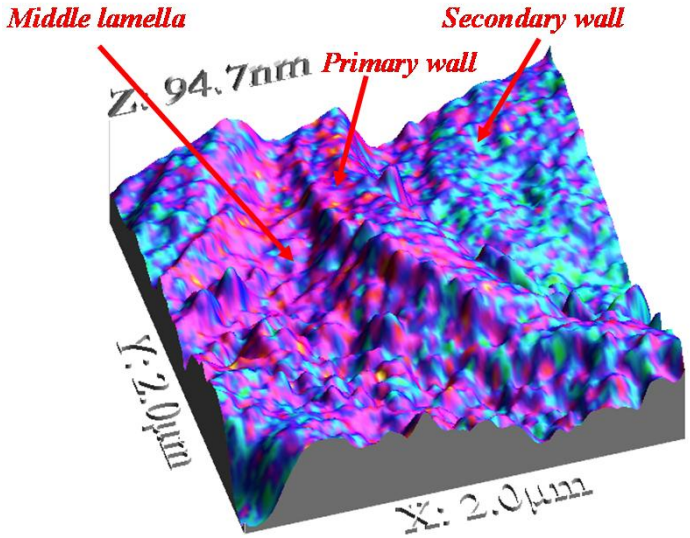
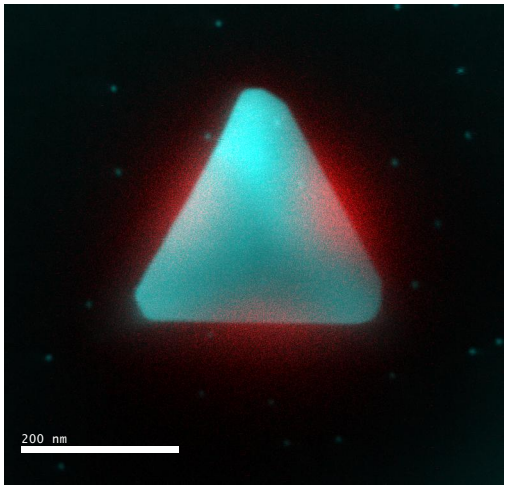
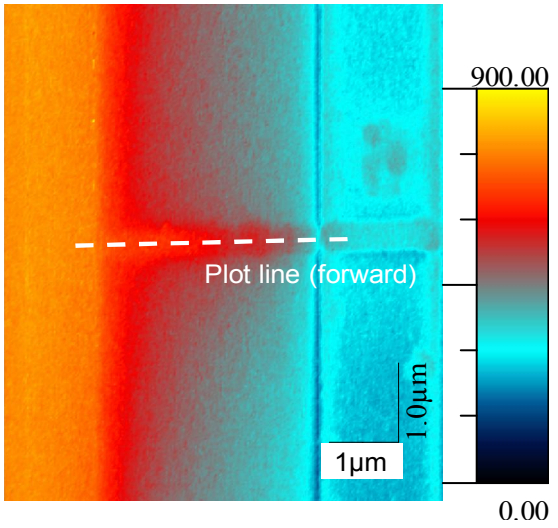






Near-field microscopy techniques for nanostructure characterization: near-field IR, AFM nanomechanics, SEM/TEM cathodoluminescence and Kelvin Probe Force Microscopy

Dr Nicolas Bogdan BERCU, Pr Michaël MOLINARI,
Dr Alexandre BERQUAND

Laboratoire de Recherche en Nanosciences LRN EA4682
Université de Reims Champagne Ardenne

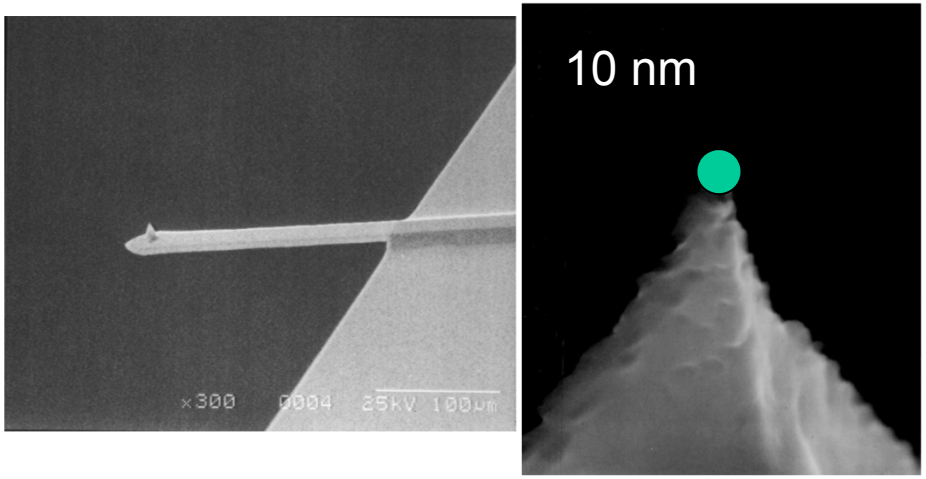
Outline

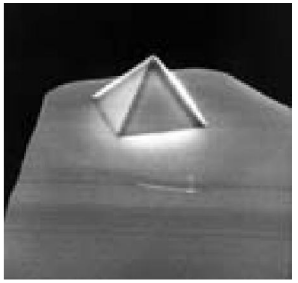
- *Overview of the near-field scanning techniques*
- *Mechanical and chemical local properties measurement by AFM techniques*
- *Nanostructure characterization by the scanning near-field and STEM CL*
- *Electrical and KPFM nanowire characterization*
- *Conclusions*

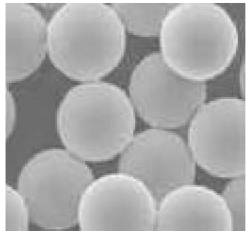
Atomic Force Microscopy

→ General Principles

• based on the displacement of a thin solid tip along the surface of the sample to analyze



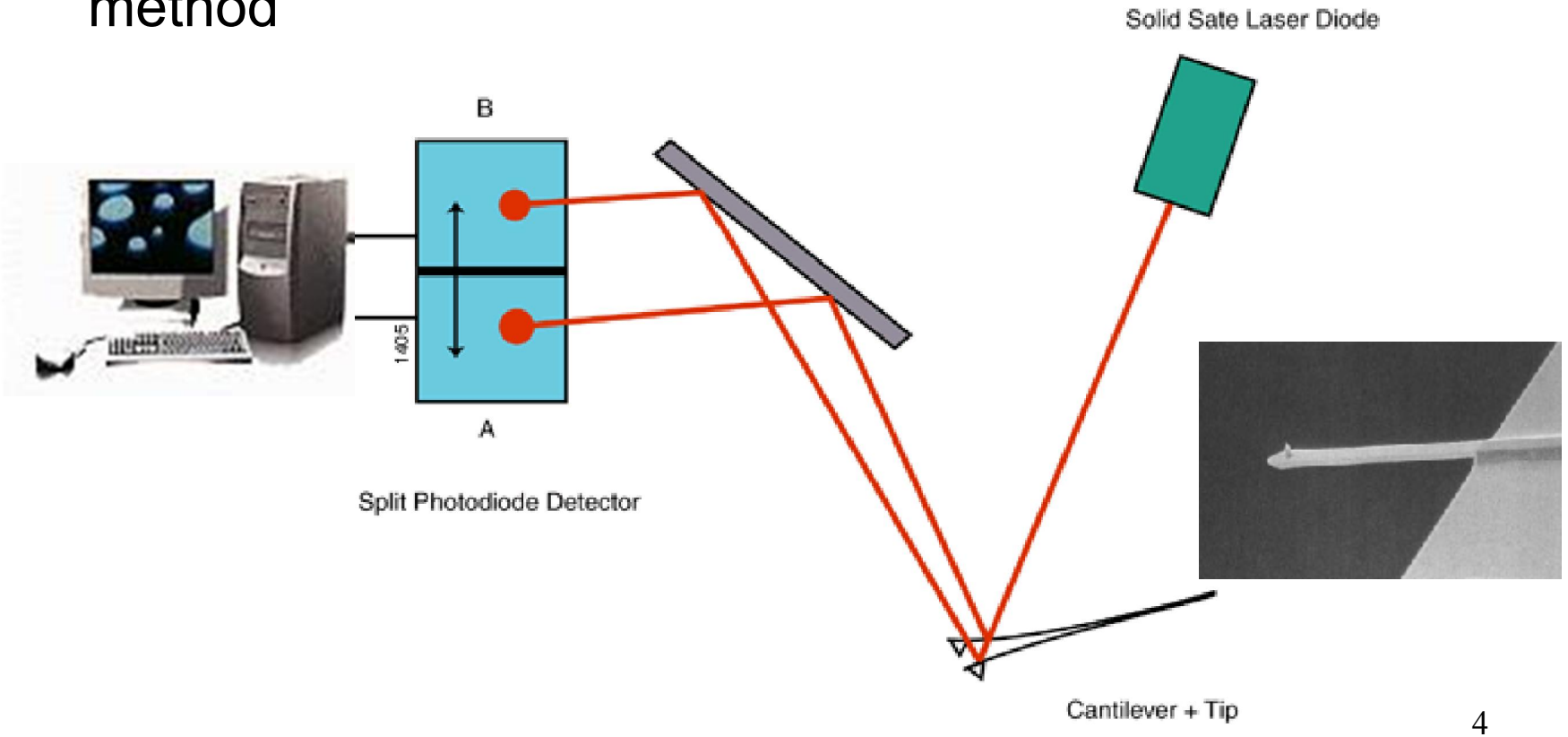




AFM Detection Technique

⇒ Step1: force – cantilever mecanical deflection (~1N/m => 1 nN/1nm)

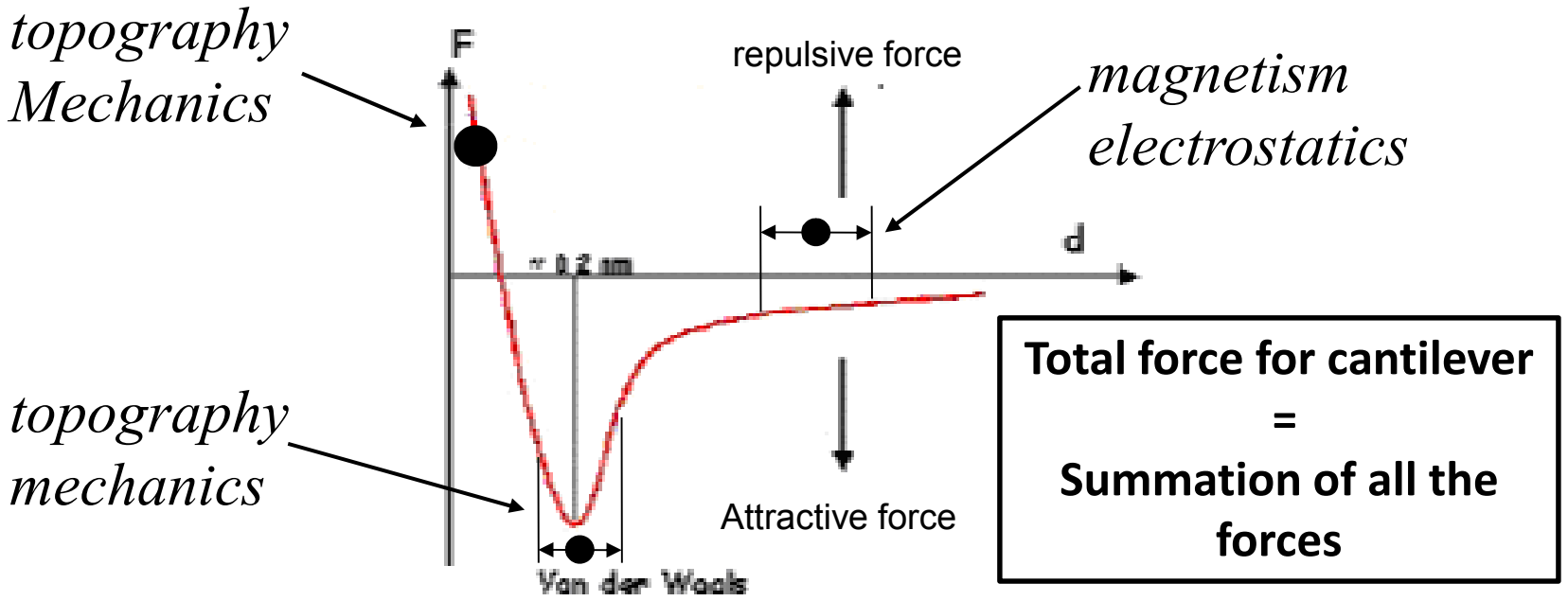
⇒ Step2: cantilever deflection detection by an optical method



Atomic Force Microscopy

→ General principles

• possibility to obtain different information to characterize the materials (adhesion, stiffness, transport, magnetism, thermal conductivity…)

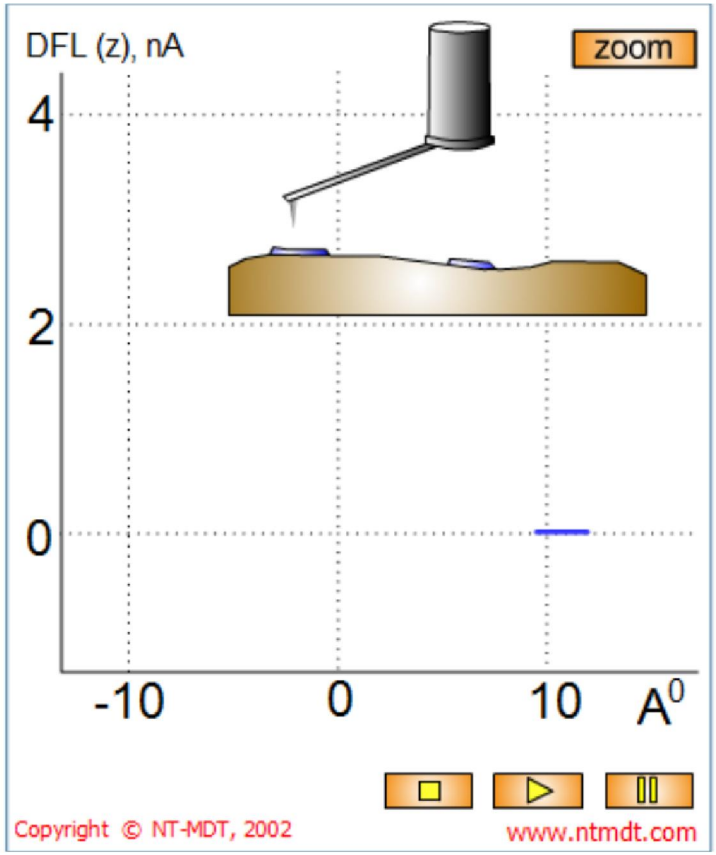


Atomic Force Microscopy

→ Nanomechanics

Force / distance measurements

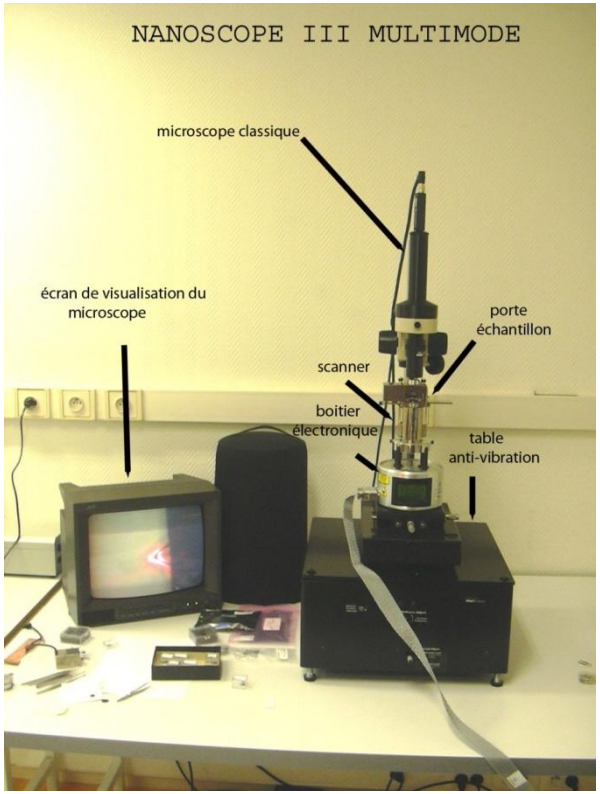
By developing the proper models, possibility to get local mechanical information such as elasticity, adhesion…

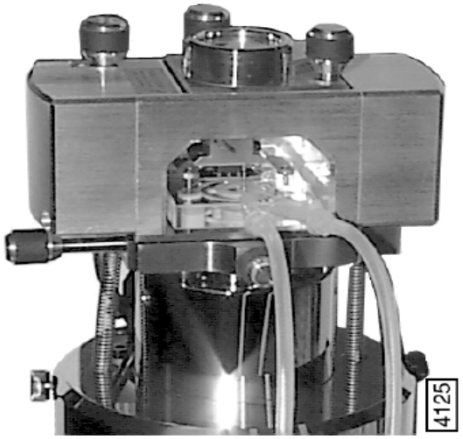


Atomic Force Microscopy

→ General Principles

• control of the working environment (fluid, humidity, temperature control…)





AFM head

Atomic Force Microscopy

→ AFM Advantages

- Non-destructive analysis
- High resolution at nanometer scale
- Minimal preparation of the sample
- Air or fluid environment
- Information about different properties (topography, stiffness, adhesion, electrical potential, …)

Atomic Force Microscopy

→ Typical commercial AFM drawbacks

– Imaging speed (several minutes per image)

