Vth Sesame meeting – Alexandria 27-29 November 2006

Nano-scale chemical mapping and surface structural modification by joint use of X-ray microbeams and tip assisted local detection

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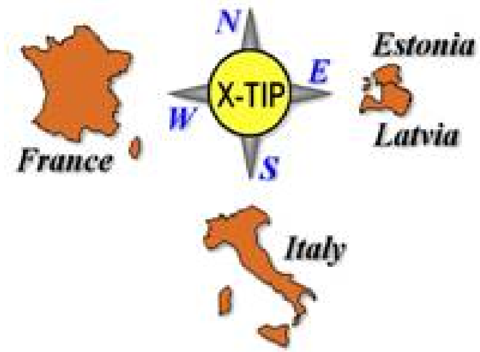
University of Trento

Italy

Outline

- Introduction
  - X-TIP Project: goals and scientific research program
- X-ray Absorption Fine Spectroscopy
  - The measurement technical modes
  - Chemical-Physical information
- Scanning Probe Microscopy (SPM)
  - Scanning Tunnelling Microscopy (STM)
  - Atomic Force Microscopy (AFM)
  - Scanning Near Field Microscopy (SNOM)
- X-tip project: some results
  - X-tip measurements
  - XEOL measurements
- Conclusions

X-TIP Project Aims



Specific Targeted Research Project (STRP)

Supported by European Commission 6th Framework Programme

Budget: 1.1 million Euro

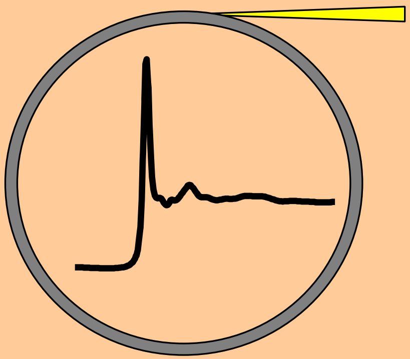
to deliver instrumentation and techniques
that merge the ability of Synchrotron Radiation spectroscopies
in providing elemental composition, chemical status and
structural information
with the lateral resolution of
Local Probe Microscopes in providing detailed surface morfology

Objectives of the X-tip project

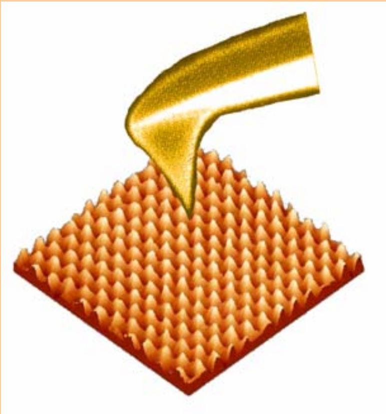
•**XAS-TEY** - Element-Specific Contrast in Local Probe Microscopy via X-Ray excited photoelectrons detection by conductive tip in Total Electron Yield collection mode [TEY].

•**XAS-SNOM** - Element-Specific Contrast in Local Probe Microscopy via X-Ray Excited Optical Luminescence (XEOL) detection by optical probe in SNOM mode.

Objectives of the X-tip project



X-Ray Absorption Spectroscopy using Synchrotron Radiation

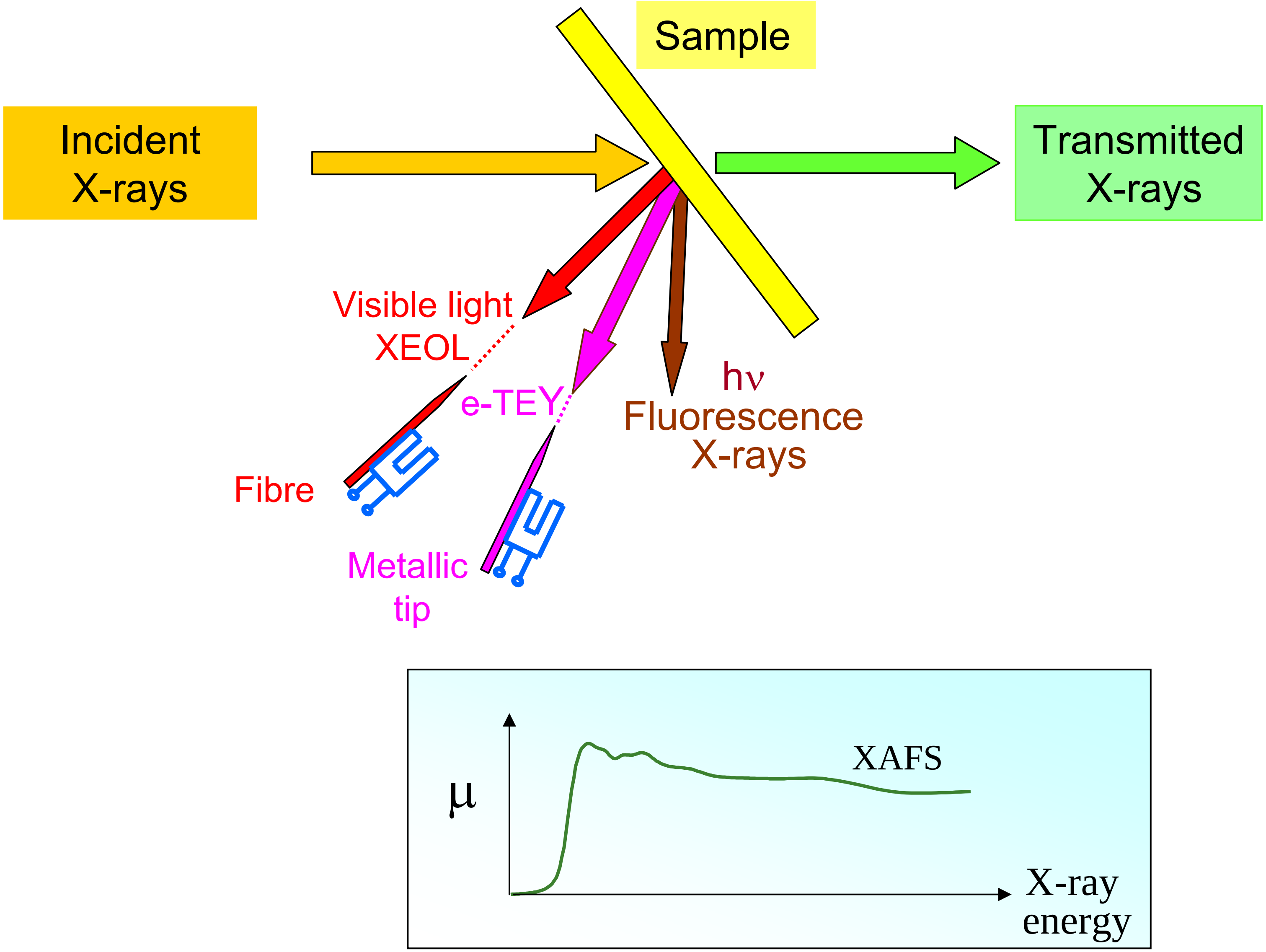


Scanning Probe Microscopy

Combined Nano-Scale Spectro-Microscopy

able to provide Mapping and Physico-Chemical characterization of nanostructures

X-ray Absorption Spectroscopy (XAS)



Info from X-ray Absorption Spectroscopy

Type of atom sorrounding the central absorber atom (typically $\Delta Z > \pm 2$)

Number of atoms sorrounding the absorber atom (± 5÷20%)

Interatomic distance (± 0.01 Å for the 1° coordination shell)

Atomic disorder (from Debye-Waller term)

Oxidation state of the absorbing atom

Ligand geometry (from intra-ligand multiple scattering)

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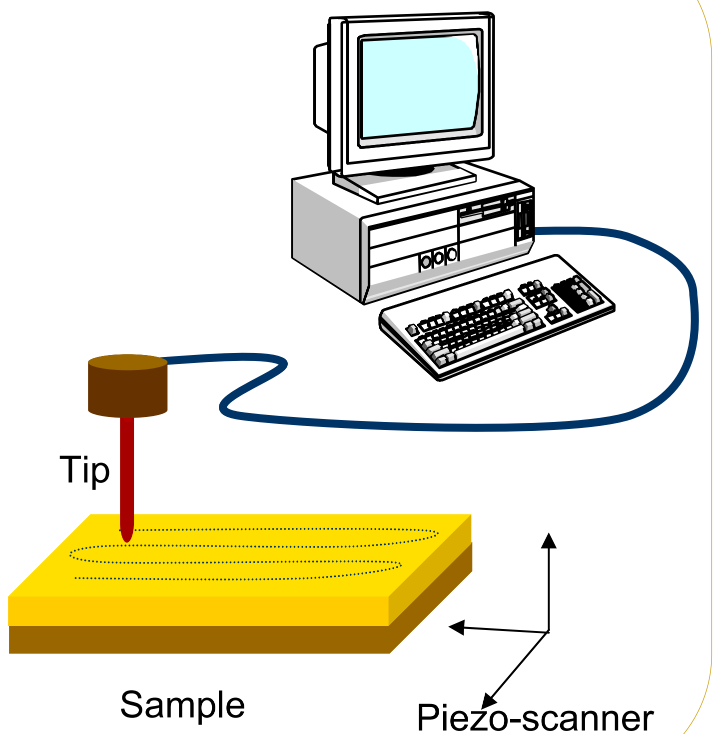
- First results
  - X-tip measurements
  - XEOL measurements
- Conclusions

SPM: Scanning Probe Microscopy



Surface image

Components

- **a pr**
- **piez**

  to m ... le);
- ***cor ... ystem***

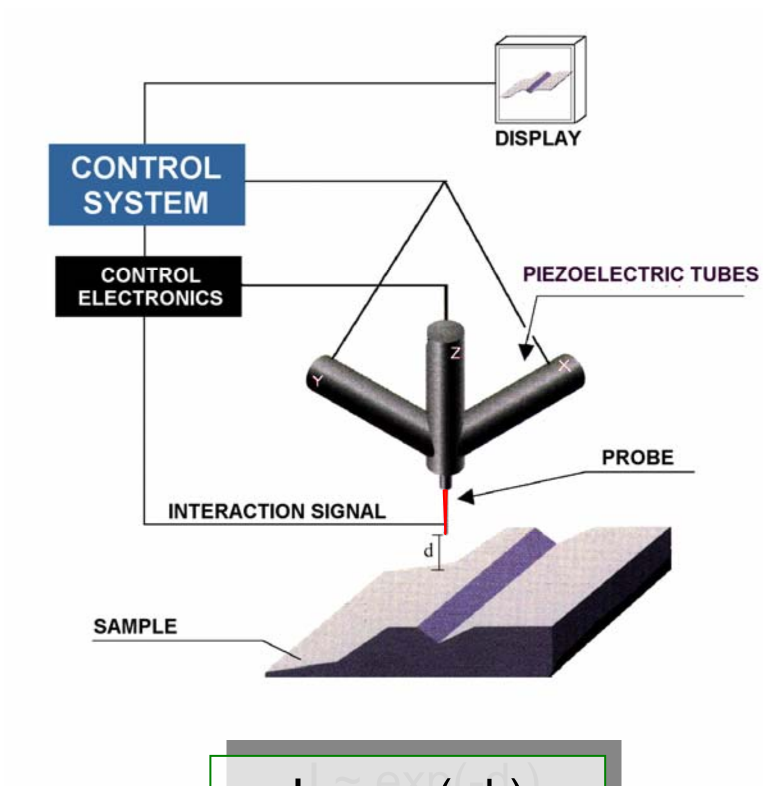
  to c ... mple

  to m ... data into

Recorded sound

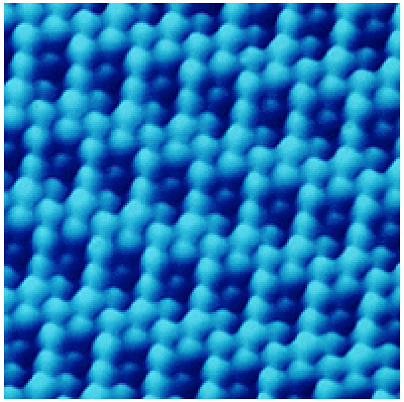
Scanning Tunnelling Microscopy (STM)

