ellis Appl. Phys. Lett. (1964)



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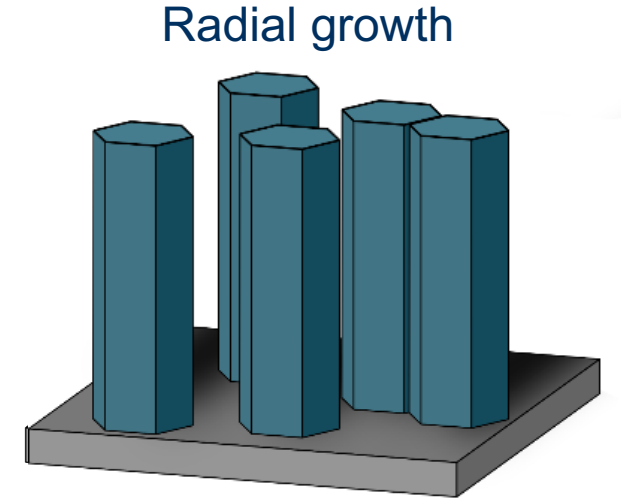
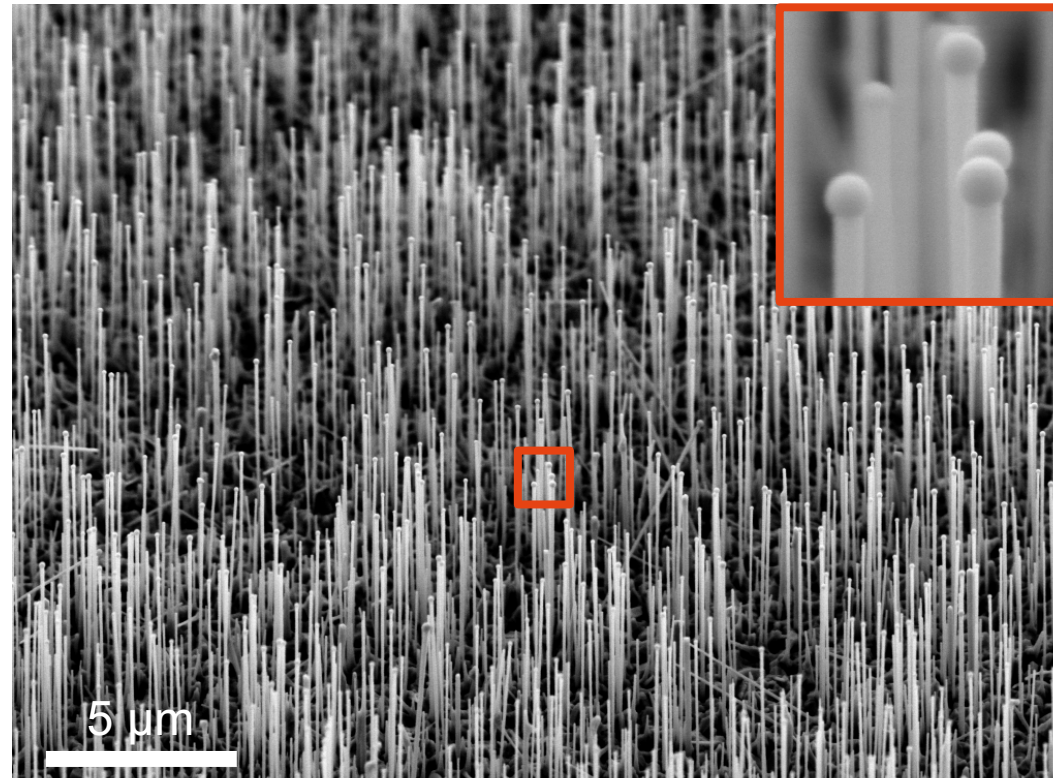
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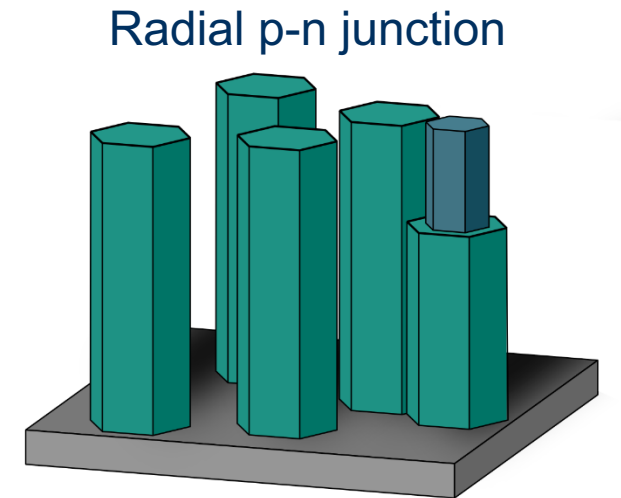
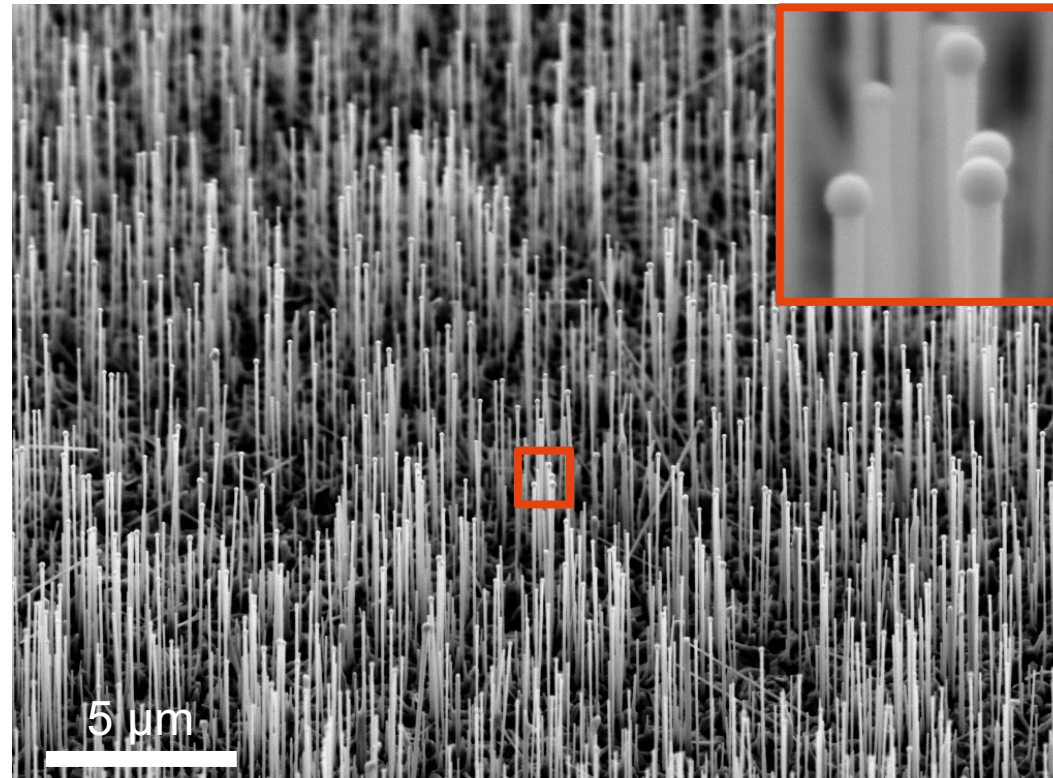
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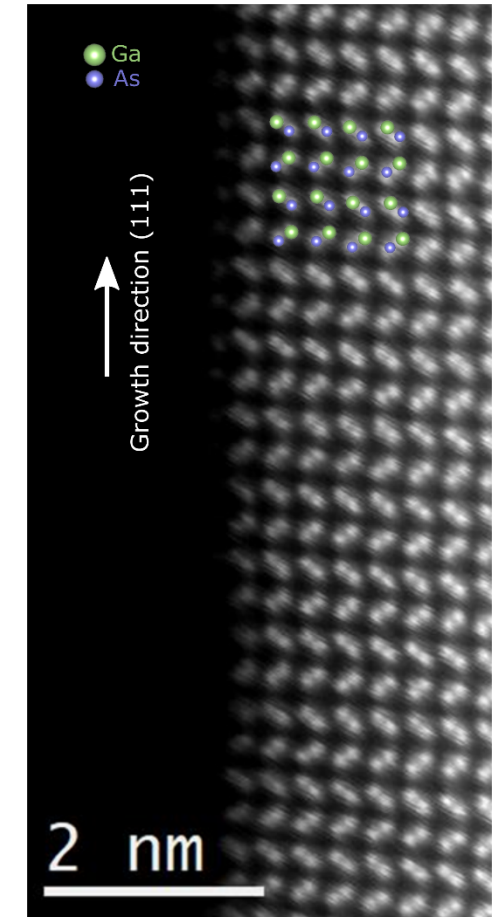
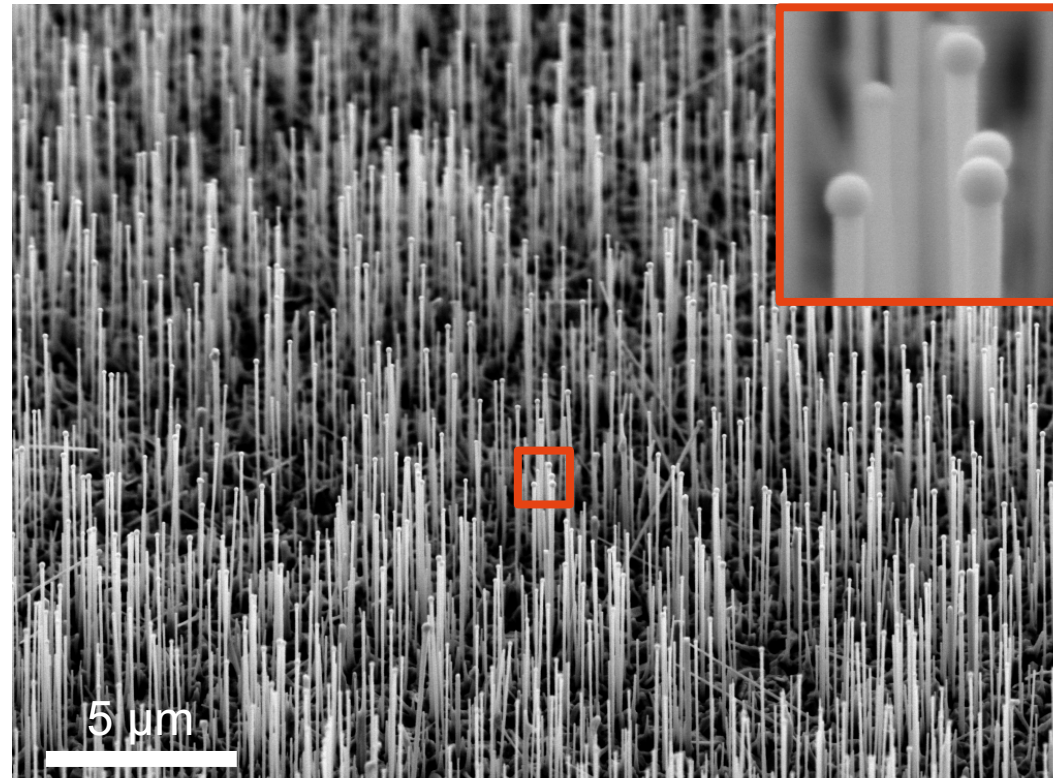
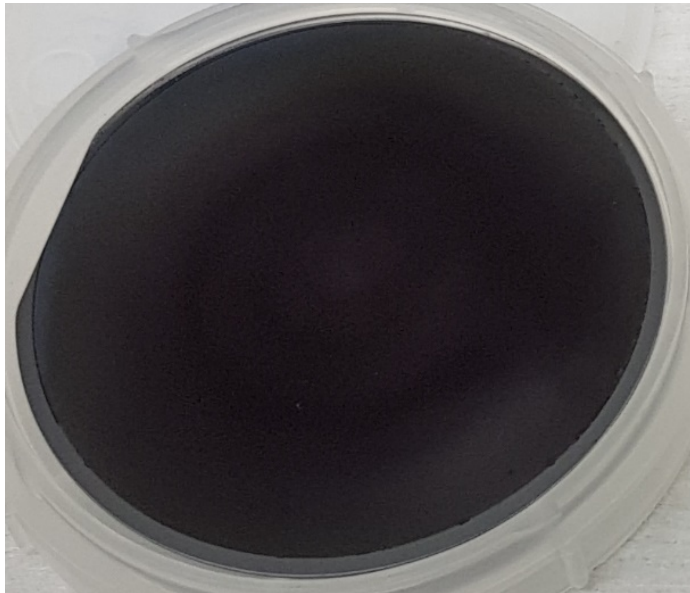
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2 – The growth of GaAs nanowires