– No chemical information

– No quantitative local mechanical measurements

– Important error for KPFM mapping on biased devices

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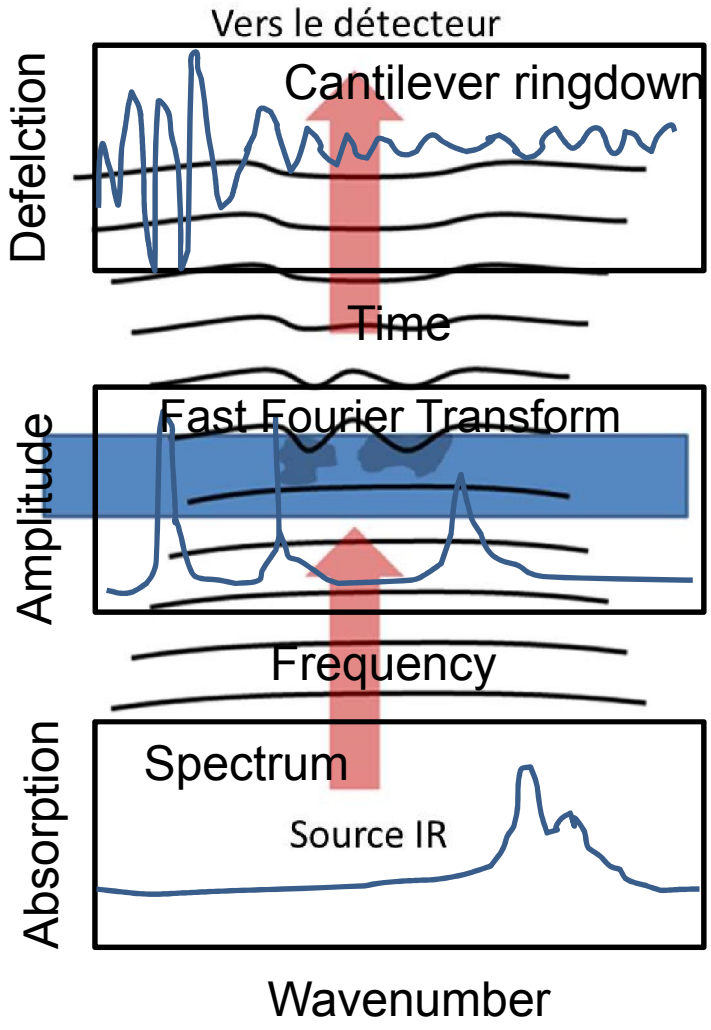
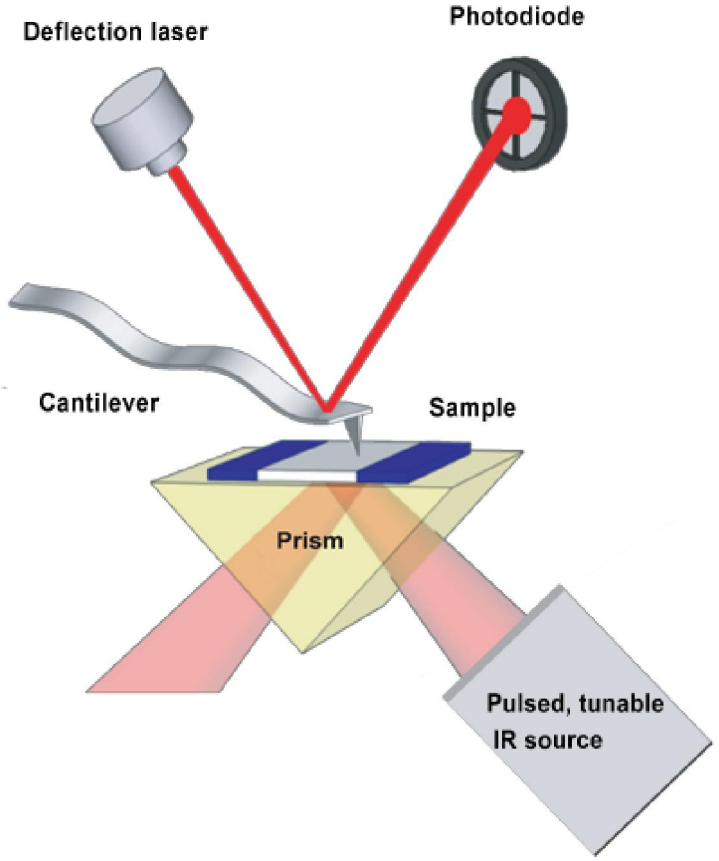
AFM + localized absorption IR

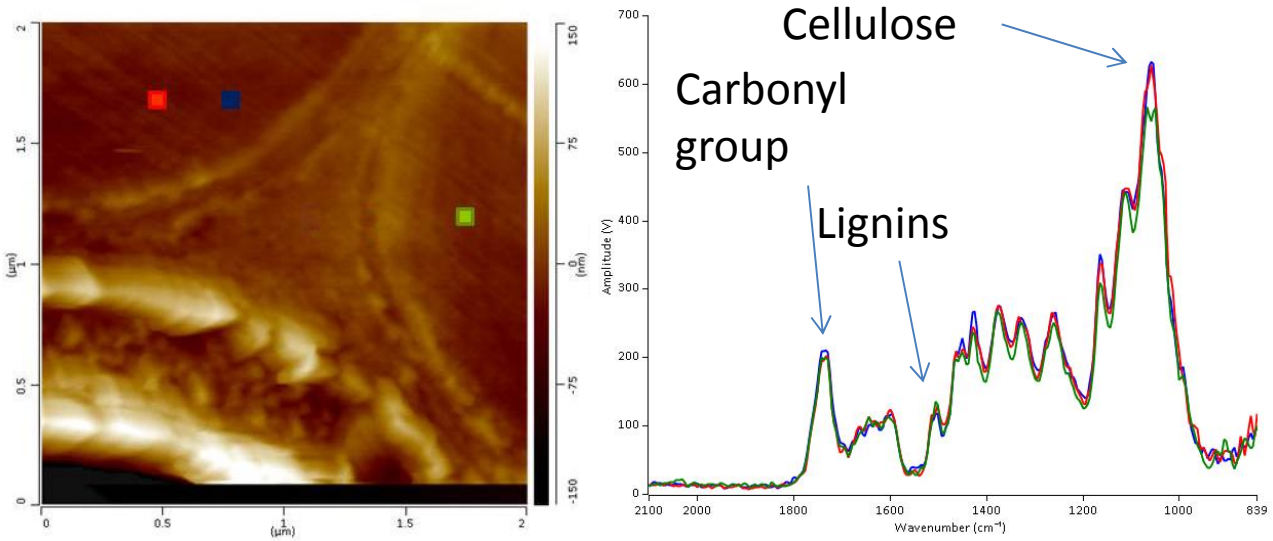




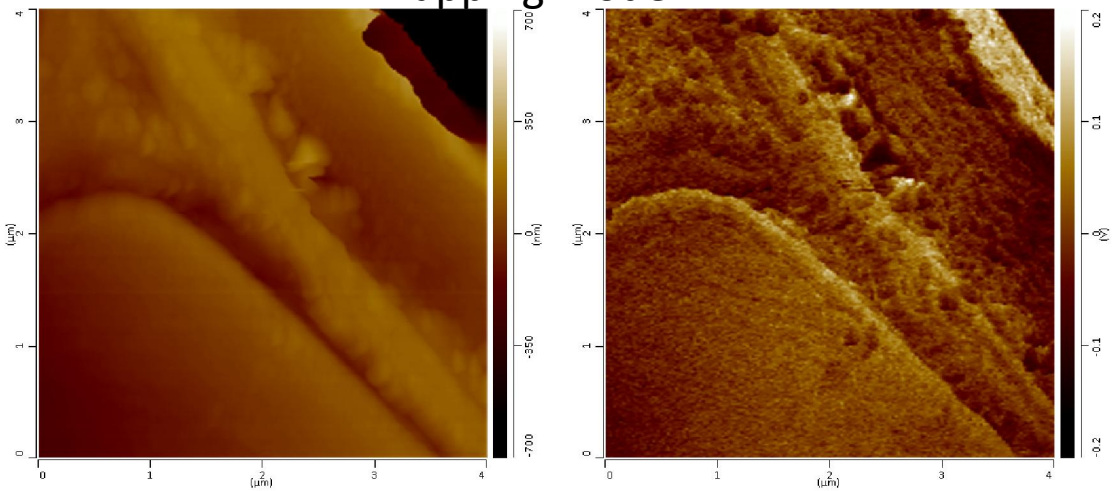
Anasys / A. Dazzi (Orsay)

AFM + localized absorption IR

Spectroscopic mode



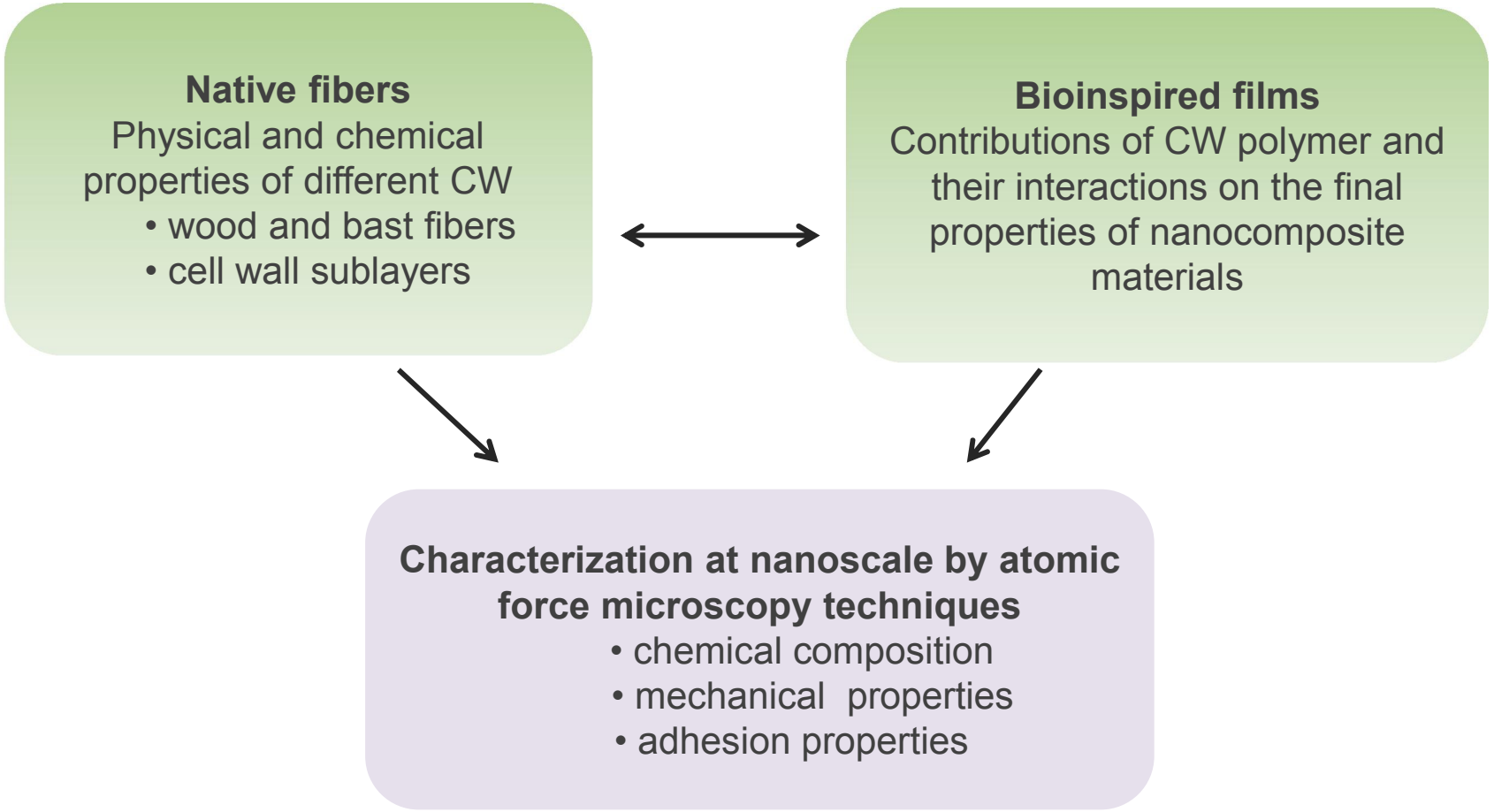
Mapping mode



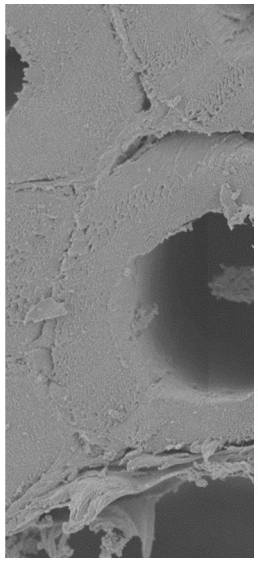
AFM-IR mapping wavelength: 1060 cm^{-1}

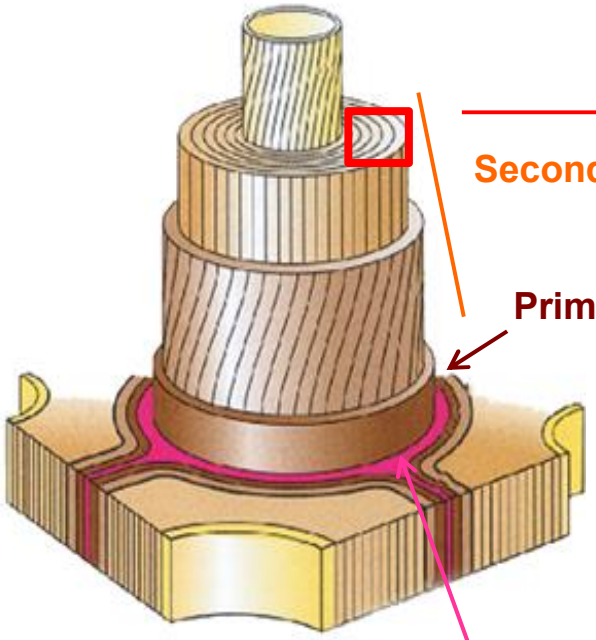
Objectives

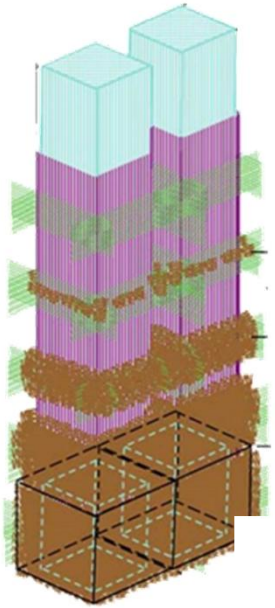
Understand the relationships between chemical composition and mechanical properties of the plant cell wall at nanoscale levels



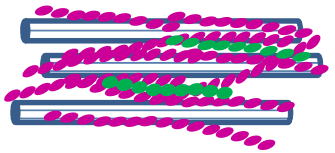
Plant Cell Wall: hierarchical composite material



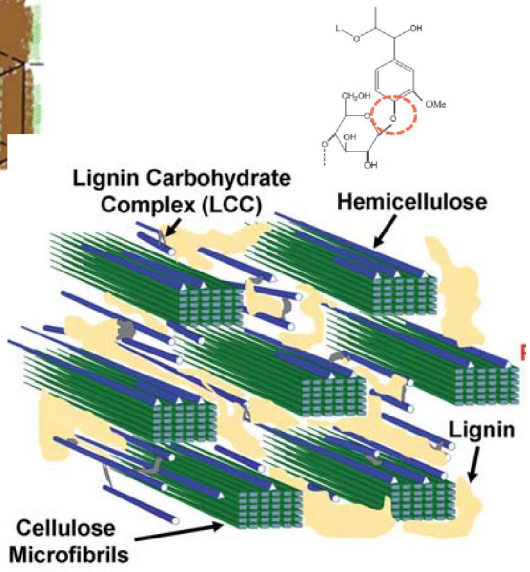


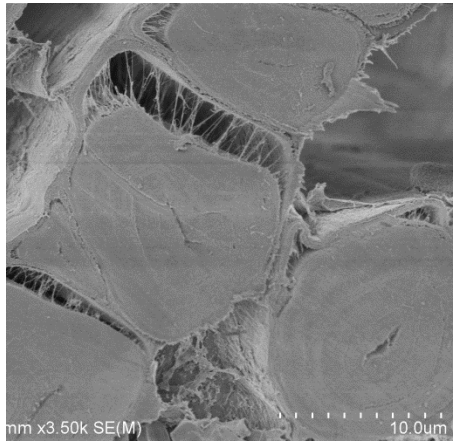


Cellulose - hemicellulose



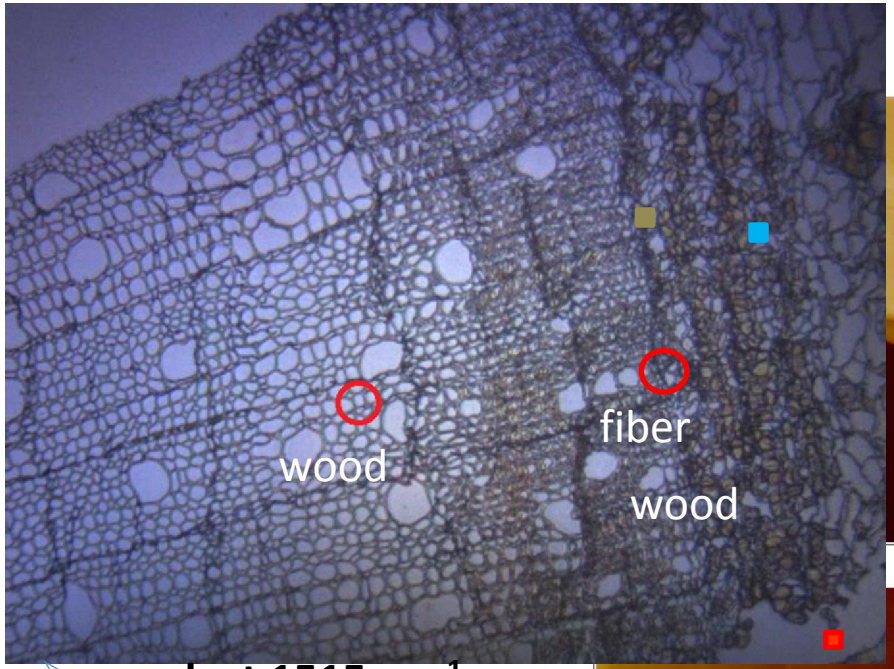
Lignin hemicellulose

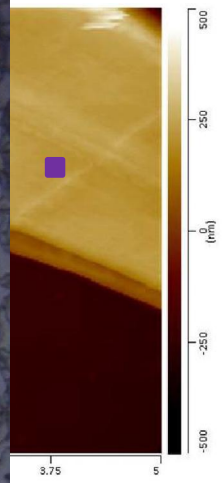


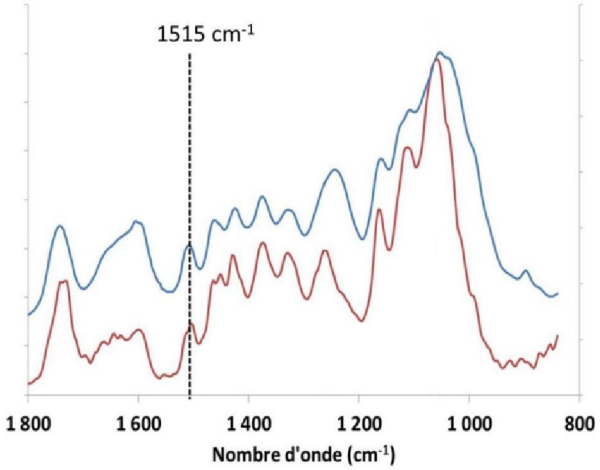


Importance of the chemical composition and interactions between polymers regarding the structure and the properties of the plant cell wall