STM



I ~ exp(-d)
d ~ Å
I ~ nA

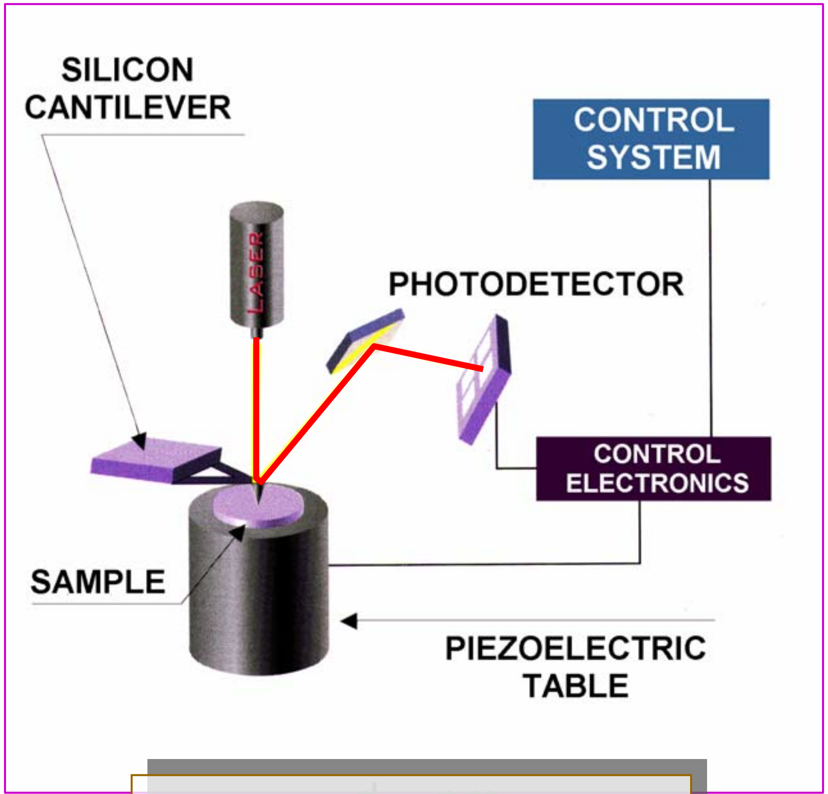
Only conductive materials



STM image of a crystal surface : single molecule resolution

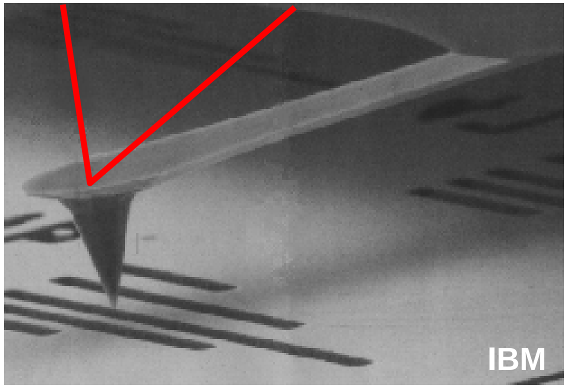
Atomic Force Microscopy

AFM



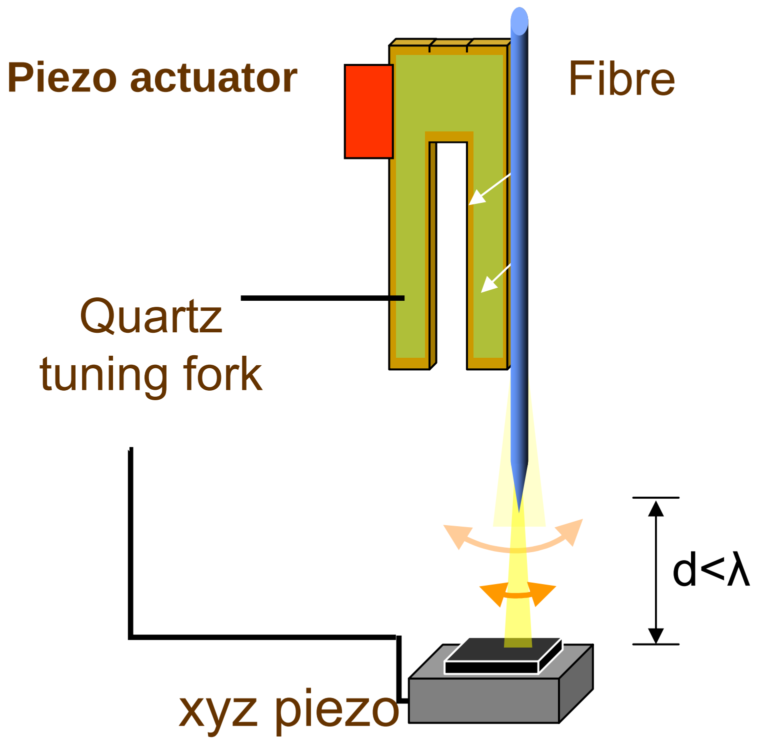
d ~ nm

$F < 10^{-16}$ N



- Both isolated and conducting surfaces
- Surface topography on atomic scale

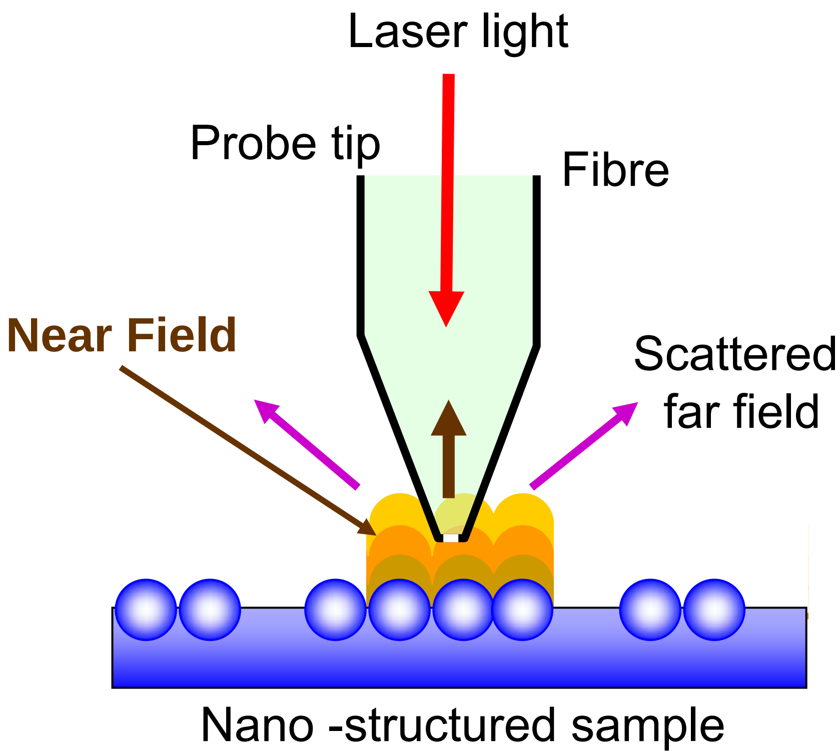
Scanning Near Optical Microscopy



- The sample is illuminated by light
- The scattered light is collected near the sample by a tapered optical fiber with a sub-wavelenght aperture
- Low light throughput
- Resolution limited to λ/10
- The tip is kept at a controlled distance from the sample surface by means of a feed back mechanism sensitive to the shear force

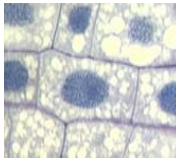
Scanning Near-field Optical Microscopy

Aperture technique

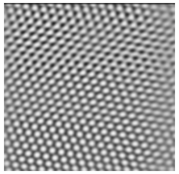


- the tip has a sub-wavelength aperture.
- Laser light illuminates the sample through the optical fibre
- it is scattered by the surface and evanescent light is produced
- the aperture picks up the reflecting evanescent light and converts it into propagating light
- which is carried up by the fibre to the detector.

Resolution of SPM



Plant Cell | Animal Cell | Bacterium | Viral ribosome | Protein | Small Molecule | Atom



1 cm| 1mm| 100µm| 10 µm| 1 µm| 100nm| 10nm| 1nm| 1Å| 0,1Å|

Resolution

0,4-0,7µm* **10nm** **5-2nm** **max 0,1nm**

Optical microscopy

Electronic microscopy : SEM

TEM

Scanning Probe Microscopy (SPM):

10nm **2Å** **0,1Å**

SNOM

AFM

STM

* The diffraction limit depends on used wavelength (λ).

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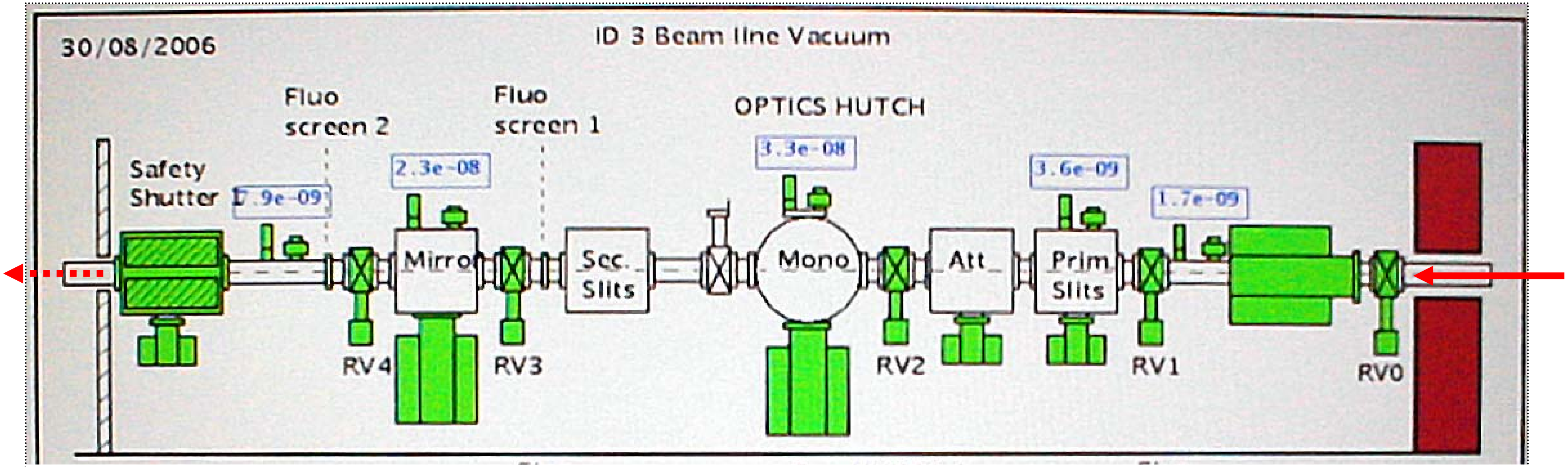
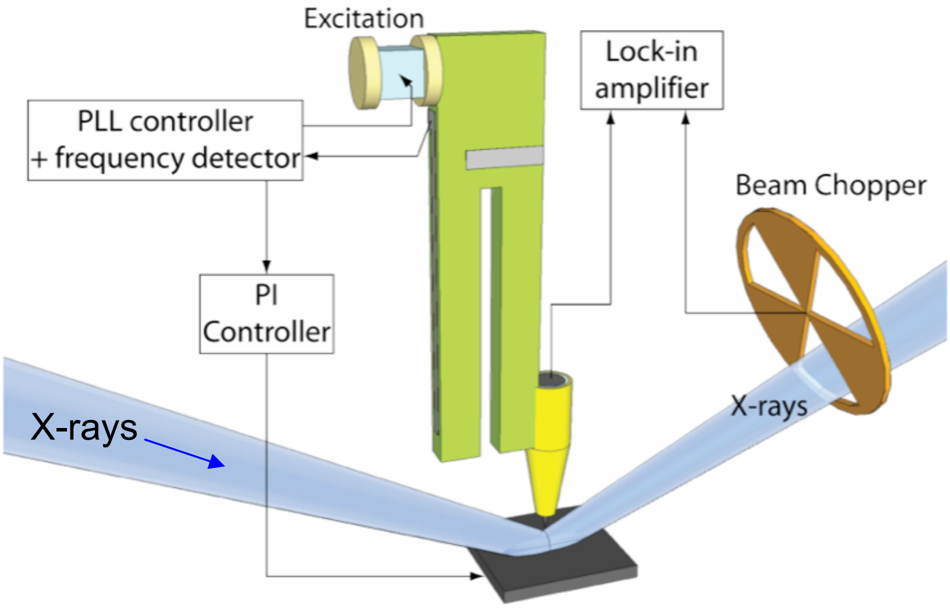
European Synchrotron Radiation Facility