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1 – Context

2 – The growth of GaAs nanowires

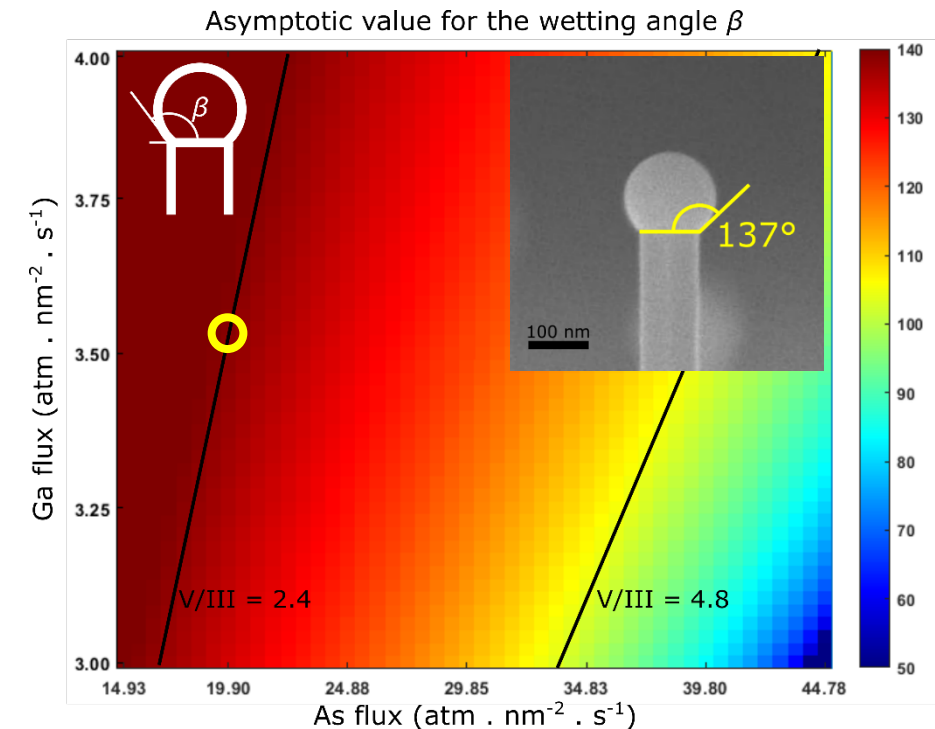
3 – Crystal phase engineering

- WZ insertion
- Extended WZ segment
- Combined characterization

4 – III-V nanowire for water splitting

3 – Extended WZ segment

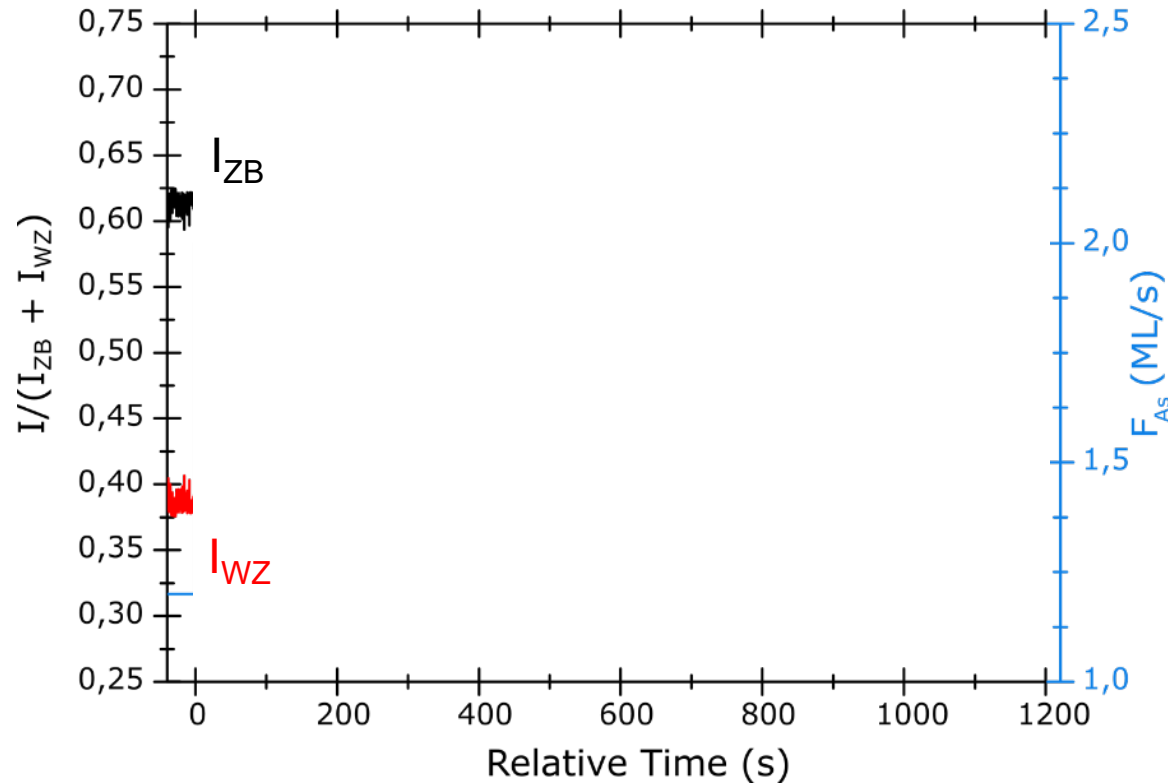
- **Master Thesis:** Inclusion of short WZ segments in a ZB nanowire
- **PhD Thesis:** sustained growth of a WZ segment ?
 - Self-assisted NW growth: a self-regulated system
M. Vettori et al. Nanoscale Adv. (2019)
 - As-rich regime:
 - Droplet volume decrease to equilibrium
 - Ga-rich regime:
 - Droplet volume increase to equilibrium



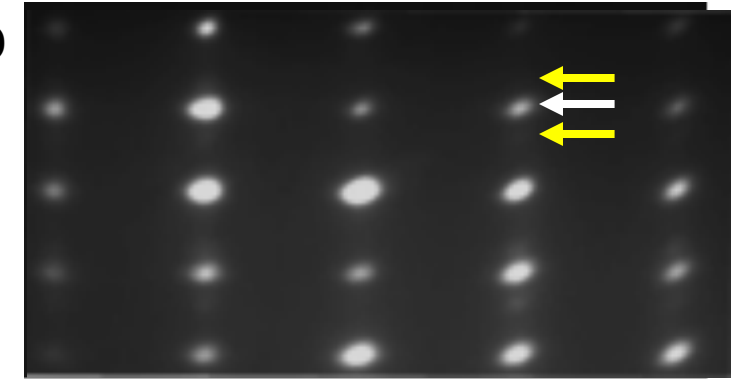
T. Dursap et al. Nanotechnology (2021)

3 – Extended WZ segment

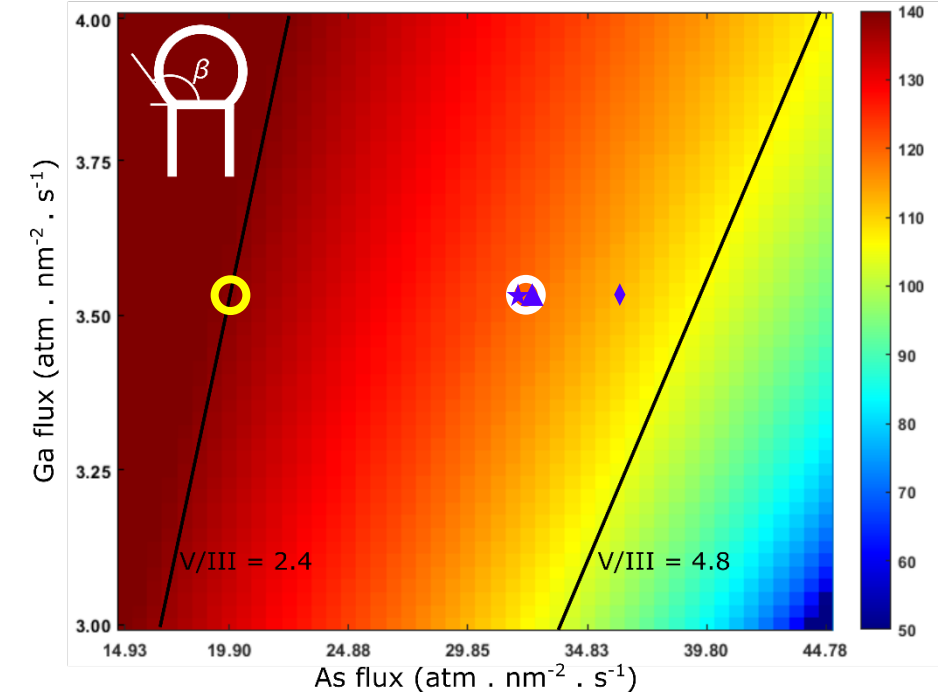
- 25 min growth at $V/III = 2.4$
- Increase **As flux** to reach $V/III = 4.0$



RHEED

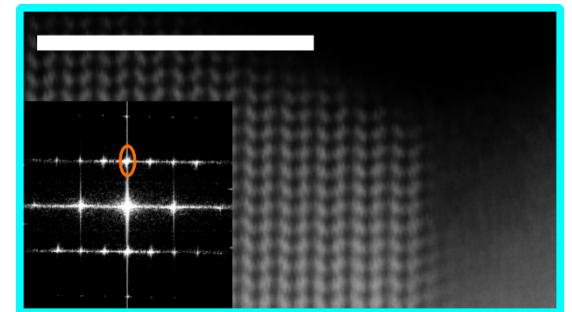
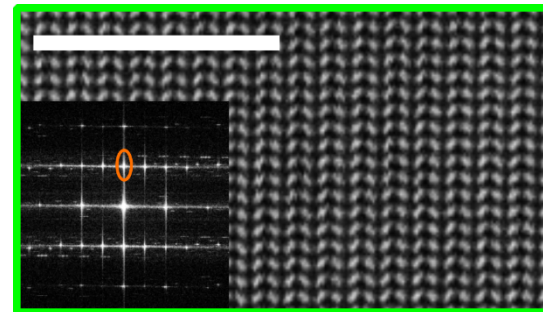
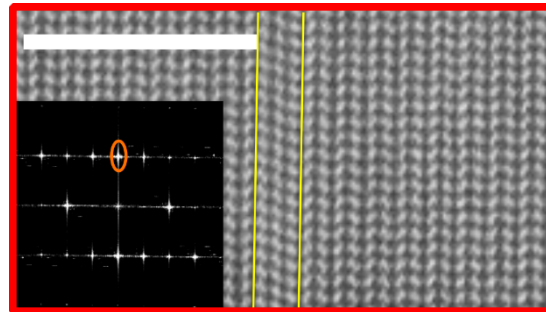
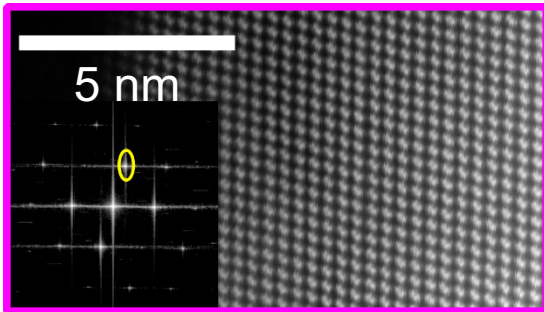
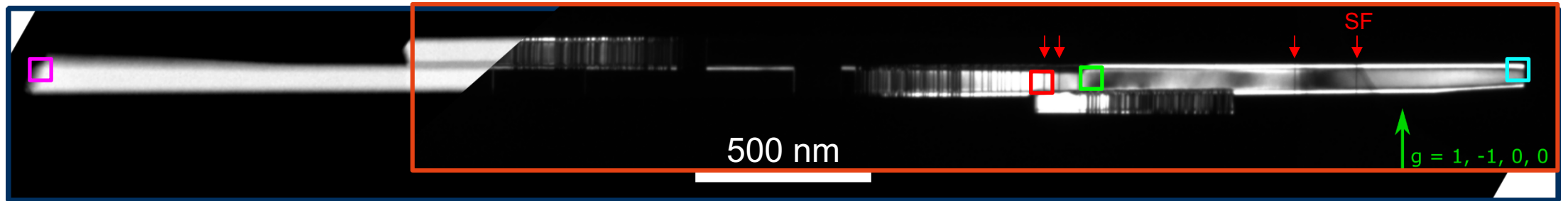


Asymptotic value for the wetting angle β

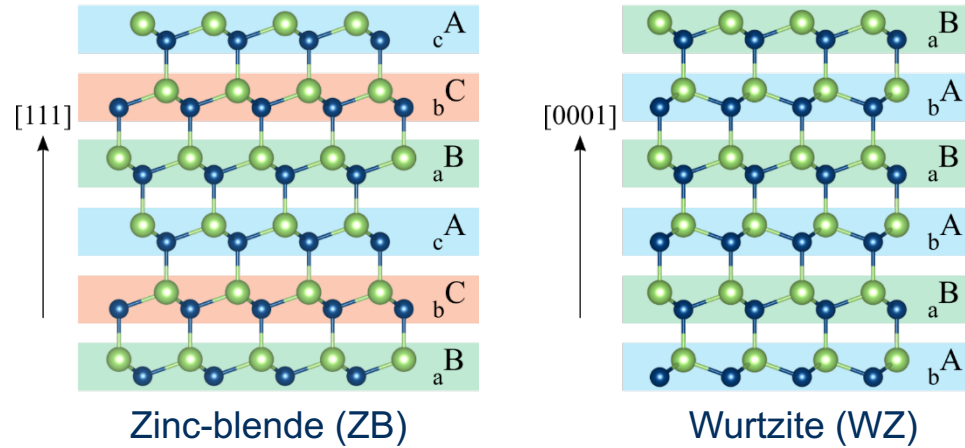


3 – Extended WZ segment

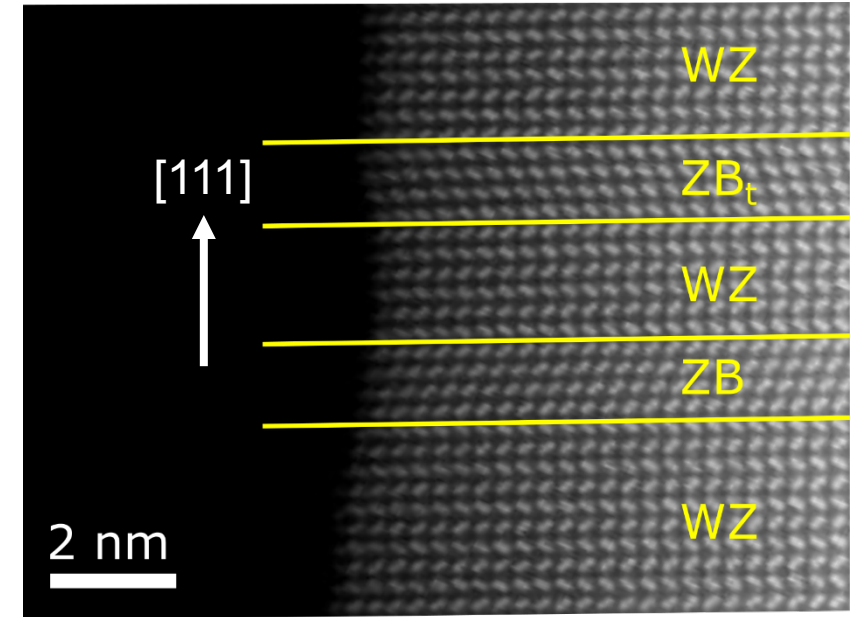
- **25 min** under **V/III = 2.4** followed by **20 min** under **V/III = 4.0**
 - STEM HAADF imaging
 - High resolution
 - Dark-field TEM