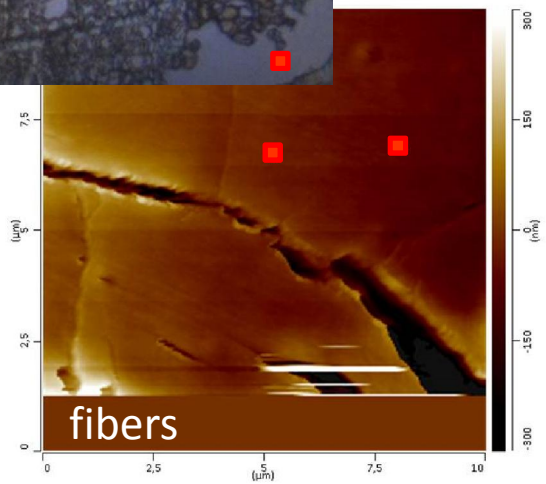
Correlation nanomechanics / nanoIR

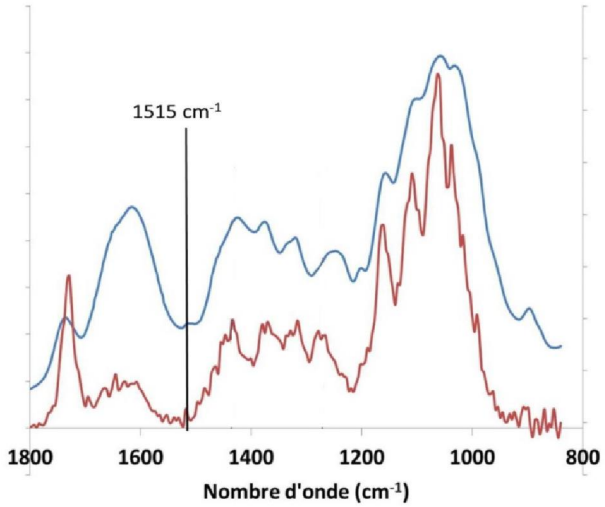




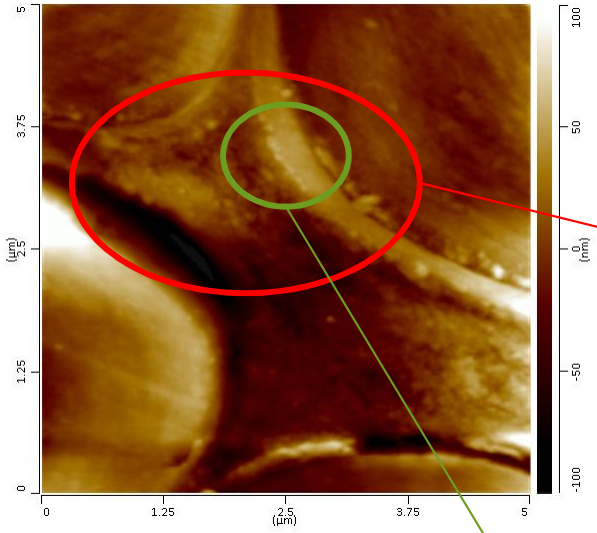


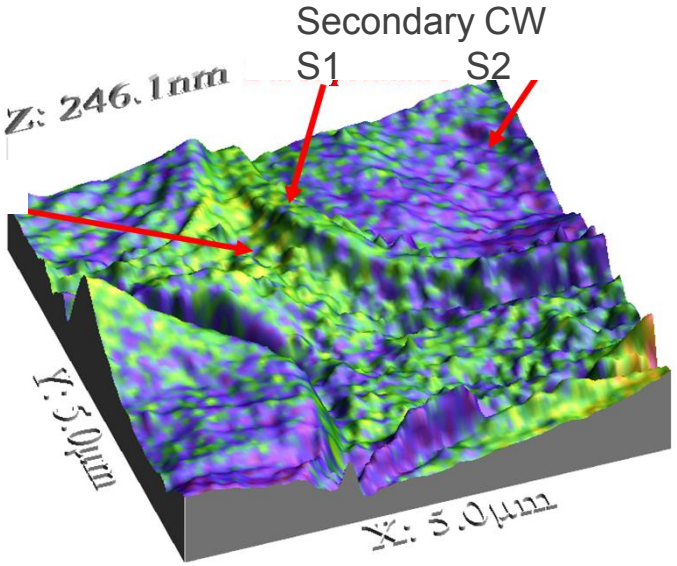
- peak at 1515 cm^{-1} for hemp wood
- Absence of this peak for hemp fibers

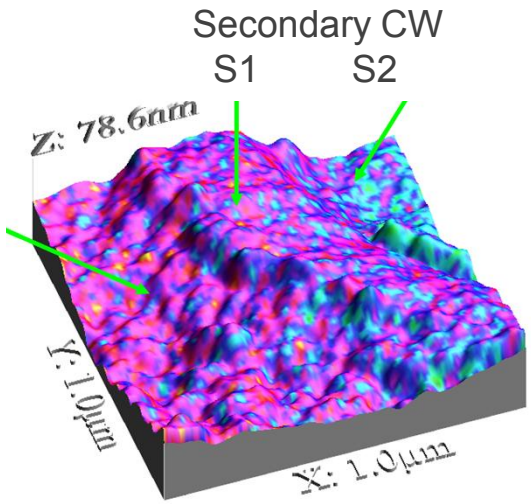




Nano-IR mapping of lignin







Bercu et al., submitted

AFM + localized absorption IR

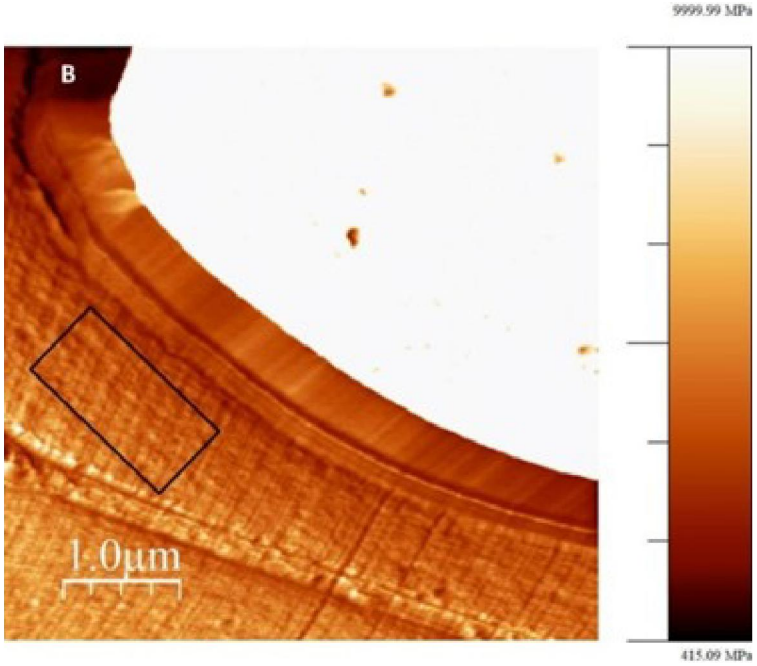
- Advantages
  - spatial resolution for IR around 50nm (spectral resolution of 4 cm^{-1} / 4500-900 cm^{-1})

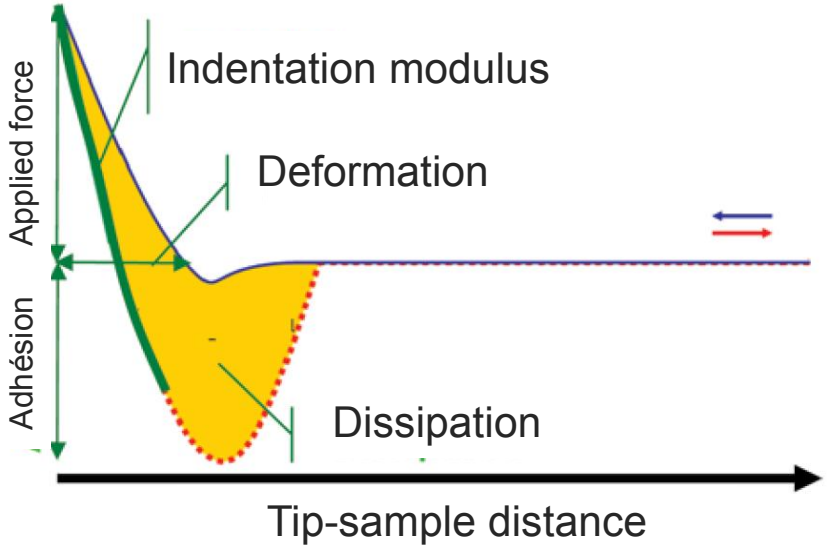
- Limitations
  - sample thickness
  - sample rugosity

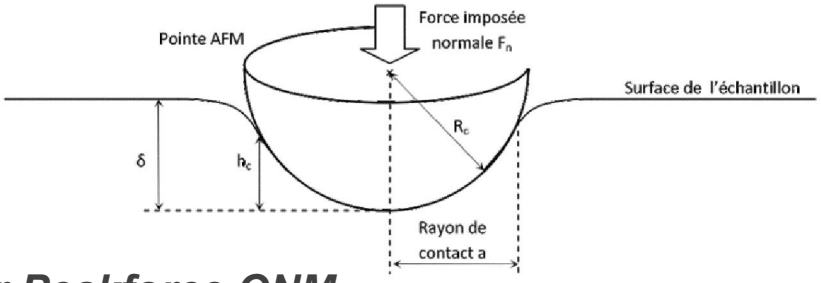
- Sample preparation

Nanomechanical properties of hemp walls

Force- distance curve







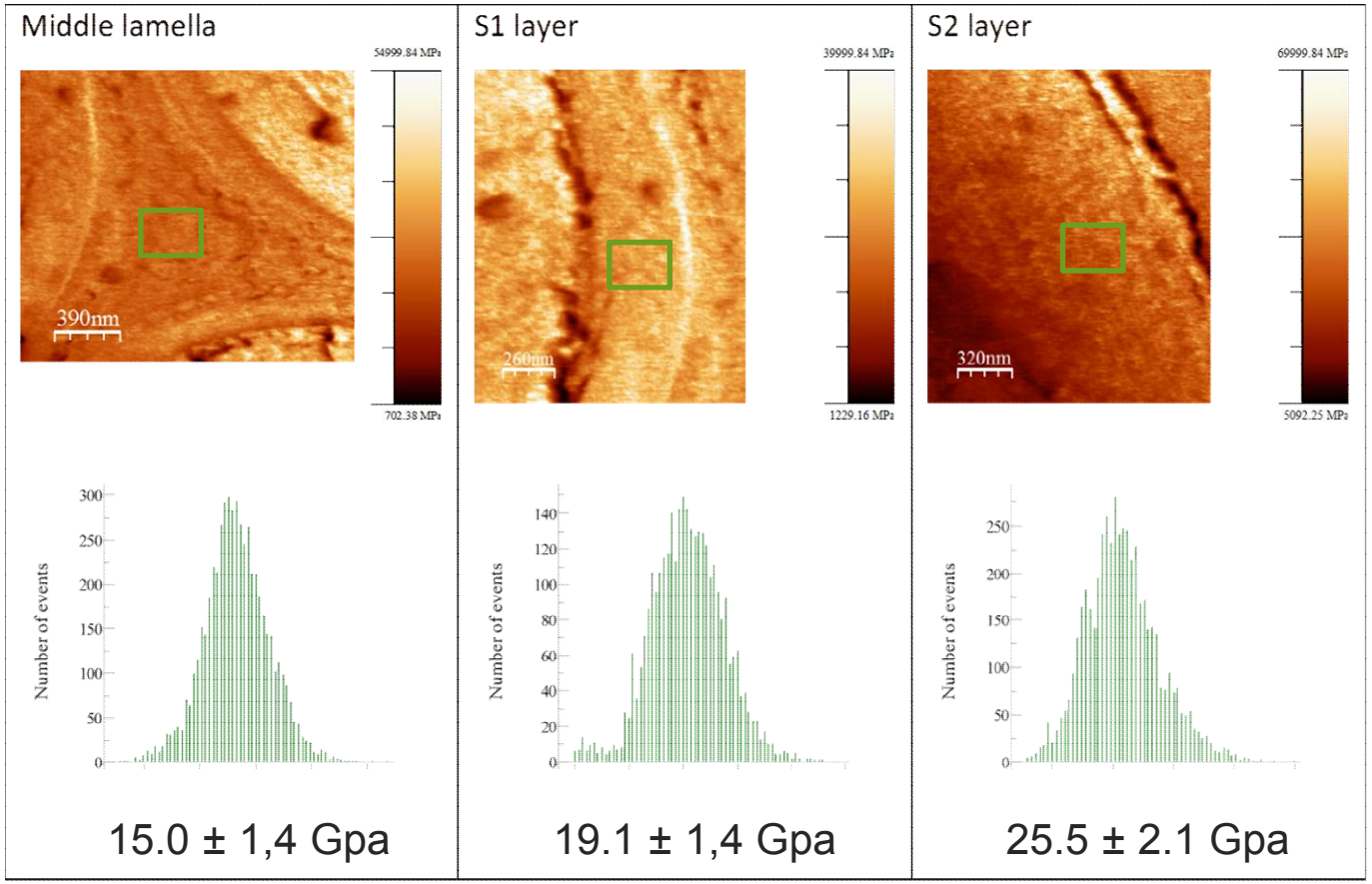
Bruker Peakforce QNM

$$F - F_{adh} = \frac{4}{3} E^* \sqrt{R(d - d_0)^3}$$

DMT model

Indentation modulus determination

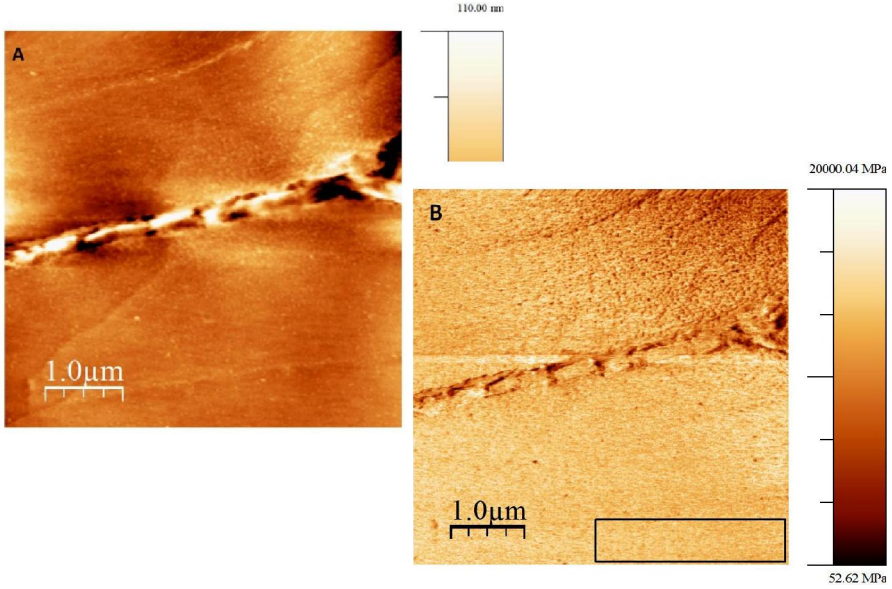
Nanomechanical properties of hemp walls

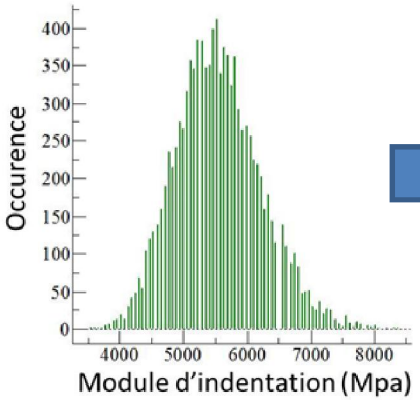


Muraille et al., submitted

Correlation nanomechanics / nanoIR

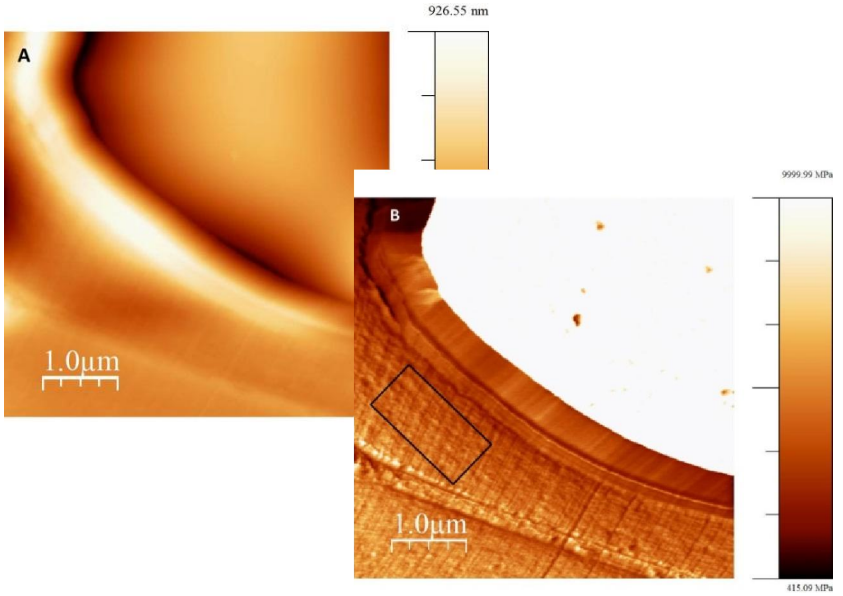
« fiber »