ESRF ID03 Beamline Layout



Cross section of the beam 2x2 μm^2

XAS – TEY expectancies



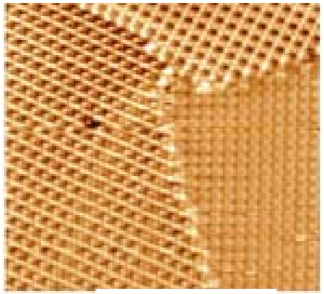
Excitation: X-rays

Measurement: Total electron yield

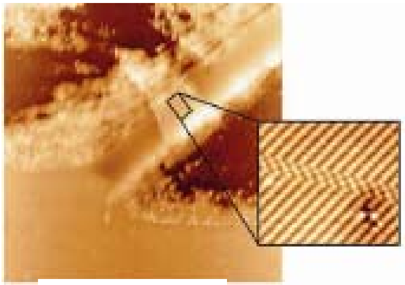
Info: Elemental composition

Chemical state

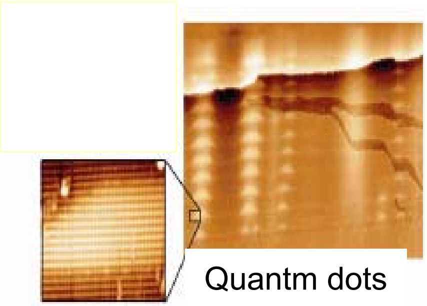
Local structure



2D oxides

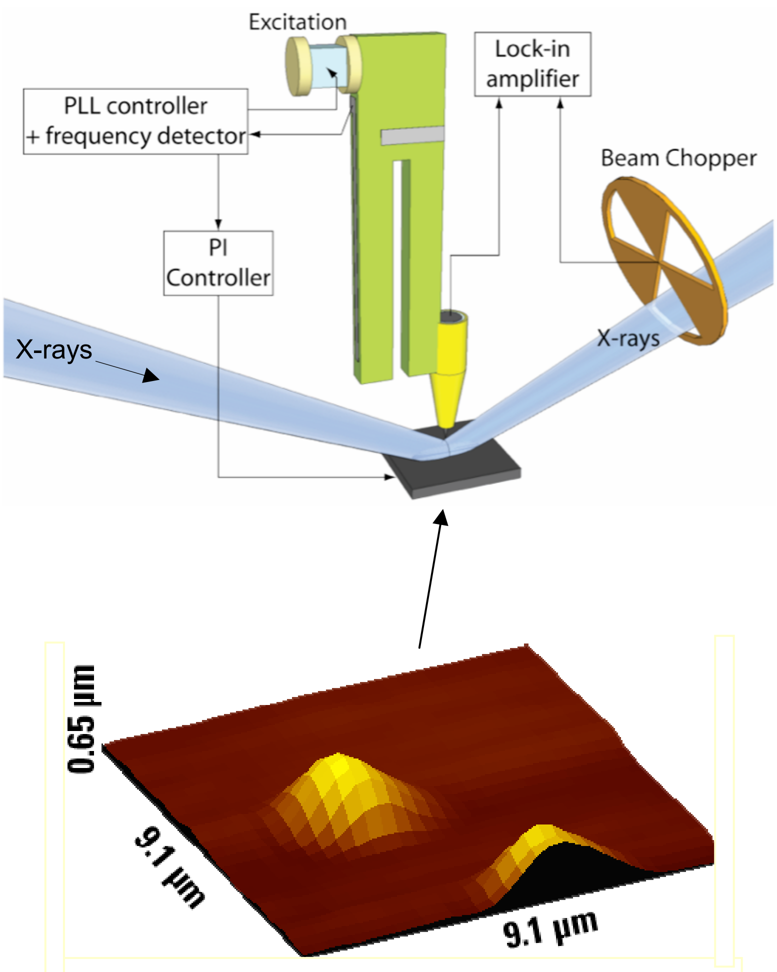


Nanowires



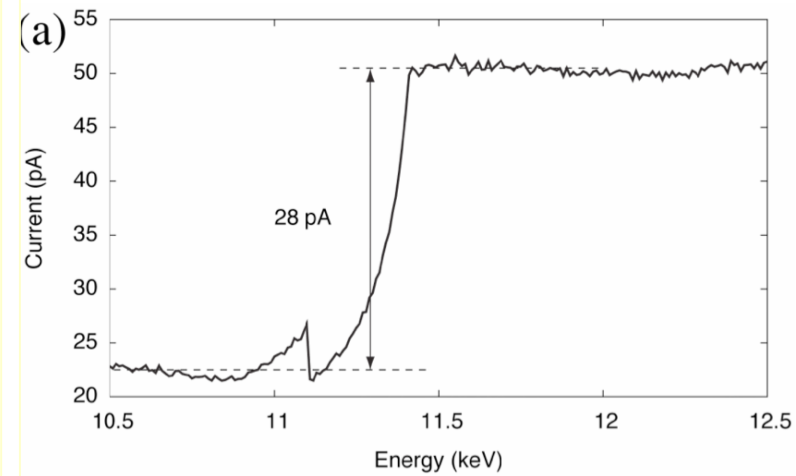
Quantm dots

XAS-TEY results

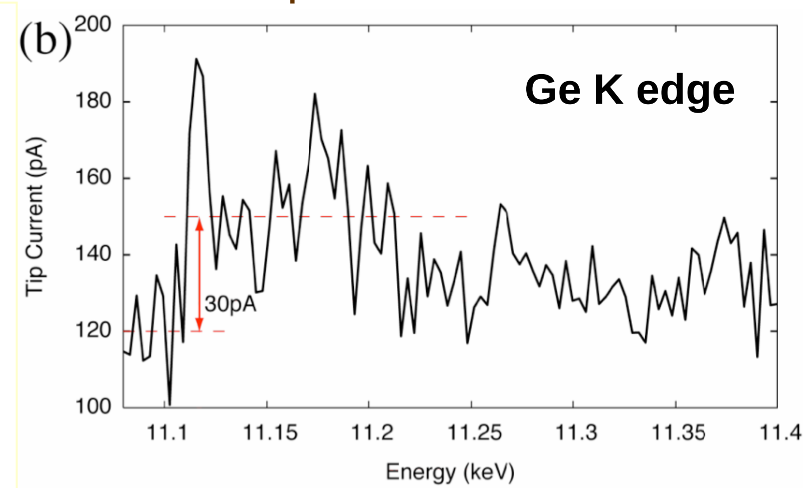


ESRF group

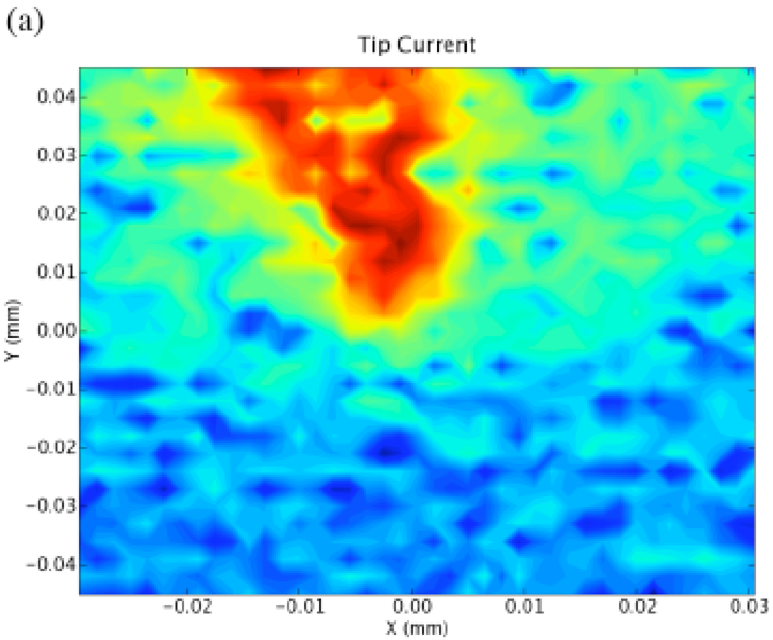
MonteCarlo simulation

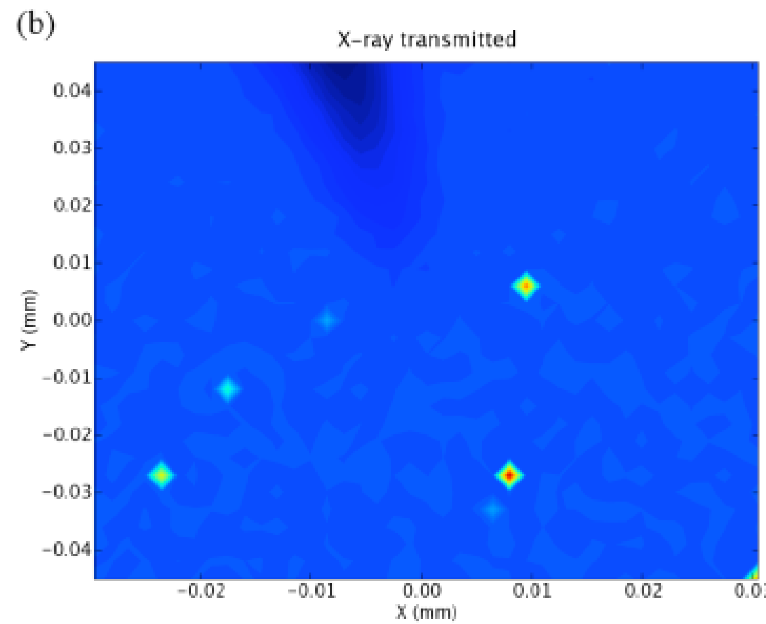


Experimental result



XAS-TEY results



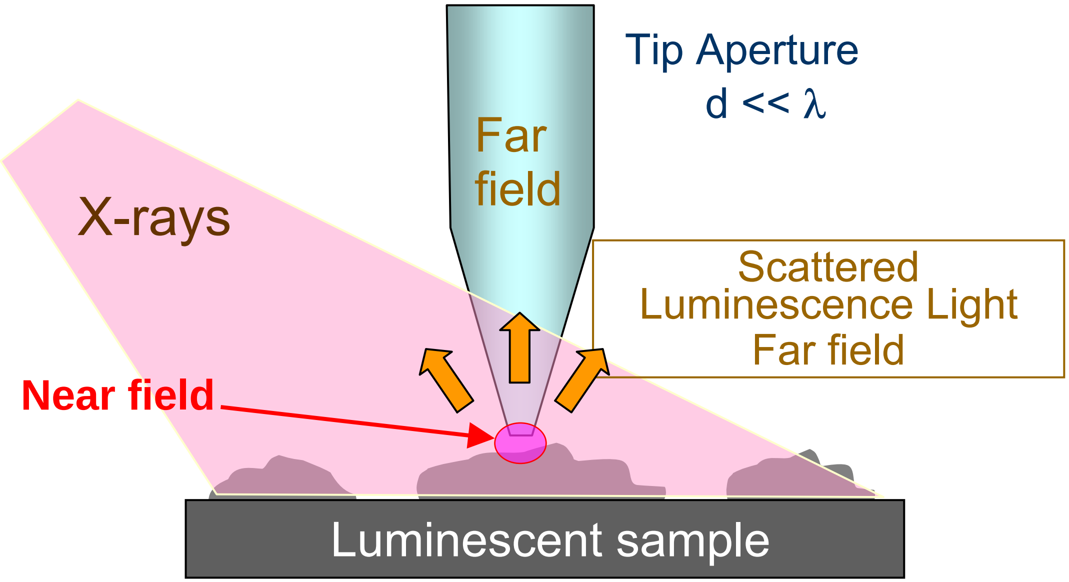


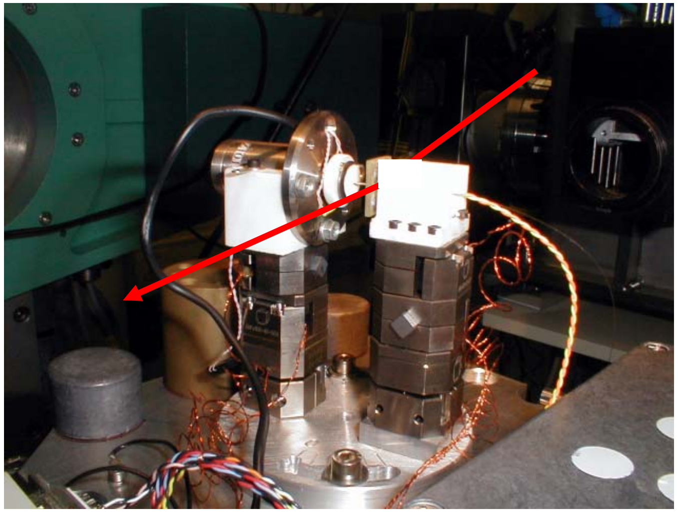
X-Tip current density

Absorption measurement in transmission mode

ESRF group

XAS - SNOM

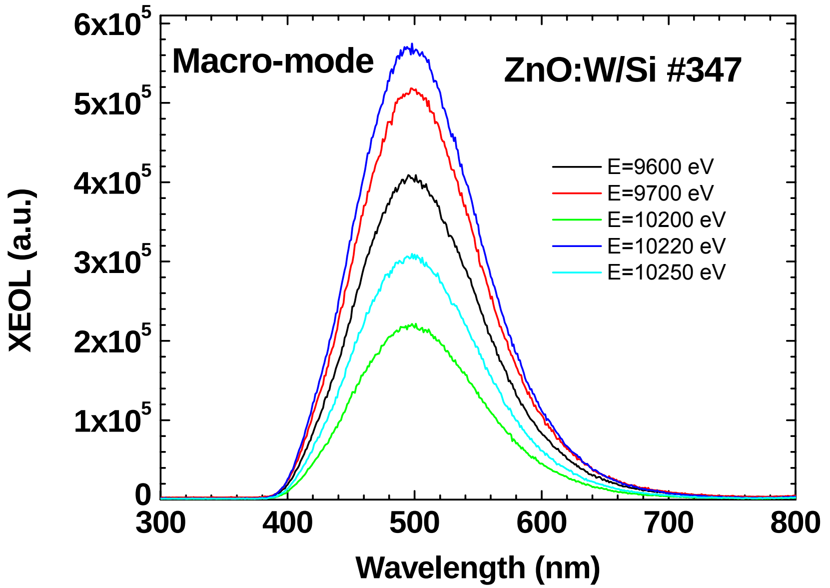




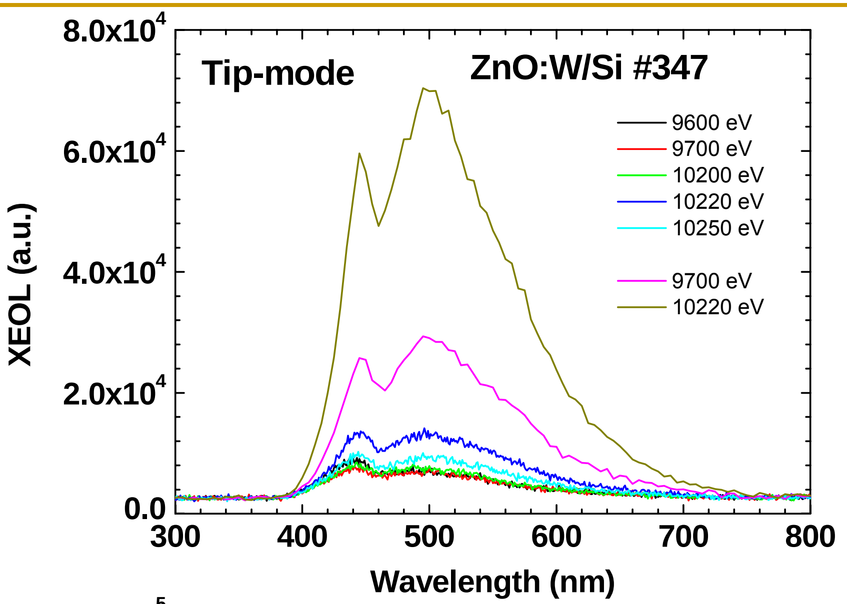
Prototype made
by the Marseille group

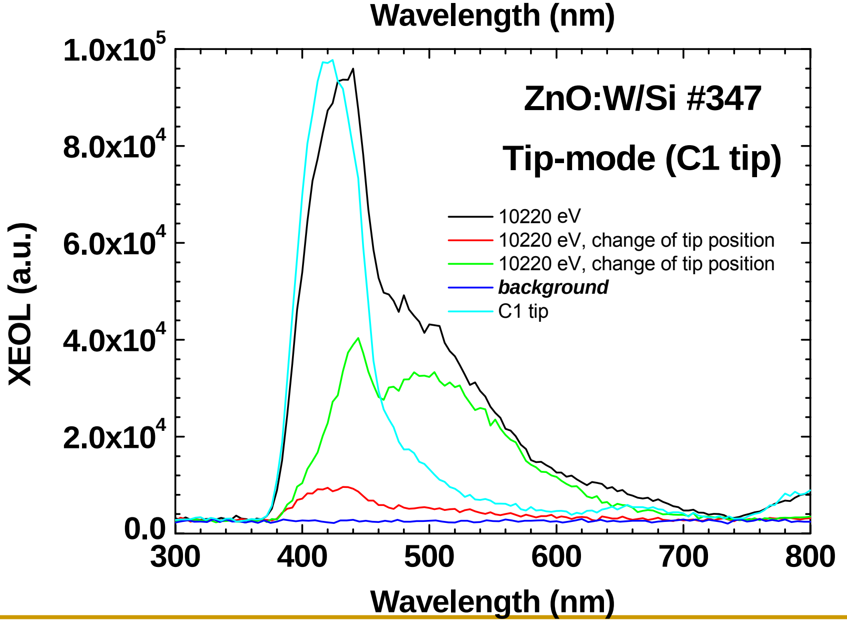
Trento- Marseille-Riga group

Thin film ZnO:W/Si

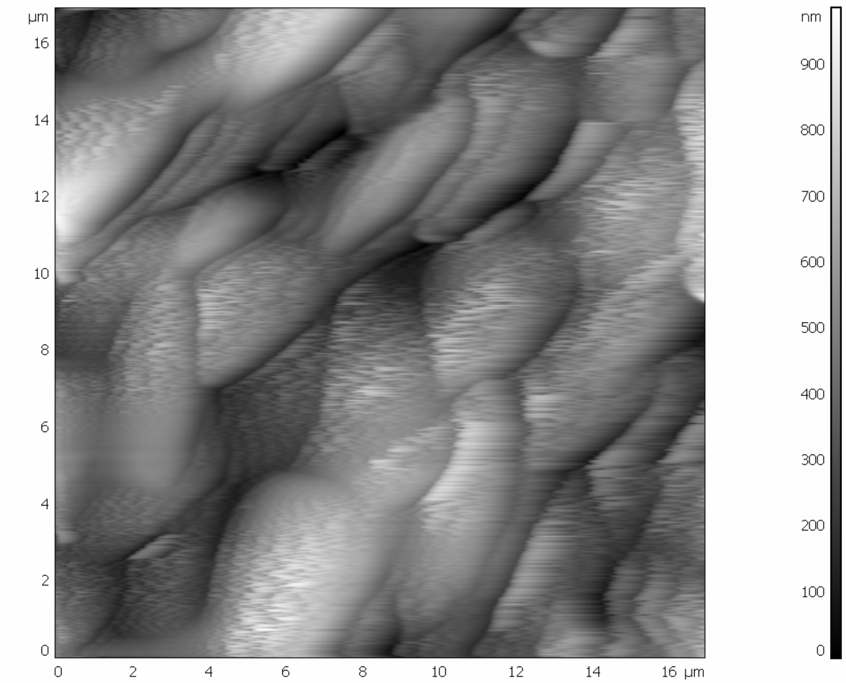


Without the tip

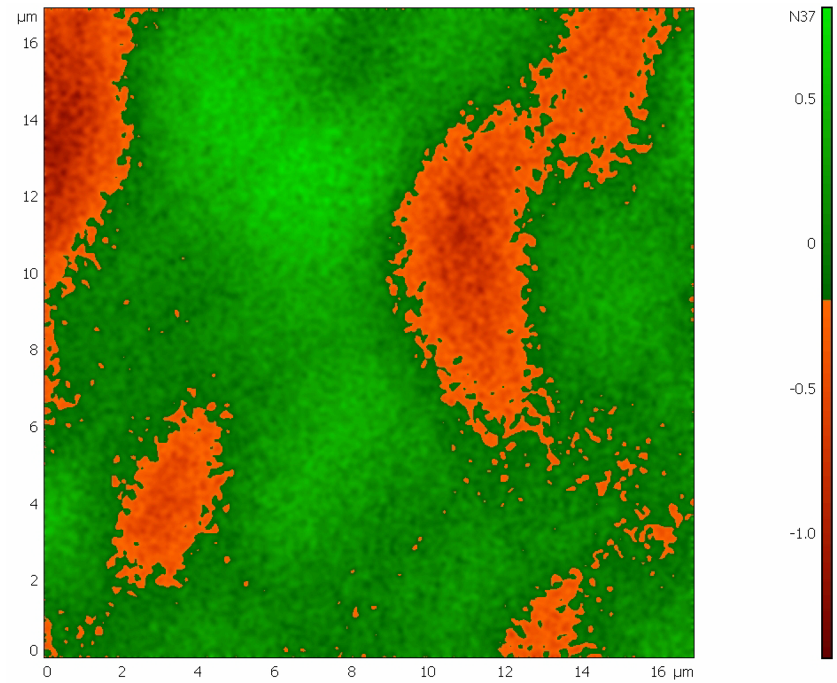




Thin film ZnO:W/Si



Topography
in share-force mode
(17 µm × 17 µm)

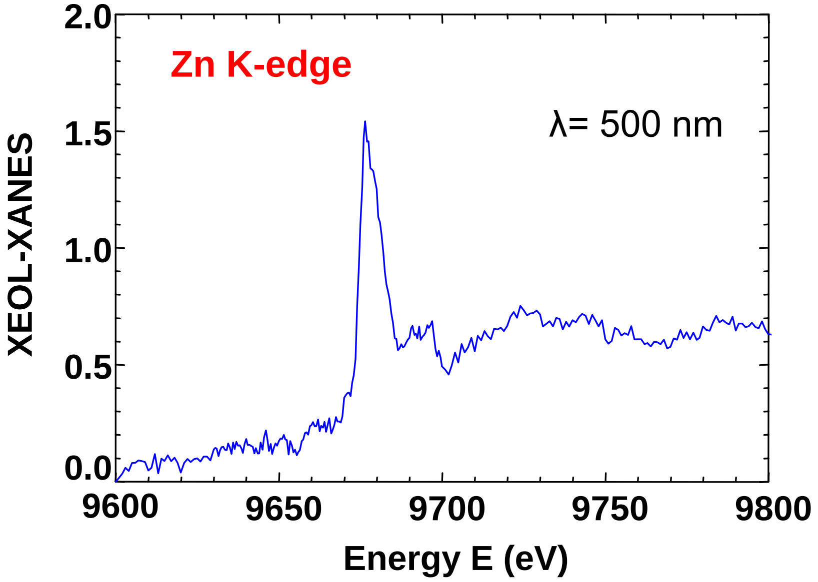


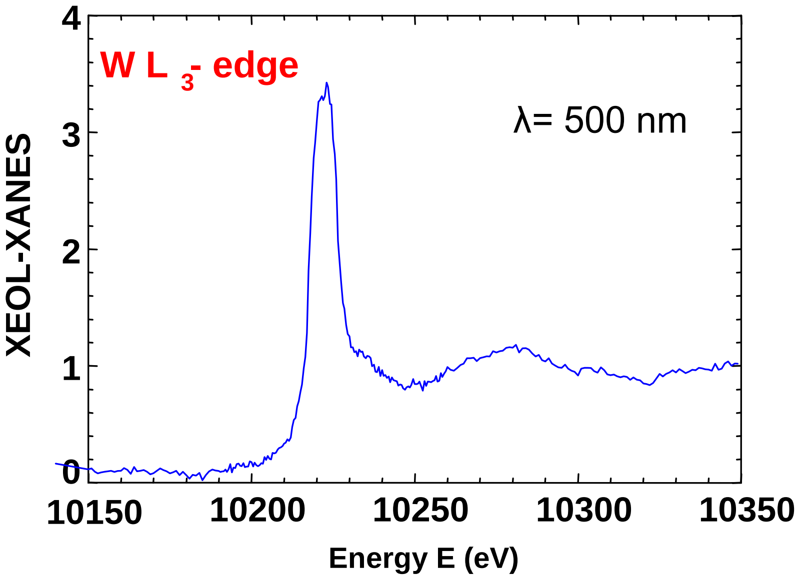
XEOL signal excited at
the W L_3-edge “white-line” maximum
(10222 eV)

Red – tungsten reach regions

Nano-XANES measured by the SNOM tip

Thin film ZnO:W/Si





Conclusions

ACHIEVEMENTS

1. X-TIP prototype is working.
2. It is possible to perform *simultaneously* topography and XEOL scanning and to detect the contrast in XEOL signal due the absorption edges of different materials.
3. It is possible to measure XANES by keeping the tip in a fixed point at the sample surface.
4. It is possible to have a map of the elements present in the nanoparticles

Conclusions

What still to do ?