3 – Combined characterization

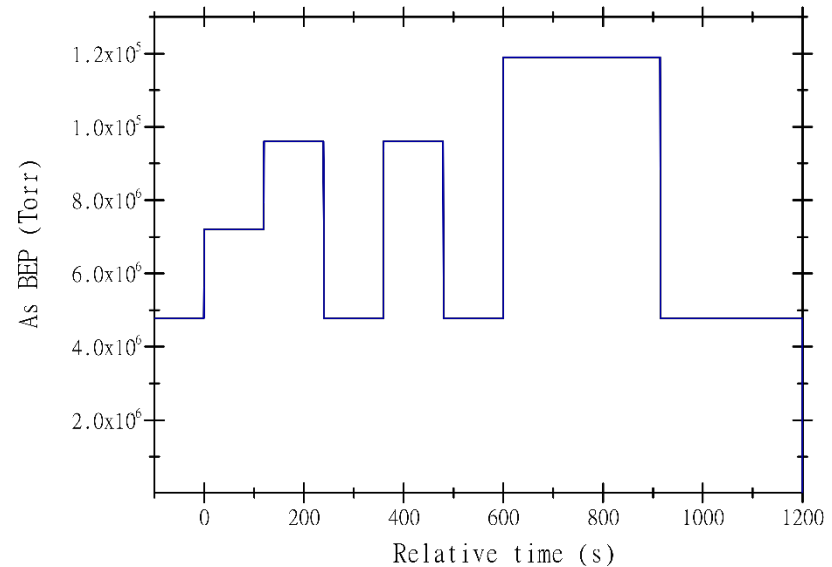


Slight in-plane lattice mismatch: -0.3%

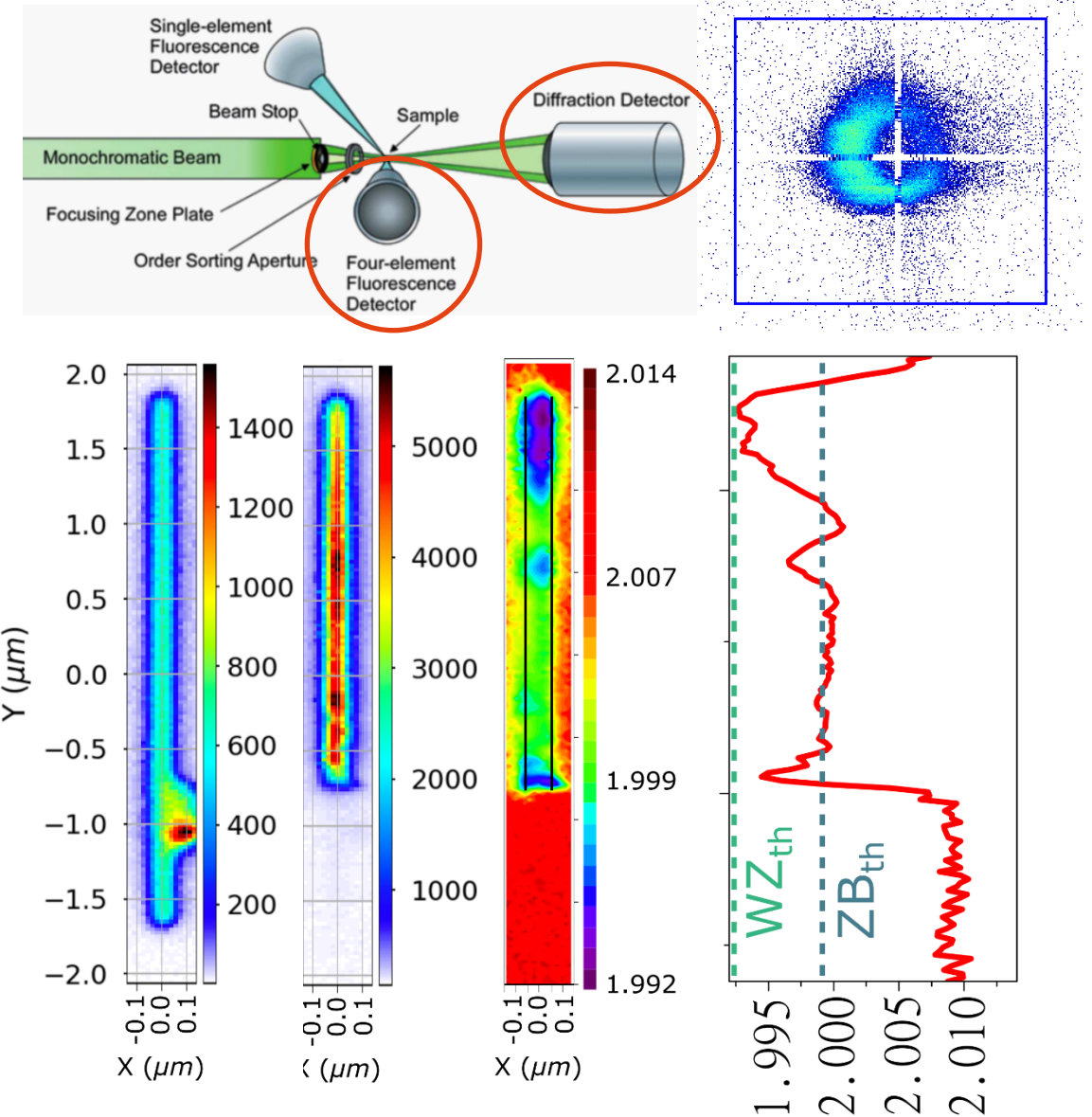


- Increase of the As flux during growth:

- Crystal phase change
- Internal strain?
- Defects ?



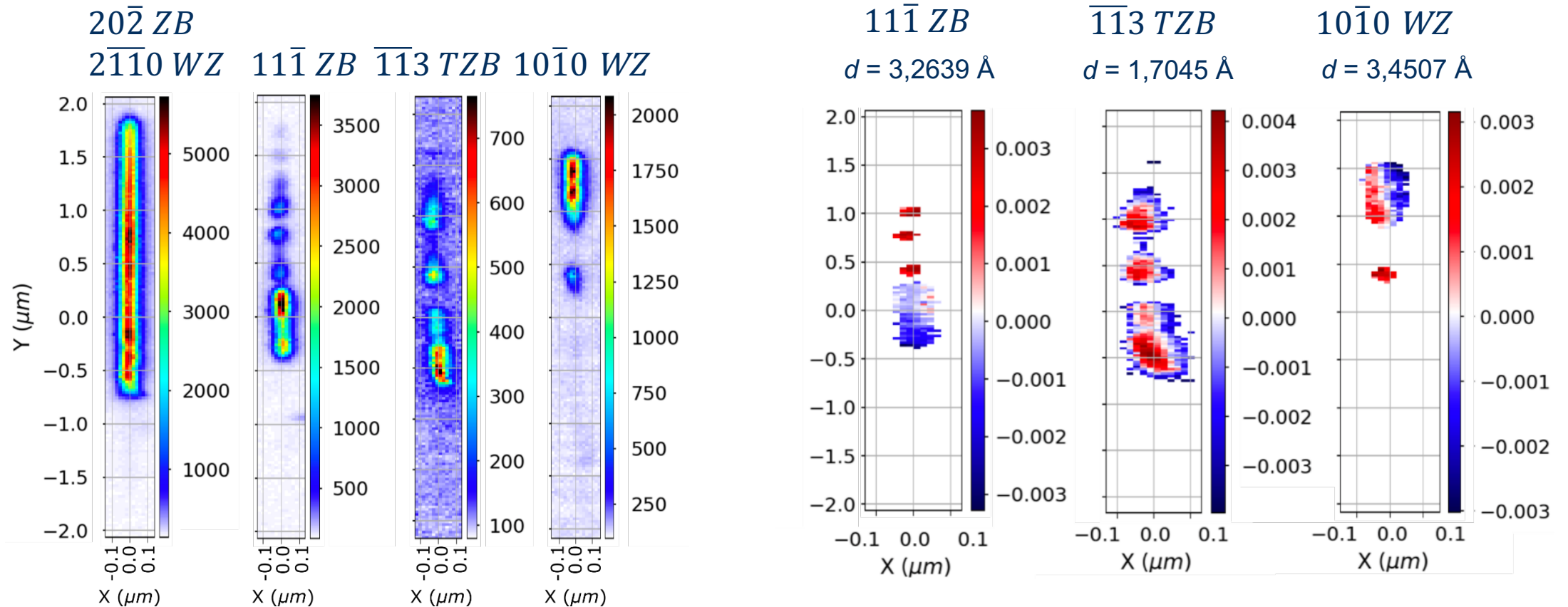
- NW localized using the **fluorescence of Ga**
- Reflection of the $20\bar{2}$ (*ZB*)/ $2\bar{1}10$ (*WZ*) plans
 - Integrated intensity
- Measurement of the **center of mass** to determine the d_{hkl}
 - Precise determination of the d_{hkl}
 - $d_{ZB} = 1,9987 \text{ \AA}$
S. Saib et al. Solid-State Elec. (2006)
 - $d_{WZ} = 1,9923 \text{ \AA}$
J. Jacobsson (2015)



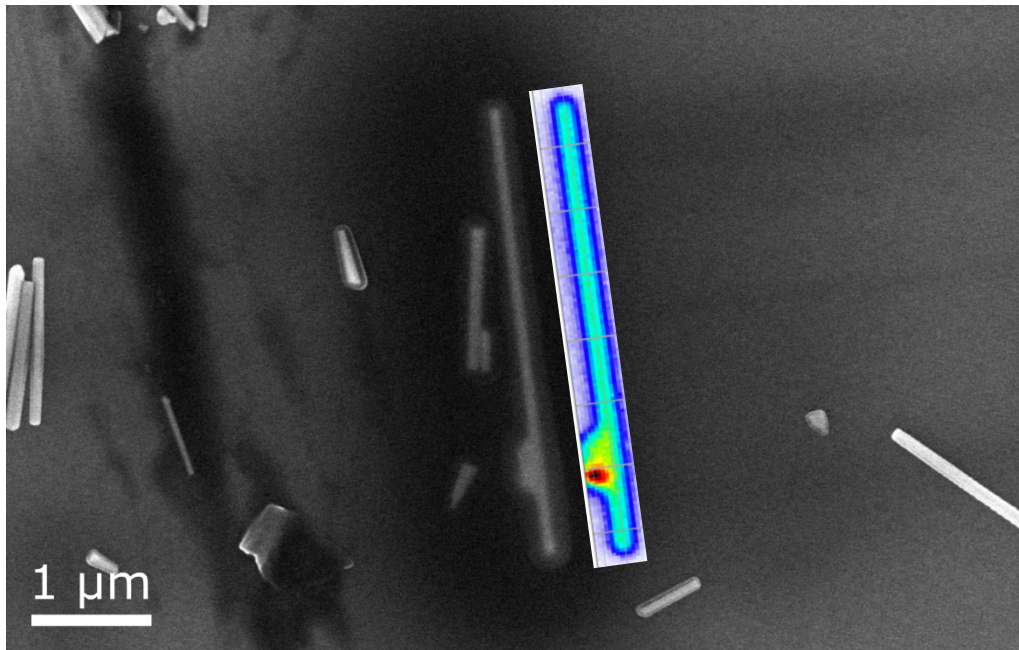
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3 – Nano-diffraction

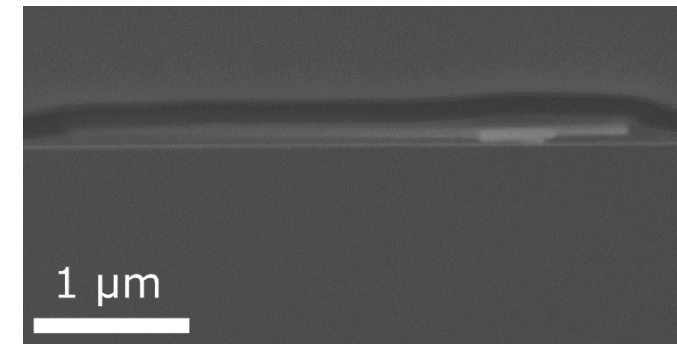
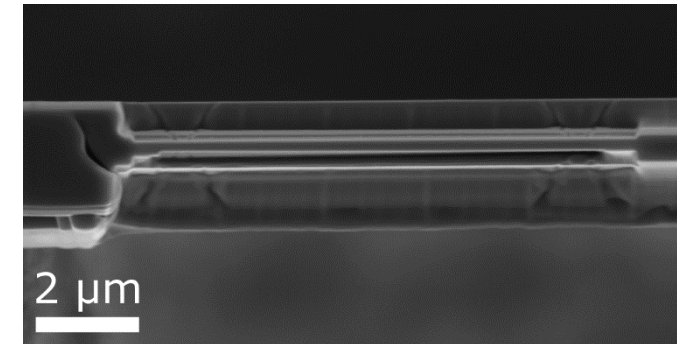
- Integrated intensity of **different reflections**
- Extract **internal strains** from the d-spacing maps



- **Nano-diffraction**
 - Spatial resolution of 25 nm
- **TEM observation**
 - High spatial resolution