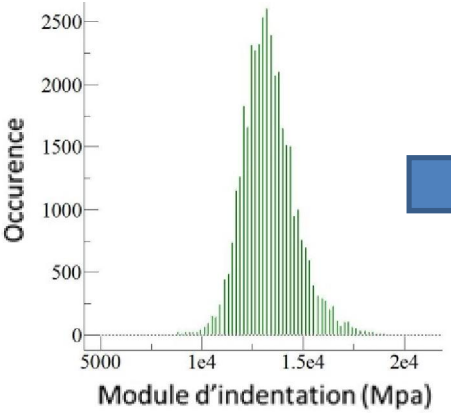




5.9 ± 0.6 GPa

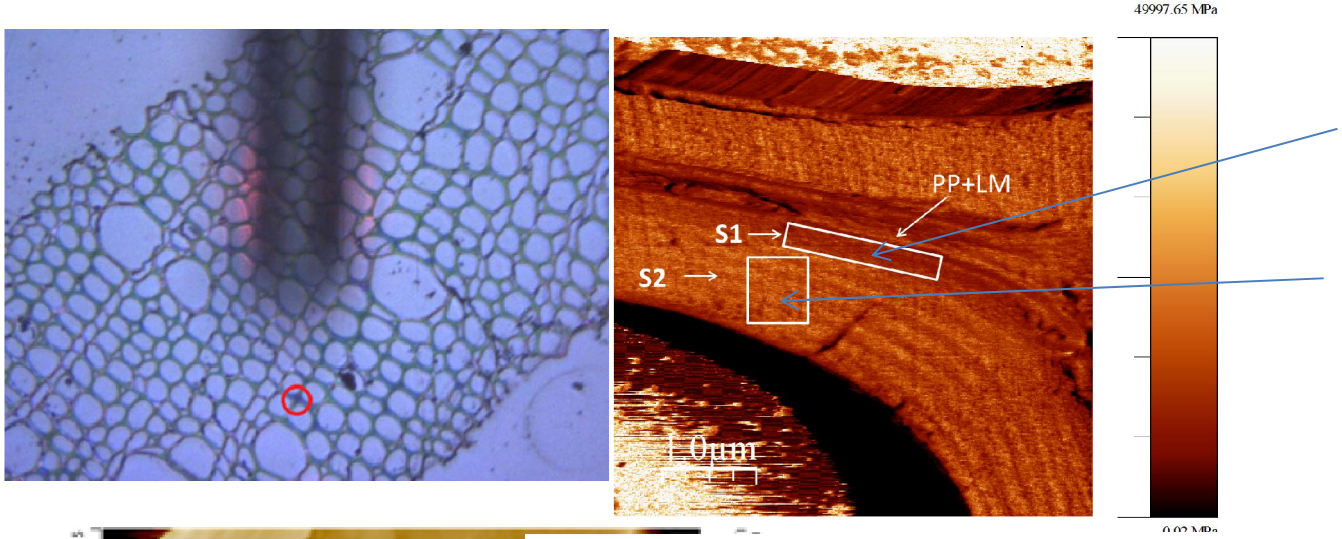
« wood »





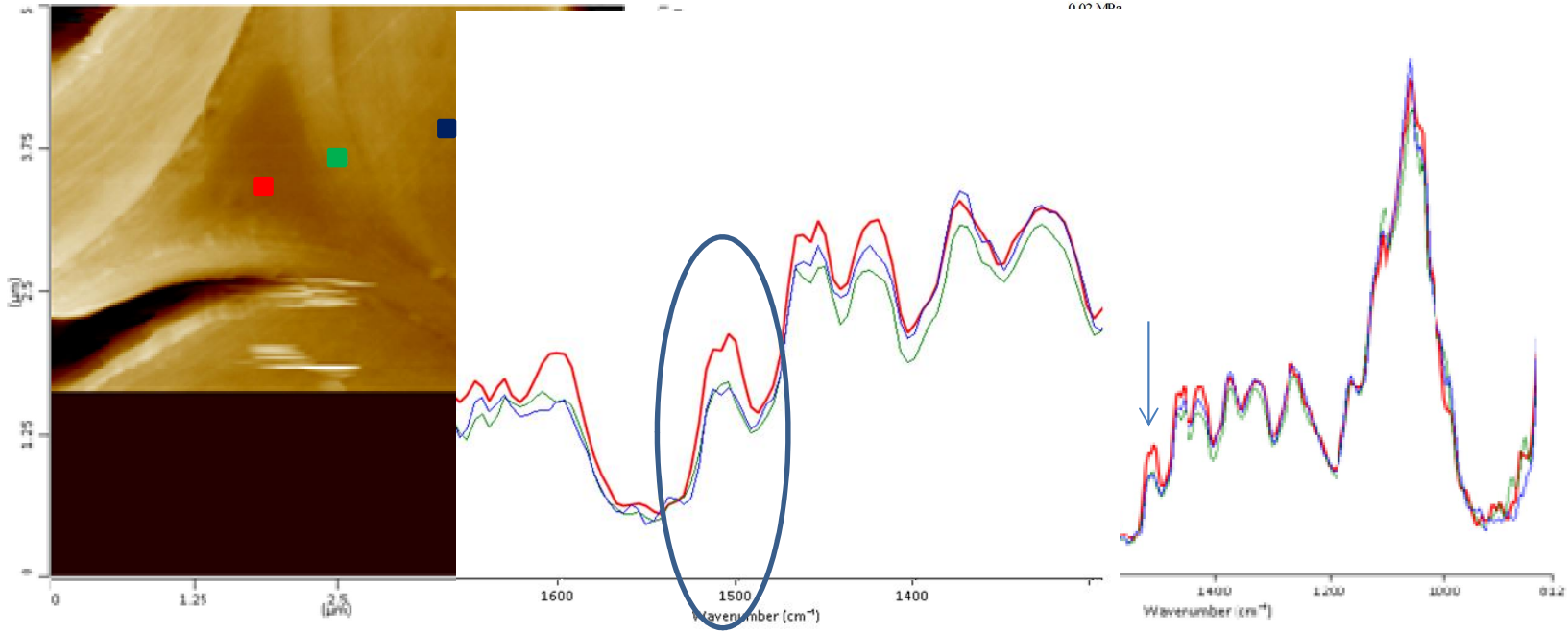
13.5 ± 1.4GPa

Correlation nanomechanics / nanoIR



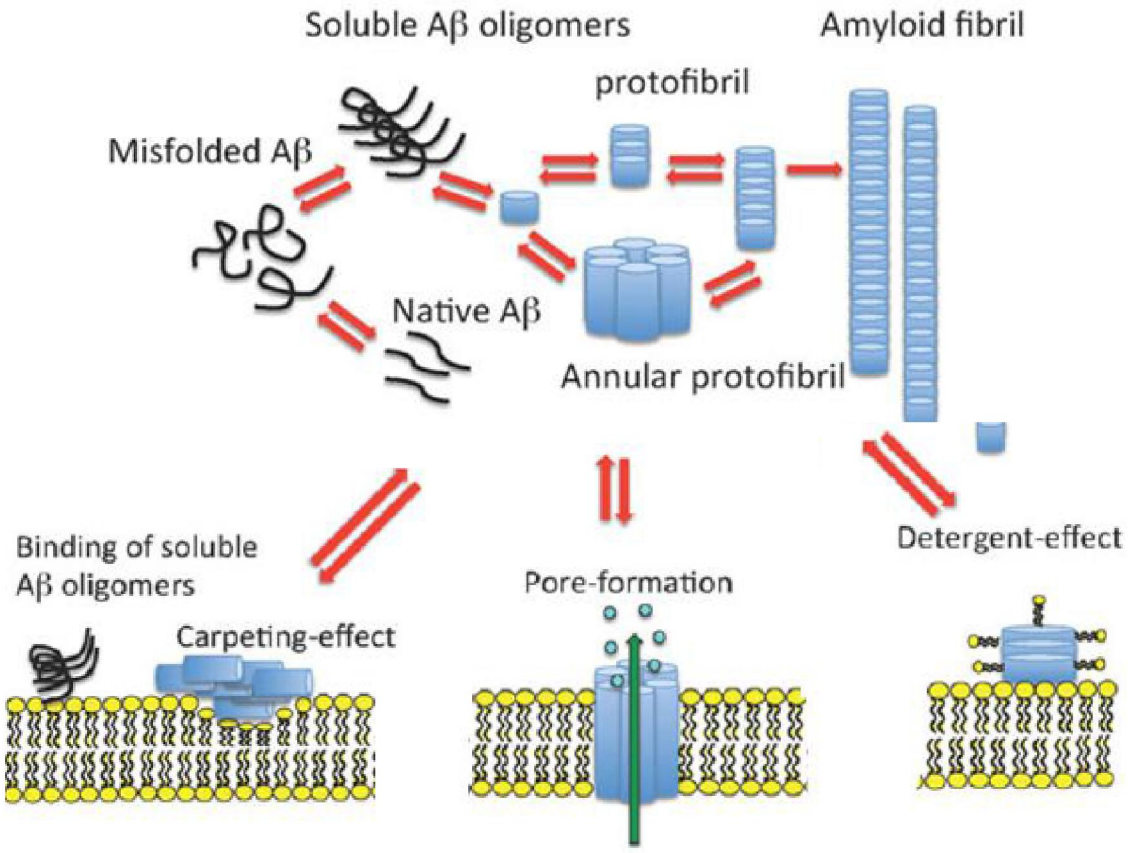
11.5 ± 0.5GPa

16.4 ± 0.7GPa



AFM + IR : applications

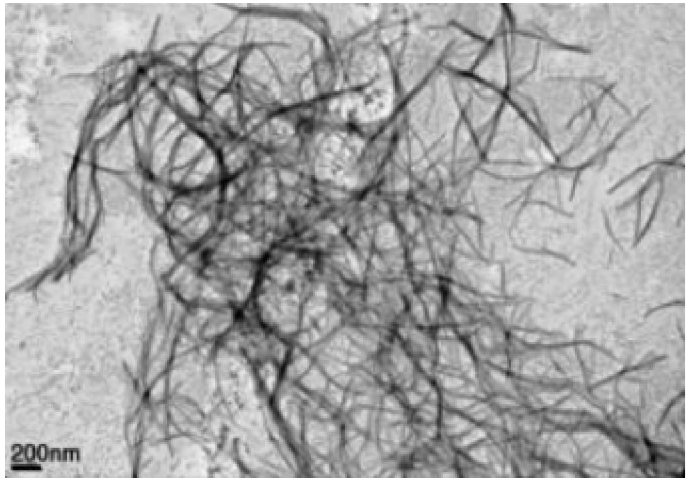
- Amyloid toxicity: morphology, structure, interactions with membranes



AFM + IR : applications

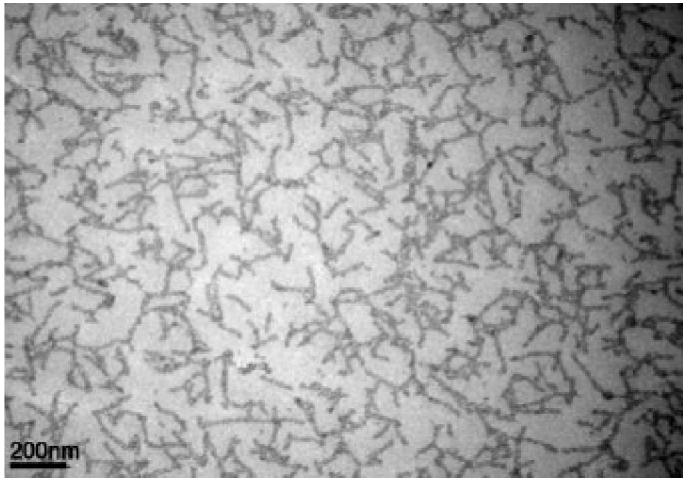
- Amyloid toxicity: morphology, structure, interactions with membranes

WT - non toxic



WT amyloids are composed of 5nm protofibrils which assemble as long fibers.

M8 - toxic

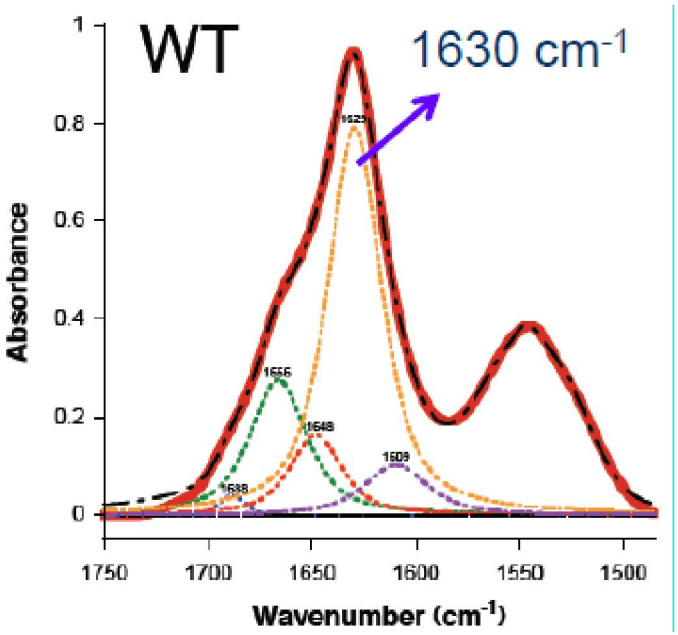


The fibrils are made up of short fibers which are assembled laterally.

AFM + IR : applications

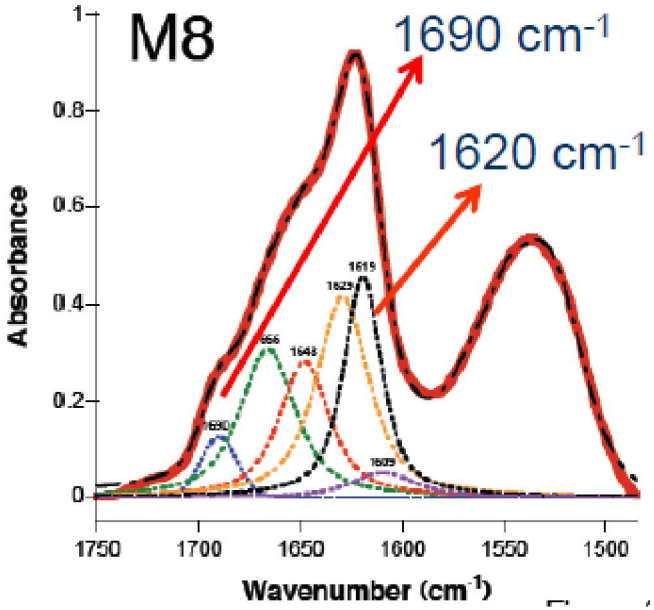
- Amyloid toxicity: morphology, structure, interactions with membranes