To reduce mechanical vibrations

To avoid tip photoluminescence under x-rays

To improve the quality of tips in order to reach
a better lateral resolution in XAS-XEOL mode

To use low energy synchrotron radiation beam-lines

Acknowledgements

To all the members of the X-tip group

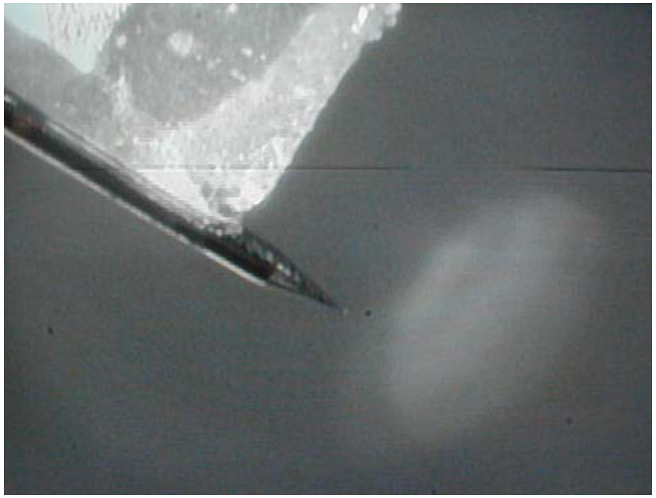
Grenoble
Marseille
Riga
Tartu

In particular to

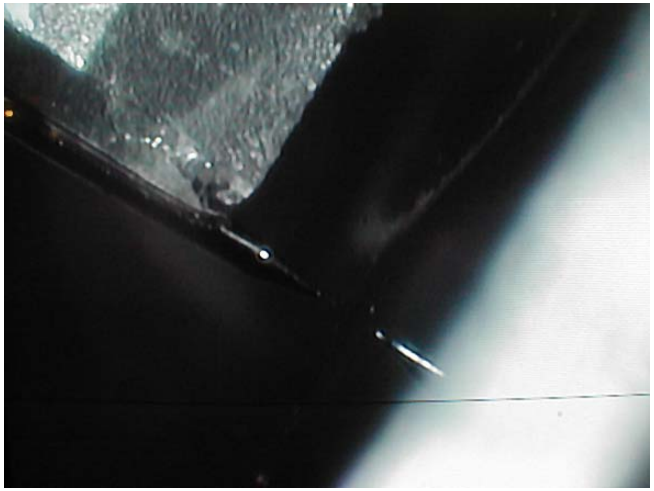
Dr. Alexei Kuzmin
Dr.Francesco Rocca
Silvia Larcheri