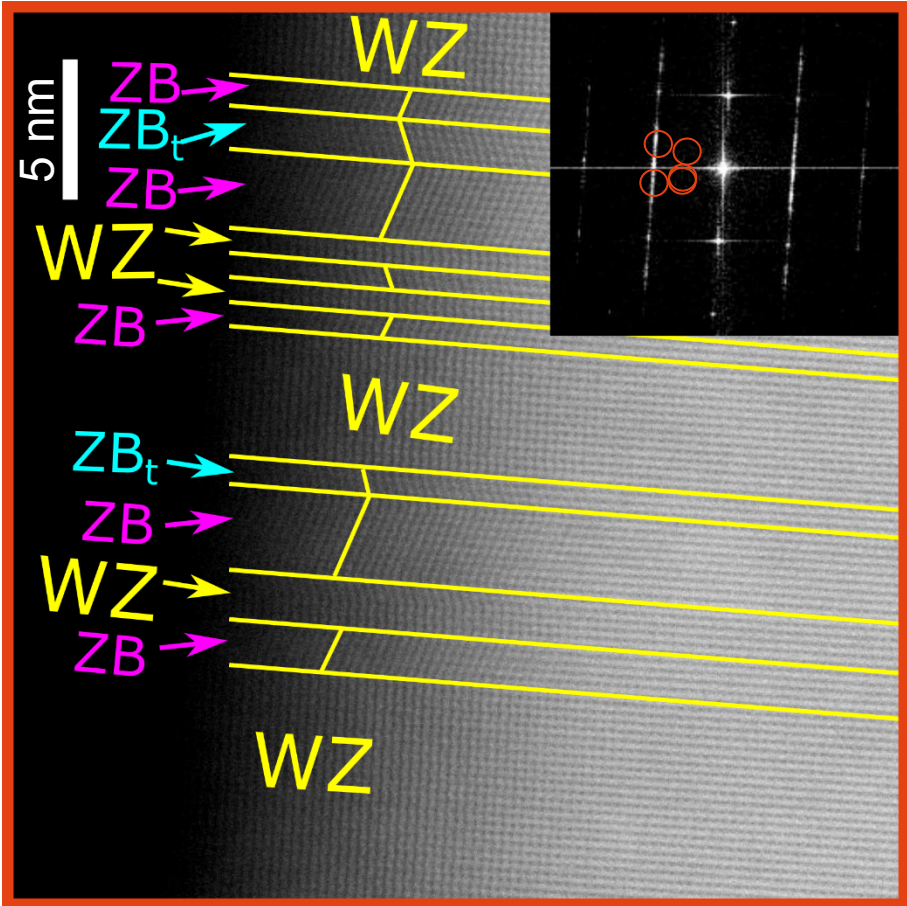
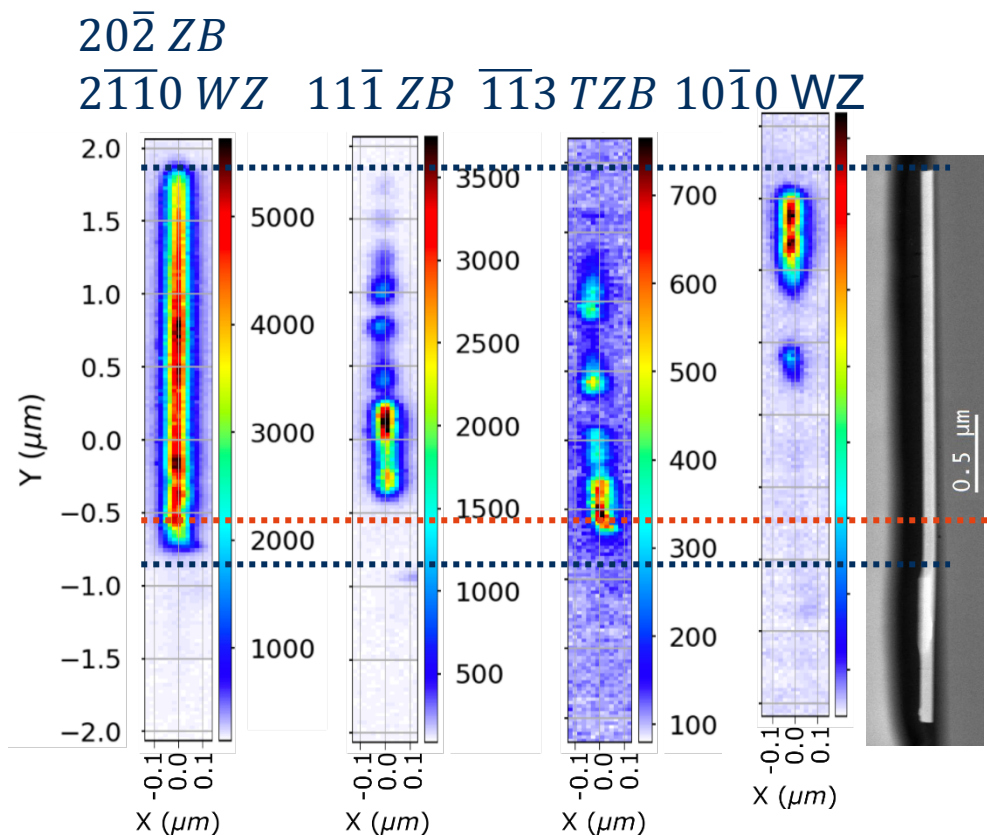


Focused Ion
Beam (FIB)

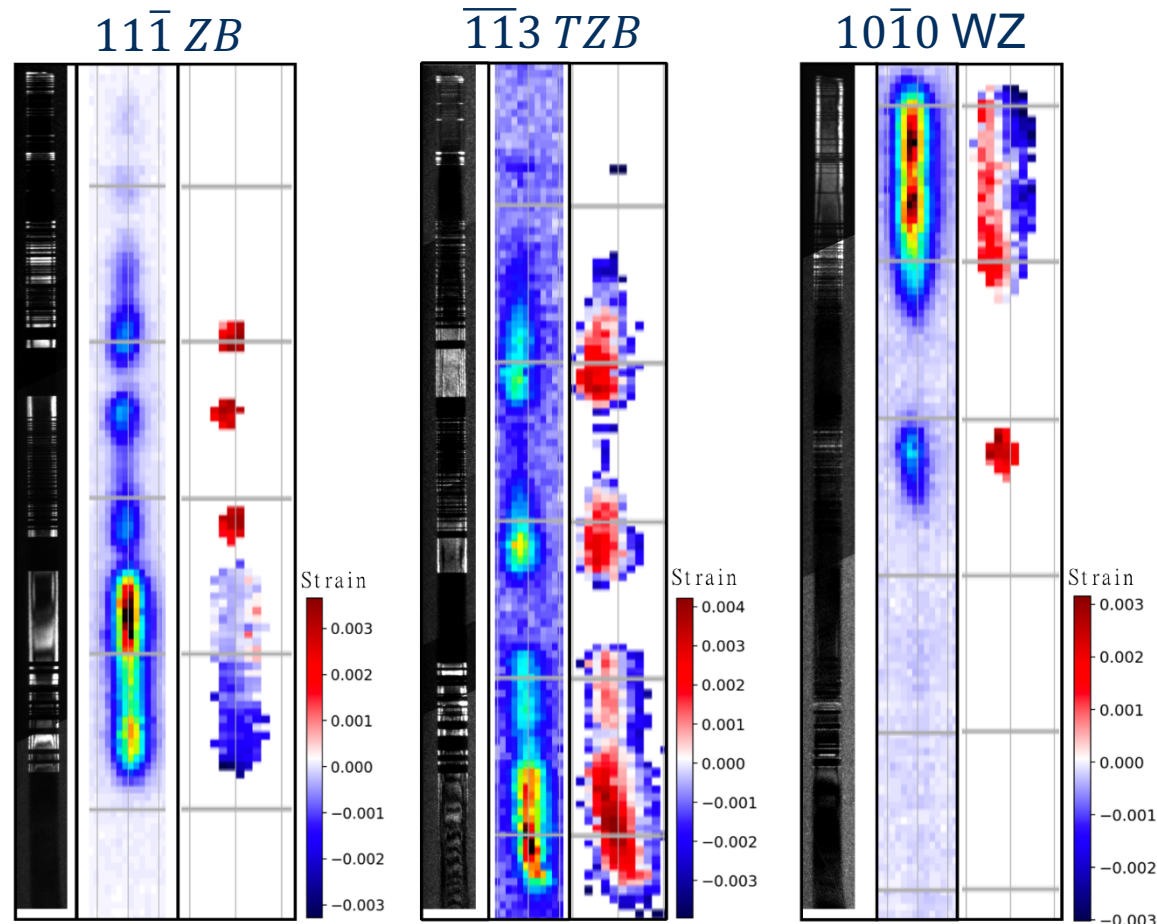


3 – High-resolution STEM

- TEM and nano-diffraction **on the same** nanowire
 - Confirm the crystal phases identified



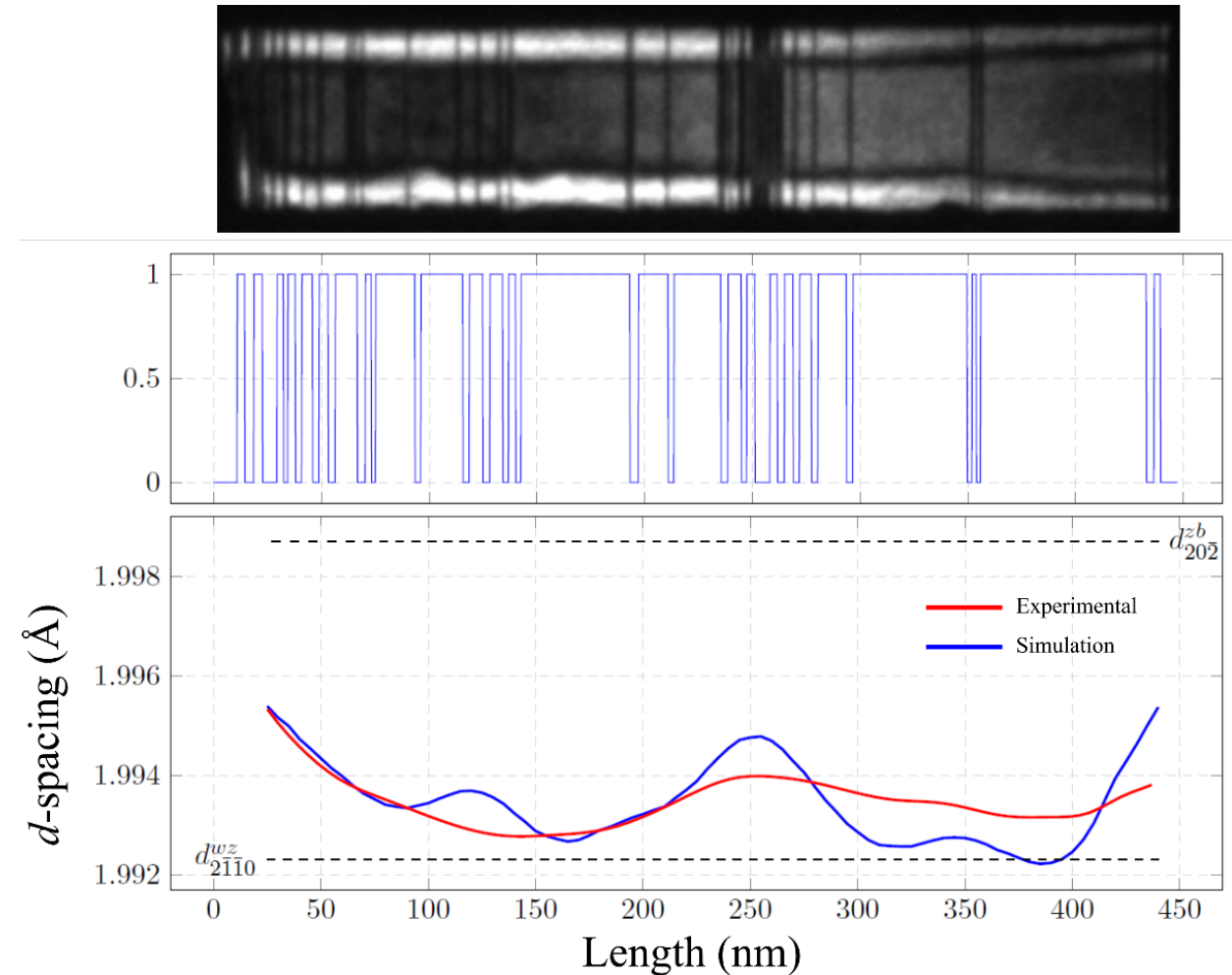
- **DF-TEM** to localize the **crystal phase** all along the nanowire



- Good match between the **DF-TEM** and **nano-diffraction** characterizations
- Evidence of **strain** around areas where the **crystal phases switch**
 - $\epsilon_{11\bar{1}} \approx 0.4 \%$
 - $\epsilon_{1\bar{1}3} \approx 0.3 \%$
 - $\epsilon_{10\bar{1}0} \approx 0.3 \%$

- **DF-TEM images** used as input for **finite element simulations**

- **1) Localization** of the phases (WZ/ZB) from **DF-TEM images**.
- **2) Computation** of the inter-reticular distance.
- Strong **contribution** of the **structural transitions** on the ***d*-spacing**.