WT - non toxic



Parallel beta-sheets

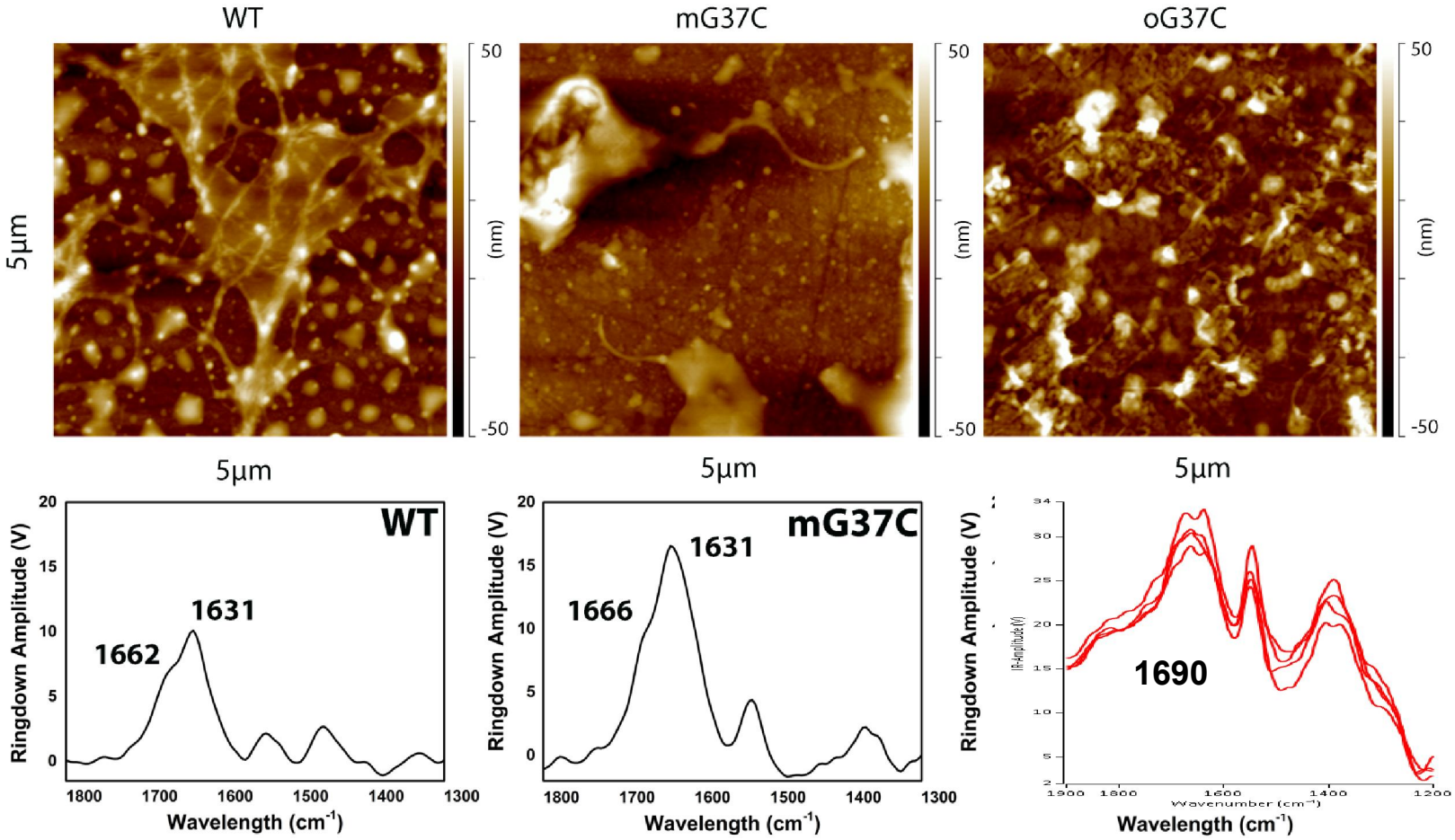
M8 - toxic



Antiparallel beta-sheets

AFM + IR : applications

- Amyloid toxicity: morphology, structure, interactions with membranes



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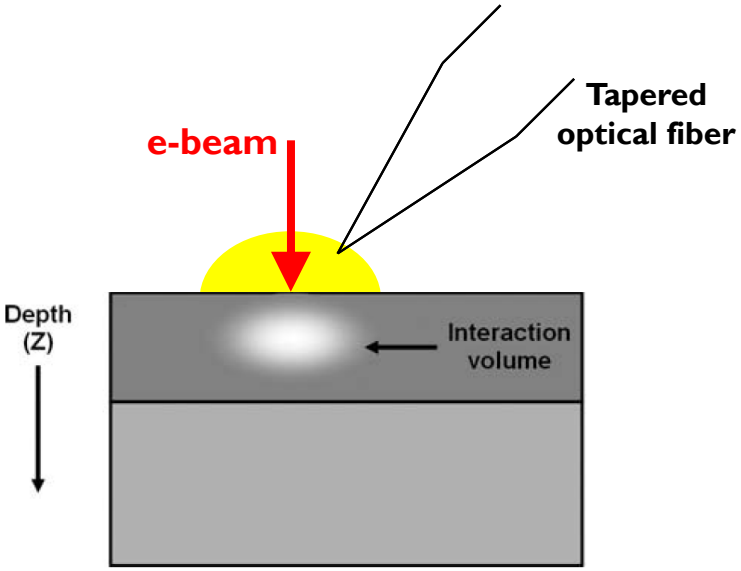
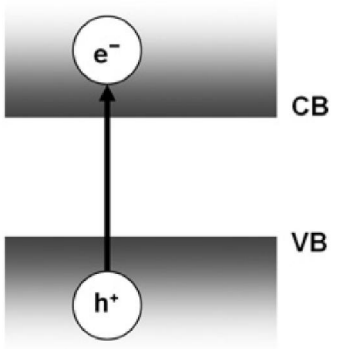
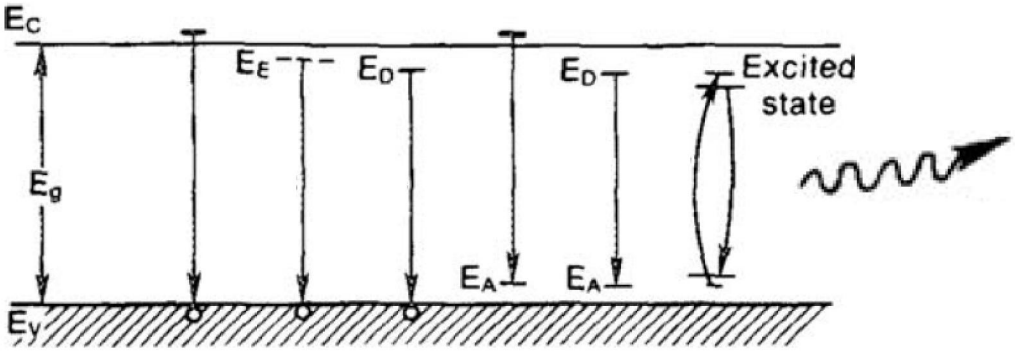
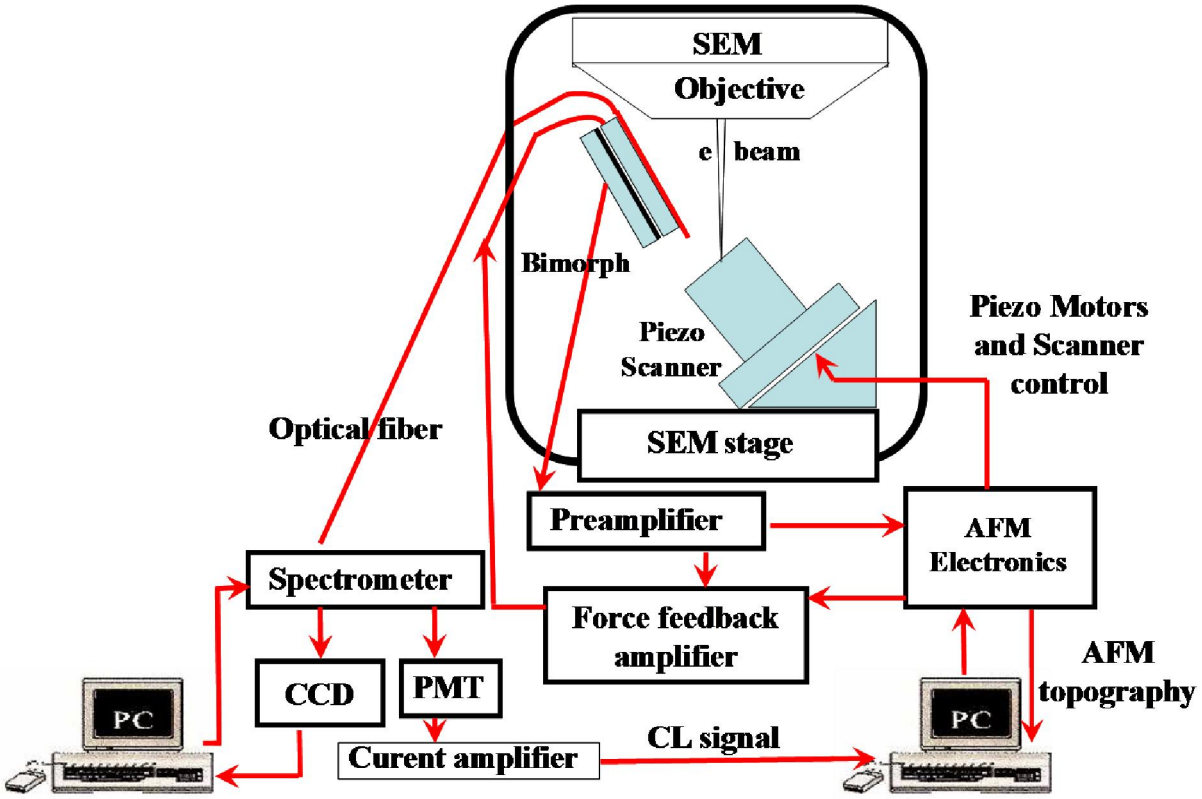
Near-field collection of cathodoluminescence







Development of a near-field CL microscope



Schematics of the scanning near-field cathodoluminescence microscope (SNCLM).

Force feedback amplifier

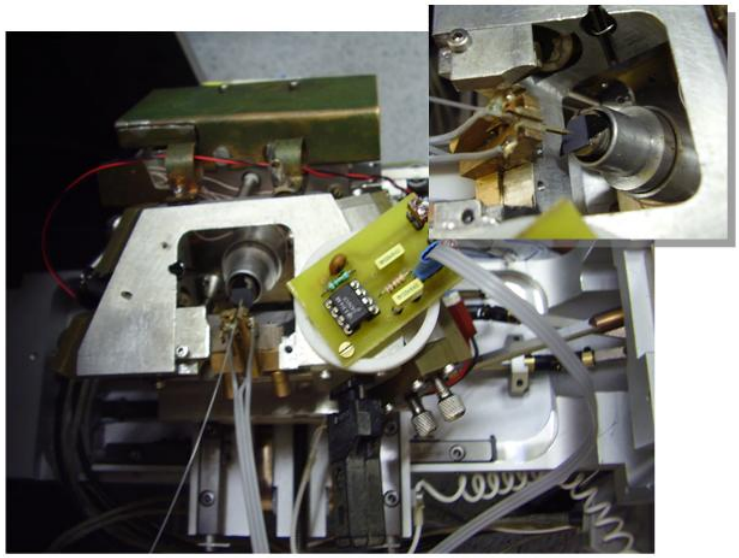
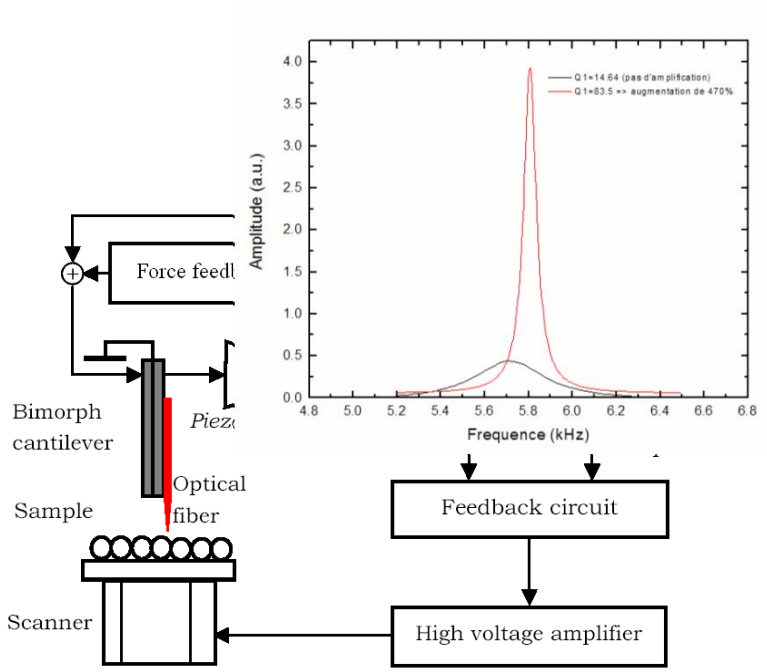
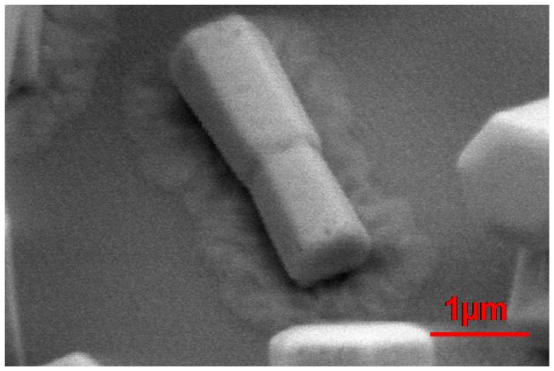


Image of the developed CL system placed on the SEM stage.

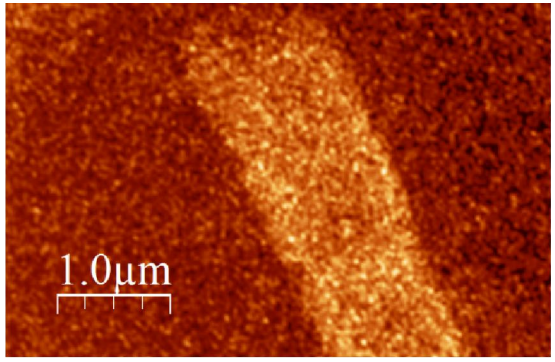


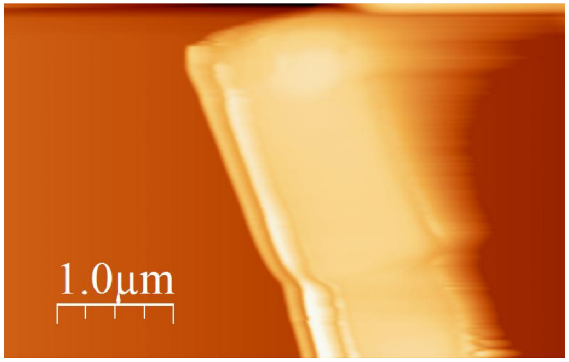
Schematic view of the feedback loop.

ZnO nanostructures imaging



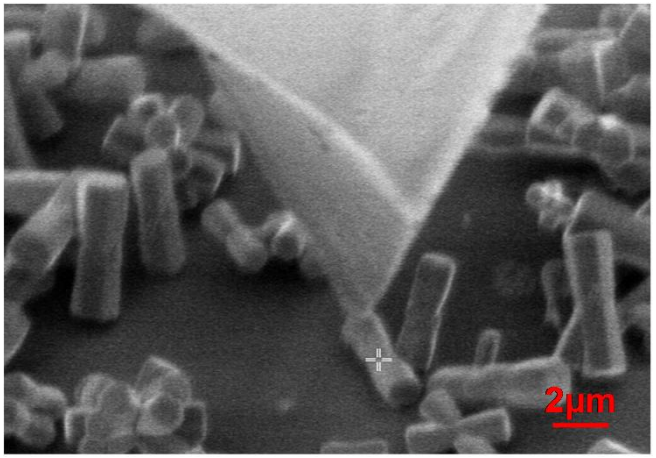
SEM image of ZnO nanostructures.



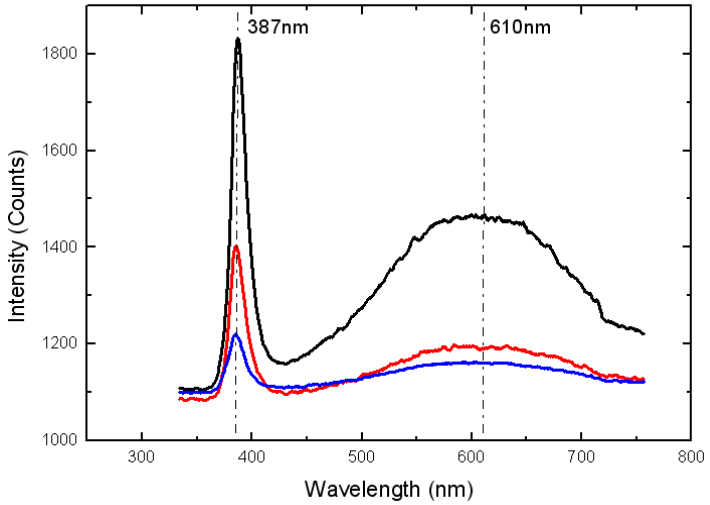


Simultaneous near-field cathodoluminescence image (left) and correspondent topography image (right) of the ZnO nanostructure.

Near-field local CL spectra

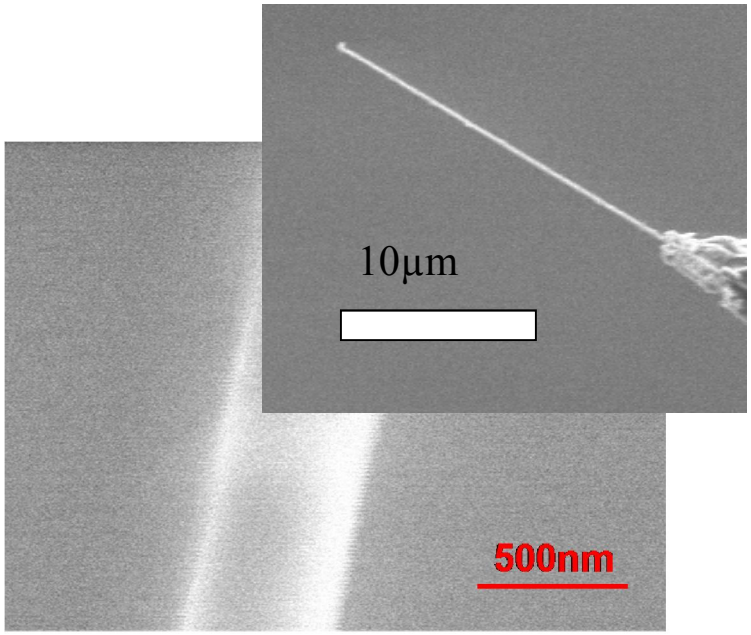


ZnO hexagonal microstructures grown on Si substrate.

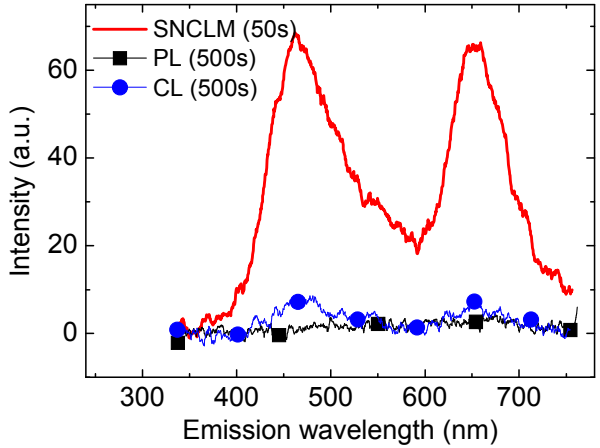


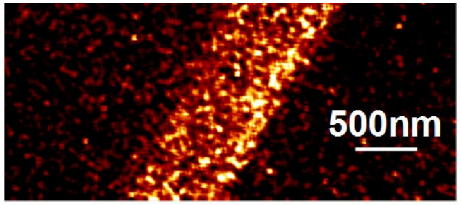
Cathodoluminescence spectra recorded in near-field on ZnO hexagonal microstructures.

Precise positioning of the fiber tip



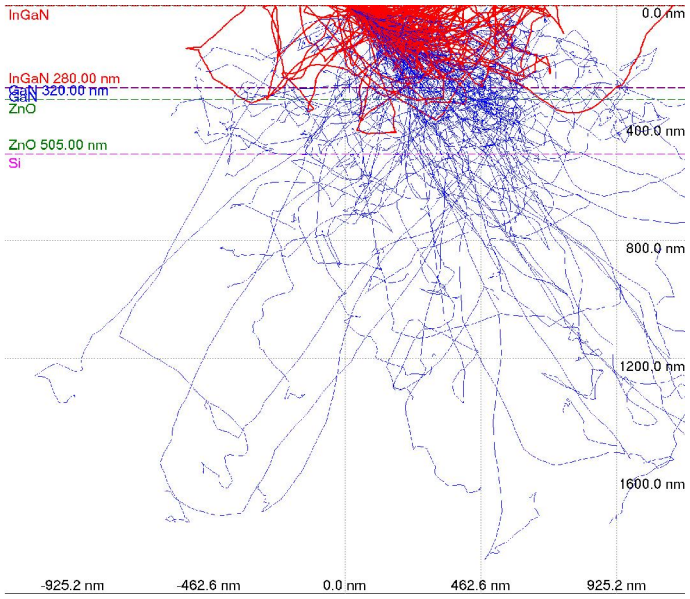
SEM image of a suspended SiC nanowire.



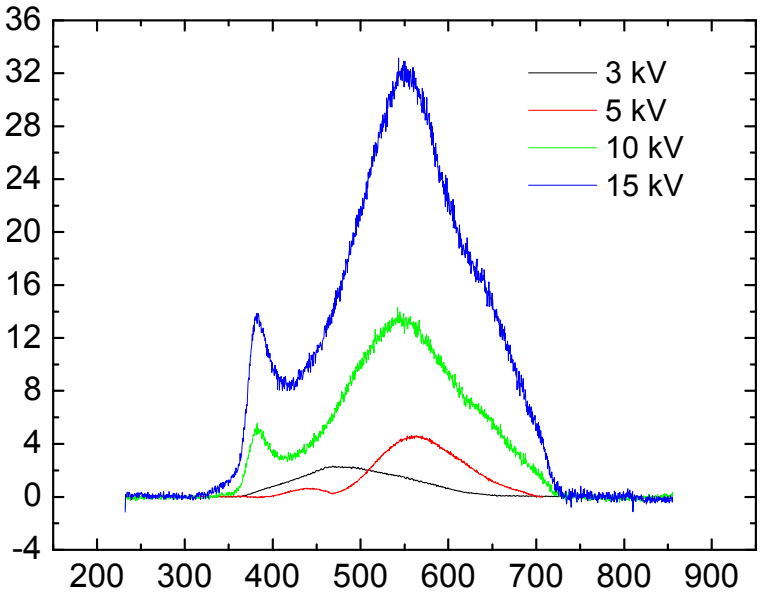


Scanning near-field CL mapping of the suspended SiC nanowire.