Many thanks to you for your attention

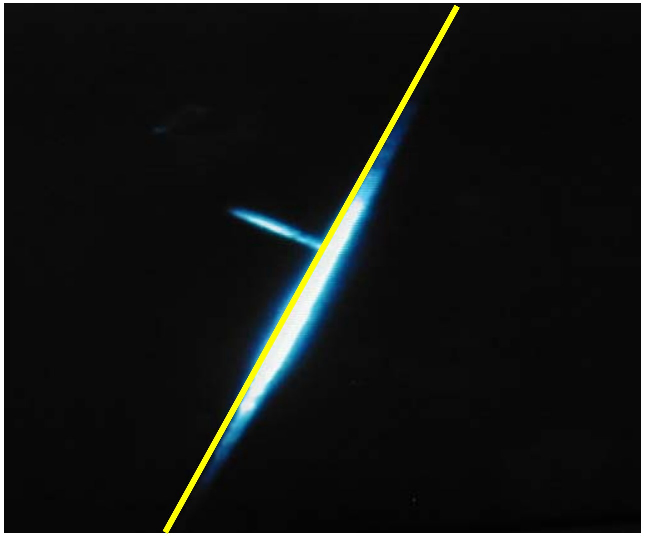
SNOM Tips



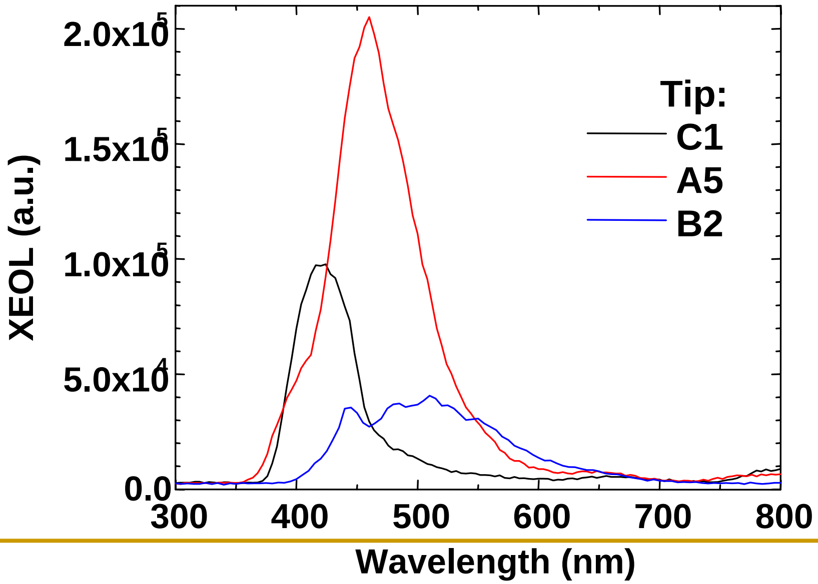
TIP on piezo-fork



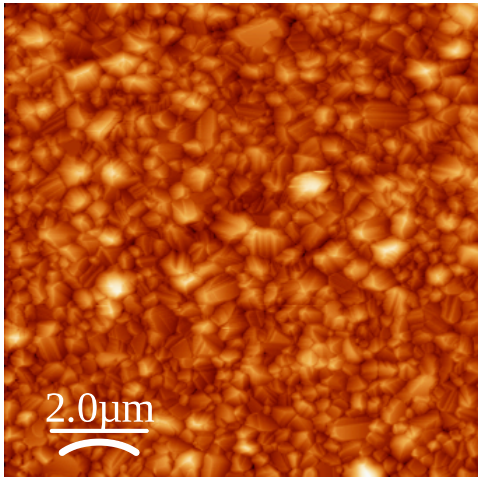
Approaching the sample surface

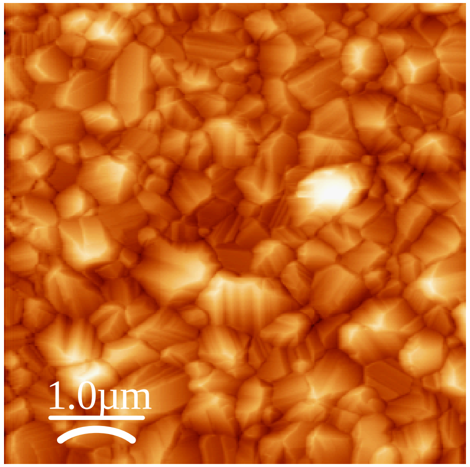


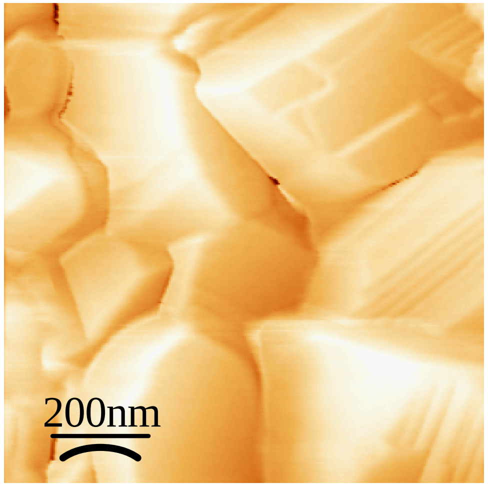
Under the x-ray beam

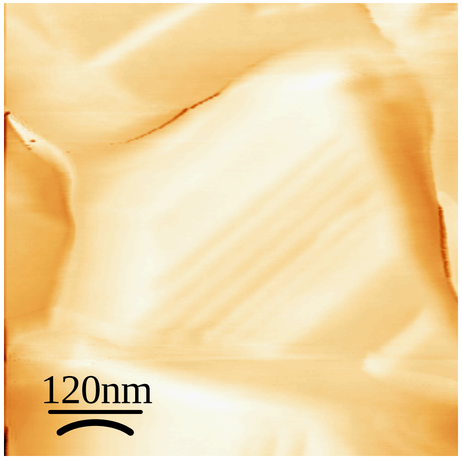


AFM: ZnO/Si 341HT



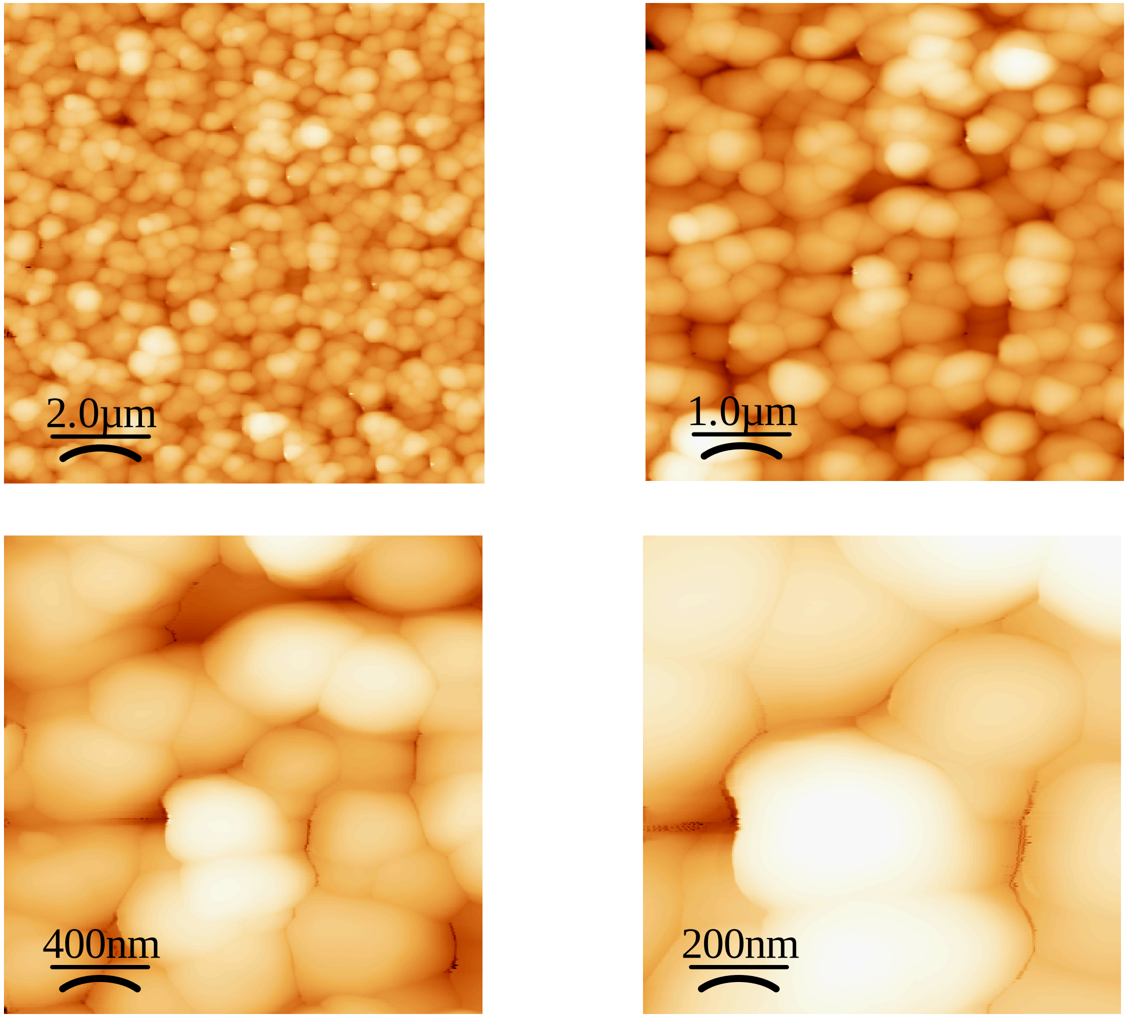






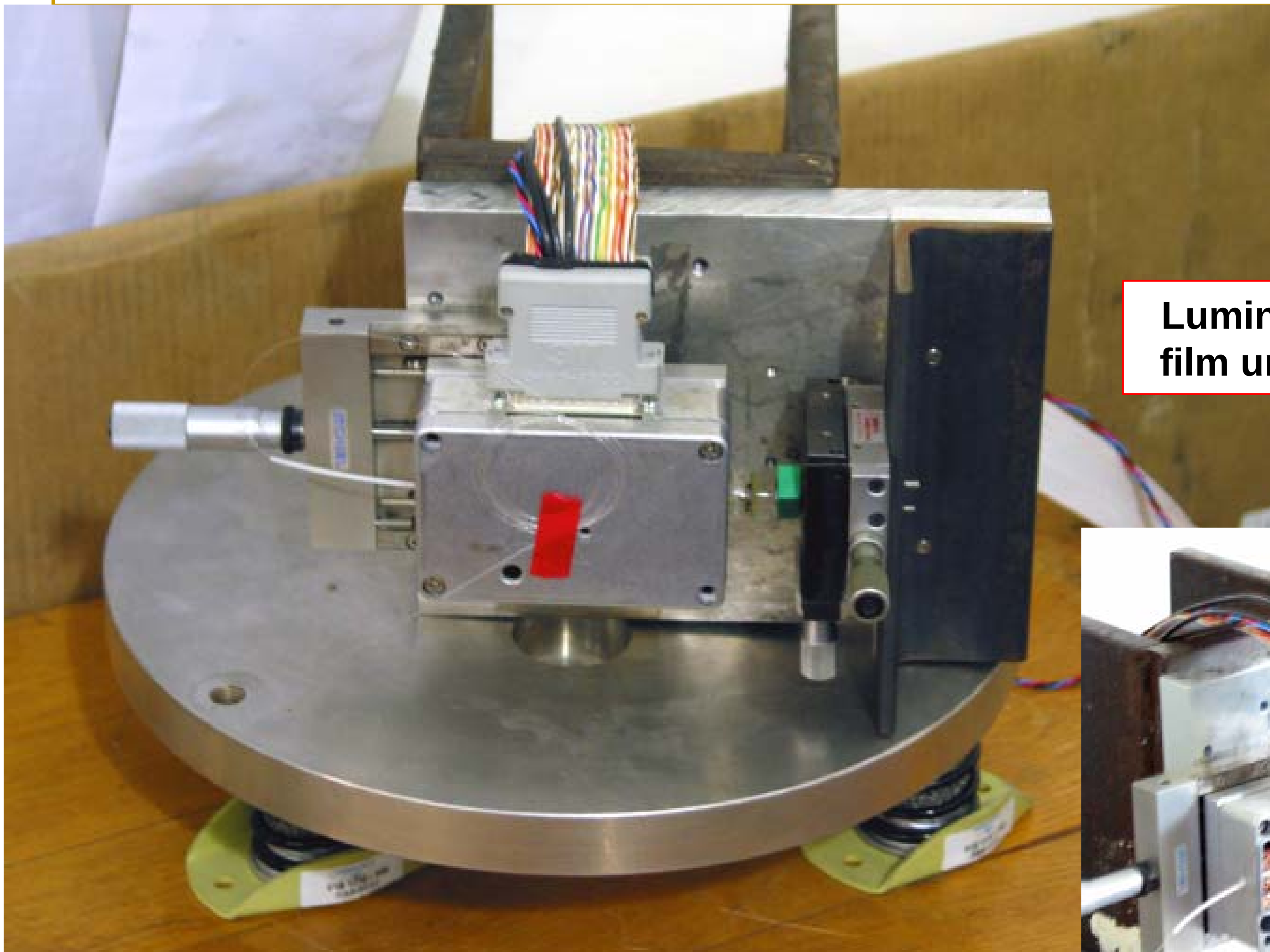
produced by oxidizing metallic Zn film

AFM: ZnO/Si

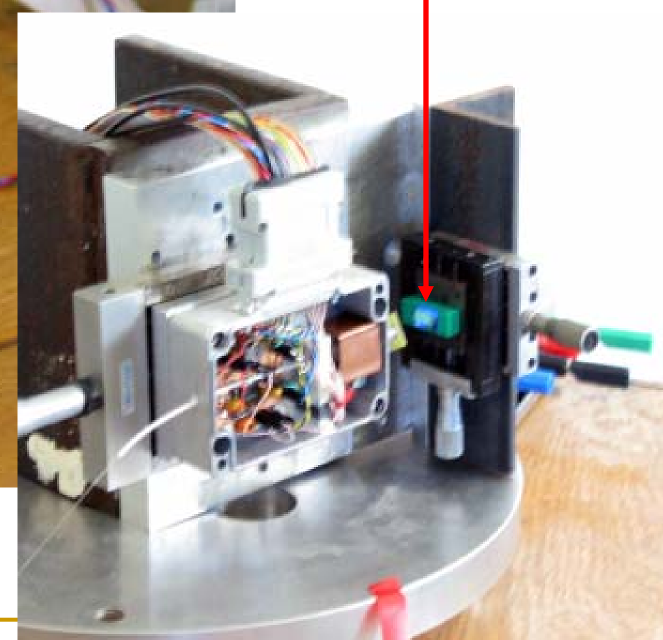


produced by sputtering in Ar-O_2

SNOM setup at Marseille University

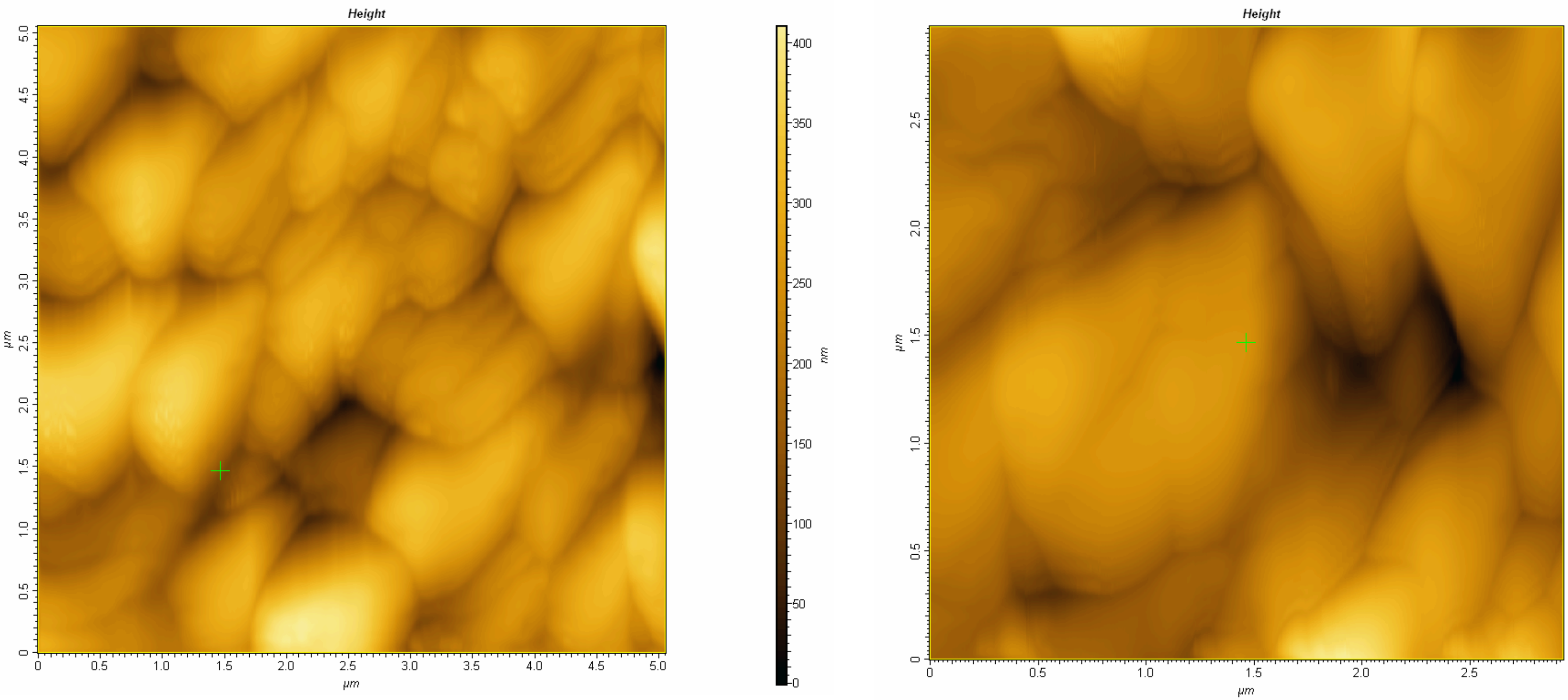


Luminescence of ZnO thin film under laser irradiation

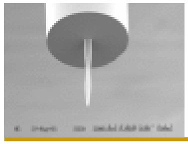


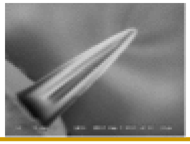
First prototype with *LovaLite* fiber

ZnO/Si – SNOM image by *LovaLite* fiber



produced by oxidizing metallic Zn film



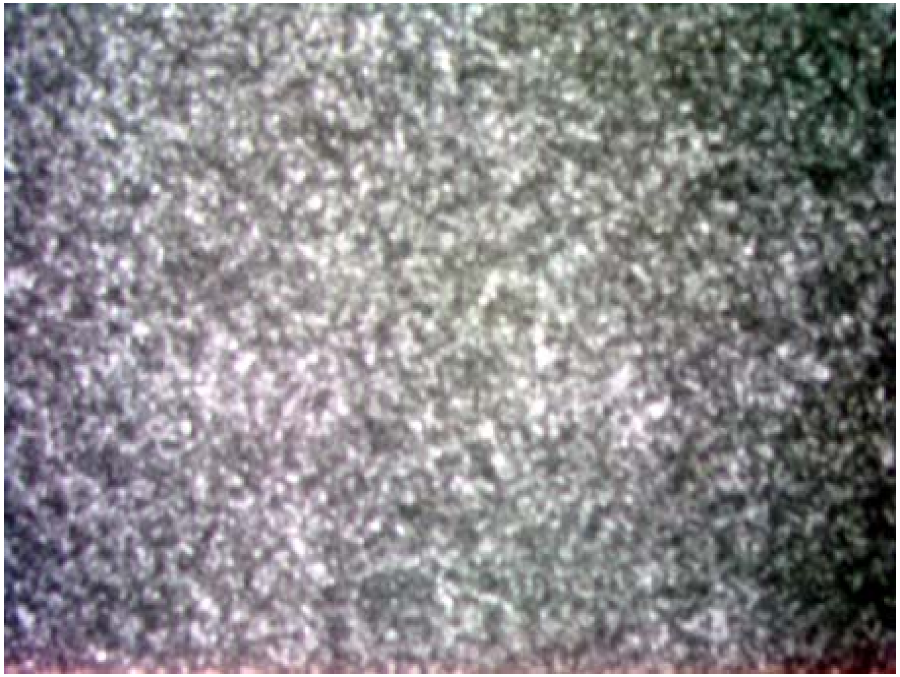


LovaLite®

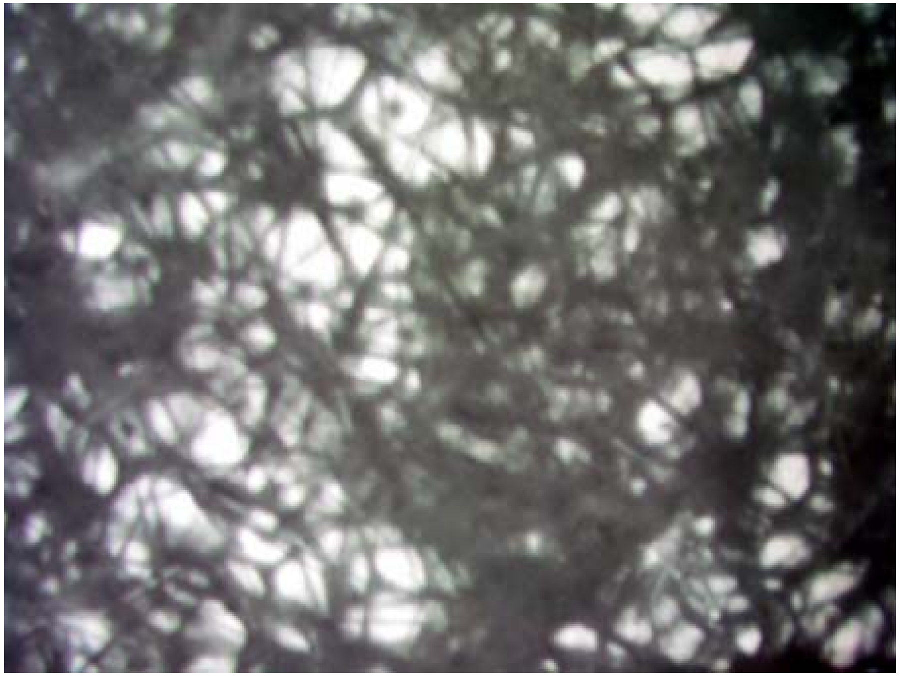
www.lovalite.com

Optical microscopy of ZnO/Si thin films

produced by magnetron sputtering and atmospheric pressure chemical vapor deposition

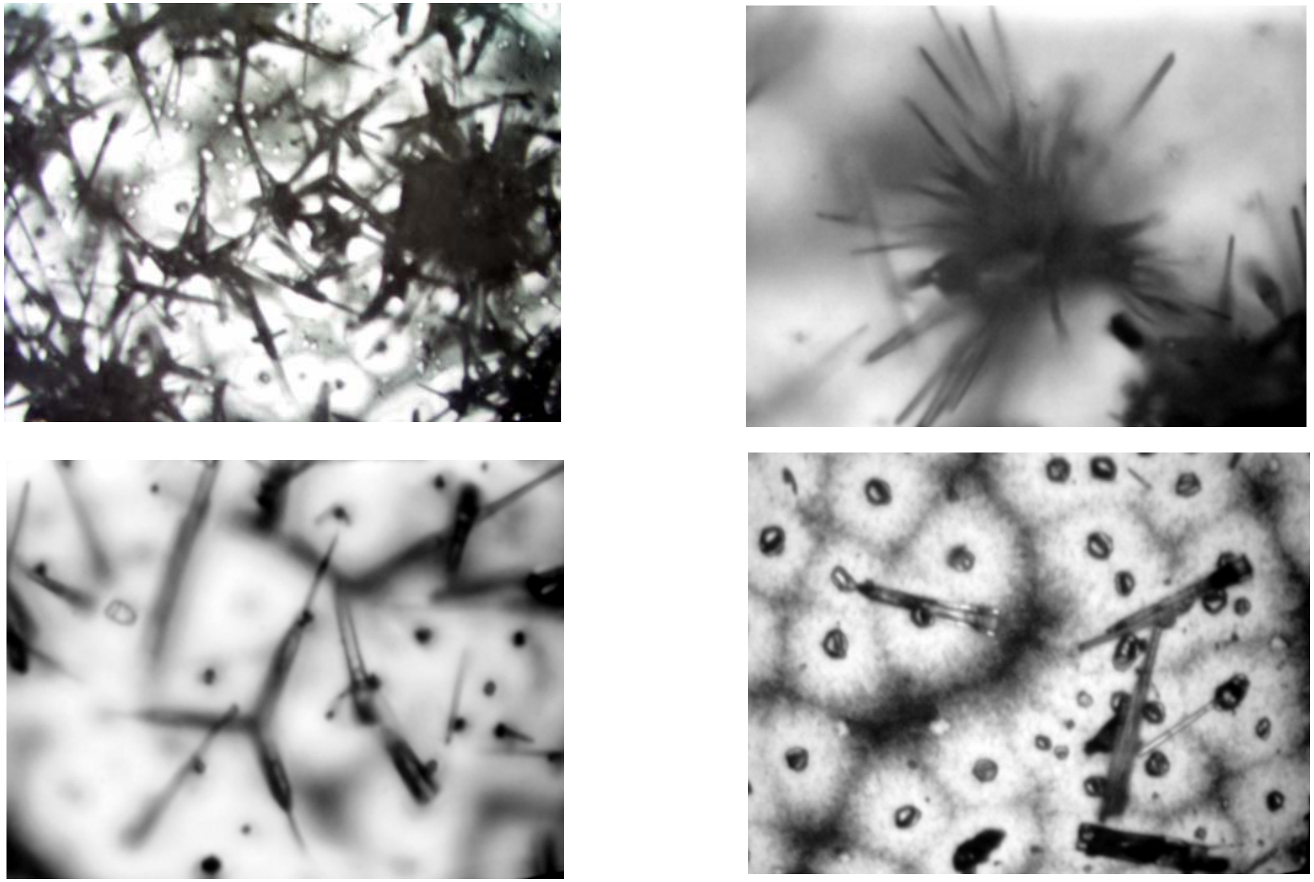


ZnO/Si 341HT
(produced by oxidizing metallic Zn film)



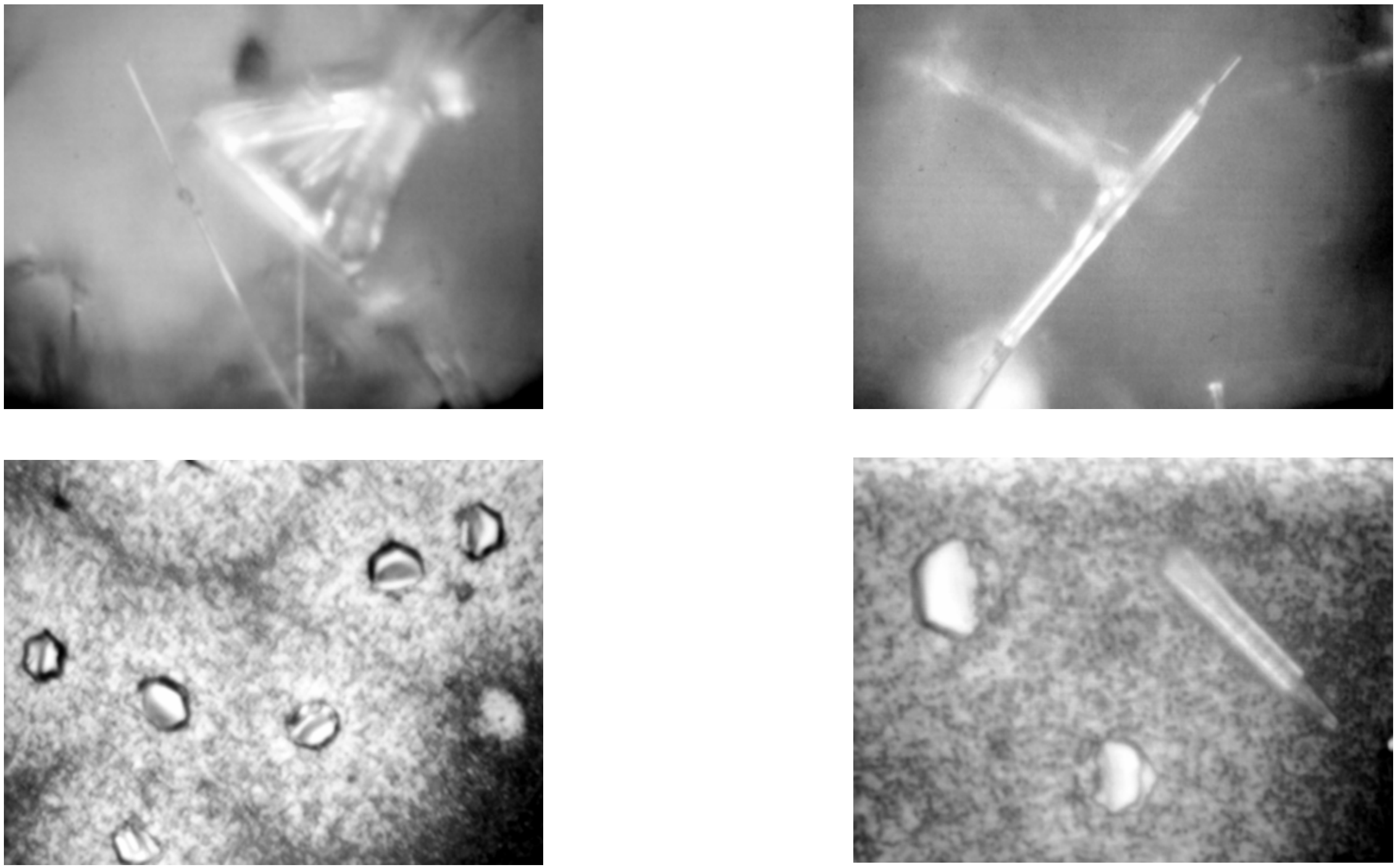
TEC sample
(produced by atmospheric pressure chemical vapor deposition (APCVD))