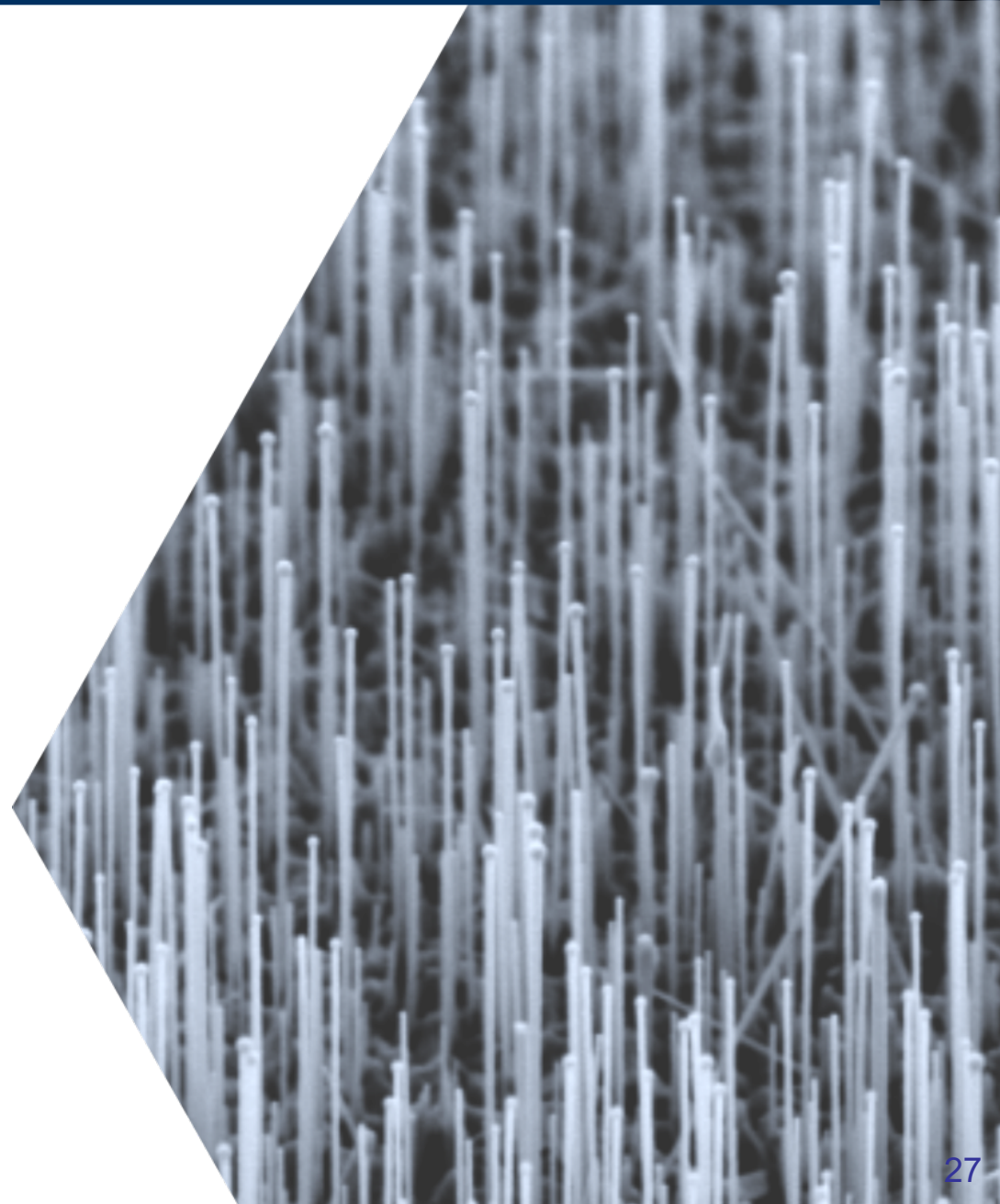
1 – Context

2 – The growth of GaAs nanowires

3 – Crystal phase engineering

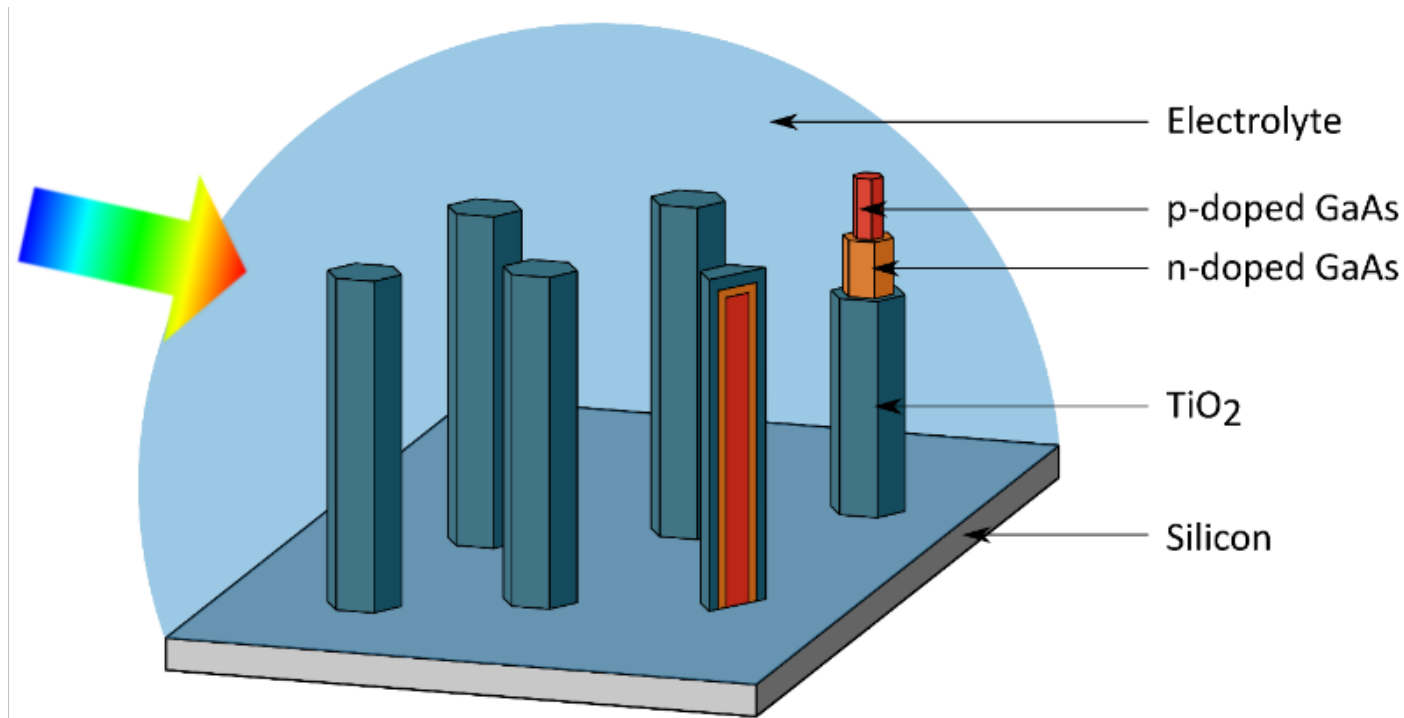
4 – III-V nanowire for water splitting

- GaAs nanowires as photocathode
- Impact of the morphology



4 – III-V nanowires for water splitting

- **III-V nanowires** for water photoelectrolysis
 - Efficiency of the nanowire geometry over thin film
 - Optimization of the nanowire-cell



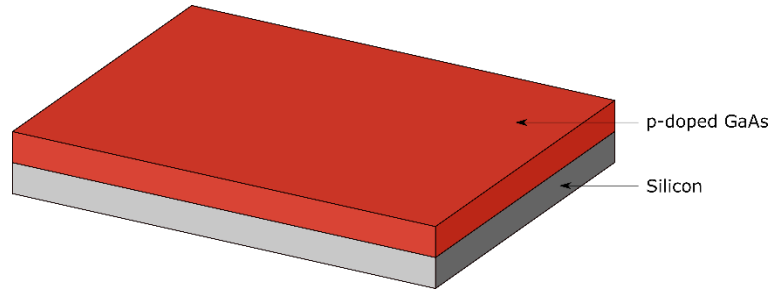
BEEP ANR project (ANR-18-CE05-0017)

Collaboration between

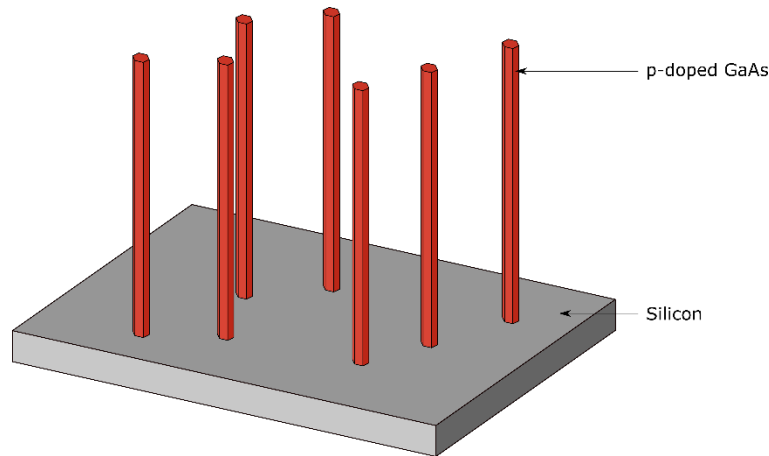
LCBM (CEA Grenoble), **SPEC** (CEA Saclay), **MATEIS**, **ICJ**, **INL**.

4 – GaAs photocathode

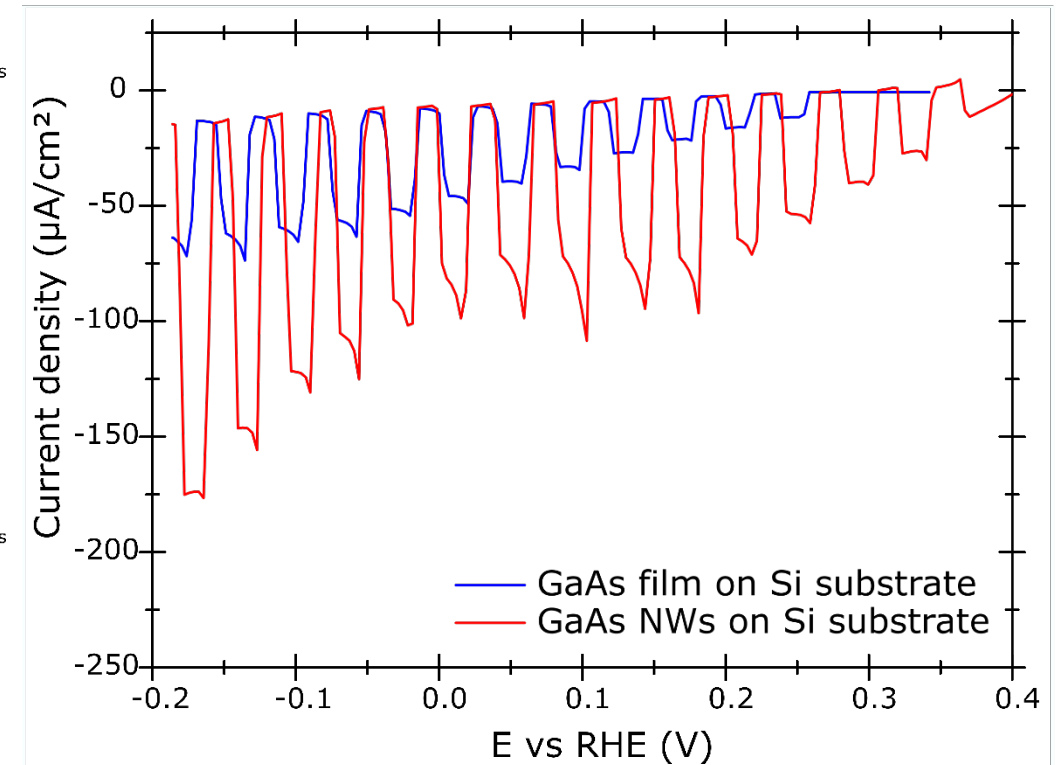
- p-doped GaAs film grew on Si(111)



- p-doped GaAs NWs grew on Si(111)



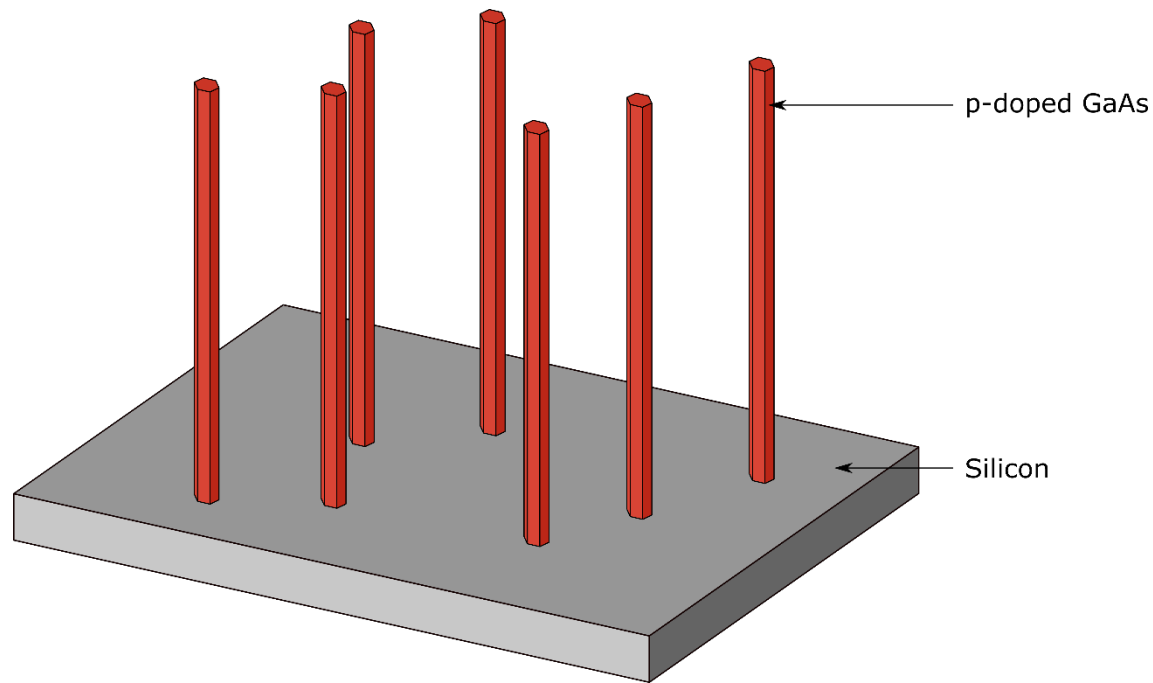
10 mV/s, 0.1 MPB pH7, 1 Sun, AM 1.5



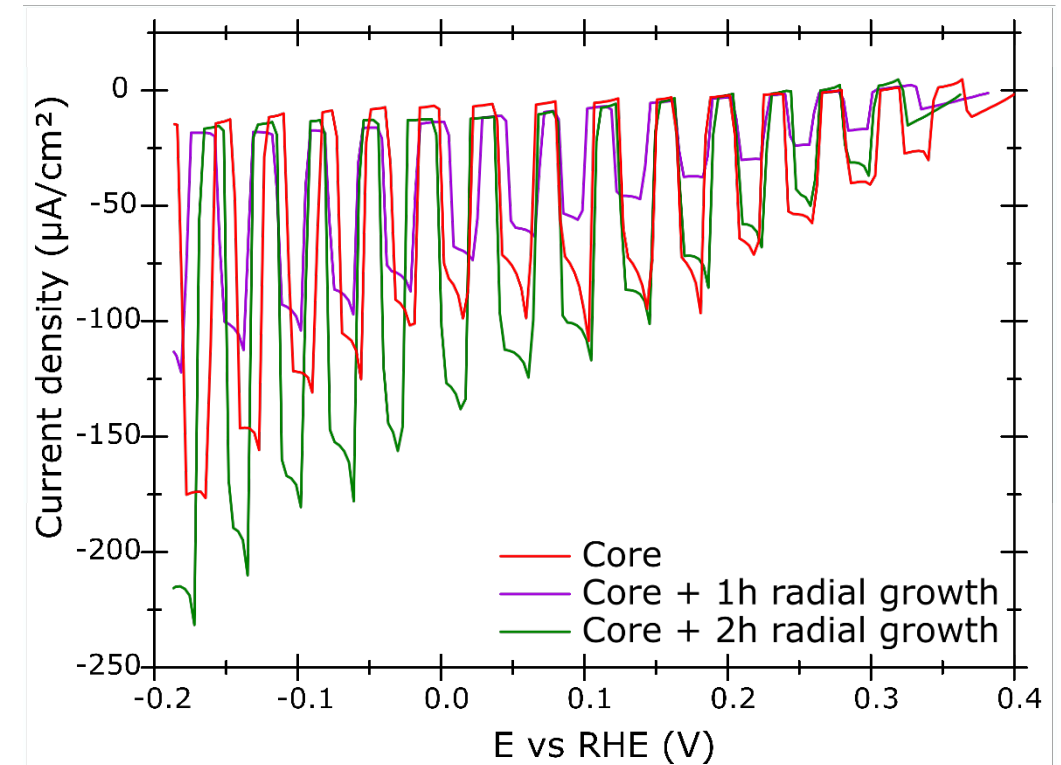
4 – Impact of the morphology

- Increase the size of the NWs by:

- $L = 2.3 \mu\text{m}$, $D = 125 \text{ nm}$
- $L = 5.2 \mu\text{m}$, $D = 380 \text{ nm}$
- $L = 9.4 \mu\text{m}$, $D = 740 \text{ nm}$

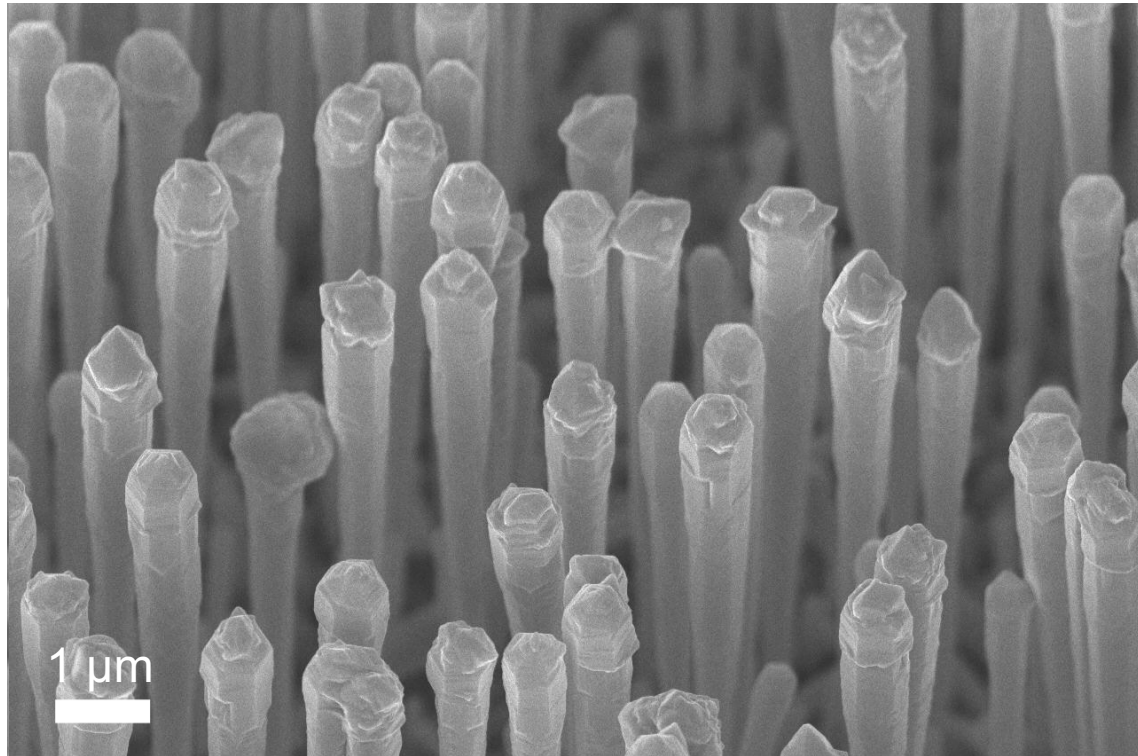


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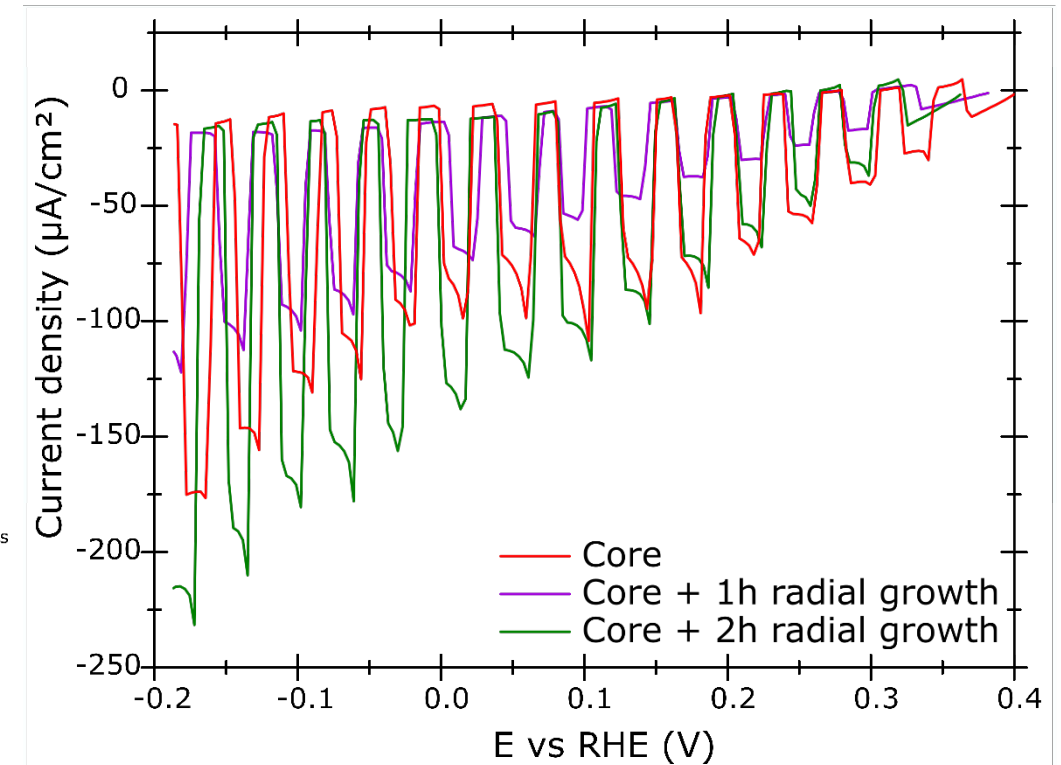


4 – Impact of the morphology

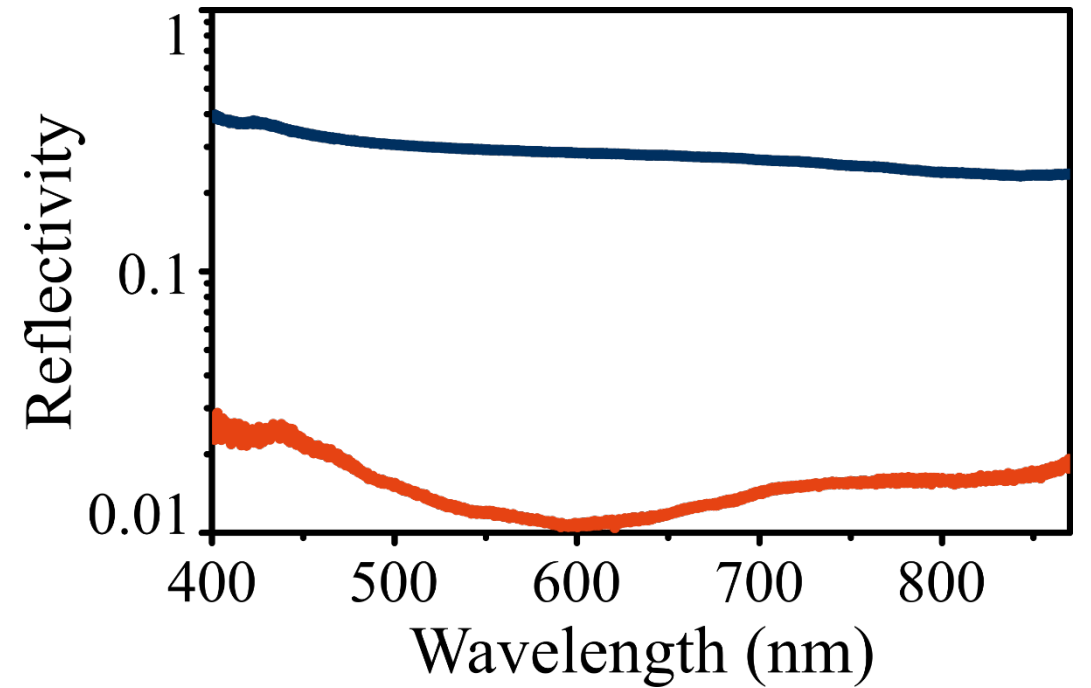
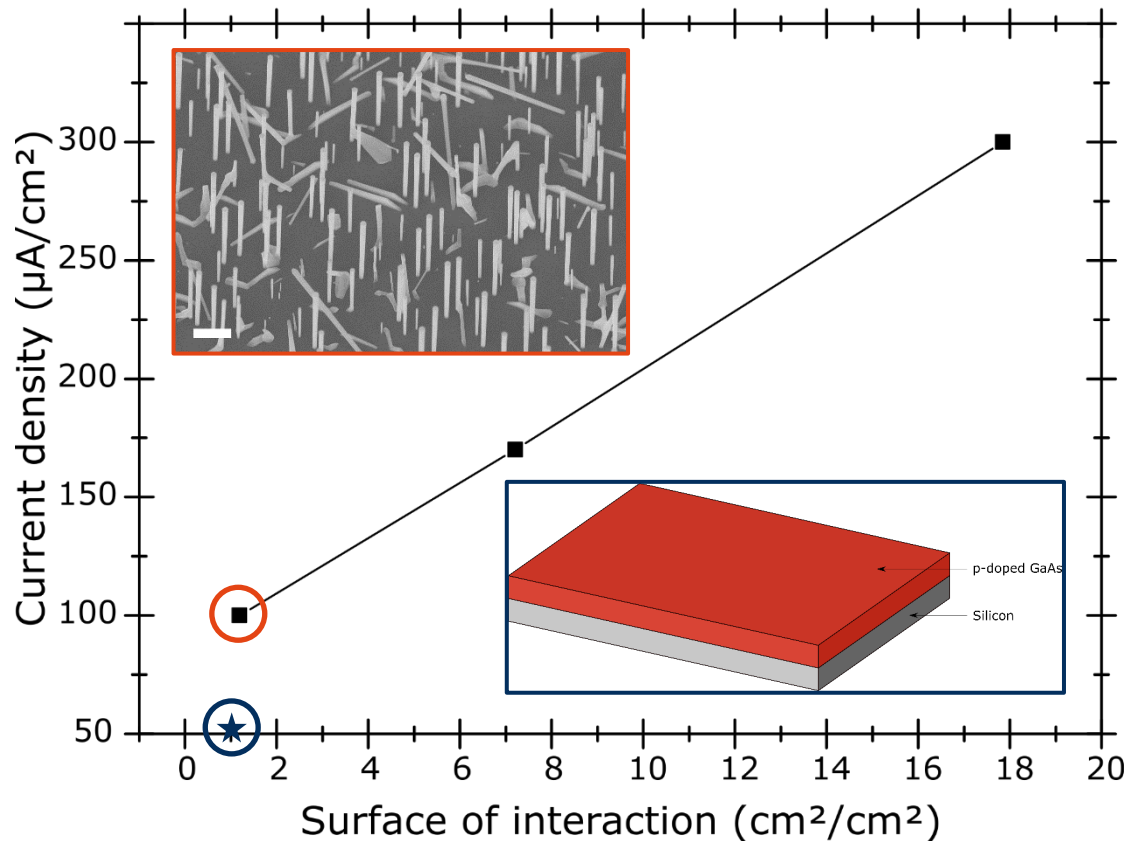
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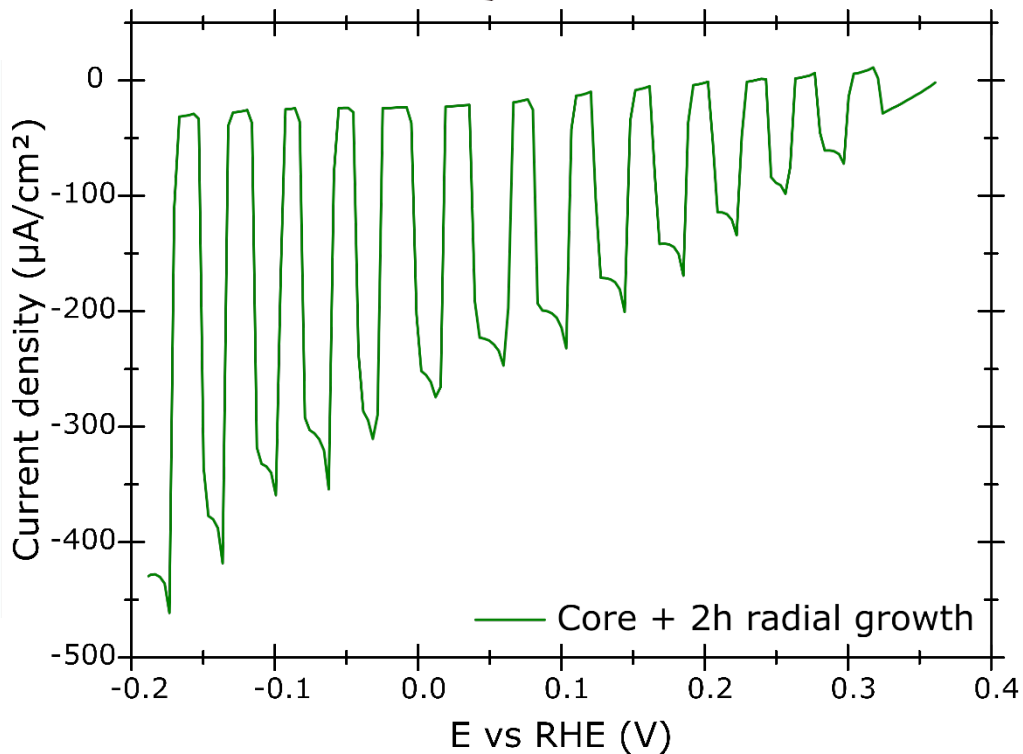
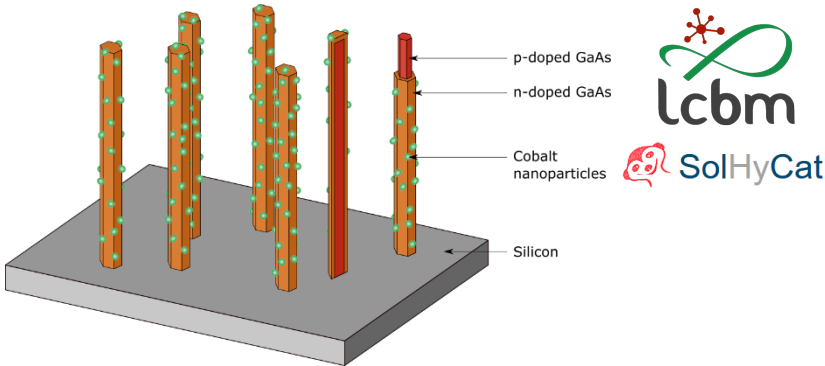
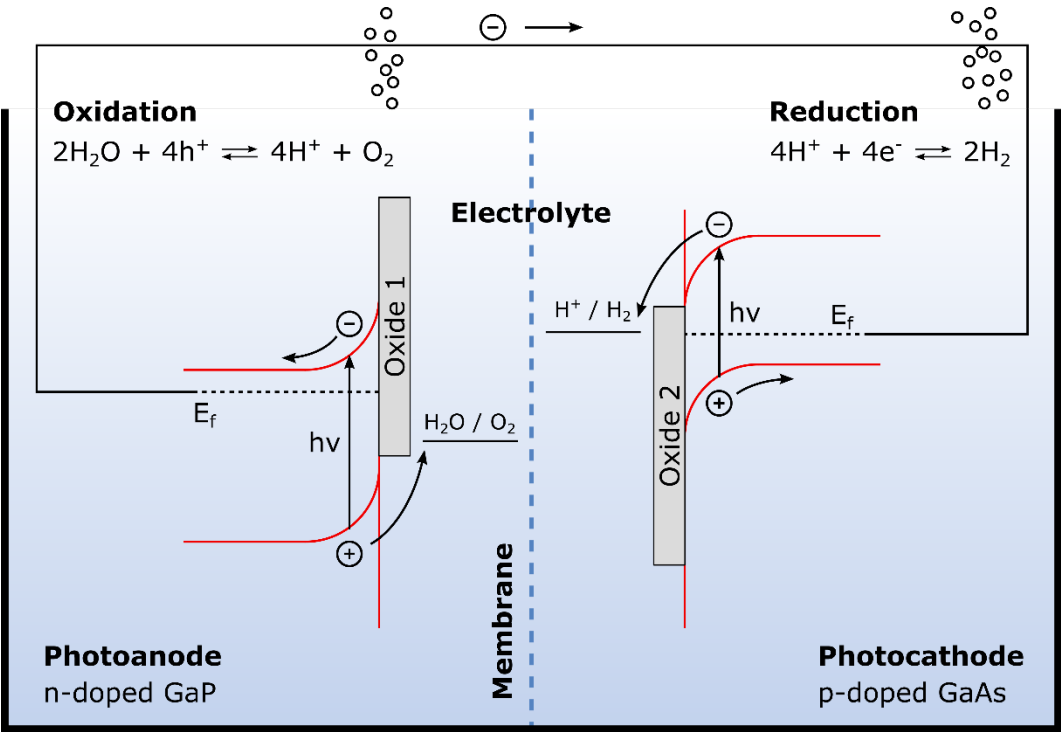
- Current density varies with the **interaction surface**
- **Enhanced** light trapping by the **NWs**