Beam energy dependent local CL spectra

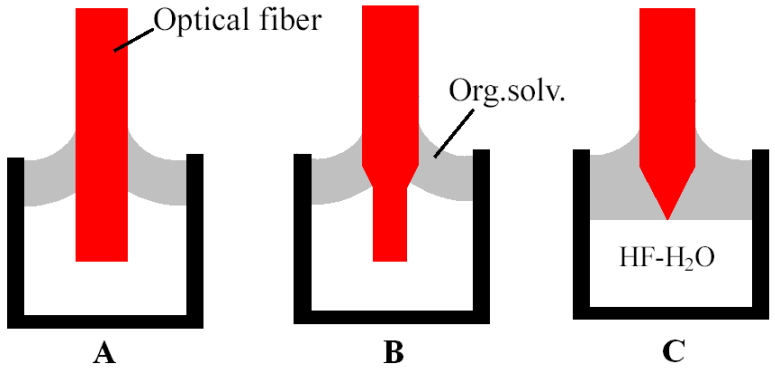


InGaN on ZnO stacked structure – Monte Carlo simulation of beam-sample interaction.

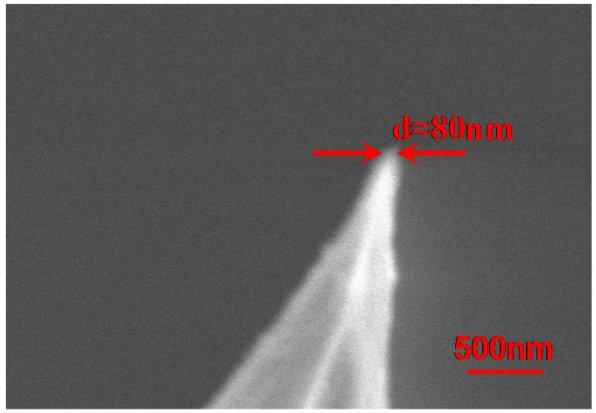


CL spectra measured on the stacked InGaN on ZnO structure at different beam energies.

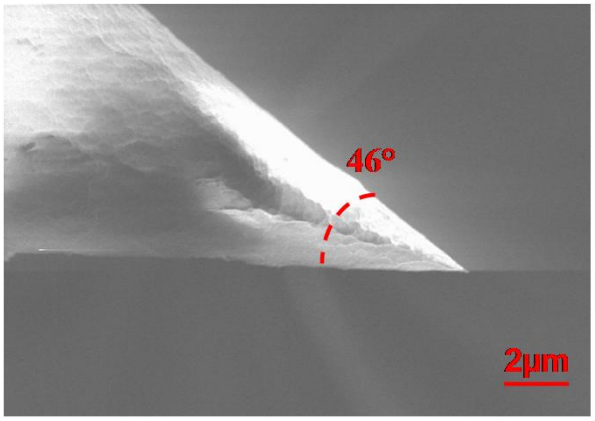
Optimized fiber chemical etching



Schematic presentation of the etching procedure.

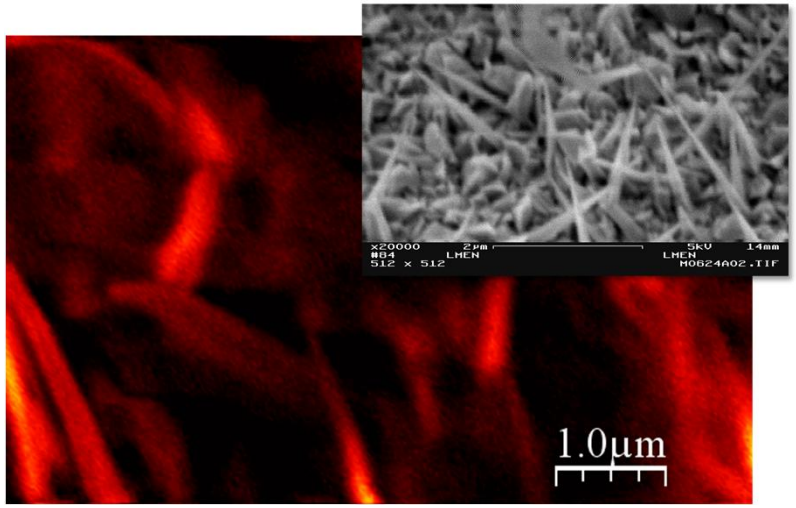


SEM image of etched optical fiber tip.

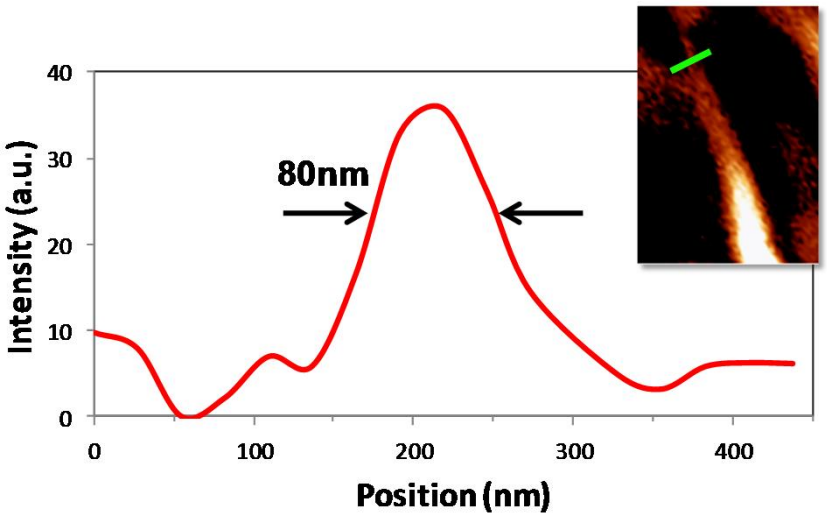


SEM image of etched optical fiber cone angle.

GaN nanowires CL mapping

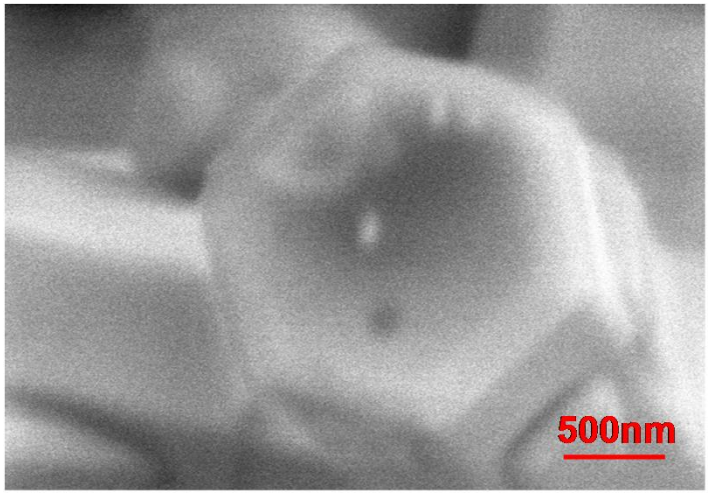


Scanning near-field CL image of GaN nanowires (Inset: SEM image).

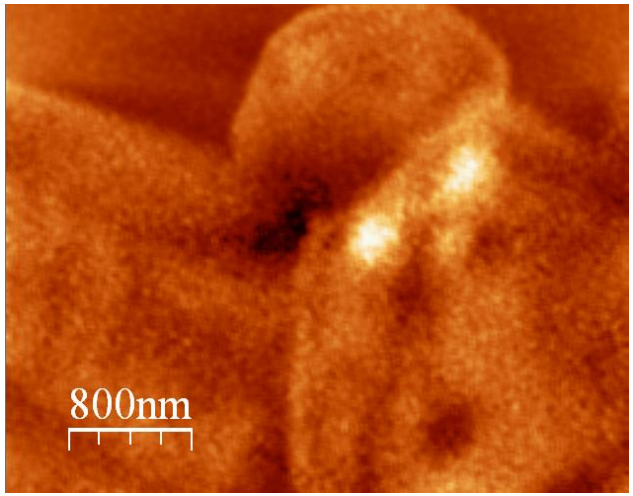


CL intensity profile along the cutline (Inset: nanowire CL image).

Defects imaging by near-field CL

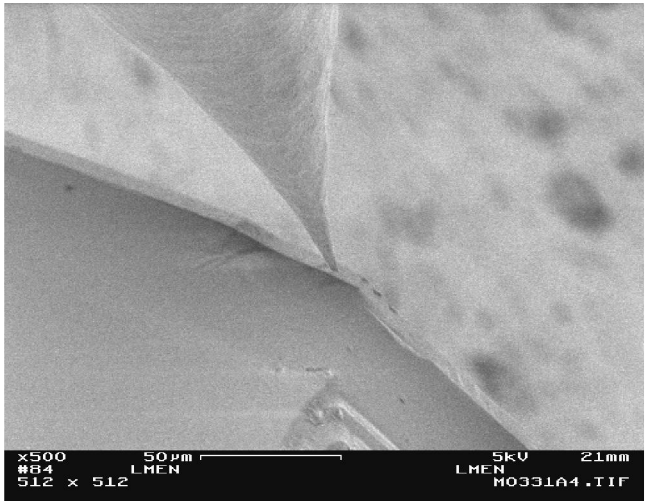


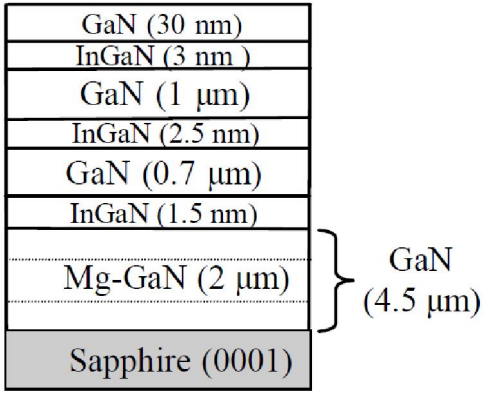
SEM image of ZnO hexagonal nanostructures showing structural defects sites.

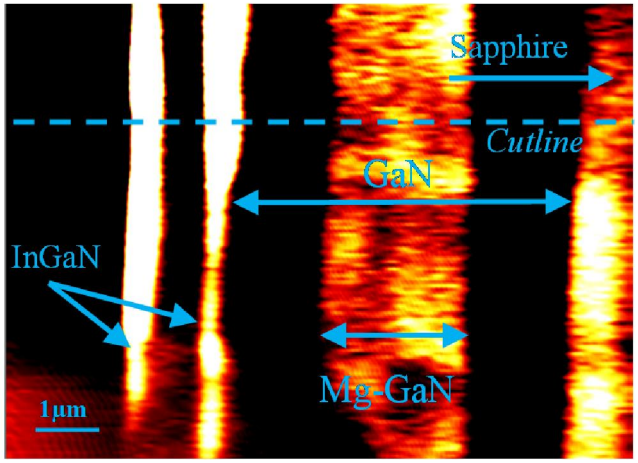


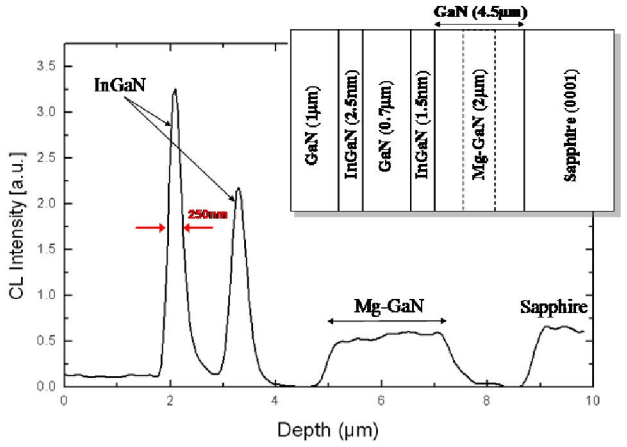
Scanning near-field CL mapping showing an enhanced defect-related CL emission at structural defects sites.

Heterostructure characterization





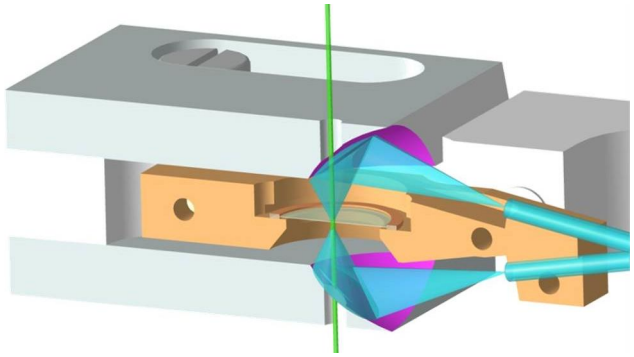


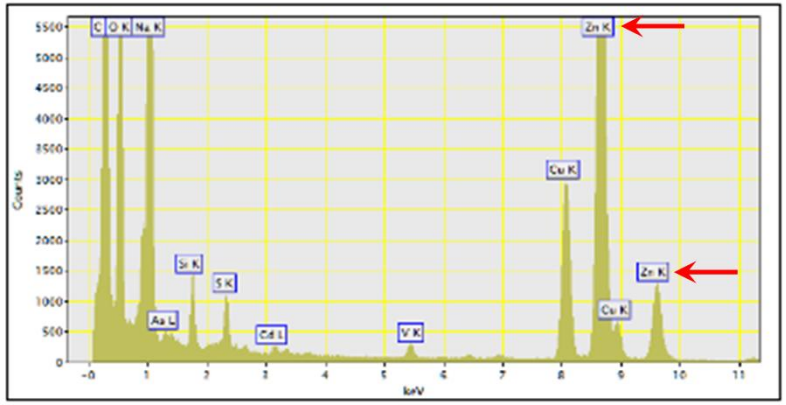


Scanning near-field CL technique overview

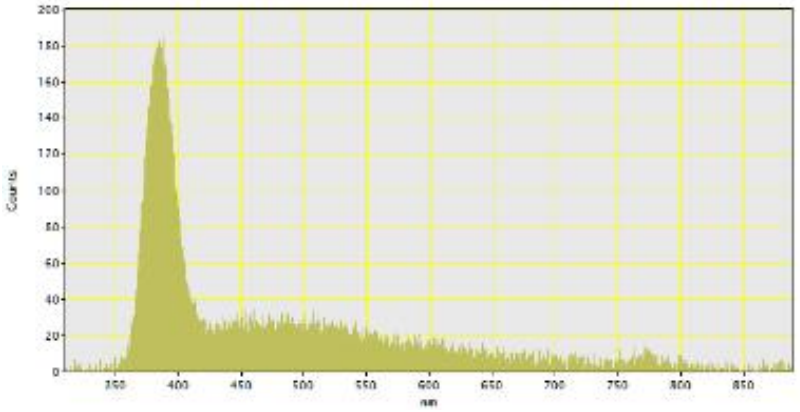
- *Robust and cost-effective actuation and detection system*
- *Good resolution compared with classical CL techniques*
- *Precise positioning of the fiber over the sample*
- *Sharp optical probes available through an optimized process*
- *Broad application field concerning SC nanowires, CNT, QDots, …*

Local EDS and STEM-CL spectra



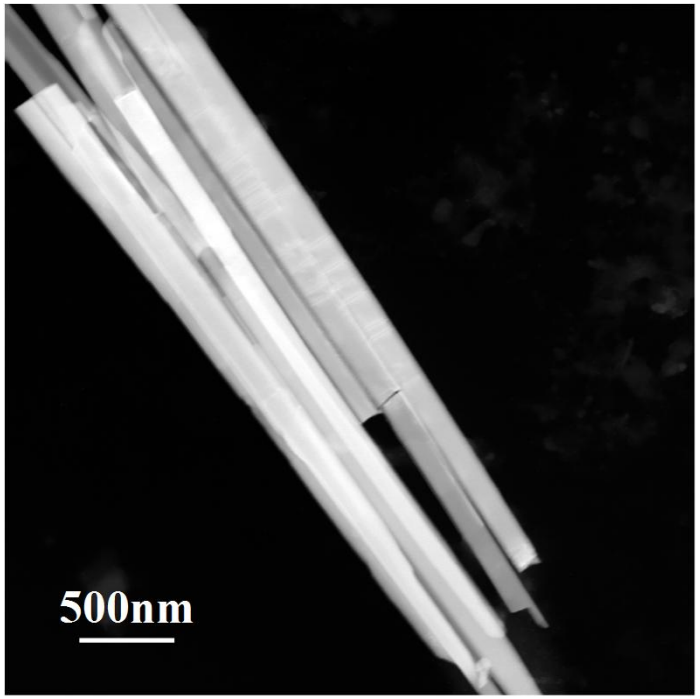


Element analysis spectrum obtained on a ZnO nanowire showing a high intensity Zn Kα line.

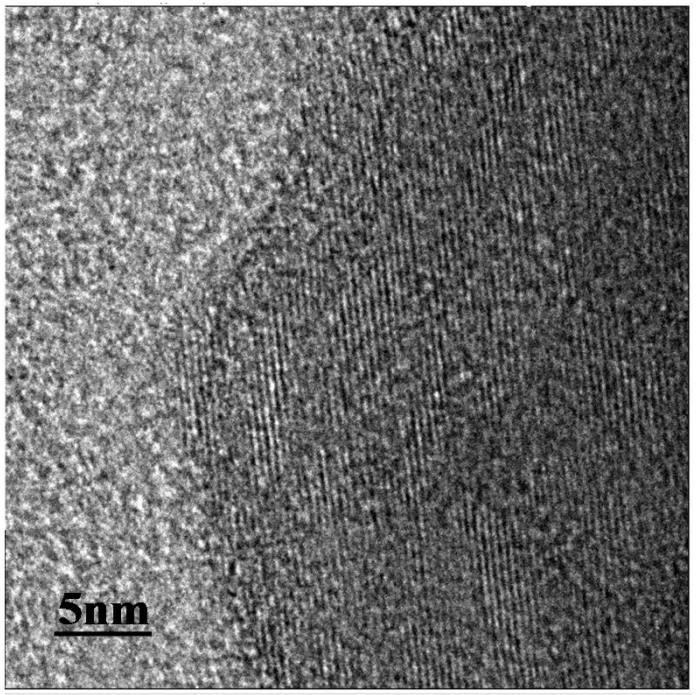


CL spectrum acquired on a ZnO nanowire showing an intense excitonic peak at 375nm and a low intensity defect related peak.

STEM nanowire imaging

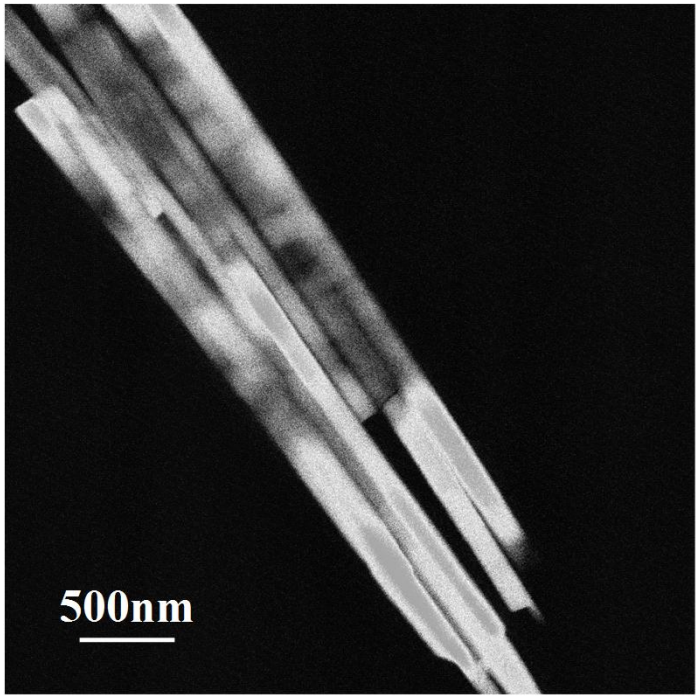


STEM image of a ZnO nanowire bundle.