TEC samples



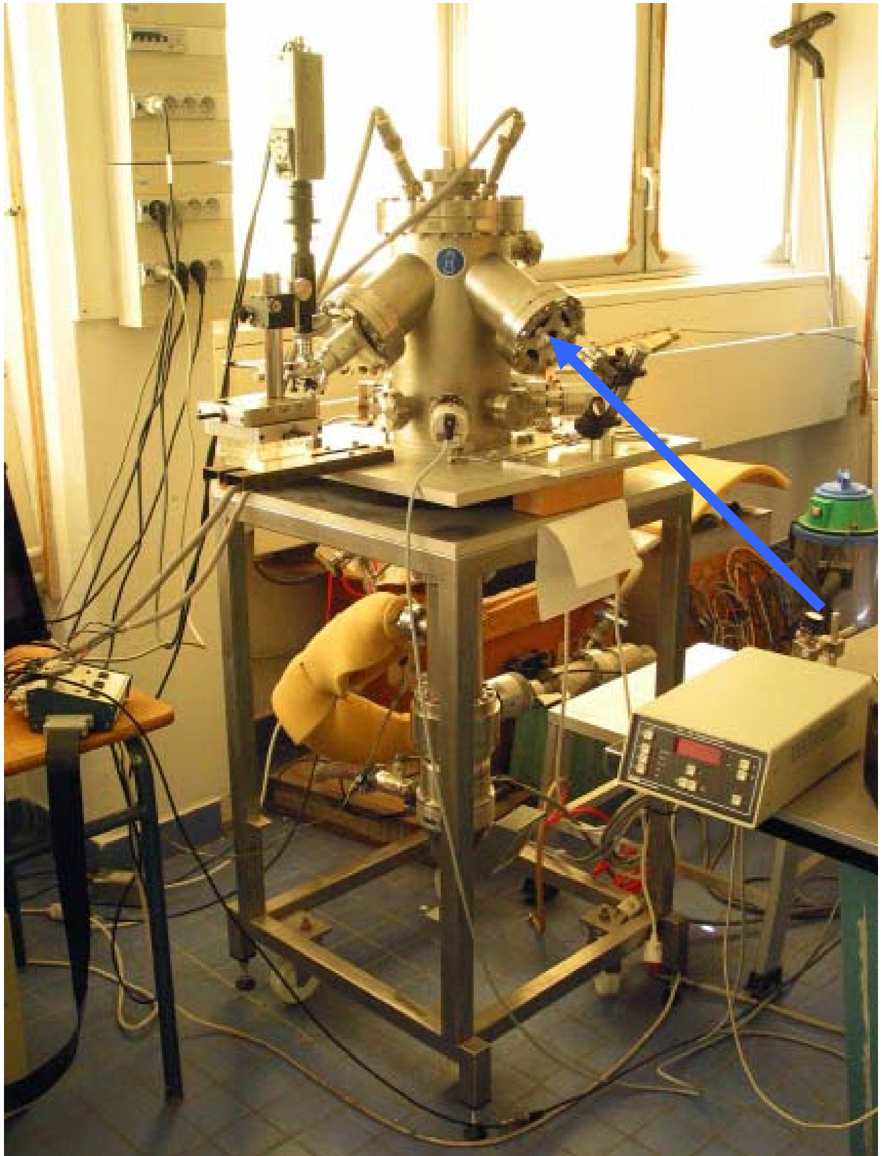
produced by atmospheric pressure chemical vapor deposition (APCVD)

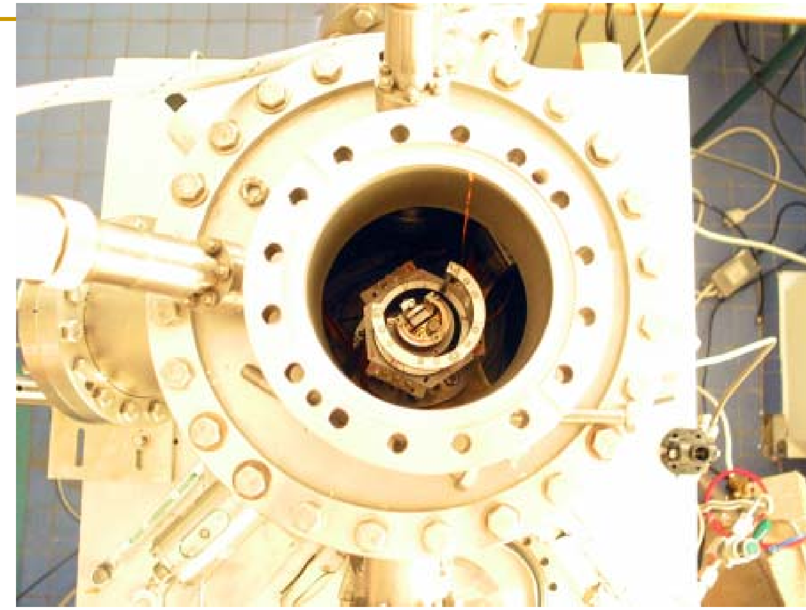
TEC samples

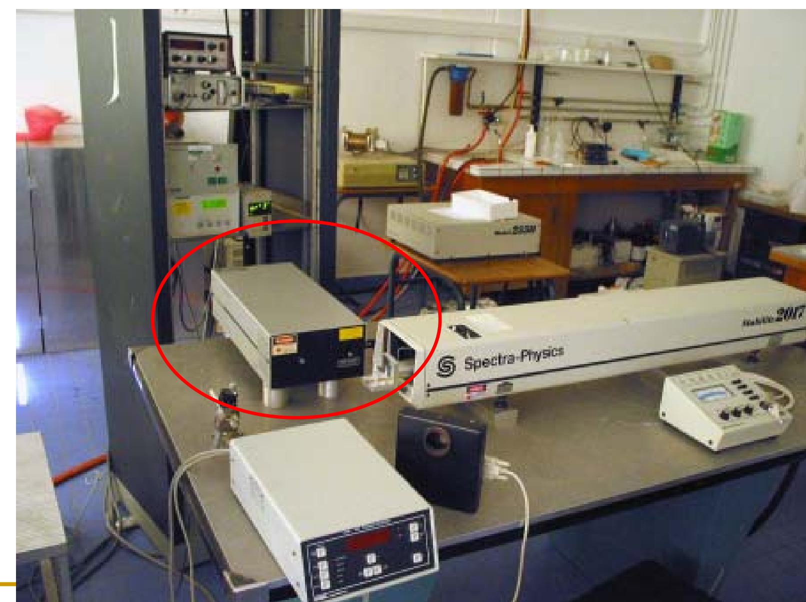


produced by atmospheric pressure chemical vapor deposition (APCVD)

STM setup with 350 nm laser excitation source







Sample preparation methods

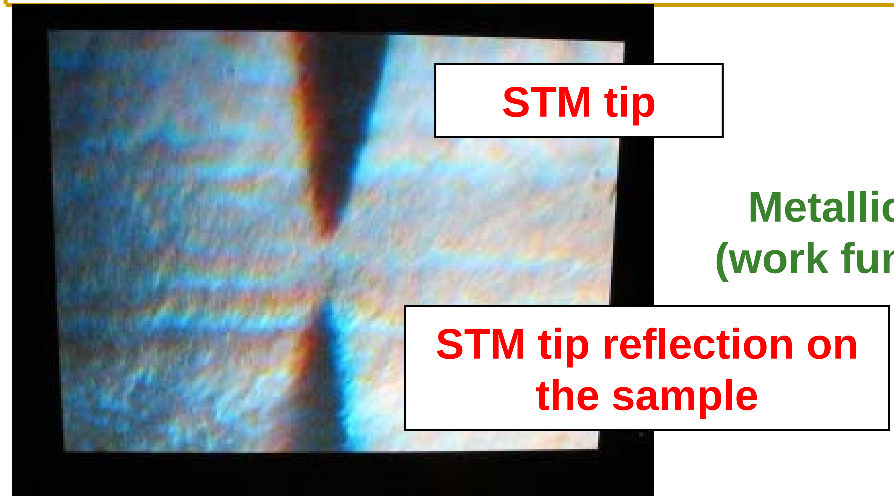
- "dc magnetron sputtering" in atmosphere of Ar-O_2 using Si substrate and Zn o W as metallic targhets

  2) tutti campioni TEC fatti con metodo "atmospheric pressure chemical vapor deposition (APCVD)" - analog di CVD ma in aria anche usando Si come substrato (abbiamo scaldato ZnO con grafite fino a ~1100 C),

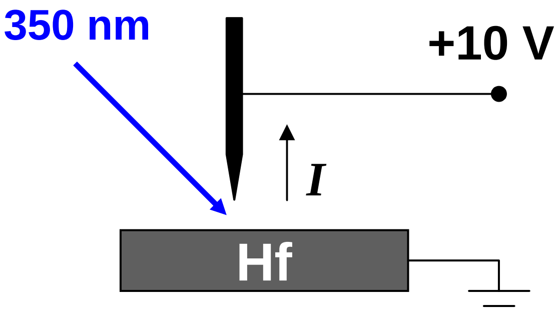
  3) campioni CER sono ceramici - misti dei polveri nano e policristallini,

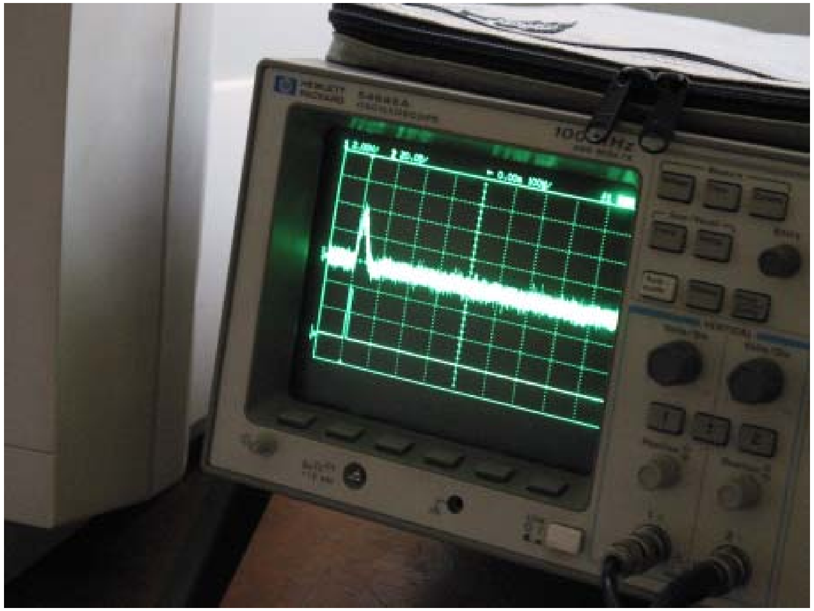
  4) campioni 31-37 fatti atraverso metodo di elettrochimica usando graphite (conduce corente) come substrato/elettrodo e "ZnCl2 aqueous electrolite solution with Pt as counter electrode".

STM measurement of current under pulsed 350 nm excitation

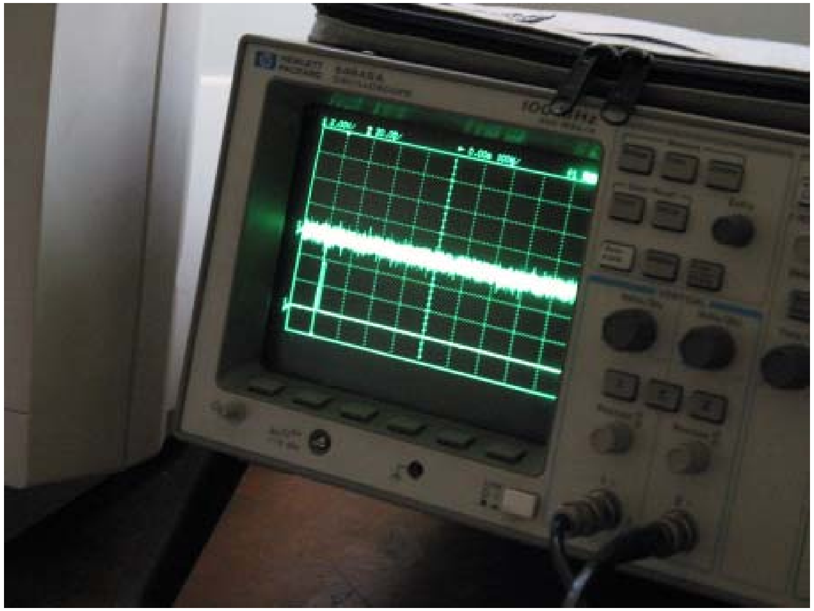


Metallic Hf sample
(work function 3.9 ev)





Laser "ON"

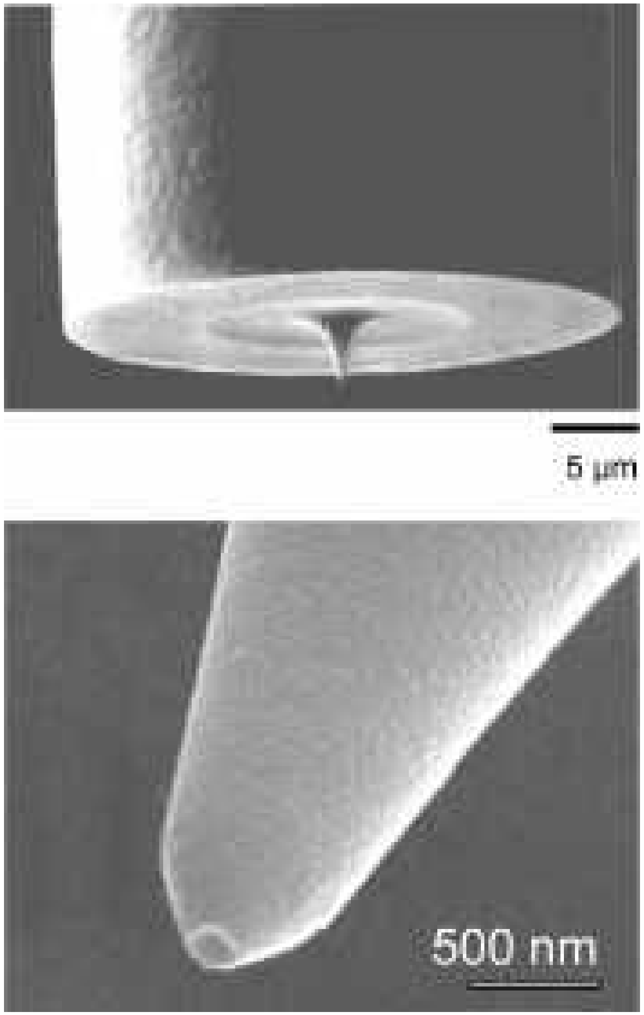


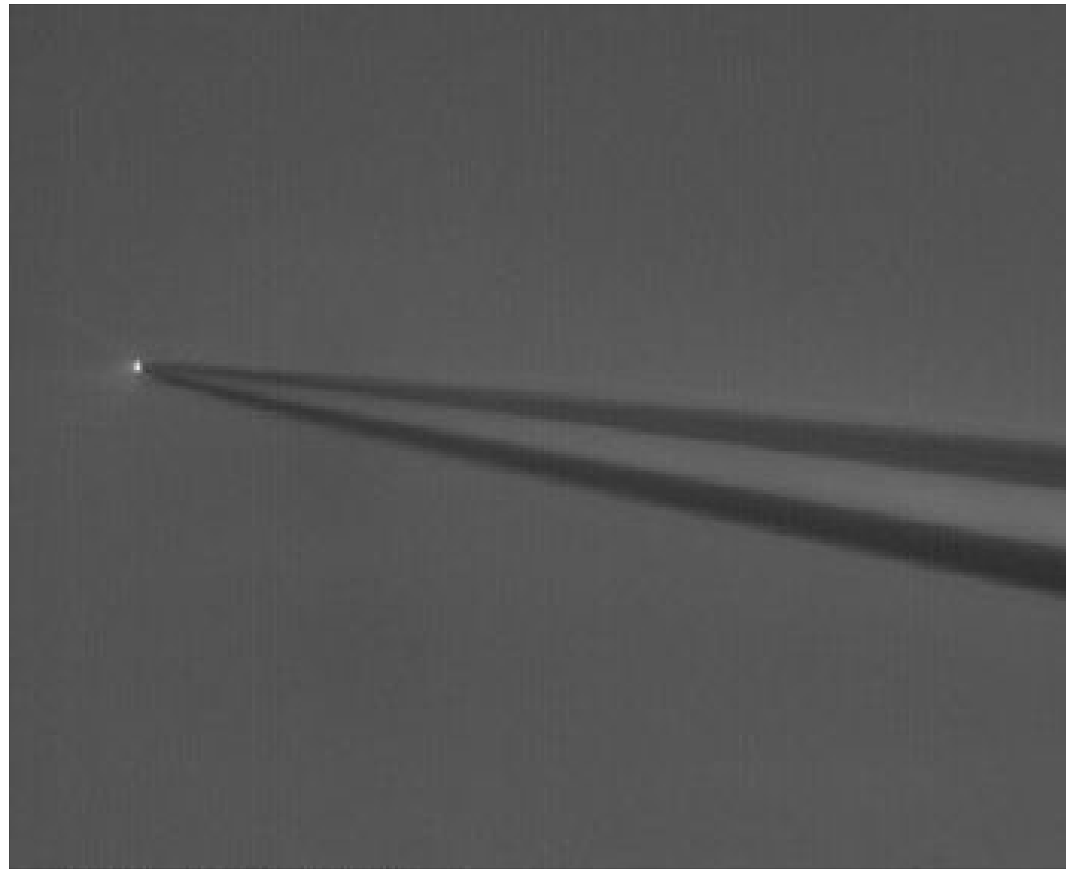
Laser "OFF"