FDTD by E. Drouard, INL

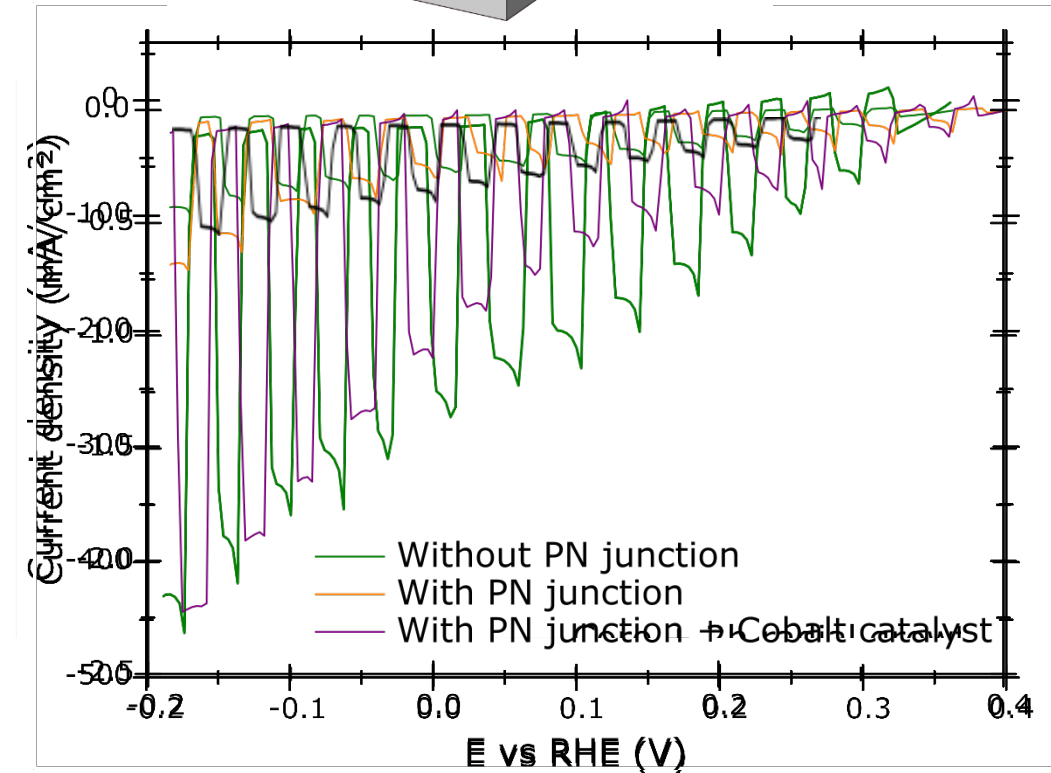
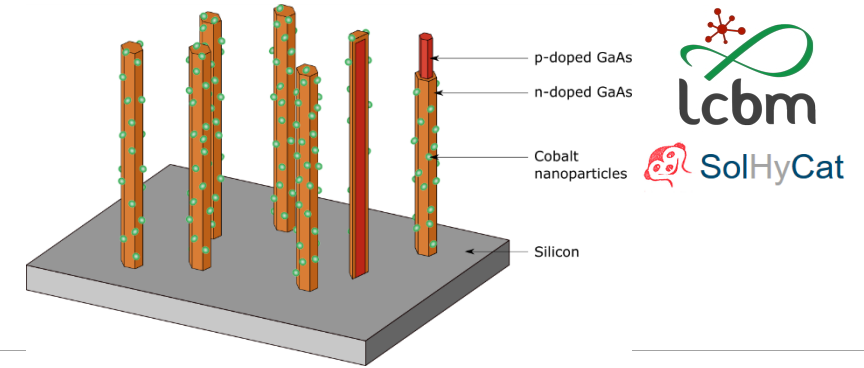
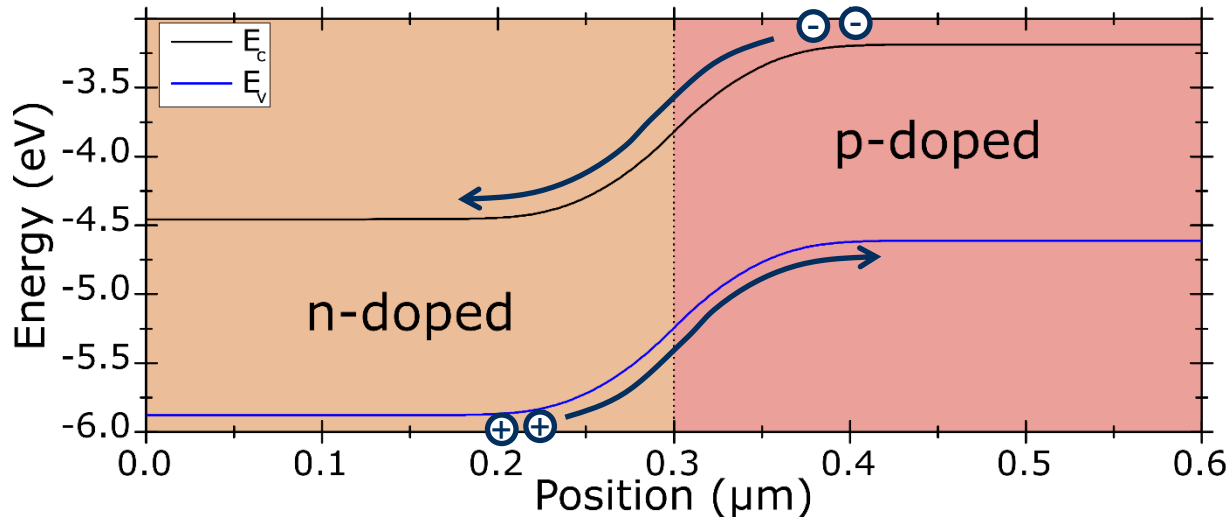
4 – Impact of the morphology

- Thick p-doped GaAs NWs



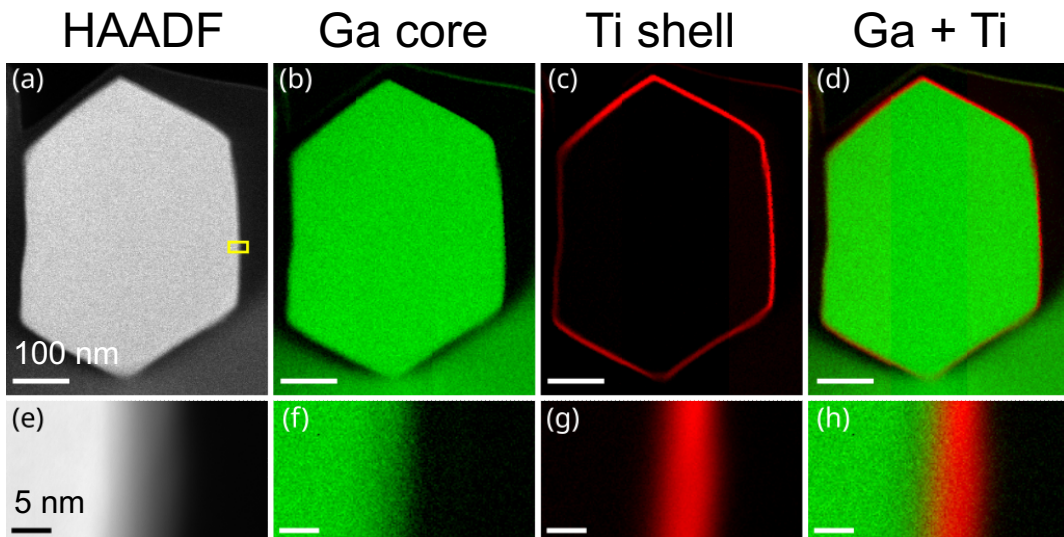
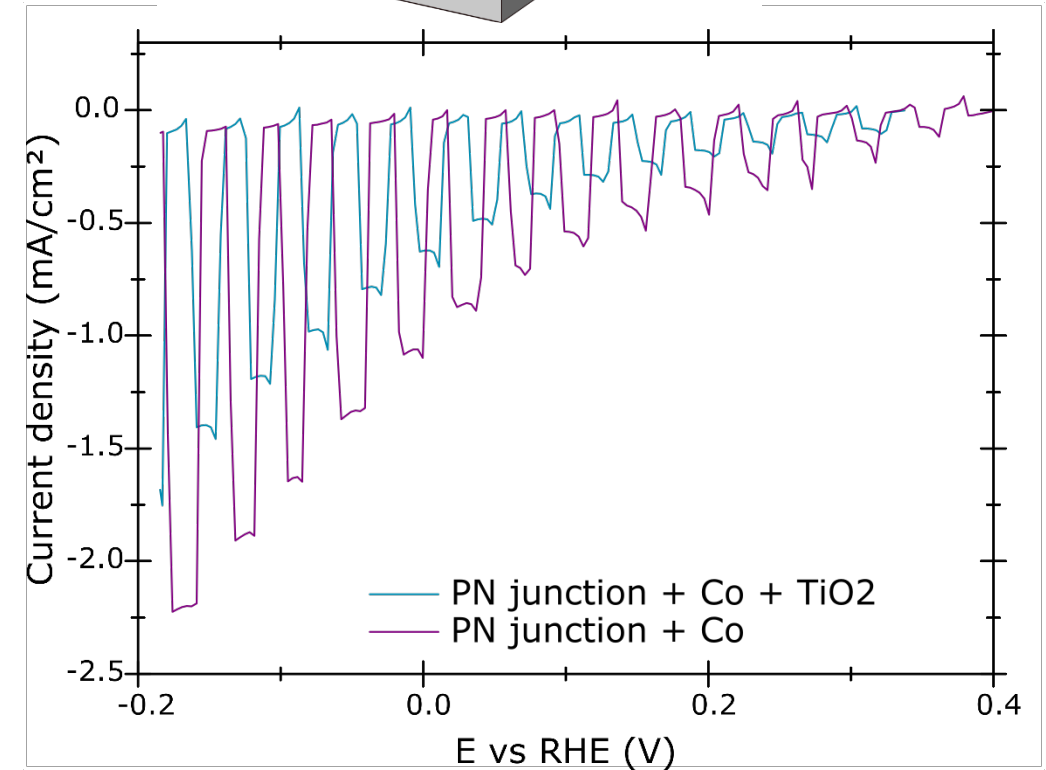
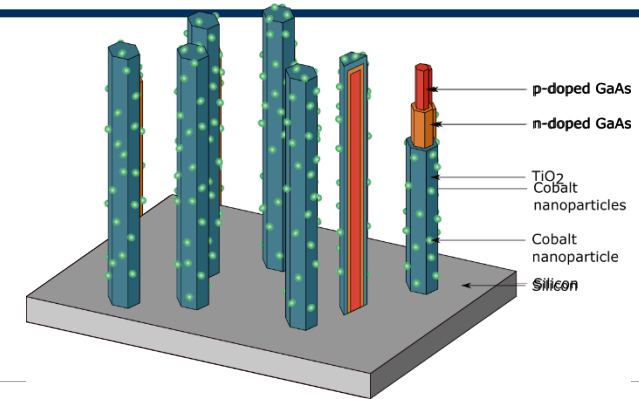
4 – Impact of the morphology