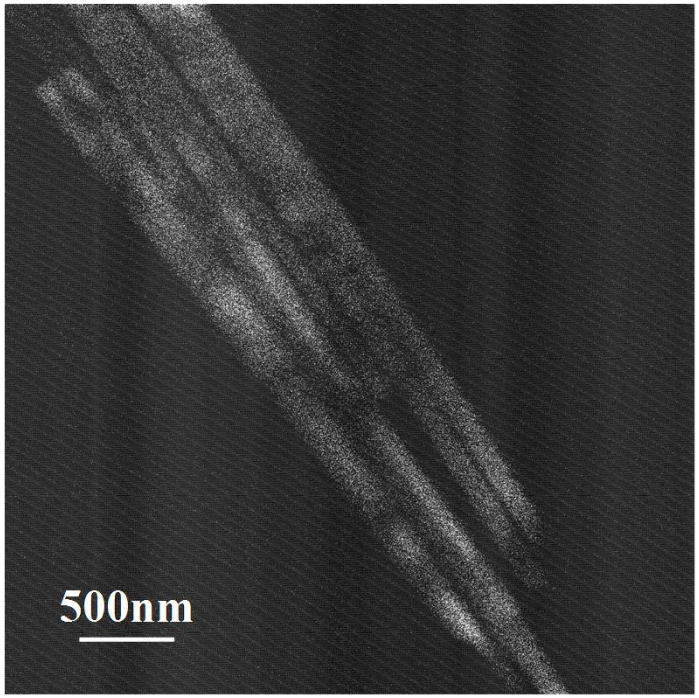


TEM image of a nanowire tip showing good crystallinity.

Mono and panchromatic STEM-CL imaging



Panchromatic CL emission image of the ZnO nanowire bundle.

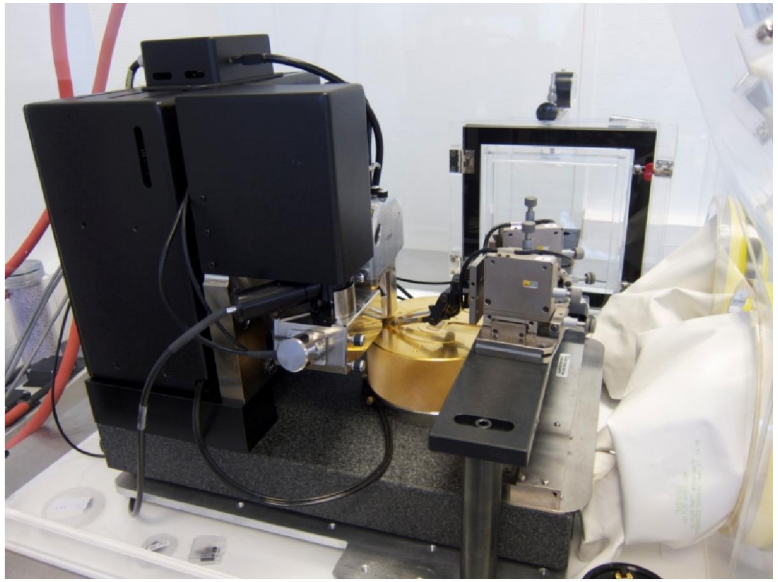


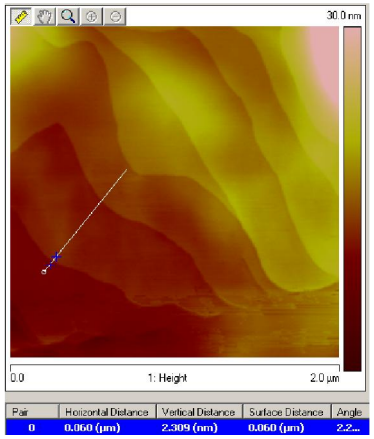
Monochromatic CL image acquired at λ=375nm of the ZnO nanowire bundle.

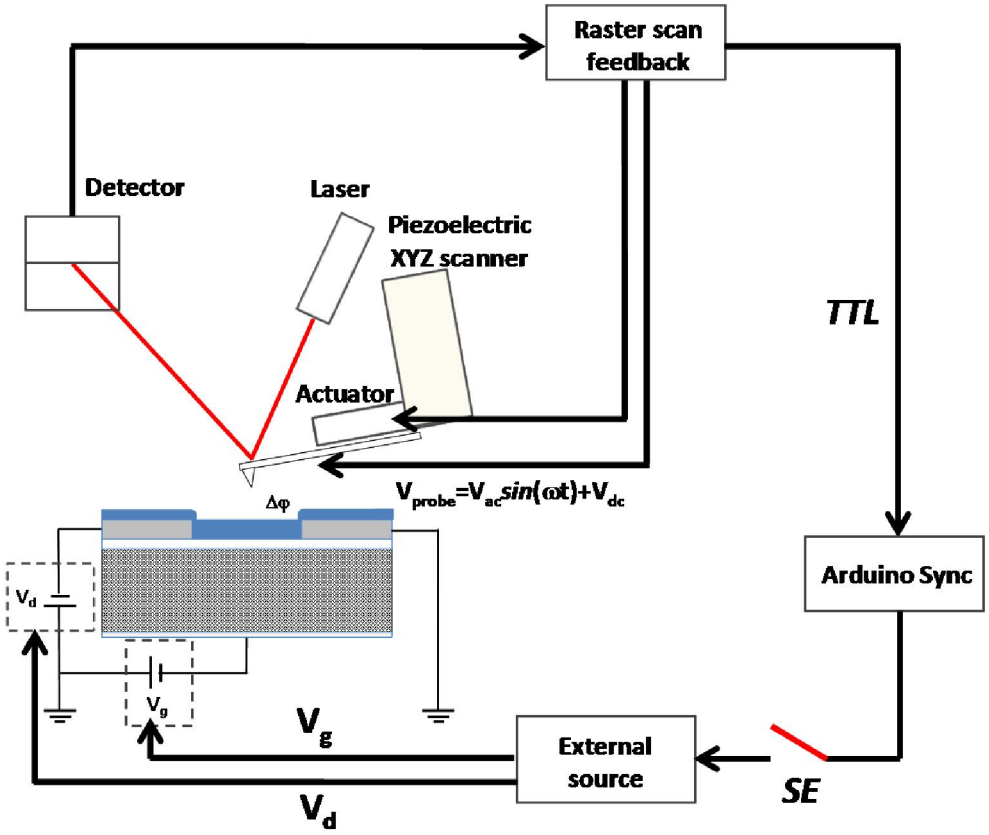
Outline

- *Overview of the near-field scanning techniques*
- *Mechanical and chemical local properties measurement by AFM techniques*
- *Nanostructure characterization by the scanning near-field and STEM CL*
- *Electrical and KPFM nanowire characterization*
- *Conclusions*

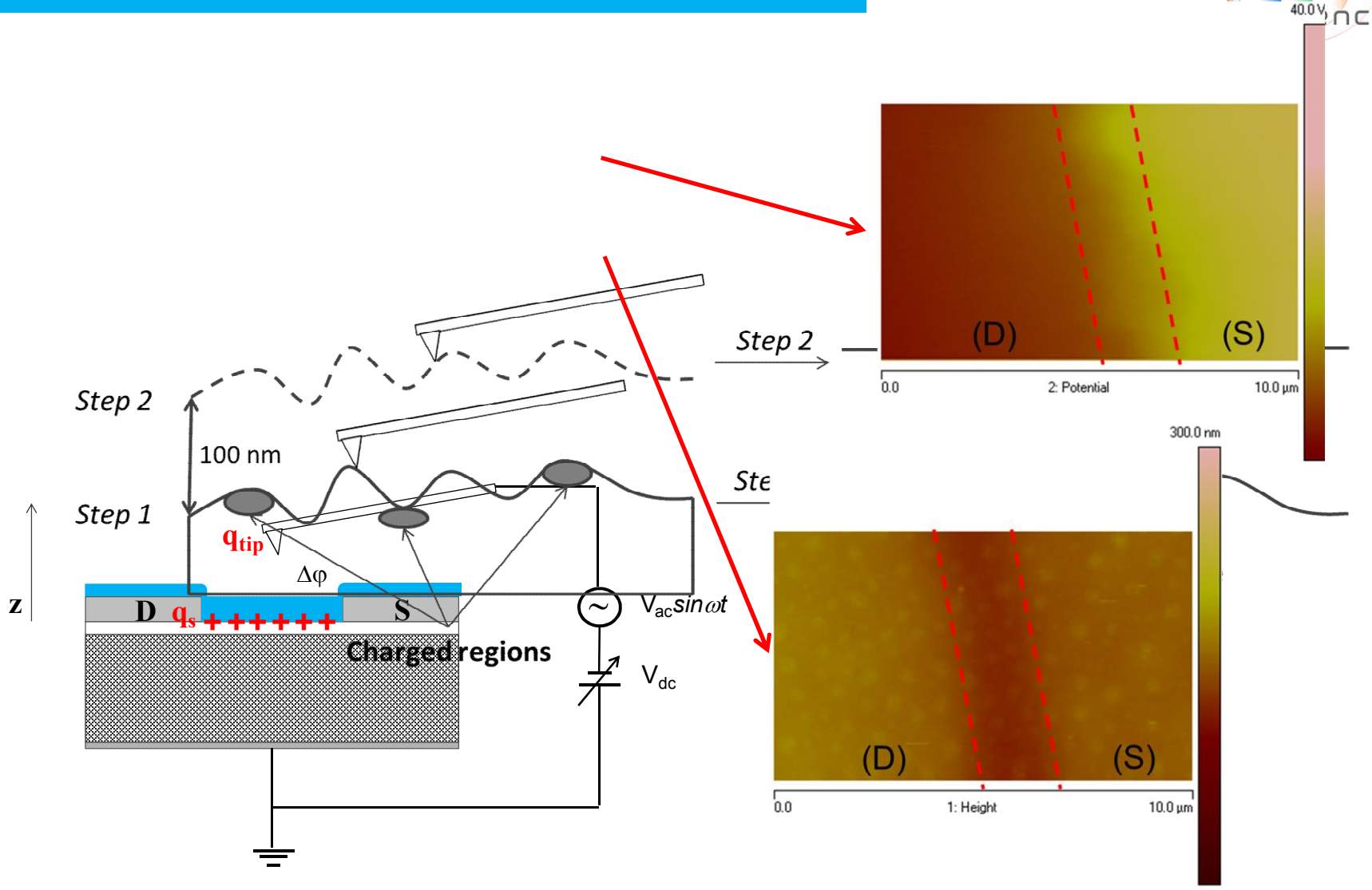
Development of a specialized KPFM



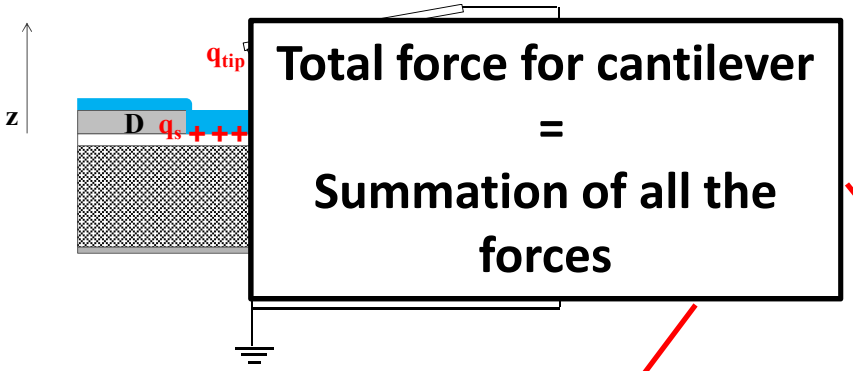




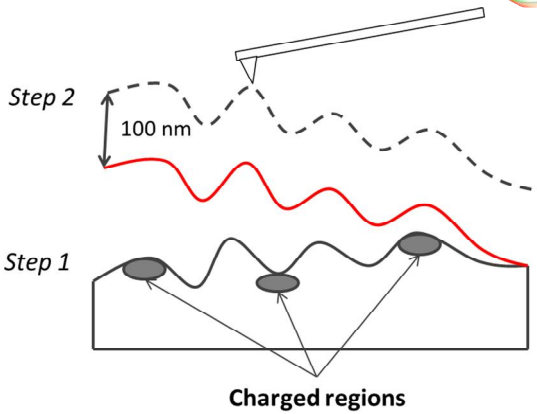
Kelvin Probe Microscopy (KPFM)

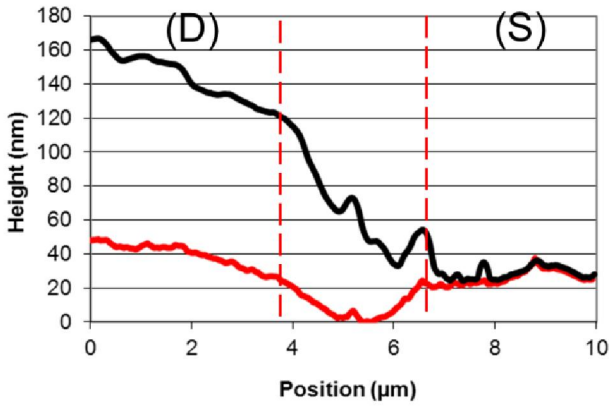


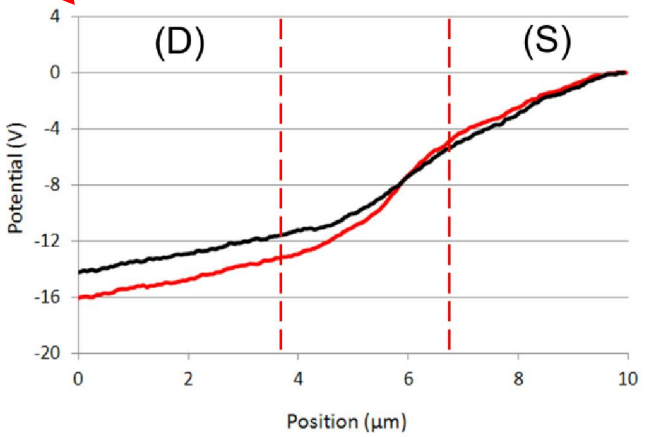
Measurements on biased transistors



Total force for cantilever
=
Summation of all the forces



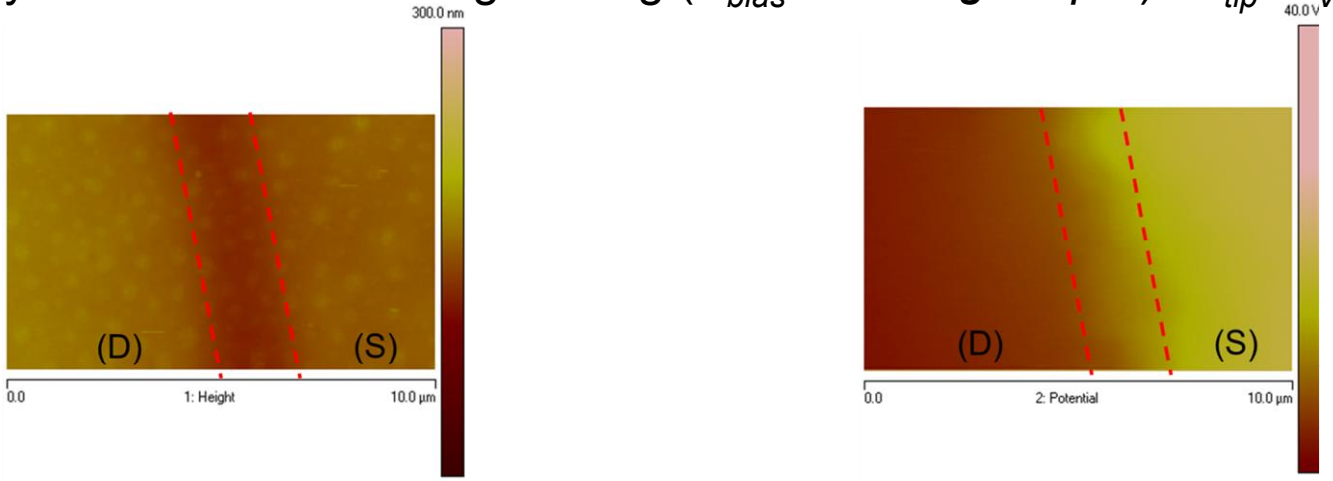




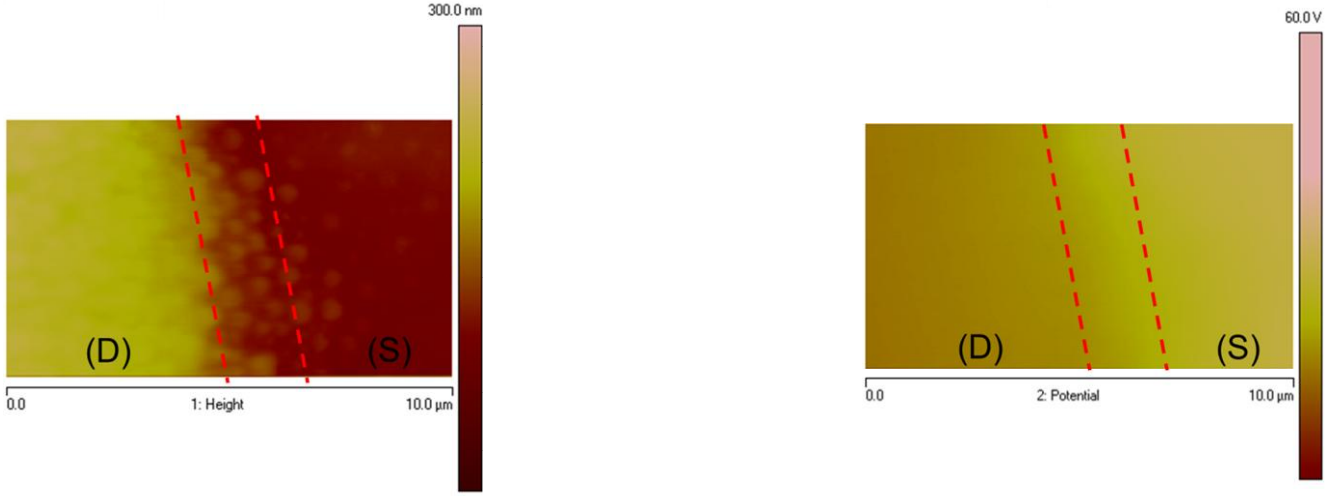
Topographic longitudinal profile (left) and potential (right) along the canal for L= 2µm, Vds=-15V DC, with bias applied all time (black) or synchronized alternate (red).