X-Tip project participants

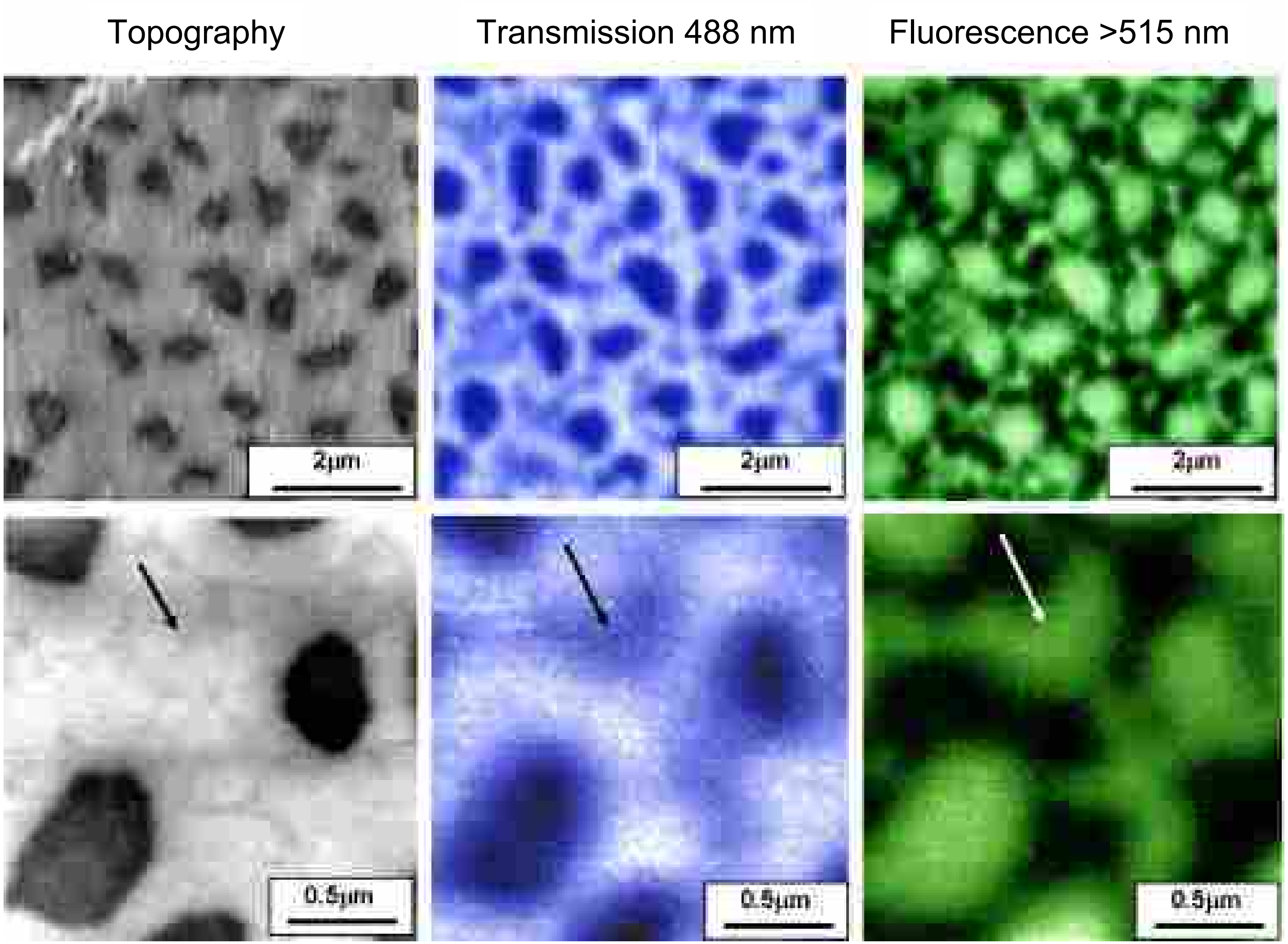
1. **ESRF -** European Synchrotron Radiation Facility, Grenoble, EU; Dr. Hab. Fabio Comin (co-ordinator)
2. **GPEC/CNRS** – Université de la Méditerranée, UMR 6631 CNRS, Marseille, France; Dr. Daniel Pailharey
3. **ISSP** – Institute of Solid State Physics, University of Latvia, Riga, Latvia; Dr.Hab. Juris Purans
4. **OGG-INFM**, Istituto Nazionale per la Fisica della Materia, Grenoble, Italy; Dr. Roberto Felici
5. **LEPES/CNRS -** Laboratoire d'Etudes des Propriétés Electroniques des Solides, CNRS, Grenoble; France Prof. Joël Chevrier
6. **UNITN -** Department of Physics, University of Trento, Italy; Prof. Giuseppe Dalba
7. **UNITA -** University of Tartu, Estonia: Institute of Physical Chemistry and Institute of Physics of the University of Tartu, Estonia, Dr. Väino Sammelselg
8. **IFN-CNR -** Institute for Photonics and Nanotechnologies, Section "ITC-Cefsa" of Trento, Italy; Dr. F. Rocca.

SNOM Pictures Aperture Probes

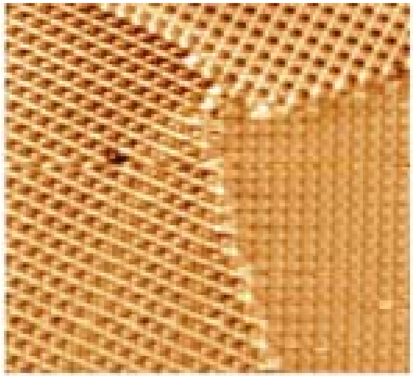




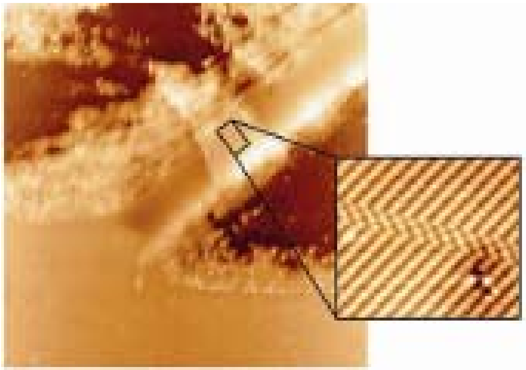
SNOM : Some images



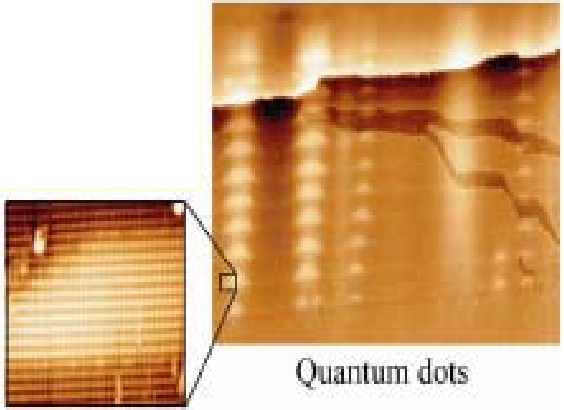
X-Tip expectances from XAS - TEY



2D-oxides



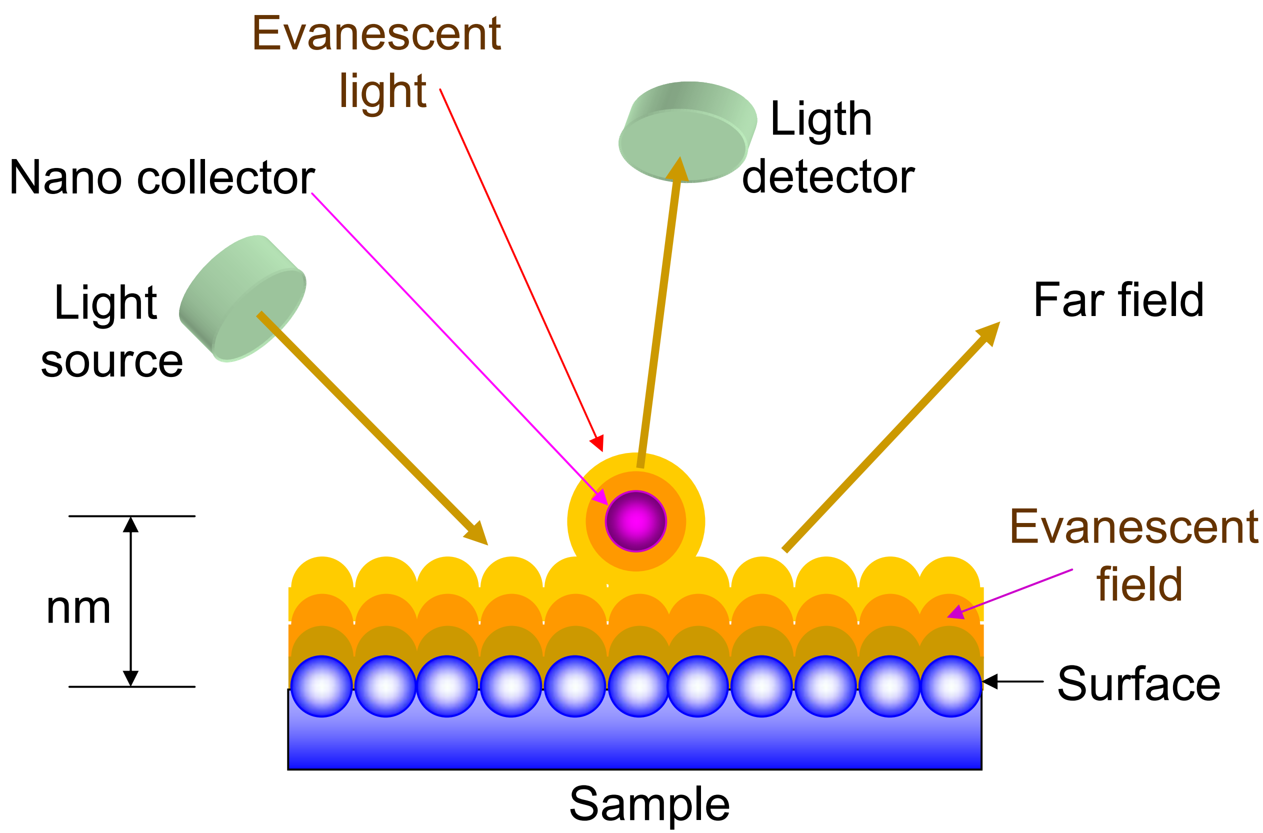
Nanowires



Quantum dots

Topological structure
+
Local distribution of elemental constituents
+
geometrical structure and chemical composition of single nanowires and dots

SNOM: Evanescent Light

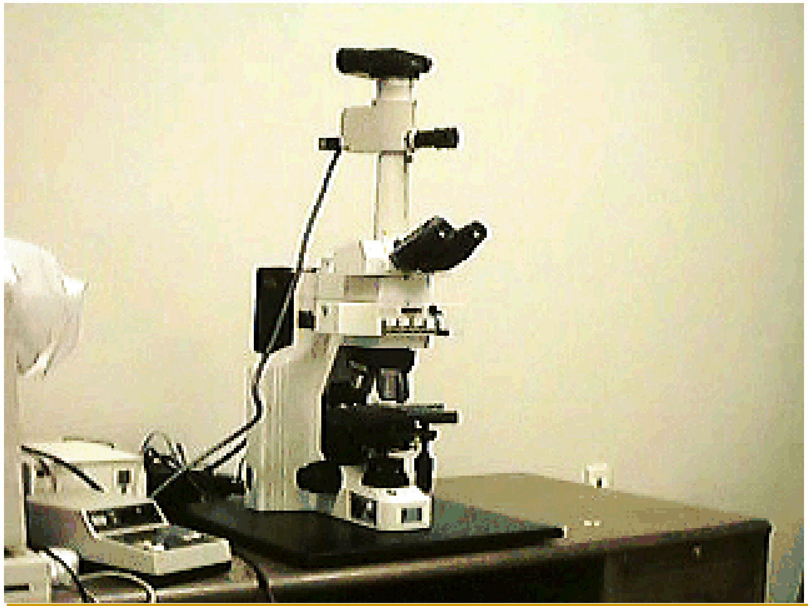


The atoms in the probe absorb evanescent photons and re-radiate propagating photons.