- Thick p-doped GaAs NWs
- Growth of core/shell **PN junction**
- Cobalt nanoparticles deposition
 - 1mM $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, 0.5M PB pH7, during 45 min under 1 sun, 1.5 AM, at -0.65 V vs Ag/AgCl



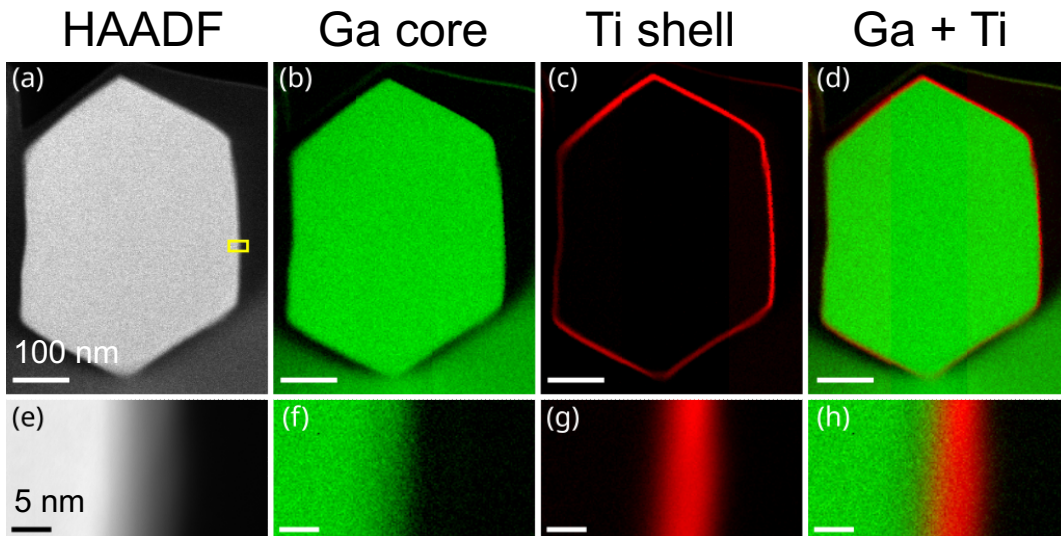
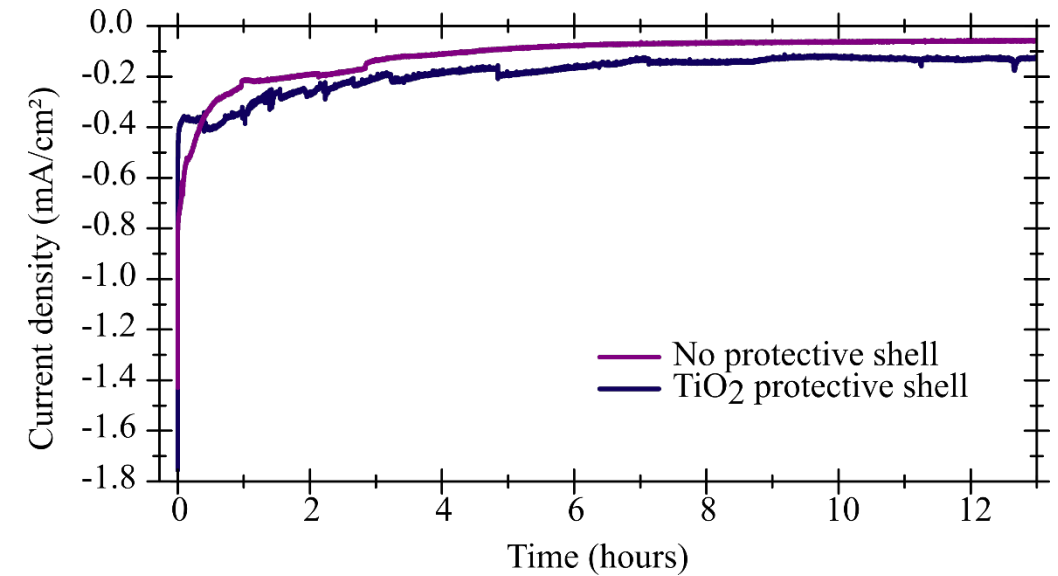
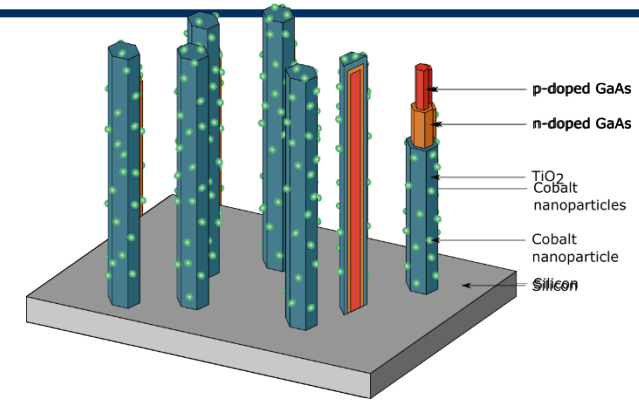
4 – GaAs photocathode

- Thick p-doped GaAs NWs
- Growth of core/shell **PN junction**
- **Co** nanoparticles deposition
 - 1mM $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, 0.5M PB pH7, during 45 min under 1 sun, 1.5 AM, at -0.65 V vs Ag/AgCl
- *Atomic layer deposition* of a TiO_2 protective shell
 - Lower current density



4 – GaAs photocathode

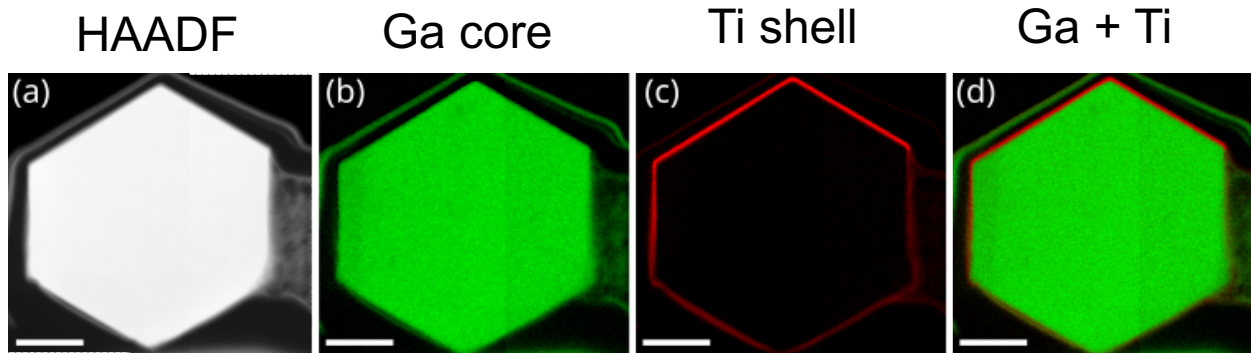
- Thick p-doped GaAs NWs
- Growth of core/shell **PN junction**
- **Co** nanoparticles deposition
 - 1mM $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, 0.5M PB pH7, during 45 min under 1 sun, 1.5 AM, at -0.65 V vs Ag/AgCl
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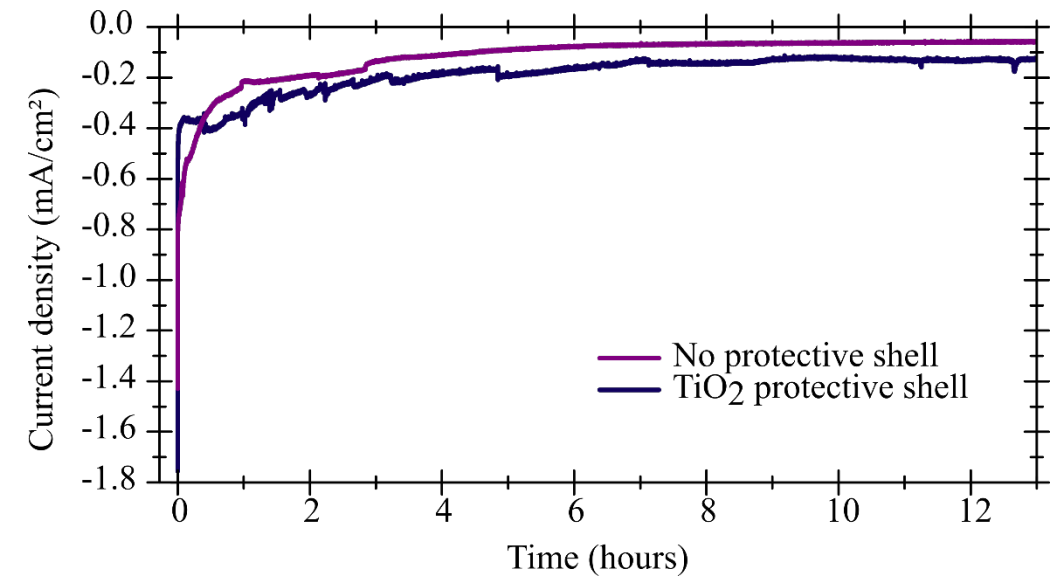
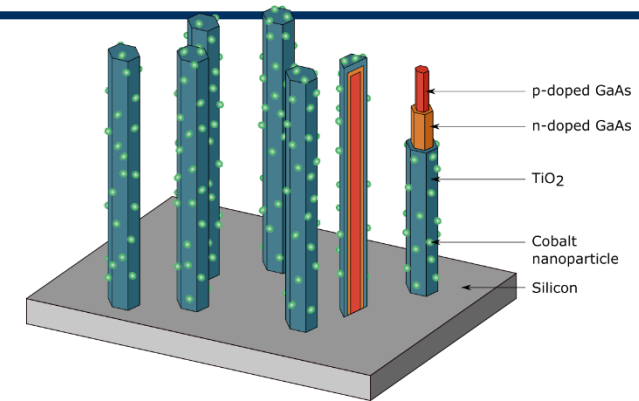
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STEM-EELS after photoelectrocatalytic HER experiments at -0.18 V vs RHE under simulated 1 sun irradiation



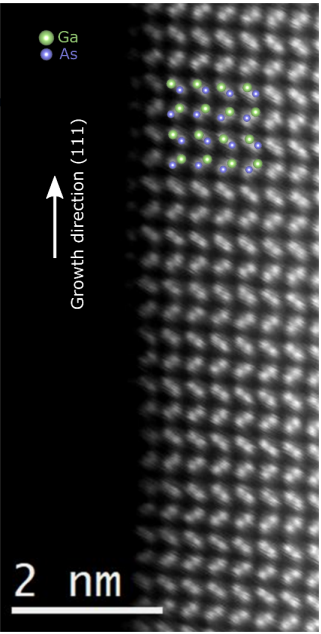
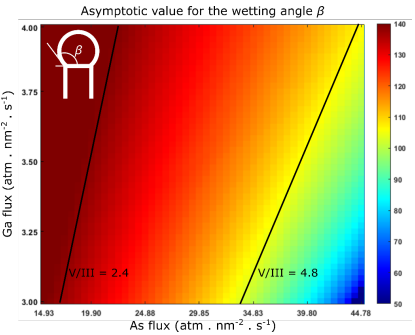
100 nm



- Experimental proof of the relevance of *in situ* RHEED for crystal phase engineering
- Robust synthesis of **WZ-pure segments μm -long in self-assisted mode.**
 - Building block for the MBE growth of **Au-free hexagonal $\text{Si}_{1-x}\text{Ge}_x$**

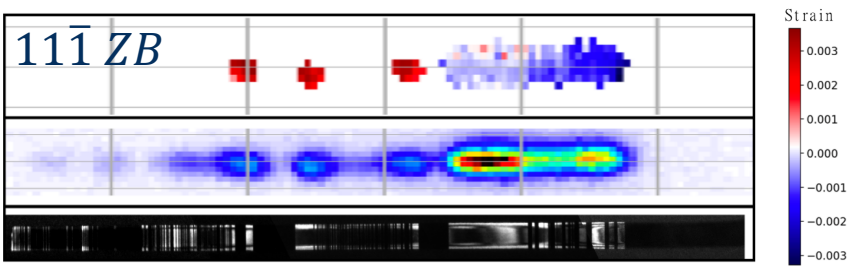
T. Dursap et al. Nanoscale Advances (2020)

T. Dursap et al. Nanotechnology (2021)

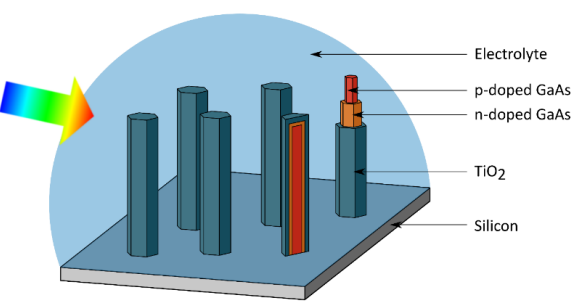


- **Correlation between phase change and strain** from X-ray nanodiffraction & TEM

T. Dursap et al. in preparation



- **Assessment of GaAs nanowire cell for photocathode**
 - Perspective: fabrication of a photo-anode / photo-cathode **tandem cell**
 - Perspective : Investigation of other materials and passivation techniques



T. Dursap et al. ACS Applied Materials Interfaces (2023),



Dr. Thomas DURSAP

- **PhD**, ECLyon - 12/05/2022
- **Postdoc** (C2N, Saclay, group of Dr. L. Vincent)
06/2022-07/2023
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11/2023

Thank you for your attention!

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