Advantages of the KPFM synchronization

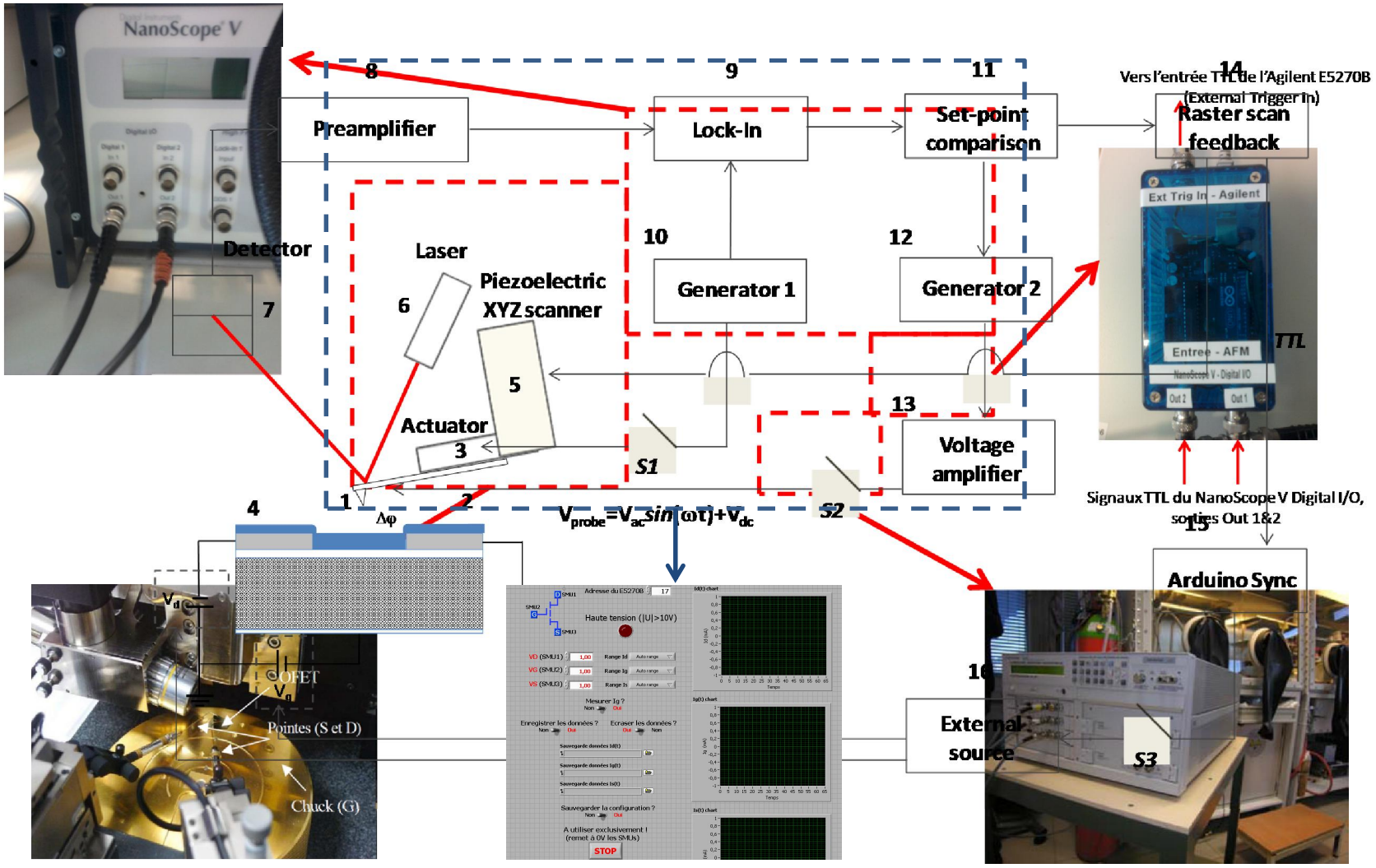
1. Synchronized alternating biasing (V_{bias}=*0 during Step 1*) : $F_{tip}=F_{VdW}+F_{capil}$



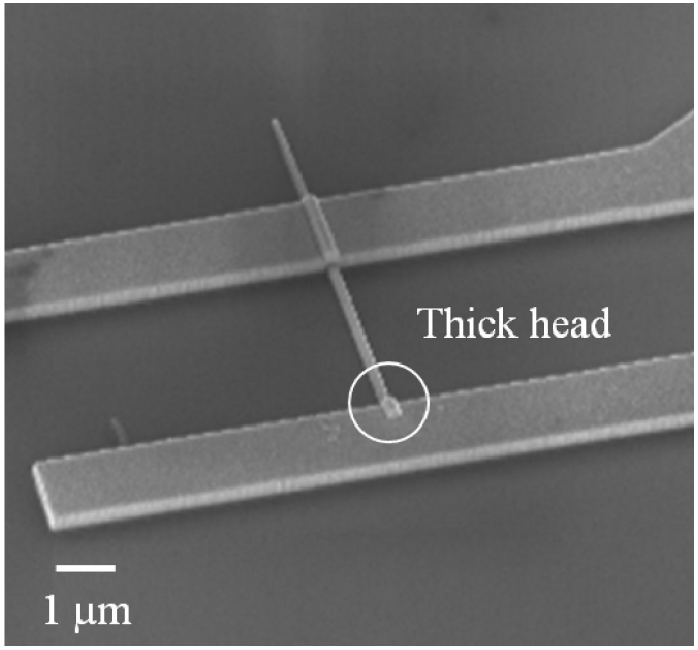
2. Continuous biasing ($V_{bias}\neq 0$ *during Step 1)* : $F_{tip}=F_{VdW}+F_{capil}$ **$+F_{el}$**



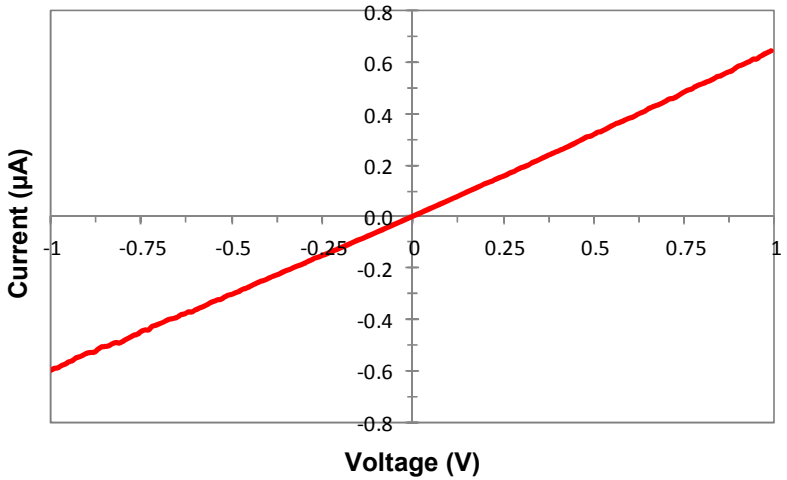
Scheme of the developed KPFM system



Nanowire contacts by e-beam lithography

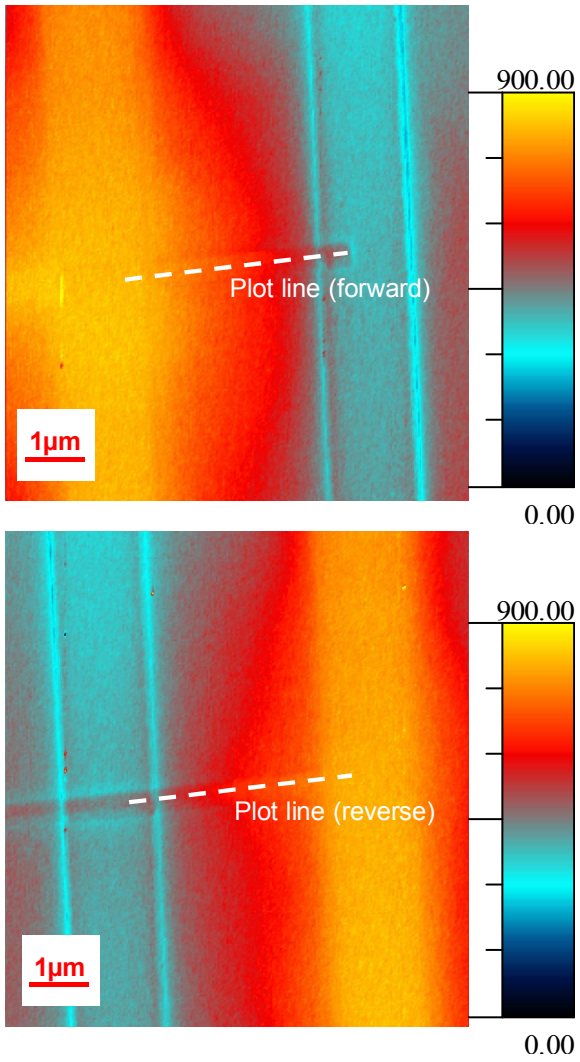


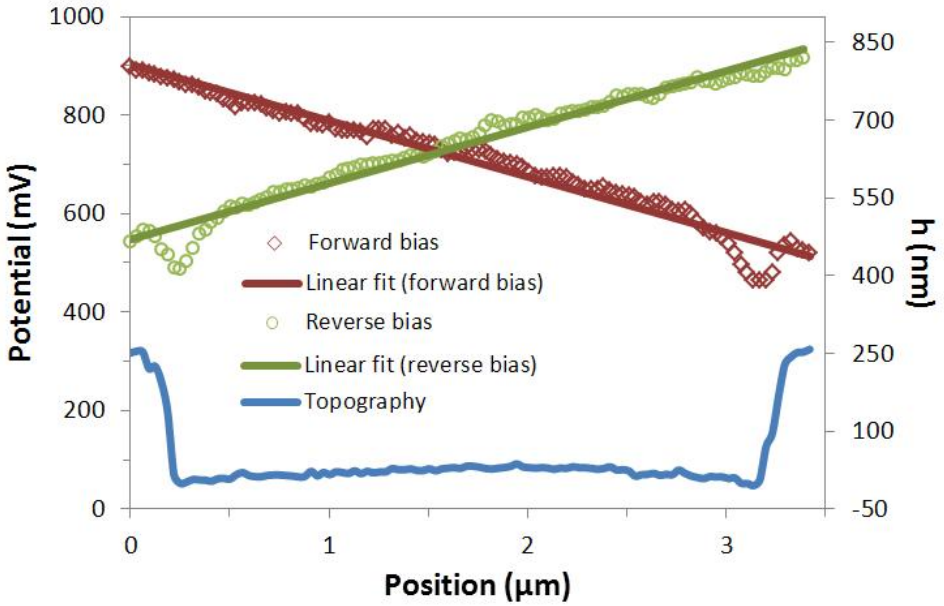
SEM image of a ZnO nanowire showing linear (ohmic) behavior.



Current-voltage measurement of a ZnO nanowire showing linear (ohmic) behavior..

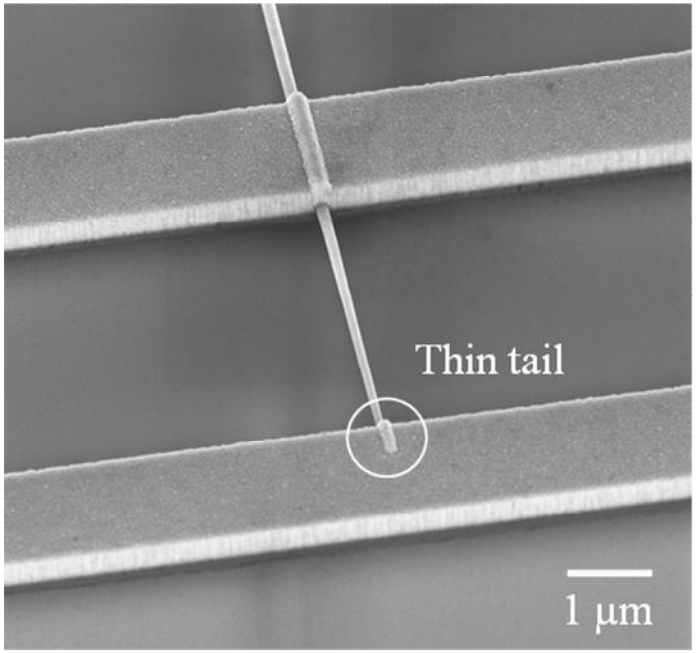
KPFM potential mapping of biased ZnO NWs



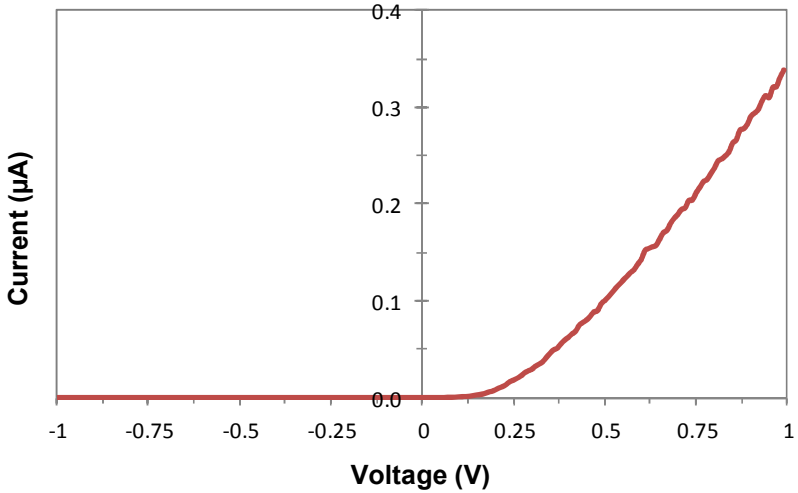


Measured topography and electrical potential variation along a ZnO nanowire with ohmic contacts..

NW shape-related linearity

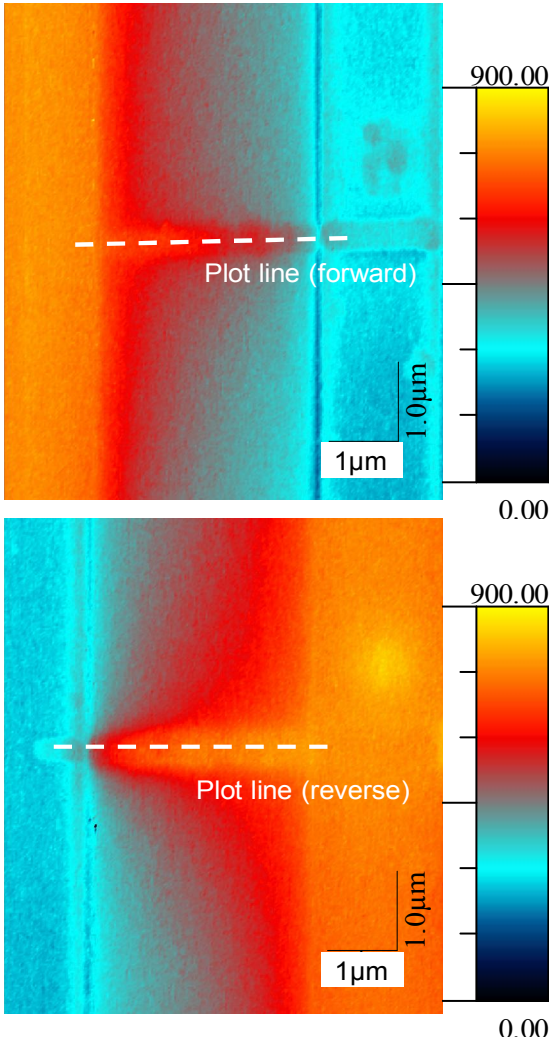


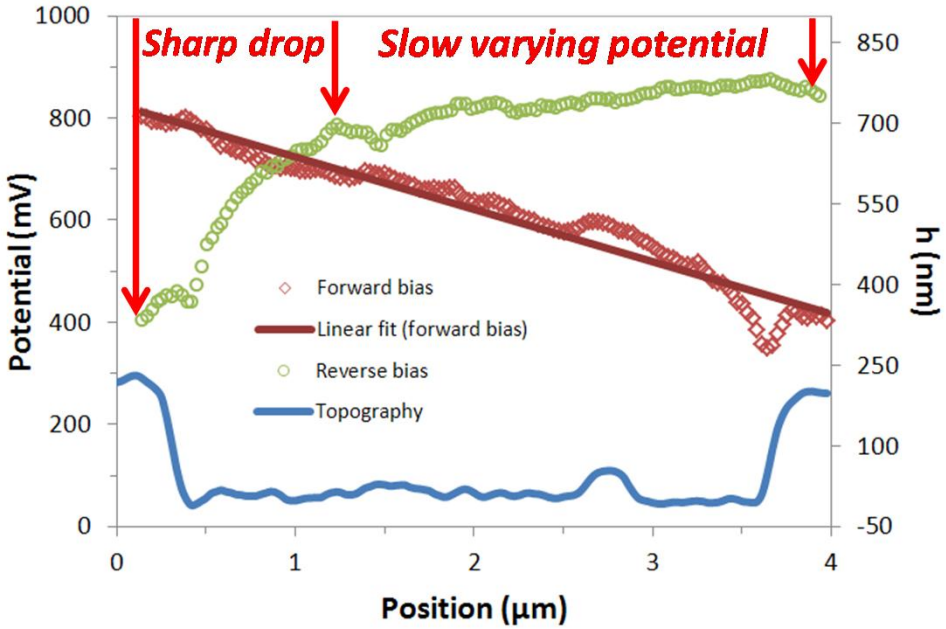
SEM image of a ZnO nanowire showing non-linear behavior.



Current-voltage measurement of a ZnO nanowire showing non-linear behavior.

KPFM potential mapping of non-linear NWs





Measured topography and electrical potential variation along a ZnO nanowire with non-linear response.

Conclusions

- Improvement of classical AFM potentialities
- Nanostructure CL mapping in near-field et STEM
- Development of resolved chemical modes
- Correlation of different properties at nanoscale (mechanical, chemical, thermal…)

Acknowledgments

- Fibers
  - INRA Reims Fractionnement des AgroRessources et Environnement: Brigitte Chabbert (CR), Véronique Aguié-Beghin (RI), Loïc Muraille (PhD)

- Toxicity peptides / membranes
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- Electrical caraterization:
  - LRN URCA: Louis Giraudet (Pr), Olivier Simonetti (Assoc Pr)

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