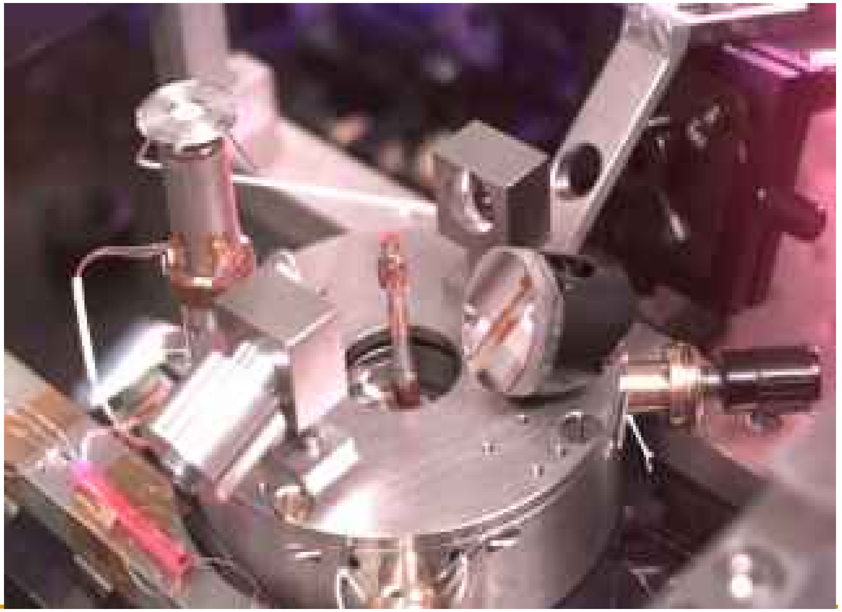
Conventional Microscopes and SNOM

- Conventional optical microscopes
  - Max ~1200× magnification
  - Look very different from a SNOM

Conventional Microscope

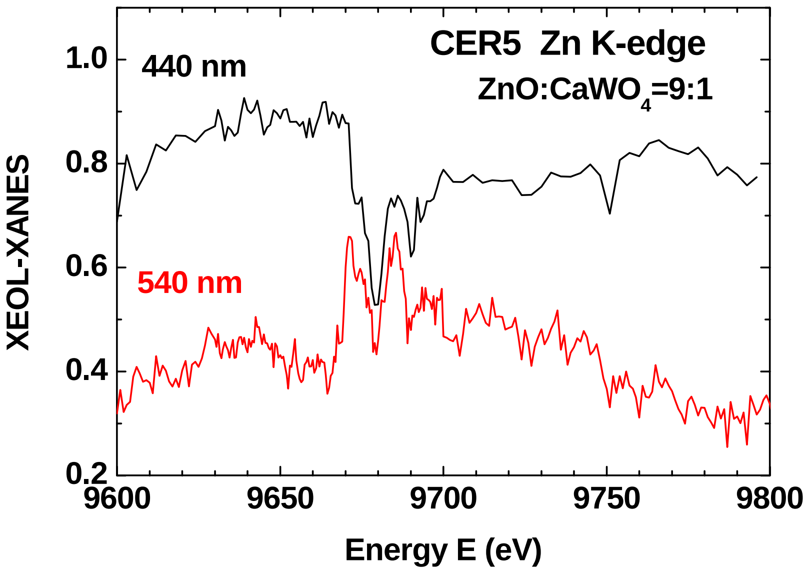


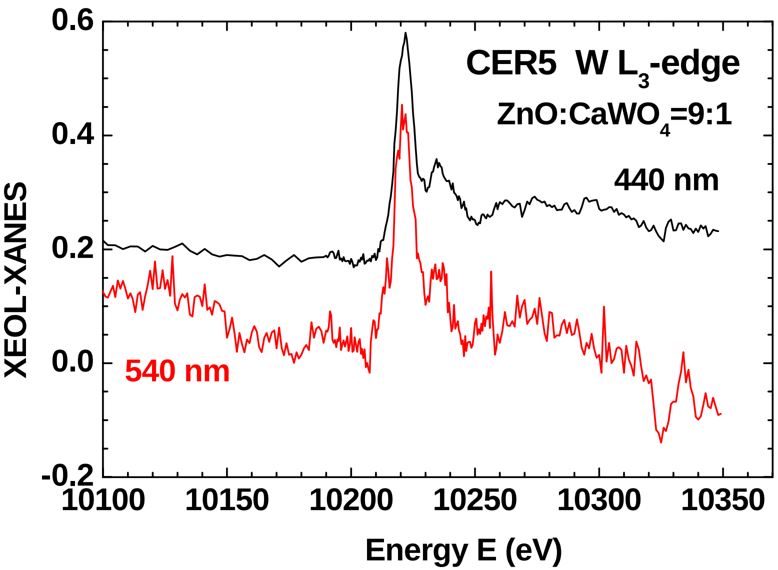
SNOM



Mixed ceramics $ZnO:CaWO_4$=9:1 (CER5)

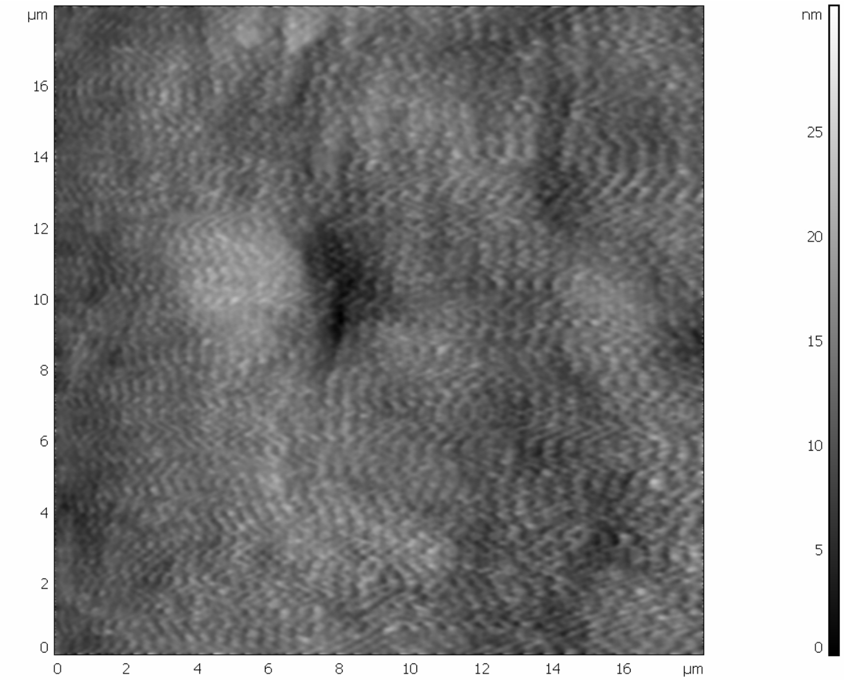
Note negative edge !



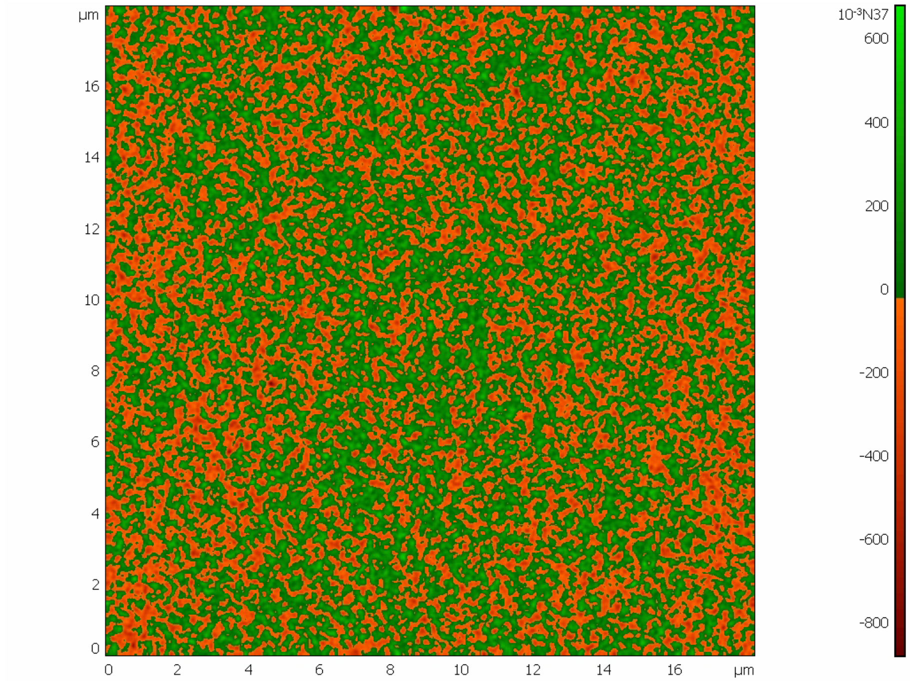


Nano-XANES measured through the SNOM tip

Thin film $ZnWO_4$+ZnO/Si



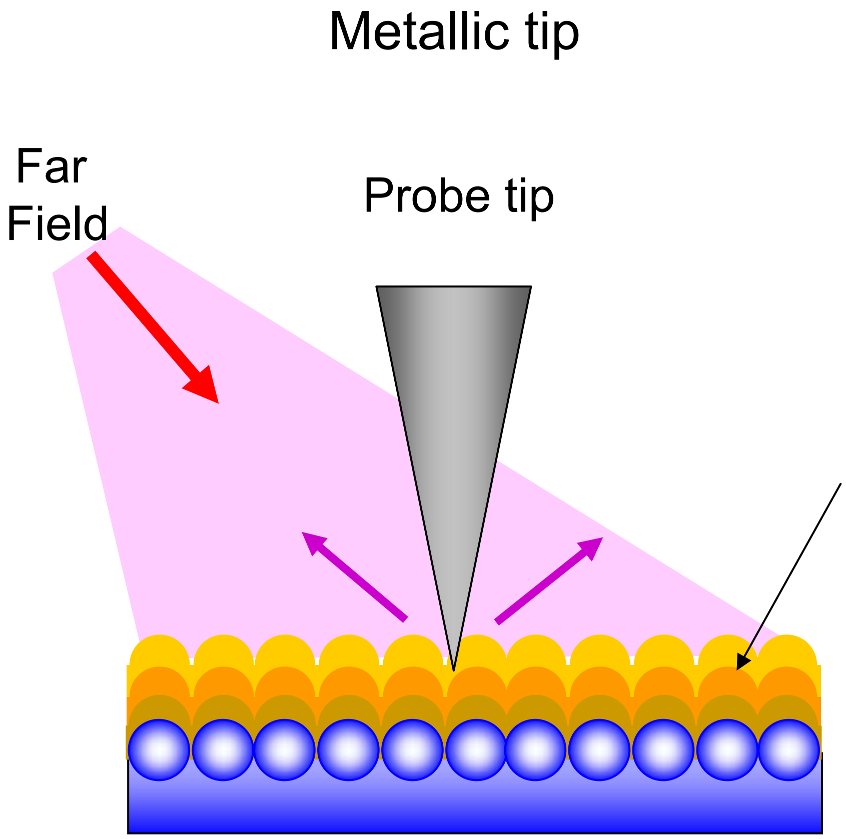
Topography
in share-force mode
(18 µm × 18 µm)



XEOL signal excited at
the W L_3-edge "white-line" maximum
(10222 eV)

Red – tungsten reach regions

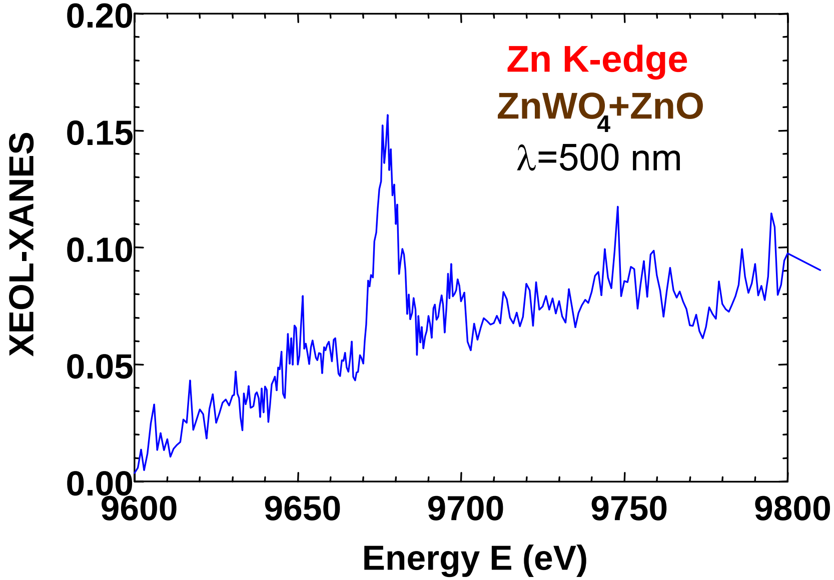
SNOM: Apertureless technique

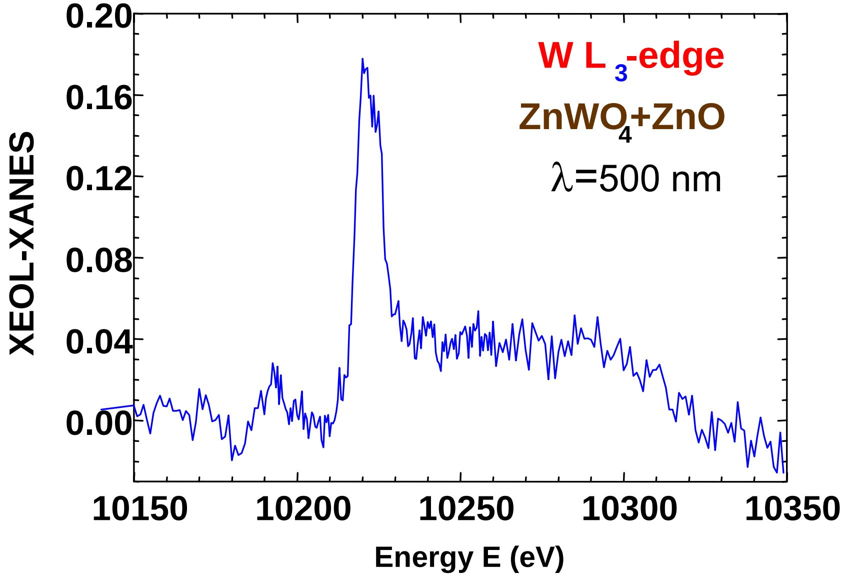


The tip is excited by the evanescent field and re-irrdiates propagating ligth

Difficulty to separate re-irradiate light the light reflected from The surface

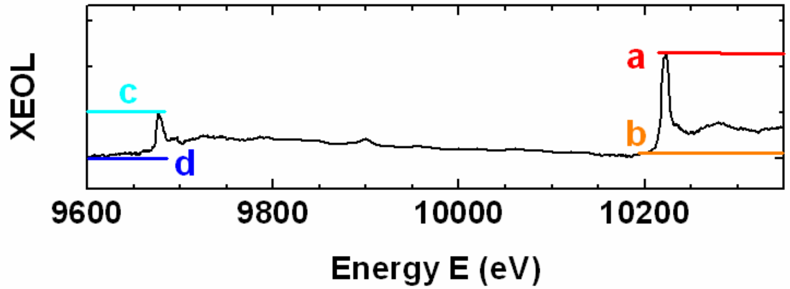
Thin film $ZnWO_4$+ZnO/Si





Nano-XANES measured through the SNOM tip

Thin film $ZnWO_4$+ZnO/Si



"white-line" maximum

Average intensity:

$I_e = 0.84$

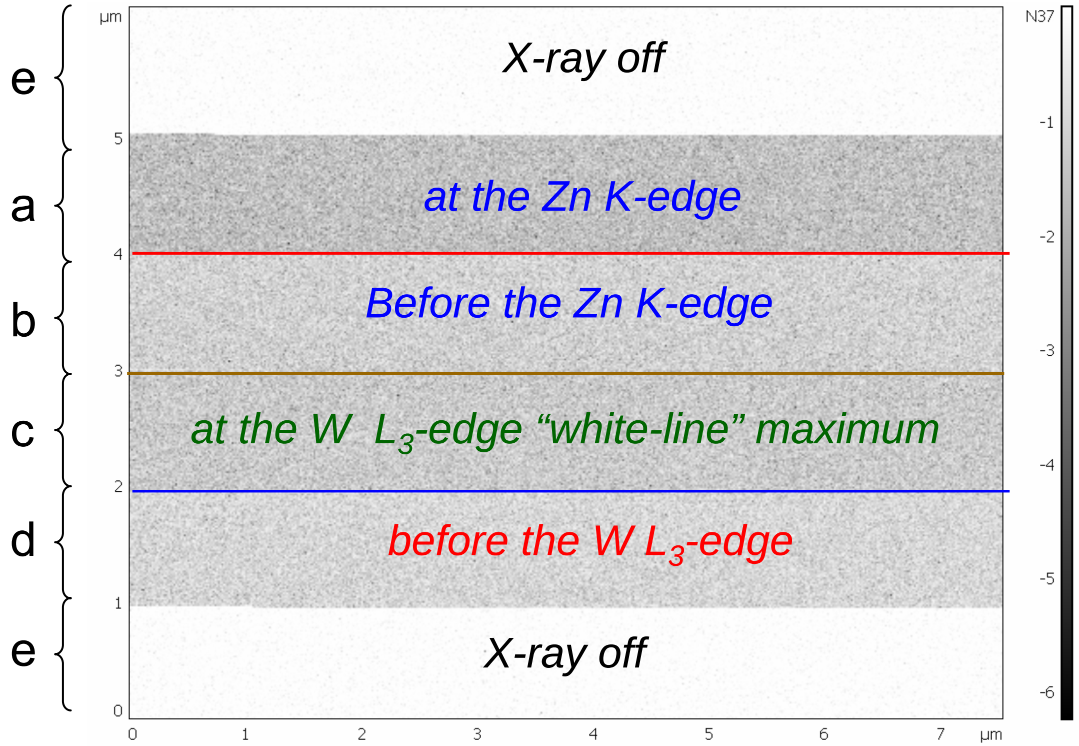
$I_a = 1.50$

$I_b = 1.12$

$I_c = 1.30$

$I_d = 1.04$

$I_e = 0.74$



Conclusions

What still to do ?

To reduce mechanical vibrations

To avoid tip photoluminescence under x-rays

To improve the sensitivity of the photo-multiplier in order to improve the photoluminescence detection

To use low energy synchrotron radiation beam-lines

To improve the quality of tips in order to reach XEOL the lateral resolution